SCM
Software for Chemistry & Materials

AMS Manual

Amsterdam Modeling Suite 2024.1

www.scm.com

Apr 05, 2024

CONTENTS

CHAPTER

ONE

GENERAL

1.1 Overview

AMS is the new driver program introduced in the 2018 release of the Amsterdam Modeling Suite. The job of AMS is to handle all changes in the simulated system's geometry, e.g. during a geometry optimization or molecular dynamics calculation, using the so-called "engines" like ADF, BAND or DFTB for the calculation of energies and forces. In summary, one might say that the AMS driver steers the engines across the potential energy surface.

Prior to the 2018 release of the Amsterdam Modeling Suite, what we now call engines used to be separate programs, each with their own input and output files and formats. Starting with the 2018 release, the engines are only accessible through the AMS driver program, that provides a unified interface to all of them.

1.2 What's new in the AMS driver?

1.2.1 New in AMS2024.1

- Use *image dependent pair potential (IDPP)* (page 77) to generate an initial path for NEB calculations
- *Reaction boost (targeted MD) restraints* (page 136) for molecular dynamics
- Dipole moment added as an option to the *BinLog* (page 108) output section for calculation of IR spectra from ab initio MD
- The *dimer method* (page 63) for transition state search
- A new Reactions Discovery tool that can be used with any *AMS engine* (page 270).
- Use engine *uncertainties* (page 270).
- Stop MD trajectories early with *exit conditions* (page 158) based on too short atom-atom distances or too high engine uncertainties.
- Store as part of the MD trajectory: temperature of individual thermostats, total BondBoost or Reactor restraint energy.

1.2.2 Removed in AMS2024.1

- Old FCF program ($AMSBIN/oldfcf) is no longer supported
  - the new *FCF program* (page 245) ($AMSBIN/fcf) has replaced the old FCF program in AMS2022.1
  - see documentation in the AMS2021.1 manual on the old FCF program (https://www.scm.com/doc.2021/AMS/Utilities/FCF_module.html)

1.2.3 New in AMS2023.1

- A new *Conformers tool* (page 295) tool allows conformer generation with any *AMS engine* (page 270).
- *Molecular orbitals energies and occupations* (page 268) can now be requested from the `Properties` block in the driver input and are printed in an engine independent manner.
- The *AMSbatch* (page 291) utility program allows executing the same AMS job for multiple systems.
- A Martinez style *Nanoreactor* (page 149) was added to the MD driver.
- The *PES scan* (page 69) task can now use all *geometry optimizers* (page 55). Previously it was limited to using the Quasi-Newton optimizer. This will make pure *lattice PES scans* (page 71) (e.g. energy-volume scans) with fast *engines* (page 270) and large cells much faster.
- The `GeometryOptimization%Convergence%Quality` keyword can now be used to *easily tighten or relax all convergence thresholds* (page 49) for geometry optimizations at once.
- The calculation of normal modes now also calculates and prints the reduced masses and force constants of the individual modes.
- The *PES point characterization* (page 200) now uses the force constants instead of the vibrational frequencies to identify transition states, making it more reliable in the presence of numerical noise.
- Environment variables in the input will now be *expanded* (page 11).
- The default value of `VibrationalAnalysis%Displacement` has been changed to 0.005 Bohr, related to precision issues with derivatives of polarizability.
- The calculation of the *vibronic density of states* (page 253) for transfer phenomena using the Adiabatic-Hessian Franck-Condon formalism has been added.
- Calculation of *vibrational polarizabilities* (page 244) under the harmonic approximation.
- For the *PES exploration* (page 169) task, it is now possible to *read an energy landscape and/or add states from the input file* (page 189). The algorithm for detecting and labeling *binding sites* (page 193) was enhanced. Importantly, the *Landscape Refinement* (page 187) job can now be run in parallel.

1.2.4 New in AMS2022.1

- The MD driver now supports Rattle/Shake methods for *constrained molecular dynamics simulations* (page 100). The *FIRE optimizer* (page 59) now supports *distance constraints* (page 52).
- The *PES scan* (page 69) task now allows the *scanning of lattice degrees of freedom* (page 71).
- The *molecule gun* (page 116) now supports the *generation of molecule mixtures* (page 121) through the `Mole-Fraction` keyword.
- The *Replay task* (page 160) for recomputing properties for trajectory frames with a different engine.
- The *PES exploration* (page 169) can now include *fragmented states* (page 185) in the energy landscape when studying adsorption processes.

- A new option allows *Geometry optimizations* (page 47) with *PES point characterization* (page 200) and no *symmetry* (page 35) to converge more reliably to minima instead of transition states or higher order saddle points: in case a geometry optimization converges to a TS, it can will now *automatically restart* (page 51) after displacing all atoms along the imaginary mode.
- The calculation of Franck-Condon factors with the *FCF program* (page 245) has been improved regarding precision, speed, and memory requirements.

1.2.5 New in AMS2021.1

- *PES exploration* (page 169) tasks for the automated discovery of stationary points on the potential energy surface.
  1. *Process Search* (page 178): a composite method for finding escape mechanisms from a state. This will find both local minima and their connecting saddle points.
  2. *Basin Hopping* (page 183): a Monte Carlo method for finding local minima.
  3. *Saddle Search* (page 180): a single-ended method for finding nearby saddle points.
- *Force bias Monte Carlo* (page 146) is now available in AMS, enabling pure MC or mixed MD/MC simulations with any engine.
- The *molecule gun* (page 116) can now generate random shooting directions in a given cone.
- A new *wall potential* (page 287) engine add-on can be used to simulate spherical nanoreactors.
- The *D4 dispersion add-on* (page 279) can now also be used for calculations on periodic systems.
- Graceful interactive termination of running jobs through the *interactive input file* (page 15).
- *Geometry optimizations* (page 47) write the optimized geometry to the results directory as an *extended XYZ file* (page 487).

1.2.6 New in AMS2020.1

- ADF has been fully integrated as an AMS engine.
- New engines: MLPotential implementing several different type of machine learning (ML) potentials. A Hybrid engine for combining other engines in QM/MM calculations. Enhanced ForceField engine (formerly UFF).
- Improvements to the *Quasi-Newton geometry optimizer* (page 57): Periodic systems can now be optimized in delocalized coordinates. Better performance for systems made up of disconnected fragments.
- Geometry optimization can now be performed with *frozen and equal strain constraints* (page 55) for the lattice degrees of freedom. This option is currently only available with the *FIRE optimizer* (page 59).
- Support for *external electric fields* (page 38): Homogeneous as well as multipole charges.
- Enhanced support for *vibrational spectroscopy* (page 207): (resonance) Raman, (resonance) vibrational Raman optical activity, vibrational circular dichroism.
- The MD driver now supports time-dependent *lattice deformations* (page 113) as well as a method for accelerating bonding reactions (*Bond Boost method* (page 133)).
- Reactive MD calculations with the AMS driver can now be analyzed with ChemTraYzer.
- It is now possible to selectively disable writing some parts of a *MD trajectory* (page 108) to save space.
- More *trajectory analysis* (page 348) options: *autocorrelation functions* (page 356) and *diffusion coefficient* (page 373)
- The *molecular composition analysis* (page 266) can now be done with respect to an adsorption support region.

- The *transition state search* (page 66) task now allows the users to specify an approximate reaction coordinate (TSRC).
- For the calculation of normal modes, the *Mobile Block Hessian* (page 213) method now allows to treat parts of the system as rigid blocks.
- New coordinates for *constrained geometry optimizations* (page 52) and *PES scans* (page 69): Sum of distances and difference of distances.
- Added the ability to include additional potential terms (i.e. springs) through the *Restraints engine add-on* (page 284).
- A running AMS driver process can be used from Python through the new AMSWorker class in the PLAMS library. The communication between PLAMS and the AMS driver happens via the new *Pipe interface* (page 25) protocol.
- Introduced *Regions* (page 36) to simplify the input syntax for options that apply to a subset of atoms only.
- Symmetrization of systems from the input and the option to input a Z-matrix.
- Low frequencies contribution to *thermodynamics properties* (page 229) can be corrected using a free rotor interpolation method.

1.2.7 New in AMS2019.3

- The *Nudged elastic band method (NEB)* (page 76) for finding minimum energy paths of transitions has been added.
- The new *PES point character property* (page 200) can be used to quickly calculate a few of the lowest vibrational modes of a system and to verify the success of a geometry optimization or transitions state search.
- *Driver level parallelism* (page 21) is now enabled and managed automatically, improving the performance and scalability of many applications.
- A *Mode Scanning* (page 215) calculation can now be *started automatically* (page 211) for all modes within a specific frequency range.
- Methods for the quick calculation of the *vibrationally resolved electronic spectra* (page 244): *Vibronic-Structure Refinement* (page 257) and *Vibronic-Structure Tracking* (page 256).
- New geometry optimizer available: *Limited-memory BFGS* (page 61)
- Input keywords that expect lists of numbers can now be specified as *ranges using a Python slice-like notation* (page 12). Input keywords that expect a single real number now also accept fractions (of integers).
- New option to include a *non-isotropic external stress* (page 282) for 1D,2D and 3D periodic systems. This can be used to study structural deformation and mechanical properties of materials under non-isotropic stress.
- New *add-on system* (page 278) for manipulating and augmenting the results returned from the *engines* (page 270):
  1. Grimme's D4 and D3 dispersion corrections can be used with any engine through the *D4Dispersion and D3Dispersion add-ons* (page 279).

1.2.8 New in AMS2019.1

- *Intrinsic Reaction Coordinate (IRC) Scan* (page 84) in now available in the AMS driver for molecular and periodic systems.
- Support for the *Grand Canonical Monte Carlo (GCMC)* (page 161) method has been added in the AMS driver.
- Molecular composition analysis for molecular dynamics simulations (see tutorial)
- *Collective Variable-driven Hyperdynamics (CVHD)* (page 126)
- *Molecule gun* (page 116) and *molecule sink* (page 121) for molecular dynamics

- *PLUMED library support* (page 124) for MD analysis and a wide variety of free energy methods
- The initial symmetry of a system is enforced during geometry optimizations with the Quasi-Newton optimizer.
- *Thermodynamic properties* (page 229) (assuming an ideal gas) are automatically computed after normal modes calculations.
- *Partial vibrational density of states (PVDOS)* (page 233) for normal modes.
- The system's symmetry is used to accelerate numerical nuclear derivatives and to provide symmetry labels for normal modes.
- The AMS driver starts up much faster, significantly speeding up scripting applications that launch AMS many times.
- New tools for mode selective vibrational analysis:
  1. *Mode Scanning* (page 215) (aka ADF's ScanFreq)
  2. *Mode Refinement* (page 216) (aka "Frequency range selection")
  3. *Mode Tracking* (page 219)

1.3 Motivation and progress

The Amsterdam Modeling Suite has grown substantially over the last decade, and in the 2017 release included programs implementing methods all the way from accurate density functional theory, through semi-empirical methods, to fast reactive force fields. Many of these programs have originally been developed by academic groups and are now maintained and expanded by SCM in collaboration with the original authors.

This rapid growth of the Amsterdam Modeling Suite had, however, led to a certain degree of unnecessary inhomogeneity within the suite: The input for the same task, e.g. a geometry optimization, differed quite a lot between the different programs in the suite. While this problem was mostly hidden for users of the graphical interface, it constituted a barrier for users of the new scripting frameworks such as PLAMS. Furthermore, the different programs produced rather different output files for the same task, making the automated extraction of results unnecessarily difficult. Finally, and most importantly, the rapid growth of the AMS suite had also led to a certain level of feature fragmentation, where some features were available in one program but not the other: ADF, for example, was able to do a linear transit calculation, while BAND was not. Constrained geometry optimization was supported in DFTB, but not in UFF. ReaxFF could be used for Grand Canonical Monte Carlo simulations, but DFTB could not.

In order to overcome these issues and make the Amsterdam Modeling Suite more powerful and user friendly, we introduced the AMS driver program with the 2018 release of the suite. The idea of this reorganization is to have only a single program called the AMS driver that under the hood uses the so-called "engines" like ADF, BAND and DFTB for the calculation of energies and gradients, where the engines are technically no longer separate programs but just libraries used by the AMS driver. In this way much of the input and output of AMS is the same, no matter which particular engine is used for a calculation. It also avoids the feature fragmentation, since any new feature in the AMS driver can immediately be used with all engines in the suite. Furthermore, the AMS driver also allows running *external programs as an engine* (page 274) providing energies and gradients, allowing end-users to perform all calculations supported by AMS with virtually any atomistic modeling program they have access to and to visualize the results in the graphical user interface of the Amsterdam Modeling Suite.

Converting all the programs of the Amsterdam Modeling Suite into engine libraries that are used by the AMS driver was a big reorganization of the entire suite, which was spread out over multiple releases between 2018 and 2020. As of the AMS2020 release, ADF itself has been integrated into the AMS driver, making the integration of all engines into the AMS driver finally complete. (The only exception is QuantumEspresso, which is integrated into the GUI, but has no connection to the AMS driver in the 2020 release.)

As with any large reorganization, it is unavoidable that some things change. For GUI users this should not create any issues, but users familiar with the existing command line and scripting interfaces will notice these changes and their existing workflows might need to be adjusted to the new setup. We know that these kind of changes can be disrupting for existing users, and where possible we try to keep backwards compatibility with previous versions, but unfortunately this is not always possible. However, overall AMS provides a much more consistent and convenient interface to command line and scripting users, and we believe that the new simplicity and expanded feature set of AMS make transitioning to the new framework well worth the effort.

1.4 Input, execution and output

With the introduction of AMS in the 2018 release of the Amsterdam Modeling Suite, there were some changes in the input and output files and formats used by our software. Users of the graphical interface should not notice these changes, but people using the software from the command line or through the scripting frameworks need to be aware of them.

This section contains the main changes. For a more complete description see:

- The extended *Input, execution and output section* (page 9).

Generally the input for AMS has the block and keyword structure that most programs in the Amsterdam Modeling Suite have already been using. See the *General remarks on input structure and parsing* (page 11) section for more details. The only new construct in the AMS input is a special `Engine` block, that selects which engine is used for the simulation and also contains all the details of its configuration. This is probably best illustrated by an example. Let us look at the following AMS input, which optimizes the geometry of the methane molecule and calculates its normal modes of vibration at the optimized geometry:

```
$AMSBIN/ams << EOF
   Task GeometryOptimization

   GeometryOptimization
      Convergence
         Gradients 1.0e-4
      End
   End

   Properties
      NormalModes true
   End

   System
      Atoms
         C       0.00000000       0.00000000       0.00000000
         H       0.63294000      -0.63294000      -0.63294000
         H      -0.63294000       0.63294000      -0.63294000
         H       0.63294000       0.63294000       0.63294000
         H      -0.63294000      -0.63294000       0.63294000
      End
   End

   Engine DFTB
      Model DFTB3
      ResourcesDir DFTB.org/3ob-3-1
   EndEngine
EOF
```

Note how DFTB is selected as the engine in the `Engine DFTB` line that opens the `Engine` block. All DFTB specific configuration is contained within this engine block, which is terminated by `EndEngine`. The fact that we want to run a geometry optimization with normal modes for methane and things like convergence criteria for the optimization are of course completely independent from which engine is actually used to perform this calculation. Therefore they are all found *outside* of the `Engine` block. In this sense, the AMS input is split up into the driver level input (everything outside of the engine block) and the engine input, which is just a single `Engine` block. This separation makes it easy to perform the same calculation at a different level of theory, by simply switching out the `Engine` block in the input. We could, for example, repeat the same calculation at the DFT-GGA level using the Band engine:

```
Engine BAND
    XC
       GGA PBE
    End
EndEngine
```

Engines like ADF and BAND that have many options and can calculate many properties, consequently also have a large number of possible keywords in their input. In order to have a better structured documentation we have split off the description of the engine inputs into separate *engine specific manuals* (page 270), while this AMS manual only documents the driver level keywords outside of the `Engine` block. All the engine specific options are found in the respective engine's manual, which documents the keywords in its `Engine` block. In general all engines can be used with all tasks in AMS. There are only a few rather obvious restrictions, for example that only engines which can handle periodic systems can be used for the calculation of phonons.

The introduction of the `Engine` block is the only real change AMS brings to the input side of things. On the output side there are a few more changes.

The first change to the output is that AMS does not put any of its output files into the present working directory, as virtually all of the standalone programs in the suite did. Instead AMS creates a `*.results` directory, which collects all result file associated with a job. Here `*` is replaced by the jobname, which is set with the `AMS_JOBNAME` environment variable:

```
AMS_JOBNAME=methane $AMSBIN/ams << EOF

... see above ...

EOF
```

This would put all results related to our geometry optimization of methane into the newly created folder `methane.results`. (The default name of the results folder is `ams.results` if `AMS_JOBNAME` is not set, see the *environment variables* (page 20) section of this manual for documentation of all environment variables used by AMS.) In this way users can easily run multiple jobs in the same directory without danger of clashing output files, which was a common problem before the introduction of AMS. This new setup is also more consistent with the graphical user interface, which already collected all files associated with a specific job into a dedicated results directory. Note that AMS will by default **not overwrite** results directories if a job is rerun or another job is run with the same jobname.

Inside of the results directory users will always find the logfile `ams.log`, which is written during a running calculation and can be used to monitor its progress. Furthermore the results directory contains binary result files in the KF format, which can be opened and inspected with the KFBrowser GUI component.

- The main `ams.rkf` written by the AMS driver. It contains high level information about the trajectory that the AMS driver took over the potential energy surface. For example, for a molecular dynamics simulation it would contain the full trajectory. The format in which this information is written is independent from which engine was used for a calculation.
- The engine specific main binary output file written by the engine (and partly by the AMS driver). This file is kept for only one special point, e.g. the final geometry in a geometry optimization. For example, for ADF this engine file is called `adf.rkf` (instead of `TAPE21` in ADF<=2019), for BAND `band.rkf`, for DFTB `dftb.rkf`. If a property, like vibrational modes, is tied to the special point on the potential energy surface, it is stored in this file. Also all engine specific properties are written to this file, like orbitals in case of a quantum mechanical engine.
- Additionally there might be a binary output file for every point on the potential energy surface that was visited during the calculation.
- Other engine specific binary (and ASCII) output files written by the engine.

Having multiple different binary output files could be confusing for people that are used to the single result file that was written by the standalone programs in ADF<=2017. After all, it brings up the question in which file the desired property is stored. The general rule is: if the property is tied to a particular point on the potential energy surface, it is stored in the engine output file belonging to that particular point. If the information depends on the entire trajectory over the PES, it is found in the main `ams.rkf` written by the AMS driver.

CHAPTER

TWO

INPUT, EXECUTION AND OUTPUT

2.1 Input

The input for AMS has a block and keyword structure. See the *General remarks on input structure and parsing* (page 11) section for more details.

The input keys *System* (page 31), *Task* (page 10), and *Engine* (page 270), are obligatory. Most other input keys in AMS are optional, like *Properties* (page 10). In the rest of this manual one can find all input keys for AMS.

The Engine specific input can be found in the respective Engine Manuals, for example, the manual for ADF, BAND, DFTB, ForceField, MOPAC, and ReaxFF.

2.1.1 Example

The AMS input has a special `Engine` block, that selects which engine is used for the simulation and also contains all the details of its configuration. This is probably best illustrated by an example. Let us look at the following AMS input, which optimizes the geometry of the methane molecule and calculates its normal modes of vibration at the optimized geometry:

```
$AMSBIN/ams << EOF
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   Properties
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   System
      Atoms
         C       0.00000000       0.00000000       0.00000000
         H       0.63294000      -0.63294000      -0.63294000
         H      -0.63294000       0.63294000      -0.63294000
         H       0.63294000       0.63294000       0.63294000
         H      -0.63294000      -0.63294000       0.63294000
      End
   End

   Engine DFTB
       Model DFTB3
```

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```
       ResourcesDir DFTB.org/3ob-3-1
   EndEngine
EOF
```

Note how DFTB is selected as the engine in the `Engine DFTB` line that opens the `Engine` block. All DFTB specific configuration is contained within this engine block, which is terminated by `EndEngine`. The fact that we want to run a geometry optimization with normal modes for methane and things like convergence criteria for the optimization are of course completely independent from which engine is actually used to perform this calculation. Therefore they are all found *outside* of the `Engine` block. In this sense, the AMS input is split up into the driver level input (everything outside of the engine block) and the engine input, which is just a single `Engine` block. This separation makes it easy to perform the same calculation at a different level of theory, by simply switching out the `Engine` block in the input. We could, for example, repeat the same calculation at the DFT-GGA level using the Band engine:

```
Engine BAND
    XC
       GGA PBE
    End
EndEngine
```

Engines like ADF or BAND that have many options and can calculate many properties, consequently also have a large number of possible keywords in their input. In order to have a better structured documentation we have split off the description of the engine inputs into separate *engine specific manuals* (page 270), while this AMS manual only documents the driver level keywords outside of the `Engine` block. All the engine specific options are found in the respective engine's manual, which documents the keywords in its `Engine` block. In general all engines can be used with all tasks in AMS. There are only a few rather obvious restrictions, for example that only engines which can handle periodic systems can be used for the calculation of phonons.

2.1.2 Tasks

The key `Task` is described in more detail in the section *Structure, Reactivity, and Molecular Dynamics* (page 45). The Task VibrationalAnalysis is described in more detail in the section *Vibrational Spectroscopy* (page 207) (Mode Scanning, Mode Refinement, Mode Tracking, VG-FC Resonance Raman) and in the section *Vibrationally resolved electronic spectra* (page 244) (VG-FC: Vertical Gradient Franck-Condon).

Below the possible arguments for `Task` are given.

```
Task [GCMC | GeometryOptimization | IRC | MolecularDynamics | NEB | PESExploration |␣
↪PESScan |
      Replay | SinglePoint | TransitionStateSearch | VibrationalAnalysis]
```

2.1.3 Properties

The block key `Properties` is described in more detail in the section *Gradients, Hessian, Stress tensor, Elasticity* (page 198), in the section *Vibrational Spectroscopy* (page 207), and in the section *Dipole moment, Polarizability, Bond orders* (page 264).

Below the possible `Properties` are summarized.

```
Properties
   BondOrders Yes/No
   Charges Yes/No
   DipoleGradients Yes/No
```

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```
   DipoleMoment Yes/No
   ElasticTensor Yes/No
   GSES Yes/No
   Gradients Yes/No
   Hessian Yes/No
   Molecules Yes/No
   NormalModes Yes/No
   OrbitalsInfo Yes/No
   Other Yes/No
   PESPointCharacter Yes/No
   Phonons Yes/No
   Polarizability Yes/No
   Raman Yes/No
   SelectedRegionForHessian string
   StressTensor Yes/No
   VCD Yes/No
   VROA Yes/No
End
```

2.1.4 General remarks on input structure and parsing

- Most keys are optionals. Defaults values will be used for keys that are not specified in the input
- Keys/blocks can either be *unique* (*i.e.* they can appear in the input only once) or *non-unique*. (i.e. they can appear multiple times in the input)
- The order in which keys or blocks are specified in the input does not matter. Possible exceptions to this rule are a) the content of non-standard blocks b) some non-unique keys/blocks)
- Comments in the input file start with one of the following characters: `#`, `!`, `::`

```
# this is a comment
! this is also a comment
:: yet another comment
```

- Empty lines are ignored
- The input parsing is **case insensitive** (except for string values):

```
# this:
UseSymmetry false
# is equivalent to this:
USESYMMETRY FALSE
```

- Indentation does not matter and multiple spaces are treaded as a single space (except for string values):

```
# this:
     UseSymmetry     false
# is equivalent to this:
UseSymmetry false
```

- Environment variables in the input will be replaced by their value. We only support simple substitution of variables (optionally surrounded by `{}`). All other parameter expansion features of the POSIX shell (https://pubs.opengroup.org/onlinepubs/9699919799/utilities/V3_chap02.html#tag_18_06_02) (e.g. default values) are **not** supported. Expansion of a variable can be prevented by prefixing the leading dollar (`$`) with a backslash (`\`). Note that variables which are not set will expand to an empty string, just like in a shell:

```
File $SOME_DIRECTORY/file.txt
File ${SOME_DIRECTORY}_BACKUP/file.txt
Key  \$WILL_NOT_EXPAND
```

2.1.5 Keys

Key-value pairs have the following structure:

```
KeyName Value
```

Possible types of keys:

bool key The value is a single Boolean (logical) value. The value can be `True` (equivalently `Yes`) or `False` (equivalently `No`.). Not specifying any value is equivalent to specifying `True`. Example:

```
KeyName Yes
```

integer key The value is a single integer number. Example:

```
KeyName 3
```

float key The value is a single float number. For scientific notation, the E-notation is used (e.g. -2.5×10^{-3} can be expressed as `-2.5E-3`). The decimal separator should be a dot (`.`), and **not** a comma (`,`). Example:

```
KeyName -2.5E-3
```

Note that fractions (of integers) can also be used:

```
KeyName 1/3    (equivalent to: 0.33333333333...)
```

string key The value is a string, which can include white spaces. Only ASCII characters are allowed. Example:

```
KeyName Lorem ipsum dolor sit amet
```

multiple_choice key The value should be a single word among the list options for that key (the options are listed in the documentation of the key). Example:

```
KeyName SomeOption
```

integer_list key The value is list of integer numbers. Example:

```
KeyName 1 6 0 9 -10
```

Note that one can also specify ranges of integers by specifying the interval and (optionally) the step size separated by colons:

```
KeyName 1:5        (equivalent to: 1 2 3 4 5)
KeyName 2:10:2     (equivalent to: 2 4 6 8 10)
KeyName 20:10:-2   (equivalent to: 20 18 16 14 12 10)
```

Note also that ranges can be freely combined with individual numbers:

```
KeyName 1:5 10 20  (equivalent to: 1 2 3 4 5 10 20)
```

float_list key The value is list of float numbers. The convention for float numbers is the same as for Float keys. Example:

```
KeyName 0.1 1.0E-2 1.3
```

Float lists can also be specified as a range with equidistant points, by specifying the interval's boundaries (inclusive) as well as the number of desired subintervals separated by colons:

```
KeyName 1.0:1.5:5  (equivalent to: 1.0 1.1 1.2 1.3 1.4 1.5)
```

Range specifications can be freely combined with each other and single numbers:

```
KeyName 0.0 1.0:1.5:5 2.0:3.0:10
```

2.1.6 Blocks

Blocks give a hierarchical structure to the input, grouping together related keys (and possibly sub-blocks). In the input, blocks generally span multiple lines, and have the following structure:

```
BlockName
   KeyName1 value1
   KeyName2 value2
   ...
End
```

Headers

For some blocks it is possible (or necessary) to specify a *header* next to the block name:

```
BlockName someHeader
   KeyName1 value1
   KeyName2 value2
   ...
End
```

Compact notation

It is possible to specify multiple key-value pairs of a block on a single line using the following notation:

```
# This:
BlockName KeyName1=value1 KeyName2=value2

# is equivalent to this:
BlockName
   KeyName1 value1
   KeyName2 value2
End
```

Notes on compact notation:

- The compact notation cannot be used for blocks with headers.
- Spaces (blanks) between the key, the equal sign and the value are ignored. However, if a value itself needs to contain spaces (e.g. because it is a list, or a number followed by a unit), the entire value must be put in either single or double quotes:

```
# This is OK:
BlockName Key1=value Key2 = "5.6 [eV]" Key3='5 7 3 2'
# ... and equivalent to:
```

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```
BlockName
   Key1  value
   Key2  5.6 [eV]
   Key3  5 7 3 2
End

# This is NOT OK:
BlockName Key1=value Key2 = 5.6 [eV] Key3=5 7 3 2
```

Non-standard Blocks

A special type of block is the *non-standard block*. These blocks are used for parts of the input that do not follow the usual key-value paradigm.

A notable example of a non-standard block is the `Atoms` block (in which the atomic coordinates and atom types are defined).

2.1.7 Including an external file

You can include an external ASCII file in the input with the `@include` directive:

```
@include FileName.in
@include "file name with spaces.in"
```

The file name should include the path, either absolute or relative to the run-directory. The content of the file is included in the input at the point where the `@include` directive occurs. The `@include` directive may occur any number of times in the input.

The `@include` feature makes it easy to pack your preferred settings in one file and use them in every run with minimum input-typing effort.

2.1.8 Units

Some keys have a default unit associated (not all keys have units). For such keys, the default unit is mentioned in the key documentation. One can specify a different unit within square brackets at the end of the line:

```
KeyName value [unit]
```

For example, assuming the key `EnergyThreshold` has as default unit `hartree`, then the following definitions are equivalent:

```
# Use defaults unit:
EnergyThreshold 1.0

# use eV as unit:
EnergyThreshold 27.211 [eV]

# use kcal/mol as unit:
EnergyThreshold 627.5 [kcal/mol]

# hartree is the atomic unit of energy:
EnergyThreshold 1.0 [hartree]
```

Available units:

- **Energy**: `hartree`, `joule`, `eV`, `kJ/mol`, `kcal/mol`, `cm1`, `MHz`
- **Forces**: `hartree/bohr`, `eV/bohr`, `hartree/angstrom`, `eV/angstrom`, `kcal/mol/angstrom`, `kJ/mol/angstrom`
- **Length**: `bohr`, `angstrom`, `meter`
- **Angles**: `radian`, `degree`
- **Mass**: `el`, `proton`, `atomic`, `kg`
- **Pressure**: `atm`, `pascal`, `GPa`, `a.u.`, `bar`, `kbar`
- **Electric field**: `V/angstrom`, `V/meter`, `a.u.`

2.2 Execution

2.2.1 Shell script

The AMS driver reads its input from standard input, i.e. what is called `STDIN` on Unix-like systems. Technically it is possible to run AMS and type the input file in interactively. This is however highly impractical and most people run AMS from a small shell script that contains the AMS text input and sends it directly to the AMS executable. For example, the content of the file 'example.run' could be like:

```
#!/bin/sh

$AMSBIN/ams << EOF

   ... AMS text input goes here:

   Block
      Keywork value
      OtherKeyword value
   End

EOF
```

The shell script 'example.run' needs be executable, if it isn't you will need to make it executable, e.g. `chmod u+x example.run`. The 'example.run' file needs to be executed as a shell script, not as input to AMS.

```
./example.run > example.out
```

2.2.2 Interactive input file

As of the 2021.1 version the AMS driver has the concept of an interactive input file. The interactive input file is a second input file, that users may create in the *results directory* (page 18) of an already running job to interact with it. The name of the interactive input file is `interactive.in`. Note that the file does not exist by default, but has to be created by the user wanting to interact with the running AMS job.

In AMS2021.1 the interactive input file may be used to request the graceful and orderly termination of a job.

```
echo "Stop" > ams.results/interactive.in
```

`Stop`

Type Bool

Default value No

Description Makes the AMS driver stop execution in an ordered manner at the next opportunity. This will not interrupt the execution in the middle of the numerical calculation of a PES point property (e.g. a Hessian).

It is generally preferably to request the termination through the interactive input file over killing a job at the operating system level. This makes sure that the job stops at a logical point and still has time to write intermediate results to disk, making restarting from such jobs easier and more reliable. From the graphical user interface, the stopping can be requested in AMSjobs by selecting the running job and clicking **Job → Request Early Stop** in the menu bar.

As of AMS2021.1, the tasks that can be stopped through the interactive input file are:

- *Molecular dynamics* (page 91) simulations will stop at the next sampling or checkpoint as if the maximum number of steps had been reached.
- *Geometry optimizations* (page 47) will stop after the current iteration and be considered converged. This can be used if a geometry optimization does not make progress anymore, e.g. because the convergence thresholds are set tighter than the noise level of the used engine.
- *Nudged elastic band* (page 76) calculations will stop after the current iteration (i.e. the calculations for all images) is complete.
- *PES scans* (page 69) will interrupt the currently running geometry optimization and skip the optimization for all further PES points.
- *PES explorations* (page 169) will terminate after the currently running expedition. No new explorers will be dispatched, but currently active explorers will be allowed to finish.

Note that the `Stop` keyword in the interactive input file will not interrupt the job in the middle of the numerical calculation of a *PES point property* (page 264), such as a Hessian or stress tensor. It will also never stop a job that is currently running an engine, and will hence not stop an engine that is calculating these properties analytically. It is possible to interrupt the numerical calculation of *PES point properties* (page 264) using the `StopProperties` keyword. We advise users to be careful with this keyword and always combine it with the `Stop` keyword, as it is generally not possible to skip the evaluation of properties, but continue with a task as the AMS driver level. (After all, the driver may need the properties that we interrupt.)

```
echo "Stop" > ams.results/interactive.in
echo "StopProperties" >> ams.results/interactive.in
```

`StopProperties`

Type Bool

Default value No

Description Makes the AMS driver stop execution during the evaluation of PES point properties. This may for example be used to interrupt the numerical calculation of a Hessian. Note that this just works at the level of the loops used for the **numerical** calculation of the properties, so engines which calculate a property analytically may not be interruptible using this keyword. It is recommended to use this keyword in combination with the generic `Stop` keyword.

As of AMS2021.1 it is not possible to restart the calculation of properties that were interrupted like this. Hence the use of the `StopProperties` keyword is limited.

2.2.3 Running AMS on compute clusters

AMS is parallelized with MPI and can therefore be run in parallel on distributed memory machines, aka compute clusters. See the installation manual for general documentation on how to set up and run all the programs from the Amsterdam Modeling Suite on compute clusters. In this section we give some more advice that is specific to the AMS driver and its engines.

Normally users use the login node to prepare their jobs and input files somewhere in their home directory, and also want the results of their jobs to end up there. Quite often, compute clusters are set up such that the user's home directory is also mounted on the compute nodes, usually via NFS (Network File System). Before the introduction of the AMS driver it was not recommended to `cd` to the home directory in the submission script and have the compute nodes execute the job directly there. This was simply due to the fact that a lot of file I/O was done on temporary files in the present working directory, which in this case would be on a slow network-mounted file system.

On the other hand, with AMS, switching to the home directory is the preferred way of running on a cluster where the home directory is mounted on the compute nodes. Running in the home directory mounted over NFS does not come with a performance penalty for AMS, but has many advantages. This is because AMS and its engines are already built under the assumption that access to this directory is slow. Basically there are three directories that are used by the AMS driver and its engines:

1. The **starting directory**, i.e. the present working directory at the time the AMS driver is started. This folder is generally read-only for AMS, except for creating the results directory there at the beginning of a calculation. Note that all relative paths in the AMS input, e.g. for loading results from previous calculations, are relative to the starting directory. The starting directory is assumed to be on a slow filesystem, but since data is normally only read once from there in the beginning of a calculation, this is in practice not a problem.
2. The **results directory**, where the results of a calculation as well as important intermediate steps (e.g. restart files) are collected. It also contains the log file which can be used to monitor a running calculations. The results directory is assumed to be on a slow filesystem, so AMS and its engines will be very careful not to do much disk I/O there. Generally something is only written to the results directory when AMS is sure that it should remain on disk when the calculation finishes. The results directory can also contain some intermediate restart files, so the contents of the result directory should be all that is needed in case the calculation crashes or is killed before it finishes normally.
3. The **scratch directory**, the location of which is set with the `$SCM_TMPDIR` environment variable, see also the installation manual. This directory should be put on a fast disk, e.g. an SSD in the compute node, as it will be used to store temporary results on disk. Users do not really need to care or know about the temporary files in the scratch directory. Normally, any files and directories created in the scratch directory are cleaned up at the end of the calculation. In case of errors, AMS tries to copy anything useful (e.g. the text output of all the different ranks) to the results directory in order to make finding the problem easier. However, for some kinds of crashes (or if the `SIGKILL` signal is sent to AMS), the cleanup of the scratch directory might not be performed, in which case users might want to manually check or remove the `amstmp_*` folders in the scratch directory.

With this setup there is no performance penalty for running directly on a network mounted home directory: Results will just be put there immediately, instead of being copied there at the end of a calculation.

Normally all batch systems provide an environment variable that is set to the directory from which the job was submitted, which is then where one should `cd` in the run script:

```
#!/bin/sh

if [ -z "$PBS_O_WORKDIR" ]; then
   # PBS batch system
   cd "$PBS_O_WORKDIR"
elif [ -z "$SLURM_SUBMIT_DIR" ]; then
   # Slurm batch system
   cd "$SLURM_SUBMIT_DIR"
elif [ -z "..." ]; then
   # add other batch systems as necessary ...
```

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```
   cd "..."
fi

export AMS_JOBNAME=myJob

$AMSBIN/ams << EOF

   # Normal AMS text input, but with all paths
   # relative to where the job was submitted from, e.g.:
   LoadSystem previousJob.results/ams.rkf

EOF
```

With this runscript the AMS driver would make a `myJob.results` folder in the directory where the job was submitted from, and there is no need to copy results around manually in the run script. Furthermore this runscript always produces exactly the same files in the same locations, no matter if it is run interactively or submitted to a compute node through the batch system. Furthermore all paths in the input file can be specified relative to the location from where the runscript is submitted (normally the folder in which the runscript is located). This removes the need to copy or specify absolute paths to previous results, e.g. when restarting calculations. Finally, files useful for monitoring the running calculation are also conveniently there and not hidden somewhere on the compute node.

2.3 Output

AMS produces two ASCII files: standard output and the `ams.log` file, and produces several binary output data files. The `ams.log` file is a very concise summary of the calculation's progress during the run. The binary output data files contain job characteristics and computational results produced by AMS and the Engine. Part of what is written to the binary output files is also written in a human readable form to standard output.

2.3.1 Results directory

Note that AMS does not put any of its binary output files and the `ams.log` file into the present working directory, as virtually all of the standalone programs in the suite did. Instead AMS creates a `*.results` directory, which collects all result file associated with a job. Here `*` is replaced by the jobname, which is set with the `AMS_JOBNAME` environment variable:

```
AMS_JOBNAME=methane $AMSBIN/ams << EOF

   ... see Input example before ...

EOF
```

This would put all results related to our geometry optimization of methane into the newly created folder `methane.results`. (The default name of the results folder is `ams.results` if `AMS_JOBNAME` is not set, see the *environment variables* (page 20) section of this manual for documentation of all environment variables used by AMS.) In this way users can easily run multiple jobs in the same directory without danger of clashing output files, which was a common problem before the introduction of AMS. This new setup is also more consistent with the graphical user interface, which already collected all files associated with a specific job into a dedicated results directory. Note that AMS will by default **not overwrite** results directories if a job is rerun or another job is run with the same jobname.

2.3.2 Logfile ams.log

Inside of the results directory users will always find the logfile `ams.log`, which is written during a running calculation and can be used to monitor its progress.

The logfile `ams.log` is generated during the calculation and flushed after (almost) each message that is sent to it by the program. Consequently, the user can inspect it and see what is going on without being delayed by potentially large system I/O buffers. Each message contains date and time of the message plus additional info.

Be alert on error messages. Take them seriously: inspect the standard output carefully and try to understand what has gone wrong. Be also alert to warnings. They are not necessarily fatal but you should understand what they are about before being satisfied with the results of the calculation. Do not ignore them just because the program has not aborted: in some cases the program may not be able to determine whether or not you really want to do what appears to be wrong or suspicious. If you believe that the program displays erratic behavior, then the standard output file may contain more detailed information. Therefore, in such case save the complete standard output file, together with the logfile `ams.log`, in case we need these files for further analysis.

2.3.3 Binary output files

The results directory contains binary result files in the KF format, which can be opened and inspected with the KFbrowser GUI component. KF stands for Keyed File: KF files are keyword oriented, which makes them easy to process by simple procedures. KF files are Direct Access binary files.

- The main `ams.rkf` written by the AMS driver. It contains high level information about the trajectory that the AMS driver took over the potential energy surface. For a geometry optimization it would for example contains the history of how the systems geometry changed during the optimization as well as the final optimized geometry. For a molecular dynamics simulation it would contain the full trajectory. The format in which this information is written is independent from which engine was used for a calculation.

Note: For a full description of the data on the `ams.rkf` file, see the *KF output files* (page 721) page.

- The engine specific main binary output file written by the engine (and partly by the AMS driver). This file is kept for only one special point, e.g. the final geometry in a geometry optimization. The ADF engine writes `adf.rkf` (instead of `TAPE21` in older versions). The BAND engine writes band.rkf (instead of `RUNKF` in older versions). The DFTB engine writes `dftb.rkf`. If a property, like vibrational modes, is tied to this special point on the potential energy surface, it is stored in this file. Also all engine specific properties are written to the main binary output file, like orbitals in case of a quantum mechanical engine.

Table 2.1: Engine specific main binary output file

Engine	**main file**
ADF	adf.rkf
BAND	band.rkf
DFTB	dftb.rkf
ForceField	forcefield.rkf
MOPAC	mopac.rkf
ReaxFF	reaxff.rkf
External	external.rkf
MLPotential	mlpotential.rkf
ASE	ase.rkf
QuantumEspresso	quantumespresso.rkf

- Additionally there might be an engine specific binary output file for every point on the potential energy surface that was visited during the calculation. Like the engine specific main binary output file they contain information tied to a specific point on the potential energy surface. These engine output files all have the extension `.rkf`, but their filename is usually somehow descriptive of the point on the PES that they correspond to. Note that one does not always get an engine output file for every PES point that was visited during the calculation. For most applications this would just be too much data.

- Other engine specific binary (and ASCII) output files written by the engine.

Having multiple different binary output files could be confusing for people that are used to the single result file that was written by the standalone programs in ADF<=2017. After all, it brings up the question in which file the desired property is stored. The general rule is: If the property is tied to a particular point on the potential energy surface, it is stored in the engine output file belonging to that particular point. This includes the Hessian, stress tensor, elastic tensor, normal modes of vibration, phonons, Raman intensities and other vibrational properties. If the information depends on the entire trajectory over the PES, it is found in the main `ams.rkf` written by the AMS driver.

2.3.4 Standard output

The standard ouput file contains in a human readable form part of the job characteristics and computational results produced by AMS and the Engine.

2.3.5 Optimized geometry in xyz format

In case of *Geometry Optimizations* (page 47), the optimized geometry is saved as an *extended XYZ file* (page 487) in the results directory with the name `output.xyz`.

Note that the optimized geometry is also stored in the binary file `ams.rkf` and is printed to the standard output.

2.3.6 AMS environment variables

The behavior of AMS related to the output can be modified through a number of environment variables.

AMS_JOBNAME Sets the name of a job. This name is used to determine the name of the results folder AMS creates, which is `$AMS_JOBNAME.results` or `ams.results` if this environment variable is not set.

AMS_RESULTSDIR If this environment variable is set, instead of creating a new results folder, AMS will use the set directory as the results folder. Not that the directory set here will *not* be created by AMS and therefore has to exist before starting AMS. Note that this environment variable can be used to prevent AMS from creating result folders, by setting `AMS_RESULTSDIR=.`. This reproduces the pre-AMS behavior of putting all result files into the directory from which a job is started.

AMS_SWITCH_LOGFILE_AND_STDOUT If this environment variable is set, AMS will redirect what is normally printed on standard output to a file (`ams.out`) in the results directory. Instead the contents of the log file (`ams.log`) will be printed to standard output while a job is running, allowing users to easily monitor the jobs progress. Note that the log file will still be created normally as if this environment variable was not set. This environment variable is just a convenience feature for users that would always redirect their output into a file and then use `tail -f` on the log file to monitor the running calculation.

This is an example run-script using the `AMS_SWITCH_LOGFILE_AND_STDOUT` and `AMS_JOBNAME` environment variables:

```
#!/bin/sh

# By setting AMS_SWITCH_LOGFILE_AND_STDOUT, the (more compact)
# logfile will be printed to standard output while the full
# text output of the calculation is redirected to the file
```

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```
# ams.out in the ams results folder

export AMS_SWITCH_LOGFILE_AND_STDOUT=true

# By default ams creates a folder 'ams.results' and puts the
# results of the calculation there. If we set AMS_JOBNAME, the
# results folder will instead be called $AMS_JOBNAME.results
# (in this case, 'H2_optimization.results')

AMS_JOBNAME=H2_optimization $AMSBIN/ams <<eor
   System
      Atoms
         H 0 0 0
         H 0 0 1
      End
   End
   Task GeometryOptimization
   Engine DFTB
      Model GFN1-xTB
   EndEngine
eor
```

2.4 Driver level parallelism

See also:

See also the GUI tutorial on the parallel scalability of the calculation of elastic tensors.

AMS is a parallel program using MPI for efficient execution on distributed memory machines, aka compute clusters. For most jobs, the AMS driver part of a calculation is computationally not particularly costly and most of the execution time is spent inside of the *compute engines* (page 270). Therefore the main parallelization of AMS is inside of the engines, making sure that a good performance is obtained for *tasks* (page 45) such as *molecular dynamics* (page 91) or *geometry optimizations* (page 47), which consist of a series of interdependent engine invocations: We need to have completed step n before we can continue with step $n + 1$.

However, not all workloads are of this sequentially dependent type. Some jobs have a lot of independent work, that can be done in parallel. This kind of trivial parallelizability can be exploited at the AMS driver level: Instead of having all cores collaborate on a single PES point and then doing all needed PES points sequentially, we can just distribute the available PES points over the all the available cores. Normally this leads to a better parallel scaling than the default parallelization inside of the engines: Parallelizing the engines is relatively complicated and often requires a lot of communication between cores. Parallelizing on the driver level on the other hand is very easy, and often the only communication required is at the very end of the calculation, when results are collected.

Note that it is perfectly possible to combine both the in-engine parallelization and the driver level parallelism: At the driver level we could split our e.g. in total 32 cores into 4 groups of 8 cores, and then have each group of 8 use the in-engine parallelization to collaborate on a specific calculation. This is especially useful if the total number of cores is larger than then number of independent calculations we have to do. It might also be that we have a very large number of calculations to do, but not enough memory to let every core work alone on its own calculation, as would be ideal from a parallel scaling point of view.

Because of the two levels of parallelism – both at the driver and the engine level – we call this setup **double parallelization**.

Starting with the AMS2019.3 release, driver level parallelism is used and configured automatically. That means that the AMS driver will automatically parallelize at the driver level when it is possible and considered advantageous. As such it should normally not be necessary for users to explicitly configure the driver level parallelism.

Driver level parallelism can be used for the calculation of the *PES point properties* (page 198) which are derivatives, if these need to be done numerically:

- Numerical calculation of *forces / nuclear gradients* (page 199). With a double sided derivative this requires $6 \times n_{\text{atoms}}$ independent calculations on geometries with one atom displaced along a cartesian coordinate.
- Numerical calculation of the *stress tensor* (page 203) for periodic systems. This requires up to 12 calculations for a double sided derivative along the 6 strain directions, but might require less in case some of the strains are symmetry equivalent.
- Numerical calculation of the *Hessian* (page 200) and normal modes of vibration. This is currently only supported for engines that calculate nuclear gradients analytically and done by numerically differentiating this first (analytic) derivative. As such it requires $6 \times n_{\text{atoms}}$ independent calculations on geometries with one atom displaced along a cartesian coordinate.
- Numerical calculation of the *elastic tensor* (page 204). This requires 84 independent geometry optimizations on systems with differently strained lattices, with each optimization having a variable number of steps.
- Numerical calculation of *phonons* (page 233). This requires at most $6 \times n_{\text{atoms}}$ displacements, but might require less in case some of the displacements are symmetry equivalent. Note that the displacements are done in a super cell system, which for many engines will increase the memory requirements, but also improve the in-engine parallel scalability.
- The forward and backward displacements along normal modes for the *Mode Scanning* (page 215), *Mode Refinement* (page 216), and *Mode Tracking* (page 219).

There are also tasks using driver level parallelism, e.g. *Nudged Elastic Band* (page 76), for which the calculations of all the images is trivially parallel.

Details of the driver level parallelism, i.e. how much to parallelize at the driver level, are generally configured for the above mentioned cases on an individual basis, because one might want a different grouping strategy for each case. For each case there is a separate `Parallel` block somewhere in the input (e.g. `ElasticTensor%Parallel` for the calculation of the elastic tensor), which has the following keywords:

```
Parallel
   nGroups integer
   nCoresPerGroup integer
   nNodesPerGroup integer
End
```

Note that only one of them should be specified in the input, depending of course on what is the desired strategy for parallelization.

`nGroups n` Splits all cores evenly into `n` groups. We recommend choosing `n` such that it divides the total number of cores without a remainder.

`nCoresPerGroup n` Each group consists of `n` cores. As such `nCoresPerGroup 1` results in the maximum possible parallelism at the driver level. We recommend choosing `n` such that it divides the total number of cores without a remainder.

`nNodesPerGroup n` Makes groups from all cores within `n` nodes, e.g. `nNodesPerGroup 1` would make every cluster node into a separate group. Note that this option should *only be used on homogeneous compute clusters*, where all used nodes have the same number of cores. Otherwise cores from different nodes will be grouped together in very surprising and unintended ways, probably resulting in suboptimal performance.

The optimal grouping strategy and number of groups depends on the total number of cores used in the calculation, the amount of independent tasks to be done in parallel, as well as the parallel scalability of the engine itself. In practice it can be a bit tricky, which is why the grouping strategy is determined automatically since AMS2019.3.

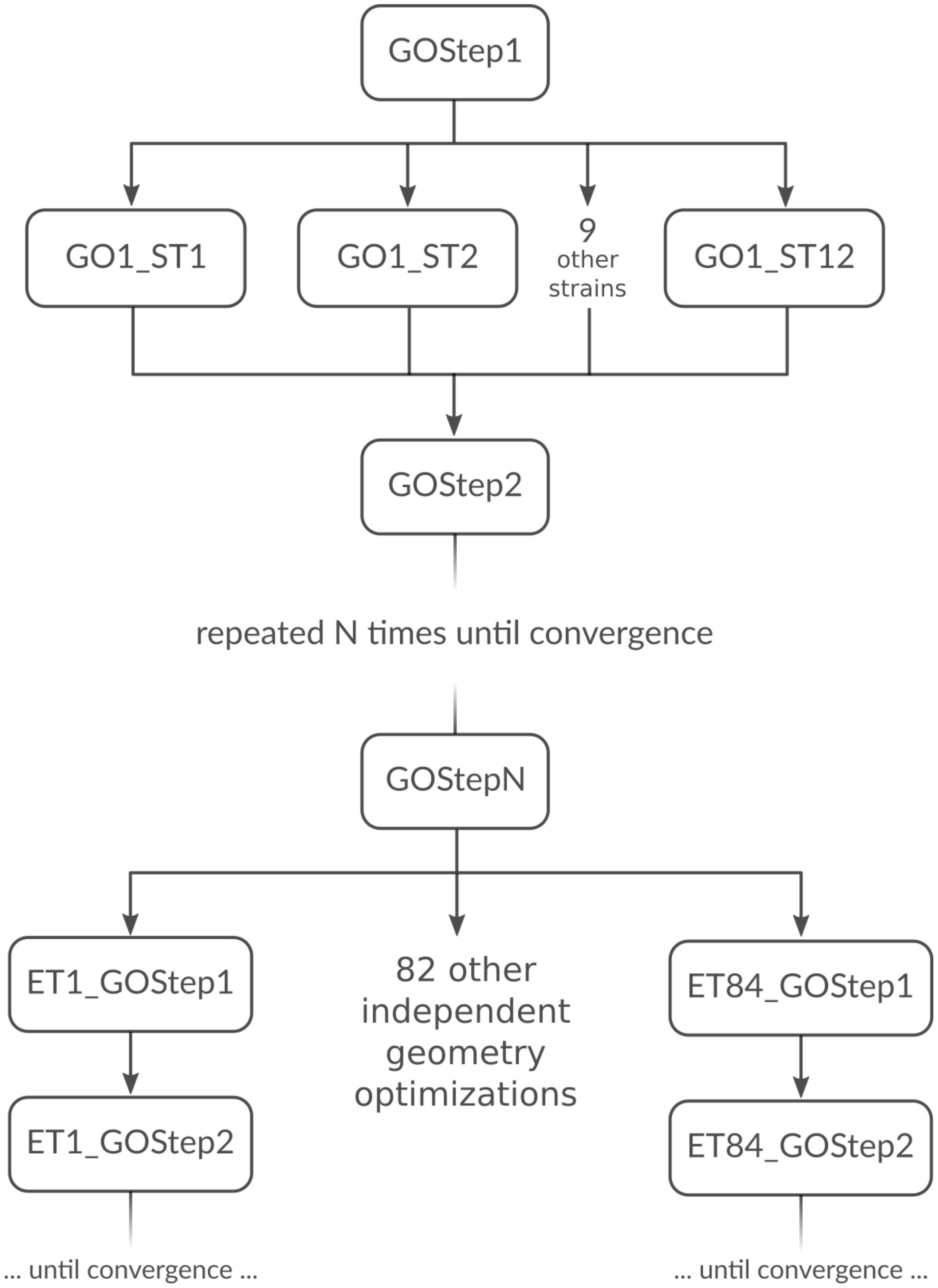
However, sometimes it can be useful to configure the groups manually. Suppose, as an example, that we want to calculate the elastic properties of a bulk material on a 32 core machine. The calculation of the *elastic tensor* (page 204) should be done on a relaxed geometry, including relaxed lattice degrees of freedom. We therefore first perform a geometry optimization, before calculating the elastic tensor. In AMS this can easily be done with the following input:

```
Task GeometryOptimization

GeometryOptimization
   OptimizeLattice True
End

Properties
   ElasticTensor True
End
```

But what is the most optimal parallel setup for this calculation? First we recognize that performing a lattice optimization requires the calculation of the *stress tensor* (page 203) at every step of the optimization. Assuming that our bulk system does not have any symmetries AMS can exploit, the numerical calculation of the stress tensor (assuming the engine can not calculate it analytically) would require 12 independent strained calculations for every step in the geometry optimization. Once the geometry optimization is converged, we have to perform 84 independent geometry optimizations to determine the elements of the elastic tensor. In summary, the graph of dependencies between all these tasks looks like this:


GOStep1
GO1_ST1
GO1_ST2
9 other strains
GO1_ST12
GOStep2
repeated N times until convergence
GOStepN
ET1_GOStep1
ET1_GOStep2
82 other independent geometry optimizations
ET84_GOStep1
ET84_GOStep2
... until convergence ...
... until convergence ...

How do we best parallelize this? For the main steps, e.g. `GOStep1` there is no question: We have nothing to do in parallel and all 32 cores work on it together to finish it as quickly as possible. For the numerical calculation of the stress tensor we have 12 tasks that can be done in parallel by the 32 cores in our machine. Now 12 obviously does not divide 32 without a remainder, so there is no way to split into equally sized groups and do all 12 strains in parallel. The greatest common divisor of 12 and 32 is 4, so it's probably best to split into 4 groups of 8 cores each. This is done with `nGroups 4`. Each group would then do 3 of the 12 strained calculations sequentially, using the in-engine parallelization to speed up the individual calculations. Once the stress tensor is computed in this way all groups merge and all 32 cores work together on `GOStep2`. This splitting and merging now continues until the geometry optimization is converged. For the elastic tensor we now have 84 tasks to perform in parallel, where each task is a completely separate geometry optimization (without optimizing the lattice) of a strained system. 84 tasks is more than double the number of cores we have. In this case it is probably not too bad to just run as parallel as possible at the driver level and make 32 "groups" of just one core to throw the 84 tasks at. This is easily done by setting `nCoresPerGroup 1` in the `ElasticTensor` block. Putting everything together we should add the following to our input file in order to optimally utilize our machine for this example calculation:

```
NumericalDifferentiation
   Parallel
      nGroups 4
   End
End

ElasticTensor
   Parallel
      nCoresPerGroup 1
   End
End
```

2.5 Python interface

There is a complete Python interface to AMS, which allows users to set up and run arbitrary AMS jobs, and to conveniently analyze the calculation results directly from Python. In this way AMS jobs can be automatized and complex multi-stage workflows implemented.

The scripting framework is called PLAMS as in "Python Library for Automating Molecular Simulation", which conveniently can also be read as "Python Layer for AMS". It is documented in a separate manual:

- PLAMS introduction
- Running AMS through PLAMS

2.6 Pipe interface

AMS can interact with other programs using a *custom communication protocol* (page 25). This enables two independent processes to communicate over a pair of data pipes (FIFOs), exchanging data in a highly efficient manner. One of the processes is the "pipe master", driving the calculation and sending the atoms, coordinates etc. to the other process to perform calculations. The other process is the "pipe worker", receiving requests from the master, performing the requested calculations and returning the results such as energies and gradients.

For technical details on the AMSPipe protocol see:

2.6.1 AMSPipe protocol specification

The AMSPipe protocol is a remote procedure call protocol used for communication between two processes on the same computer. One of these processes is the "pipe master", submitting geometries and requests for calculations and receiving the results. The other process is the "pipe worker", which listens for calls from the master, executes the requested calculations and returns their results.

Communication takes place over a pair of pipes, a "call pipe" (master to worker) and a "reply pipe" (worker to master). Each pipe carries a sequence of messages, which are processed in order. Each message is an associative object (like a JSON object or a Python dict) containing a single item. The key of this item denotes the name of the message, while the value of this item is another object containing the payload.

Each message sent over the call pipe constitutes a method call. The name of the message is equal to the name of the method being called, while the payload object contains any arguments. For methods without arguments, the payload is an empty object.

Once the worker receives a call message, it will execute the specified method and potentially write a sequence of zero or more messages to the reply pipe, containing the results of the calculation. After the execution of the method is completed, the worker will write a "return" messages to the reply pipe, denoting the success or failure of the method call.

Any method whose name starts with "Set" doesn't send a "return" message. Instead, errors encountered during the execution of a Set method are buffered by the worker to be returned the next time a "return" message is generated. While an error is buffered, any further method calls are ignored by the worker and are not executed. Once a non-Set call is seen by the worker, such a call will also be discarded without being executed, but a "return" message will be immediately generated with the buffered error data. The buffered error will then be cleared and normal processing of calls resumes.

As a special case, the "Exit" method may be called at any time and will be immediately executed by the worker, terminating the protocol session. The "Exit" method never returns a "return" message, discarding any potentially buffered error.

All values are always in atomic units: Hartree for energies, Bohr for distances, Hartree/Bohr for gradients etc.

Low-level message encoding

All messages are encoded using Universal Binary JSON. AMSPipe implementations MAY encode messages using the UBJSON optimized container format (with explicit length and/or strong typing). Implementations MUST support decoding UBJSON containers whether or not they're written using optimized format.

UBJSON arrays in messages MUST NOT contain other arrays or objects. Multi-dimensional arrays MUST be flattened on encoding (and unflattened on decoding as necessary). Flattening SHOULD preserve the original order of elements in memory. All arrays MUST be accompanied by an additional integer array holding the original dimensions before flattening. The name of this auxiliary array is equal to the name of the main array with a `_dim_` suffix. The dimensions are written in Fortran (column-major) order, so that the first value in the `_dim_` array corresponds to the index that changes the fastests when iterating over consecutive elements of the flattened array.

Arrays also MUST NOT contain elements of incompatible types. The elements of an array MUST be either all integers, all real numbers, all Boolean, or all strings. UBJSON type "char" is equivalent to a UBJSON "string" of length 1 (elements of type "char" and "string" MAY thus be mixed in an array). An empty array is equivalent to an array that is not present at all.

When sending messages over stream transport mechanisms (such as UNIX pipes), each message MUST be prefixed with a 32-bit native endian integer length.

Return messages and error handling

The "return" message consists of the following fields:

- "status" (integer): Zero for success or one of the error codes listed below.
- "method" (string, optional): Name of the method in which the error occurred.
- "argument" (string, optional): Name of the argument in error.
- "message" (string, optional): Human-readable error message.

The "status" field can have one of the following values:

0: success No error, method executed successfully.

1: decode_error Message could not be decoded correctly (invalid UBJSON encoding or a violation of one of the constraints above).

2: logic_error Programmer error, such as methods called in an incorrect sequence or with an invalid worker state.

3: runtime_error An error occurred during the execution of a method (outside of the AMSPipe protocol).

4: unknown_version (Only returned from "Hello".) Requested protocol version is not supported by the worker.

5: unknown_method A method of the requested name is not supported by the worker.

6: unknown_argument The argument in "argument" is not known to the worker and couldn't be processed. If multiple arguments to given single call are unknown, "argument" will be set to the one at the lowest nesting depth (if an argument contains nested objects). If multiple fields at the same nesting depth are unknown, the first one in ASCII sort order will be returned.

7: invalid_argument An argument doesn't have the correct type or dimensions, or it has an invalid value.

Methods

Hello(version)

- "version" (integer):

Attempt to activate a given version of the AMSPipe protocol. Only version 1 is defined at the moment.

Other methods (with the exception of "Hello" and "Exit") MUST NOT be called until a Hello has completed successfully. Pipe masters SHOULD attempt a Hello with the highest supported protocol version and iterate downwards if an unknown_version error is returned. Once a Hello has succeeded, it MUST NOT be called again during the lifetime of a pipe session.

Exit()

Terminate the worker and disconnect both pipes. This method never returns.

The worker MAY also discard any remembered calculations.

SetCoords(coords)

- "coords" (real(3,:)):

Replace the Cartesian coordinates in the current chemical system. The number of atoms must match.

SetLattice(vectors)

- "vectors" (real(:,:)):

Replace the lattice matrix of the current chemical system. If "vectors" is absent or of dimensions (0,0), make the system non-periodic.

SetSystem(atomSymbols, coords, totalCharge)

- "atomSymbols" (string(:)):
- "coords" (real(3,:)):
- "totalCharge" (real):

Define a new chemical system.

Solve(request, keepResults, prevTitle)

- **"request" (object):**
  - "title" (string): Unique string key identifying this calculation.
  - "quiet" (bool): If true, the worker SHOULD keep any standard output from the calculation to a minimum.
  - "gradients" (bool): Calculate gradients on atoms.
  - "stressTensor" (bool): Calculate the stress tensor.
  - "elasticTensor" (bool):
  - "hessian" (bool):
  - "dipoleMoment" (bool):
  - "dipoleGradients" (bool):
- "keepResults" (bool, default false): Remember worker state for future restart.
- "prevTitle" (string, optional): Title of a previously stored calculation to restart from.

Run a single point calculation on the current chemical system and return a "results" object if successful. If the calculation fails with a runtime error, a "results" object MAY still be returned (possibly with just some of the requested properties).

All Boolean fields in "request" default to false if not present. All non-Boolean fields in "request" except for "title" are optional and their default values are worker-dependent. The master SHOULD NOT explicitly set any Boolean fields in "request" to False. The worker MAY raise an unknown argument error if an unknown Boolean is set to False. The worker SHOULD raise an unknown argument error as usual if an unknown Boolean is set to True or if an unknown non-Boolean is set. Workers SHOULD raise these errors before performing any time-consuming calculations so that the master can efficiently retry the call.

If "keepResults" is not specified or set to false, the worker will discard all data from the calculation after returning a "results" object. If "keepResults" is set to true, the worker will remember any internal state related to the calculation. This internal state can later be reused for restart by passing the "title" of the stored calculation as "prevTitle". The pipe master SHOULD call DeleteResults to discard the stored state as soon as it is no longer needed.

A "results" object consists of the following fields. Workers MAY include additional fields not listed here. A master MUST NOT signal an error due to any fields it does not expect or understand.

- **"results" (object):**
  - "messages" (string(:)): Runtime error or warning messages generated by the calculation.
  - "energy" (real):
  - "gradients" (real(3,:)):
  - "stressTensor" (real(:,:)):
  - "elasticTensor" (real(:,:)):
  - "hessian" (real(:,:)):

  - "dipoleMoment" (real(:,:)):
  - "dipoleGradients" (real(:,:)):
  - "charges" (real(:)):

DeleteResults(title)

- "title" (string): Title of a previously remembered calculation.

Discard any worker state corresponding to a previously remembered calculation.

Forward and backward compatibility considerations

The AMSPipe protocol is designed to support combining new masters with old workers and vice versa. Major, incompatible changes in the protocol will be handled by increasing the protocol version number. Negotiating a suitable protocol version is then handled by call(s) to Hello at the beginning of a pipe session.

The following requirements are in place to ensure that the protocol stays extensible within a single protocol version:

- Workers MUST raise an unknown_method error on any call to a method they don't implement. If the method name starts with Set, such an error will be buffered to be returned later. If the method name doesn't start with Set, a "return" message will be generated immediately.
- Workers MUST raise unknown_argument errors any time they encounter an argument to a known method that they don't know how to handle. The master SHOULD then retry the call without such an argument or choose an alternative sequence of calls if possible.
- The master SHOULD ignore unexpected messages of unsupported type on the reply pipe.

Namely, the following changes are permitted without increasing the protocol version number:

- Adding new methods to the protocol.
- Adding new optional arguments to existing methods.
- Adding new fields to returned objects.
- Adding new reply message types.

2.6.2 AMS as a pipe master

The AMS driver can play the role of a pipe master, allowing users to combine the features of the AMS driver with potentials implemented in external programs. Unlike a *traditional external engine* (page 274), the overhead introduced by the pipe interface is entirely negligible, because the external program is only started once at the beginning of the run and all communication is handled by an efficient binary protocol instead of text files. This mode is enabled by using `Engine Pipe` in the input for the master.

```
Engine Pipe
   WorkerCommand /path/to/pipe/worker
EndEngine
```

`WorkerCommand`

Type String

Description The command to execute to run the external worker. The command is executed in a subdirectory of the results directory.

All calculations requested by the driver will then be forwarded over the pipe to the worker for processing.

Note: AMS currently must be run in serial (`NSCM=1`) when serving as a pipe master.

A Python module implementing the worker side of the AMSPipe protocol is available in `scm.amspipe`. To facilitate interfacing with various existing computational engines, this module provides the `ASEPipeWorker` class. This class can wrap any ASE calculator object and make it serve as a pipe worker.

```
calculator = ase.calculators.lj.LennardJones()
# calculator.parameters = …

engine = scm.amspipe.ASEPipeWorker(calculator=calculator)
engine.run()
```

See also:

Example: ASE calculator as a pipe worker (page 482)

2.6.3 AMS as a pipe worker

AMS can also serve as a pipe worker, allowing external drivers to take advantage of its *engines* (page 270). This mode is enabled by using `Task Pipe`. No *Geometry, System definition* (page 31) is required on the input because the system will be supplied by the pipe master.

Hint: For most users it will easiest to use this functionality through the new AMSWorker class in the PLAMS library. This class hides all the details of the underlying AMSPipe protocol and provides users an easy way to get very fast access to energies, gradients and other properties from any of the engines in the AMS driver. See the respective page in the PLAMS manual for details.

See also:

Example: AMS as a pipe worker (page 484)

Additionally AMS can also be driven through the FlexMD library using `AMSPipeForceJob`:

```
forcejob = AMSPipeForceJob(mdmol)
forcejob.settings.engine = 'ReaxFF'
forcejob.settings.engineSettings = { 'ForceField': 'Glycine.ff' }
```

CHAPTER

THREE

GEOMETRY, SYSTEM DEFINITION

The definition of the system to simulate, i.e. the positions and types of the nuclei, the total charge, and potentially lattice vectors, is enclosed in the `System` block:

```
System header
   Atoms header # Non-standard block. See details.
      ...
   End
   Lattice header # Non-standard block. See details.
      ...
   End
   FractionalCoords Yes/No
   AllowCloseAtoms Yes/No
   GeometryFile string
   Symmetrize Yes/No
   LatticeStrain float_list
   SuperCell integer_list
   Charge float
   BondOrders # Non-standard block. See details.
      ...
   End
End
```

3.1 Geometry, Lattice

The geometry of the system is specified with the `Atoms` and `Lattice` blocks.

`System`

Type Block

Recurring True

Description Specification of the chemical system. For some applications more than one system may be present in the input. In this case, all systems except one must have a non-empty string ID specified after the System keyword. The system without an ID is considered the main one.

`Atoms`

Type Non-standard block

Description The atom types and coordinates. Unit can be specified in the header. Default unit is Angstrom.

`Lattice`

Type Non-standard block

Description Up to three lattice vectors. Unit can be specified in the header. Default unit is Angstrom.

FractionalCoords

Type Bool

Default value No

Description Whether the atomic coordinates in the Atoms block are given in fractional coordinates of the lattice vectors. Requires the presence of the Lattice block.

The `Atoms` block contains one line per atoms, similar to the lines found in an `.xyz` file: First the name of the element, then three real numbers representing the coordinates of that atom in Angstrom. The following `Atoms` block shows how one would define a water molecule:

```
System
   Atoms
      O   0.0   0.0       0.59372
      H   0.0   0.76544  -0.00836
      H   0.0  -0.76544  -0.00836
   End
End
```

Note that it is possible to specify a different unit of length in the header of the block (that is in the line after the keyword opening the block) by putting the name of the unit in `[` and `]` brackets. So the same water molecule could also be specified as follows:

```
System
   Atoms [Bohr]
      O   0.0   0.0       1.12197
      H   0.0   1.44647  -0.01580
      H   0.0  -1.44647  -0.01580
   End
End
```

It is also possible to specify the input geometry as a Z-Matrix, by putting the string `Z-Matrix` in the header of the block:

```
System
   Atoms Z-Matrix
      C
      H   1 1.089000
      H   1 1.089000  2  109.4710
      H   1 1.089000  2  109.4710  3  120.0000
      H   1 1.089000  2  109.4710  3 -120.0000
   End
End
```

Periodic systems require the specification of 1 (for chains), 2 (for slabs) or 3 (for bulk) lattice vectors in addition to the nuclear coordinates. Every lattice vector is specified on a separate line of three numbers, representing the vectors x,y and z-component. Note that for chain systems, the single lattice vector **must** point along the x-axis, while for slab systems the two lattice vectors **must** be in the xy-plane. Consider the following input for graphene:

```
System
   Atoms
      C   0.0   0.0      0.0
      C   1.23  0.71014  0.0
```

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```
   End
   Lattice
      2.46  0.0      0.0
      1.23  2.13042  0.0
   End
End
```

As with the `Atoms` block, the length unit in which the lattice vectors are given can be changed by specifying the desired unit in the header of the block (enclosed in `[` and `]`). It is also possible to define a system given the fractional coordinates of the atoms using the `FractionalCoords` keyword. The numbers in the `Atoms` block are then interpreted as fractional coordinates according to the lattice vectors in the `Lattice` block. Note that for chain and slab systems, the coordinates perpendicular to the periodic direction (z and y for chains, z for slabs) are of course still in Angstrom (or alternatively the unit set in the header of the `Atoms` block). Using the `FractionalCoords` keyword we could specify the geometry of table salt (NaCl) as follows:

```
System
   Lattice
      0.0   2.75  2.75
      2.75  0.0   2.75
      2.75  2.75  0.0
   End
   FractionalCoords True
   Atoms
      Na  0.0  0.0  0.0
      Cl  0.5  0.5  0.5
   End
End
```

Instead of specifying the geometry of the system directly in the input file it can also be read from an external file.

System

GeometryFile

Type String

Description Read the geometry from a file (instead of from Atoms and Lattice blocks). Supported formats: .xyz

Note that the `GeometryFile` key replaces both the `Atoms` and the `Lattice` blocks in the input. So if you specify the `GeometryFile` keyword in the input, the `Atoms` and `Lattice` blocks must not appear there. At the moment only the *extended XYZ file format* (page 487) is supported.

3.1.1 Modifying the geometry

Finally there are a number of keywords that *modify* the system geometry:

System

Symmetrize

Type Bool

Default value No

Description Whether to symmetrize the input structure. This might also rototranslate the structure into a standard orientation. This will symmetrize the atomic coordinates to machine precision. Useful if the system is almost symmetric or to rototranslate a symmetric molecule into a standard orientation.

`LatticeStrain`

Type Float List

Description Deform the input system by the specified strain. The strain elements are in Voigt notation, so one should specify 6 numbers for 3D periodic system (order: xx,yy,zz,yz,xz,xy), 3 numbers for 2D periodic systems (order: xx,yy,xy) or 1 number for 1D periodic systems.

`SuperCell`

Type Integer List

Description Create a supercell of the input system (only possible for periodic systems). The integer numbers represent the diagonal elements of the supercell transformation; you should specify as many numbers as lattice vectors (i.e. 1 number for 1D, 2 numbers for 2D and 3 numbers for 3D periodic systems).

`SuperCellTrafo`

Type Integer List

Description Create a supercell of the input system (only possible for periodic systems) $\vec{a}_i' = \sum_j T_{ij}\vec{a}_j$. The integer numbers represent the supercell transformation T_{ij}: 1 number for 1D PBC, 4 numbers for 2D PBC corresponding to a 2x2 matrix (order: (1,1),(1,2),(2,1),(2,2)) and 9 numbers for 3D PBC corresponding to a 3x3 matrix (order: (1,1),(1,2),(1,3),(2,1),(2,2),(2,3),(3,1),(3,2),(3,3)).

`PerturbCoordinates`

Type Float

Default value 0.0

Unit Angstrom

Description Perturb the atomic coordinates by adding random numbers between [-PerturbCoordinates,PerturbCoordinates] to each Cartesian component. This can be useful if you want to break the symmetry of your system (e.g. for a geometry optimization).

`PerturbLattice`

Type Float

Default value 0.0

Description Perturb the lattice vectors by applying random strain with matrix elements between [-PerturbLattice,PerturbLattice]. This can be useful if you want to deviate from an ideal symmetric geometry, for example if you look for a phase change due to high pressure.

`MapAtomsToUnitCell`

Type Bool

Default value No

Description For periodic systems the atoms will be moved to the central cell.

These modifications are applied immediately after the system block is read. To the rest of AMS (and the input) it looks exactly as if the modified system was specified explicitly in the `System` block input. That means that the `SuperCell` keyword is not easily usable with input options that require the specification of atom indices, e.g. the *constraints* (page 52) block. Note that the randomization of the coordinates is applied after a potential supercell creation.

3.2 Symmetry

Symmetry can be used in AMS optimizations of molecules and of periodic structures.

In case of molecules at the start of an AMS calculation one can symmetrize an almost symmetric structure. In the *Appendix Symmetry* (page 491) one can find molecular orientation requirements that AMS needs such that AMS can use the (sub)symmetry of a molecule. If the system is symmetrized (and no symmetry is given in the System block key) the molecular structure is rotranslated into this standard orientation. In the *Appendix Symmetry* (page 490) one can also find Schönfliess symbols for molecular point groups and symmetry labels that are used in AMS for molecules to label normal modes.

```
System header
   Symmetrize Yes/No
   Symmetry [...]
End
```

```
Symmetry
   SymmetrizeTolerance float
   Tolerance float
End
```

```
UseSymmetry Yes/No
```

System

Symmetrize

Type Bool

Default value No

Description Whether to symmetrize the input structure. This might also rototranslate the structure into a standard orientation. This will symmetrize the atomic coordinates to machine precision. Useful if the system is almost symmetric or to rototranslate a symmetric molecule into a standard orientation.

Symmetry

Type Multiple Choice

Default value AUTO

Options [AUTO, NOSYM, C(LIN), D(LIN), C(I), C(S), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(2V), C(3V), C(4V), C(5V), C(6V), C(7V), C(8V), C(2H), C(3H), C(4H), C(5H), C(6H), C(7H), C(8H), D(2), D(3), D(4), D(5), D(6), D(7), D(8), D(2D), D(3D), D(4D), D(5D), D(6D), D(7D), D(8D), D(2H), D(3H), D(4H), D(5H), D(6H), D(7H), D(8H), I, I(H), O, O(H), T, T(D), T(H), S(4), S(6), S(8)]

Description Use (sub)symmetry with this Schoenflies symbol. Can only be used for molecules. Orientation should be correct for the (sub)symmetry. If used icw Symmetrize, the symmetrization will not reorient the molecule.

Symmetry

SymmetrizeTolerance

Type Float

Default value 0.05

Description Tolerance used to detect symmetry in case symmetrize is requested.

Tolerance

Type Float

Default value 1e-07

Description Tolerance used to detect symmetry in the system.

UseSymmetry

Type Bool

Default value Yes

Description Whether to use the system's symmetry in AMS. Symmetry is recognized within a tolerance as given in the Symmetry key.

3.3 Regions

Some options of the AMS driver and its engines require specifying a subset of a system's atoms. For example one might want to freeze part of the system in a molecular dynamics calculation. We refer to these subsets of atoms as "regions". Atoms are assigned to regions by specifying the region names behind the atomic coordinates in the `Atoms` block of the input:

```
System
   Atoms
      C       1.22110608      -0.00000000       1.65928963     region=ring_1
      C       0.37734253      -1.16134090       1.65928963     region=ring_1
      C       0.37734253       1.16134090       1.65928963     region=ring_1
      C      -0.98789557      -0.71774815       1.65928963     region=ring_1
      C      -0.98789557       0.71774815       1.65928963     region=ring_1
      H       2.30849293      -0.00000000       1.64874914     region=ring_1
      H       0.71336355      -2.19550724       1.64874914     region=ring_1
      H       0.71336355       2.19550724       1.64874914     region=ring_1
      H      -1.86761001      -1.35689810       1.64874914     region=ring_1
      H      -1.86761001       1.35689810       1.64874914     region=ring_1
      Fe      0.00000000       0.00000000       0.00000000
      H       0.71336355       2.19550724      -1.64874914     region=ring_2
      H       0.71336355      -2.19550724      -1.64874914     region=ring_2
      C       1.22110608      -0.00000000      -1.65928963     region=ring_2
      C       0.37734253       1.16134090      -1.65928963     region=ring_2
      C       0.37734253      -1.16134090      -1.65928963     region=ring_2
      C      -0.98789557       0.71774815      -1.65928963     region=ring_2
      C      -0.98789557      -0.71774815      -1.65928963     region=ring_2
      H       2.30849293      -0.00000000      -1.64874914     region=ring_2
      H      -1.86761001       1.35689810      -1.64874914     region=ring_2
      H      -1.86761001      -1.35689810      -1.64874914     region=ring_2
   End
End
```

In the above example of a ferrocene molecule, we have created two separate regions for the two cyclopentadienyl rings. The region names (`ring_1` and `ring_2` in the example above) can be freely chosen by the user. Note that an atom can be in more than one region, in which case the region names should be separated by commas:

```
System
   Atoms
      ...
      Mg   0.0   0.0   0.0    region=metal_centers,mol_1
```

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```
      ...
   End
End
```

Technically the region is handled as an *atomic attribute* (page 41).

3.4 Charge, atomic masses, input bond orders

AMS allows to set user-defined masses for particular atoms. This can be used to simulate isotopes of different atoms. Masses are specified by adding the desired mass (in Dalton) at the end of the atom's line. The following input shows the system specification for a heavy water molecule:

```
System
   Atoms
      O   0.0    0.0        0.59372
      H   0.0    0.76544   -0.00836    mass=2.014
      H   0.0   -0.76544   -0.00836    mass=2.014
   End
End
```

(Observe that the mass specified this way is an example of the *atomic attributes* (page 41) system.)

Finally the `System` block also contains the specification of the system's total charge as well as optionally defined bond orders.

System

Charge

Type Float

Default value 0.0

GUI name Total charge

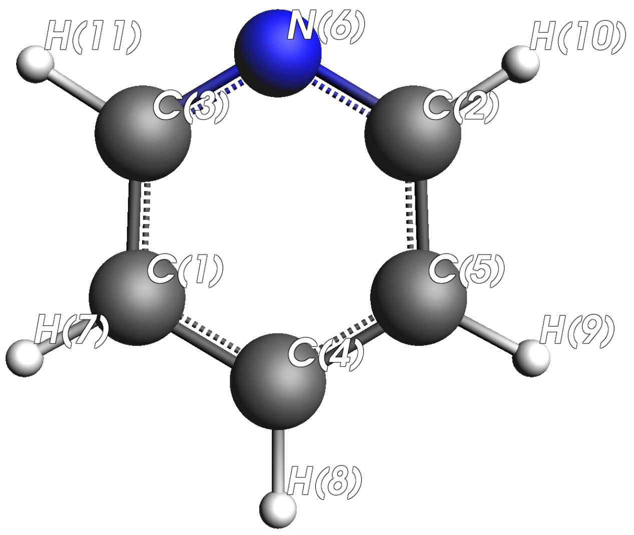
Description The system's total charge in atomic units.

BondOrders

Type Non-standard block

Description Defined bond orders. Each line should contain two atom indices, followed by the bond order (1, 1.5, 2, 3 for single, aromatic, double and triple bonds) and (optionally) the cell shifts for periodic systems. May be used by MM engines and for defining constraints. If the system is periodic and none of the bonds have the cell shift defined then AMS will attempt to determine them following the minimum image convention.

The following example shows the System block with defined bond orders for pyridine:



```
System
    Atoms
       C  0.0  -1.19129014   -0.47777633
       C  0.0   1.1420834     0.90885782
       C  0.0  -1.1420834     0.90885782
       C  0.0   0.0          -1.18887601
       C  0.0   1.19129014   -0.47777633
       N  0.0   0.0           1.5894377
       H  0.0  -2.14522862   -0.99205897
       H  0.0   0.0          -2.27338592
       H  0.0   2.14522862   -0.99205897
       H  0.0   2.05492975    1.4973896
       H  0.0  -2.05492975    1.4973896
    End
    BondOrders
        1 3  1.5
        1 4  1.5
        1 7  1.0
        2 5  1.5
        2 6  1.5
        2 10 1.0
        3 6  1.5
        3 11 1.0
        4 5  1.5
        4 8  1.0
        5 9  1.0
    End
End
```

Note that the specified bond orders are currently only used by the ForceField engine and for generating distance constraints via the `All bonds` option in the constraints block.

3.5 Homogeneous electric field and multipole charges

A homogeneous electric field and multipole charges can be requested at the AMS level. Currently this option is supported by the engines ADF, BAND, DFTB, and MOPAC.

Homogeneous electric field:

```
System
   ElectrostaticEmbedding
      ElectricField ex ey ez
   End
End
```

ElectrostaticEmbedding

ElectricField

Type Float List

Unit V/Angstrom

Description External homogeneous electric field with three Cartesian components: ex, ey, ez, the default unit being V/Å.

In atomic units: Hartree/(e bohr) = 14.39964 V/Angstrom; the relation to SI units is: 1 Hartree/(e bohr) = 5.14 … e11 V/m.

Supported by the engines adf, band, dftb and mopac.

For periodic systems the field may only have nonzero components orthogonal to the direction(s) of periodicity (i.e. for 1D periodic system the x-component of the electric field should be zero, while for 2D periodic systems both the x and y components should be zero. This options cannot be used for 3D periodic systems.

Point and multipole charges:

```
System
   ElectrostaticEmbedding
      MultipolePotential
         Coordinates
            x y z   q   py pz px
            x y z   q   py pz px
            ...
         End
      End
   End
End
```

ElectrostaticEmbedding

MultipolePotential

Type Block

Description External point charges (and dipoles).

ChargeModel

Type Multiple Choice

Default value Point

Options [Point, Gaussian]

Description A multipole may be represented by a point (with a singular potential at its location) or by a spherical Gaussian distribution.

ChargeWidth

Type Float

Default value -1.0

Description The width parameter in a.u. in case a Gaussian charge model is chosen. A negative value means that the width will be chosen automatically.

Coordinates

Type Non-standard block

Description Positions and values of the multipoles, one per line. Each line has the following format:

x y z q, or x y z q µx µy µz.

Here x, y, z are the coordinates in Å, q is the charge (in atomic units of charge) and µx, µy, µz are the (optional) dipole moment components (in atomic units, i.e. e*Bohr).

Periodic systems are not supported.

Note: When running geometry optimizations (or other similar tasks) in combination with point charges, you should be aware that the system might end up on top of the point charge(s), resulting in non-physical situations. You should consider using *constraints* (page 52), *restraints* (page 284) or explicitly setting *rigid motions* (page 610) options.

3.6 Load a System from file

Instead of specifying the system to simulate in the `System` block of the input, it is also possible to read the system used in a previous calculation from the binary `.rkf` result files of AMS. This is done with the `LoadSystem` block in the input:

```
LoadSystem header
   File string
   Section string
End
```

LoadSystem

Type Block

Recurring True

Description Block that controls reading the chemical system from a KF file instead of the [System] block.

File

Type String

Description The path of the KF file from which to load the system. It may also be the results directory containing it.

Section

Type String

Default value Molecule

Description The section on the KF file from which to load the system.

Note that the `LoadSystem` block is mutually exclusive with the `System` block: The system *either* needs to be specified in the input, *or* loaded from a previous results file.

Any `.rkf` file written by AMS should be suitable to load a system from. For *engine output files* (page 19) the loaded geometry is just the one for which the engine was invoked when it wrote this file. For the *main result file* (page 19) `ams.rkf` written by the AMS driver, which geometry is loaded depends on the *task* (page 45) that AMS was performing when this file was written. Generally the `ams.rkf` file contains two systems:

- The input system corresponding just to the `System` block that was read in by AMS. This system is written to the `InputMolecule` section on the `ams.rkf`, and can be loaded from there using the `LoadSystem%Section` keyword. This can be useful in order to repeat a previous AMS calculation for the same system, but with different settings, e.g. a different engine.
- The system which was the result of a previous AMS calculation, e.g. a geometry optimization or transition state search. This system is written to the `Molecule` section on the `ams.rkf`. What exactly is considered the resulting geometry of a calculation depends in the *task* (page 45) of the previous calculation. (For tasks that do not change the geometry (like a single point calculation) or where no configuration is particularly special (e.g. a PES scan), the result system is normally just the same as the input system.)

3.7 Atom attributes

There is in general the possibility to add text after the coordinates of an atom, we call these atomic attributes. The text should be of the form key=value, separated by spaces:

```
System
   Atoms
      O   0.0   0.0        0.59372   key1=1 key2=y
      H   0.0   0.76544   -0.00836   file=ams.rkf
      H   0.0  -0.76544   -0.00836
   End
End
```

You can enter any arbitrary key/value list, but that will have no effect in general. Although there is one important effect that atoms with different atomic attributes (even unrecognized ones) are considered different elements during the symmetry detection.

The order in which keys are specified has no effect.

Examples of atomic attributes are the region, and mass.

3.8 Force field related extensions

For forcefield there are two dedicated *atomic attributes* (page 41), the ForceField.Type and ForceField.Charge. Obviously these attributes are ignored by all other engines, although it can reduce the symmetry of the system:

```
System
   Atoms
      O   0.0   0.0        0.59372   ForceField.Type=O ForceField.Charge=-0.1
      H   0.0   0.76544   -0.00836   ForceField.Type=H ForceField.Charge=+0.05
      H   0.0  -0.76544   -0.00836   ForceField.Type=H ForceField.Charge=+0.05
```

(continues on next page)

(continued from previous page)

```
   End
End
```

3.8.1 Load charges for a forcefield into regions

When you want to use a forcefield, the charges obtained by a previous calculation can be loaded into a specific region (with the same molecule). Currently the order of the atoms has to be the same for this to work.

Once loaded, it is as if the user had typed in the ForceField.Charge attributes.

System

LoadForceFieldCharges

Type Block

Recurring True

Description This is a mechanism to set the ForceField.Charge attribute in the input. This information is currently only used by the ForceField engine.

CheckGeometryRMSD

Type Bool

Default value No

Description Whether the geometry RMSD test should be performed, see MaxGeometryRMSD. Otherwise only basic tests are performed, such as number and atom types. Not doing the RMSD test allows you to load molecular charges in a periodic system.

File

Type String

Description Name of the (kf) file

MaxGeometryRMSD

Type Float

Default value 0.1

Unit Angstrom

Description The geometry of the charge producing calculation is compared to the one of the region, and need to be the same within this tolerance.

Region

Type String

Default value *

Description Region for which the charges should be loaded

Section

Type String

Default value AMSResults

Description Section name of the kf file

Variable

Type String

Default value Charges

Description Variable name of the kf file

3.8.2 Load forcefield atom types

After you have done a forcefield calculation the atom types are stored. You can load those for a next calculation.

Once loaded, it is as if the user had typed in the ForceField.Type atom attributes.

`System`

`LoadForceFieldAtomTypes`

Type Block

Description This is a mechanism to set the ForceField.Type attribute in the input. This information is currently only used by the ForceField engine.

`File`

Type String

Description Name of the (kf) file. It needs to be the result of a forcefield calculation.

CHAPTER

FOUR

STRUCTURE AND REACTIVITY, MOLECULAR DYNAMICS

4.1 Single point calculations

A single point calculation is the simplest task available in the AMS driver. It simply runs the *engine* (page 270) once for the given geometry. In other words, the AMS driver does not explore the potential energy surface (PES), but simply samples a "single point" of it.

A single point calculation is performed by selecting it with the `Task` keyword:

```
Task SinglePoint
```

Note that a single point calculation in AMS includes the calculation of *PES point properties* (page 198). Many of these, such as the nuclear gradients and the Hessian, are derivatives at this PES point with respect to nuclear displacements. These derivatives might be done numerically by the AMS driver, in which case it would technically run the engine multiple times and sample PES points around the initial point. However, in AMS this is still considered a single point calculation. Take for example the calculation of the normal modes of vibration of a molecule. This used to be a separate task in the 2017 release of the DFTB program, but in AMS is just a single point calculation with a request for normal modes:

```
Task SinglePoint

Properties
   NormalModes True
End
```

See the manual section on *PES point properties* (page 198) for an overview of which properties can be calculated with the `SinglePoint` task in AMS.

4.2 Bond energy calculations

The way to calculate bonding energies is always the same, regardless of the engine. It is about combining ground state energies for several systems.

4.2.1 Ground state energy

Let system A have a ground state energy E(A)

The ground state energy of a system is obtained by a full relaxation with respect to the geometry coordinates and (if relevant) to the electronic degrees of freedom. In case of periodic materials the lattice vectors need relaxation as well.

Electronic degrees of freedom are specific for the method underpinning the engine. A simple force field may have a charge equilibration scheme , whereas more advanced engines such DFT- and DFTB-based ones have orbitals. The electronic relaxation can become a non-trivial problem in case of *open shell* (page 47) systems.

4.2.2 Formation energy

Say we have a reaction of two molecules (A and B) forming a new one (C).

A + B -> C

The interaction energy follows from three *ground state* (page 46) calculations

E(bond) = E(C) - E(A) - E(B)

Let us look at a slightly more complicated reaction. The (metastable) material Octanitrocubane with the formula C_8 (NO $_2$ $)_8$ can be formed from 8 CO_2 molecules and four N_2 molecules. The formation energy is

E(bond) = E(Octanitrocubane) - 8 E(CO_2) - 4 E(N_2)

the result being positive as this reaction is highly endothermic.

4.2.3 Atomization energies

Let us now look at atomization energies. For instance, the cohesive energy the NaCl crystal is

E(cohesive energy) = E(NaCl-crystal) - E(Na-atom) - E(Cl-atom)

(Atomization energies can also be calculated for molecules.)

For engines with electronic degrees of freedom, the tricky part here is how to calculate the atomic energies, in particular E(Cl-atom), because they are open shell systems. See the notes on a *atomic corrections* (page 47).

Of course you need to weigh the atomic energies by how often they occur in the system (molecule or crystal).

4.2.4 Chemisorption energies

What is the adsorption energy of a molecule on a surface?

The main thing here is whether the "real" system has translational symmetry. For instance in an experiment this may be the case and correspond to a certain coverage. This can be perfectly modeled in a periodic calculation

E(chemisorption) = E(mol@surface) - E(mol) - E(bare surface)

You need to choose the right super cell to get the correct coverage (how many adsorbed atoms per unit cell).

If the experiment is about the adsorption of a single molecule you need to try to converge the result with progressively larger super cells.

The other main issue is that almost always in the experimental setup the surface is macroscopically thick. Therefore the slab thickness is an issue to be tested. Fortunately, often less than 10 layers are needed.

4.2.5 Atomic corrections

Sometimes we need to calculate the ground state energy of a single atom. As there are no geometric variables, the only degrees of freedom are electronic. In general atoms are *open shell* (page 47) systems. The idea is to let the engine run without any restrictions imposed on the spin-polarization, or the symmetry of the orbitals.

One possible trick is to run two atoms quite far away (10-20 angstrom), thus reducing the exact spherical symmetry.

Calculating atomic corrections can be very tricky, as there may be many nearly degenerate orbitals near the fermi level. Also SCF convergence can be very difficult. There is not a single solution for all atoms.

4.2.6 Open shell systems

The idea is to let the engine run without any restrictions imposed on the spin-polarization, or the symmetry of the orbitals.

Calculating open shell systems can be very tricky, as there may be many close lying states (of which the lowest is searched for). Also SCF convergence can be very difficult.

From a theoretical point of view these states should ultimately be described by multi-determinantal wave functions, lacking from methods such as DFT.

There may be no automatic way to find the absolute minimum. If possible try to avoid the need to do such calculations.

4.2.7 Impurities

Let's say that we want to introduce a single impurity in a crystal. Currently we do not support such a method. But using periodic boundary conditions (PBCs) we can approximate this.

Say we want to introduce a single Li atom in an Al crystal. This can be done by considering progressively larger super cells.

First we make a 2x2x2 super cell, with 8 Al atoms, then we insert one Li, thus modeling an "impurity", with a 1/8 Li/Al ratio, rather than a 1/infinity. With bigger super cells this approximation becomes better.

The insertion energy is then

E(8Al+Li) - E(8Al) - E(Li-atom)

See also the comments for Atomization energies.

4.3 Geometry optimization

A geometry optimization is the process of changing the system's geometry (the nuclear coordinates and potentially the lattice vectors) to minimize the total energy of the systems. This is typically a local optimization, i.e. the optimization converges to the next local minimum on the potential energy surface (PES), given the initial system geometry specified in the `System` block. In other words: The geometry optimizer moves "downhill" on the PES into the local minimum.

See also:

Examples (page 379) and silicon lattice optimization and phonons tutorial

Geometry optimizations are performed by selecting them as the `Task`. The details of the optimization can be configured in the corresponding block:

```
Task GeometryOptimization
```

```
GeometryOptimization
   Convergence
      Energy float
      Gradients float
      Quality [VeryBasic | Basic | Normal | Good | VeryGood | Custom]
      Step float
      StressEnergyPerAtom float
   End
   MaxIterations integer
   CalcPropertiesOnlyIfConverged Yes/No
   OptimizeLattice Yes/No
   KeepIntermediateResults Yes/No
   PretendConverged Yes/No
   MaxRestarts integer
   RestartDisplacement float
End
```

4.3.1 Convergence criteria

GeometryOptimization

Type Block

Description Configures details of the geometry optimization and transition state searches.

Convergence

Type Block

Description Convergence is monitored for up to 4 quantities: the energy change, the Cartesian gradients, the Cartesian step size, and for lattice optimizations the stress energy per atom. Convergence criteria can be specified separately for each of these items.

Energy

Type Float

Default value 1e-05

Unit Hartree

Value Range value > 0

GUI name Energy convergence

Description The criterion for changes in the energy. The energy is considered converged when the change in energy is smaller than this threshold times the number of atoms.

Gradients

Type Float

Default value 0.001

Unit Hartree/Angstrom

Value Range value > 0

GUI name Gradient convergence

Description Threshold for nuclear gradients.

Quality

Type Multiple Choice

Default value Custom

Options [VeryBasic, Basic, Normal, Good, VeryGood, Custom]

GUI name Convergence

Description A quick way to change convergence thresholds: 'Good' will reduce all thresholds by an order of magnitude from their default value. 'VeryGood' will tighten them by two orders of magnitude. 'Basic' and 'VeryBasic' will increase the thresholds by one or two orders of magnitude respectively.

`Step`

Type Float

Default value 0.01

Unit Angstrom

Value Range value > 0

GUI name Step convergence

Description The maximum Cartesian step allowed for a converged geometry.

`StressEnergyPerAtom`

Type Float

Default value 0.0005

Unit Hartree

Value Range value > 0

Description Threshold used when optimizing the lattice vectors. The stress is considered 'converged' when the maximum value of stress_tensor * cell_volume / number_of_atoms is smaller than this threshold (for 2D and 1D systems, the cell_volume is replaced by the cell_area and cell_length respectively).

A geometry optimization is considered converged when all the following criteria are met:

1. The difference between the bond energy at the current geometry and at the previous geometry step is smaller than `Convergence%Energy` times the number of atoms in the system.
2. The maximum Cartesian nuclear gradient is smaller than `Convergence%Gradient`.
3. The root mean square (RMS) of the Cartesian nuclear gradients is smaller than 2/3 `Convergence%Gradient`.
4. The maximum Cartesian step is smaller than `Convergence%Step`.
5. The root mean square (RMS) of the Cartesian steps is smaller than 2/3 `Convergence%Step`.

Note: If the maximum and RMS gradients are 10 times smaller than the convergence criterion, then criteria 4 and 5 are ignored.

The `Convergence%Quality` sets the criteria as follows:

Quality	Energy (Ha)	Gradients (Ha/Å)	Step (Å)	StressEnergyPerAtom (Ha)
VeryBasic	10^{-3}	10^{-1}	1	5×10^{-2}
Basic	10^{-4}	10^{-2}	0.1	5×10^{-3}
Normal	10^{-5}	10^{-3}	0.01	5×10^{-4}
Good	10^{-6}	10^{-4}	0.001	5×10^{-5}
VeryGood	10^{-7}	10^{-5}	0.0001	5×10^{-6}

Some remarks on the choice of the convergence thresholds:

- Molecules may differ very much in the stiffness around the energy minimum. Using the standard convergence thresholds without second thought is therefore not recommended. Strict criteria may require a large number of steps, while a loose threshold may yield geometries that are far from the minimum (with respect to atom-atom distances, bond-angles etc…) even when the total energy of the molecule might be very close to the value at the minimum. It is good practice to consider first what the objectives of the calculation are. The default settings in AMS are intended to be reasonable for most applications, but inevitably situations may arise where they are inadequate.
- The convergence threshold for the coordinates (`Convergence%Step`) is not a reliable measure for the precision of the final coordinates. Usually it yields a reasonable estimate (order of magnitude), but to get accurate results one should tighten the criterion on the gradients, rather than on the steps (coordinates). (The reason for this is that with the Quasi-Newton based optimizers the estimated uncertainty in the coordinates is related to the used Hessian, which is updated during the optimization. Quite often it stays rather far from an accurate representation of the true Hessian. This does usually not prevent the program from converging nicely, but it does imply a possibly incorrect calculation of the uncertainty in the coordinates.)
- Note that tight convergence criteria for the geometry optimization require accurate and noise-free gradients from the engine. For some engines this might mean that their numerical accuracy has to be increased for geometry optimization with tight convergence criteria, see e.g. the `NumericalQuality` keyword in the BAND manual.

The maximum number of geometry iterations allowed to locate the desired structure is specified with the `MaxIterations` keyword:

`GeometryOptimization`

`MaxIterations`

Type Integer

Value Range value >= 0

GUI name Maximum number of iterations

Description The maximum number of geometry iterations allowed to converge to the desired structure.

`CalcPropertiesOnlyIfConverged`

Type Bool

Default value Yes

Description Compute the properties requested in the 'Properties' block, e.g. Frequencies or Phonons, only if the optimization (or transition state search) converged. If False, the properties will be computed even if the optimization did not converge.

`PretendConverged`

Type Bool

Default value No

Description Normally a non-converged geometry optimization is considered an error. If this keyword is set to True, the optimizer will only produce a warning and still claim that the optimization is converged. (This is mostly useful for scripting applications, where one might want to consider non-converged optimizations still successful jobs.)

If the geometry optimization does not converge within this many steps it is considered failed and the iteration aborted, i.e. *PES point properties* (page 198) block will not be calculated at the last geometry. The default maximum number of steps is chosen automatically based on the used optimizer and the number of degrees of freedom to be optimized. The default is a fairly large number already, so if the geometry has not converged (at least to a reasonable extent) within that many iterations you should step back and consider the underlying cause rather than simply increase the allowed number of iterations and try again.

4.3.2 Automatic restarts

While a geometry optimization aims to find a (local) PES minimum, it may occur that it ends up finding a saddle point instead. The `PESPointCharacter` property keyword can be used to quickly calculate the lowest few Hessian eigenvalues to determine what kind of stationary PES point the optimization found. More information on this feature can be found on its *Documentation Page* (page 200). Since AMS2022.1, geometry optimizations with enabled PES point characterization can automatically restart when a transition state (or higher order saddle point) is found: the geometry is distorted along the lowest frequency mode and the optimizer run again. The applied distortion is often symmetry breaking in this case, so this automatic restarting is only enabled if the system does not have any symmetry operators or the use of symmetry is explicitly disabled using the `UseSymmetry` keyword. Furthermore the automatic restarting must be explicitly enabled by setting the `MaxRestarts` option to a value >0. Of course the PES point characterization needs to be enabled too:

```
GeometryOptimization
   MaxRestarts 5
End

UseSymmetry False

Properties
   PESPointCharacter True
End
```

Details of the automatic restarting can configured with the following keywords:

`GeometryOptimization`

`MaxRestarts`

Type Integer

Default value 0

Description If a geometry optimization of a system with no symmetry operators (or with explicitly disabled symmetry: `UseSymmetry False`) and enabled PES point characterization converges to a transition state (or higher order saddle point), it can be restarted automatically after a small displacement along the imaginary vibrational mode. In case the restarted optimization again does not find a minimum, this can happen multiple times in succession. This keyword sets the maximum number of restarts. The default value is 0, so the automatic restarting is disabled by default.

`RestartDisplacement`

Type Float

Default value 0.05

Unit Angstrom

Description If a geometry optimization of a system with no symmetry operators (or with explicitly disabled symmetry: `UseSymmetry False`) and enabled PES point characterization converges to a transition state (or higher order saddle point), it can be restarted automatically after a small displacement along the imaginary vibrational mode. This keywords sets the size of the displacement for the furthest moving atom.

4.3.3 Lattice optimization

For periodic systems the lattice degrees of freedom can be optimized in addition to the nuclear positions.

GeometryOptimization

OptimizeLattice

Type Bool

Default value No

Description Whether to also optimize the lattice for periodic structures. This is currently supported with the Quasi-Newton, FIRE, and L-BFGS optimizers.

See also *Constrained optimization* (page 52) for constrained lattice optimizations.

4.3.4 Keep all results files

The `GeometryOptimization` block also contains some technical options:

GeometryOptimization

KeepIntermediateResults

Type Bool

Default value No

Description Whether the full engine result files of all intermediate steps are stored on disk. By default only the last step is kept, and only if the geometry optimization converged. This can easily lead to huge amounts of data being stored on disk, but it can sometimes be convenient to closely monitor a tricky optimization, e.g. excited state optimizations going through conical intersections, etc. …

4.3.5 Constrained optimization

The AMS driver also allows to perform constrained optimizations, where a number of specified degrees of freedom are fixed to particular values.

See also:

Example demonstrating all supported constraints (page 387)

The desired constraints are specified in the `Constraints` block at the root level of the AMS input file:

```
Constraints
   Atom integer
   AtomList integer_list
   FixedRegion string
   Coordinate integer [x|y|z] float?
   Distance (integer){2} float
   All ... [Bonds|Triangles] ...
   Angle (integer){3} float
   Dihedral (integer){4} float
   SumDist (integer){4} float
   DifDist (integer){4} float
   BlockAtoms integer_list
   Block string
```

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```
   FreezeStrain [xx] [xy] [xz] [yy] [yz] [zz]
   EqualStrain  [xx] [xy] [xz] [yy] [yz] [zz]
End
```

`Constraints`

Type Block

Description The Constraints block allows geometry optimizations and potential energy surface scans with constraints. The constraints do not have to be satisfied at the start of the calculation.

The different types constraints are described with examples below.

Note that in principle an arbitrary number of constraints can be specified and thus combined. However, it is the user's responsibility to ensure that the specified constraints are actually *compatible with each other*, meaning that it is theoretically possible to satisfy all of them at the same time. The AMS driver does **not** detect this kind of problems, but the optimization will show very unexpected results. Furthermore, for calculations involving block constraints the following restrictions apply:

- There should be no other constrained coordinates used together with block constraints although this may work in many situation.
- The user should absolutely avoid specifying other constraints that include atoms of a frozen block.

Fixed atoms

The following constraints can be used to fix atoms in space.

`Atom atomIdx` Fix the atom with index `atomIdx` at the initial position, as given in the `System%Atoms` block.

`AtomList [atomIdx1 .. atomIdxN]` Fix all atoms in the list at the initial position, as given in the `System%Atoms` block.

`FixedRegion regionName` Fix all atoms in a *region* (page 36) to their initial positions.

`Coordinate atomIdx [x|y|z] coordValue?` Constrain the atom with index `atomIdx` (following the order in the `System%Atoms` block) to have a cartesian coordinate (`x`, `y` or `z`) of `coordValue` (given in Angstrom). If the `coordValue` is missing, the coordinate will be fixed to its initial value.

Internal degrees of freedom

The following options allow constraints of internal degrees of freedom, such as distances, angles and dihedral angles.

`Distance atomIdx1 atomIdx2 distValue` Constrain the distance between the atoms with index `atomIdx1` and `atomIdx2` (following the order in the `System%Atoms` block) to `distValue`, given in Angstrom.

`Angle atomIdx1 atomIdx2 atomIdx3 angleValue` Constrain the angle (1)–(2)–(3) between the atoms with indices `atomIdx1-3` (as given by their order in the `System%Atoms` block) to `angleValue`, given in degrees.

`Dihedral atomIdx1 atomIdx2 atomIdx3 atomIdx4 dihedValue` Constrain the dihedral angle (1)–(2)–(3)–(4) between the atoms with indices `atomIdx1-4` (as given by their order in the `System%Atoms` block) to `dihedValue`, given in degrees.

`SumDist atomIdx1 atomIdx2 atomIdx3 atomIdx4 sumDistValue` Constrain the sum of the distances R(1,2)+R(3,4) between the atoms with indices `atomIdx1-4` (as given by their order in the `System%Atoms` block) to `sumDistValue`, given in Angstrom.

DifDist atomIdx1 atomIdx2 atomIdx3 atomIdx4 difDistValue Constrain the difference between the distances R(1,2)-R(3,4) of the atoms with indices `atomIdx1-4` (as given by their order in the `System%Atoms` block) to `difDistValue`, given in Angstrom.

Note that the above constraints do **not** need to be satisfied at the beginning of the optimization.

The `Distance` keyword described above can be used to set up constraints for specific pairs of atoms in the system. For some applications, this input can be cumbersome and one would rather specify a constraint for **all** bonds of a particular type. Since the AMS2022.1 release, there is a simplified input for this using the `All` keyword. The `All` keyword allows generating distance constraints for matching *bonds defined in the System block* (page 37). The bonds for which distance constraints will be generated can be selected based on the elements of the bonded atoms, as well as the bond order defined in the System block. The following example would constrain all carbon-carbon single bonds to a distance of 1.4 Angstrom, and all bonds with hydrogen atoms to their initial distance:

```
Constraints
   All single bonds C C to 1.4
   All bonds H *
End
```

It is also possible to constrain neighboring bonds and the angle between them using the combination `All triangles`. This is mostly useful for water molecules, which can then easily be made entirely rigid:

```
All triangles H O H
```

Warning: It is very easy to generate a large number of interdependent distance constraints using the `All triangles` keyword. Interdependent distance constraints can impair optimizer performance and should be avoided. Consider for example the input `All triangles H C H` for methane: there are 6 triangles matching this description in CH4, generating 18 interdependent distance constraints. A rigid CH4 would be better set up using a block constraint.

See below for a full description of the `Constraints%All` keyword.

Constraints

All

Type String

Recurring True

Description Fix multiple distances using one the following formats: All [bondOrder] bonds at1 at2 [to distance] All triangles at1 at2 at3

The first option constrains all bonds between atoms at1 at2 to a certain length, while the second - bonds at1-at2 and at2-at3 as well as the angle between them.

The [bondOrder] can be a number or a string such as single, double, triple or aromatic. If it's omitted then any bond between specified atoms will be constrained. Atom names are case-sensitive and they must be as they are in the Atoms block, or an asterisk '*' denoting any atom. If the distance is omitted then the bond length from the initial geometry is used.

Important: only the bonds present in the system at the start of the simulation can be constrained, which means that the bonds may need to be specified in the System block.

Valid examples: All single bonds C C to 1.4 All bonds O H to 0.98 All bonds O H All bonds H * All triangles H * H

Block constraints

Block constraints can be used to treat parts of the System as a rigid unit in the optimization.

`BlockAtoms [atomIdx1 ... atomIdxN]` Creates a block constraint (freezes all internal degrees of freedom) for a set of atoms identified by the list of integers `[atomIdx1 ... atomIdxN]`. These atom indices refer to the order of the atoms in the `System%Atoms` block.

`Block regionName` Creates a block constraint (freezes all internal degrees of freedom) for a all atoms in a *region* (page 36) defined in the `System%Atoms` block. Example:

```
System
   Atoms
      C  0.0  0.0  0.0    region=myblock
      C  0.0  0.0  1.0    region=myblock
      C  0.0  1.0  0.0
   End
End
Constraints
   Block myblock
End
```

Lattice constraints

For lattice optimizations, the following constraints can be used on the lattice degrees of freedom:

`FreezeStrain [xx] [xy] [xz] [yy] [yz] [zz]` Exclusively for lattice optimizations: Freezes any lattice deformation corresponding to a particular component of the strain tensor. Accepts a set of strain components [xx, xy, xz, yy, yz, zz] to be frozen.

`EqualStrain [xx] [xy] [xz] [yy] [yz] [zz]` Exclusively for lattice optimizations: Accepts a set of strain components [xx, xy, xz, yy, yz, zz] which are to be kept equal. The applied strain will be determined by the average of the corresponding stress tensors components.

Restraints

Not all optimizers support constraints. An alternative is to use so-called restraints. These are not exact constraints, but rather a number of springs that pull the system towards the preferred constraints, see *Restraints* (page 284).

4.3.6 Optimization under pressure / external stress

Pressure (page 282) or *non-isotropic external stress* (page 282) can be included in your simulation via the corresponding *engine addons* (page 278).

4.3.7 Optimization methods

The AMS driver implements a few different geometry optimization algorithms. It also allows to choose the coordinate space in which the optimization is performed:

```
GeometryOptimization
   Method [Auto | Quasi-Newton | FIRE | L-BFGS | ConjugateGradients | Dimer]
   CoordinateType [Auto | Delocalized | Cartesian]
End
```

GeometryOptimization

Method

Type Multiple Choice

Default value Auto

Options [Auto, Quasi-Newton, FIRE, L-BFGS, ConjugateGradients, Dimer]

GUI name Optimization method

Description Select the optimization algorithm employed for the geometry relaxation. Currently supported are:

the Hessian-based Quasi-Newton-type BFGS algorithm,

the fast inertial relaxation method (FIRE),

the limited-memory BFGS method,

and the conjugate gradients method. The default is to choose an appropriate method automatically based on the engine's speed, the system size and the supported optimization options.

CoordinateType

Type Multiple Choice

Default value Auto

Options [Auto, Delocalized, Cartesian]

GUI name Optimization space

Description Select the type of coordinates in which to perform the optimization. 'Auto' automatically selects the most appropriate CoordinateType for a given Method.

If 'Auto' is selected, Delocalized coordinates will be used for the Quasi-Newton method, while Cartesian coordinates will be used for all other methods.

We **strongly** advise leaving both the `Method` as well as the `Coordinate` type on the `Auto` setting. There are many restrictions as to which optimizer and coordinate type can be used together with which kind of optimization. The following (roughly) sketches the compatibility of the different optimizers and options:

Optimizer	Constraints	Lattice opt.	Coordinate types
Quasi-Newton	All, except strain	Yes	All
FIRE	Fixed coordinates, distances, strain	Yes	Cartesian
L-BFGS	No	Yes	Cartesian
Conjugate gradients	No	No	Cartesian

Furthermore for optimal performance the optimizer should be chosen with the speed of the engine: a faster engine in combination should use an optimizer with little overhead (FIRE), while slower engines should use optimizers that strictly minimize the number of steps (Quasi-Newton). This is all handled automatically by default, and we recommend changing `Method` and `Coordinate` only in case there are problems with the automatic choice.

The following subsections list the strengths and weaknesses of the individual optimizers in some more detail, motivating why which optimizer is chosen automatically under which circumstances.

Quasi-Newton

This optimizer implements a quasi Newton approach[1][2][3], using the Hessian for computing changes in the geometry so as to reach a local minimum. The Hessian itself is typically *approximated* (page 58) in the beginning and updated in the process of optimization. It uses delocalized coordinates by default both for molecules and periodic systems. The molecular part is based mainly on the work by Marcel Swart[4]. Cartesian coordinates are used in the presence of an external electric field and/or frozen atom constraints.

The Quasi-Newton (QN) optimizer supports all types of constraints and can be used for both molecular and periodic systems, including lattice optimizations. For cases where the optimization can be performed in delocalized coordinates, the number of steps taken to reach the local minimum is usually smaller than when optimizing in Cartesian ones. For fast compute *engines* (page 270), the overhead of the QN optimizer can become a bottleneck of the calculation, thus a more light-weight optimizer such as *FIRE* (page 59) may give an better overall performance. In principle, a QN optimization in delocalized coordinates may run out of memory for a very large system (say over 1000 atoms) because of the SVD step. However, since it is going to be used for a moderate-to-slow engine we still recommend sticking to it for the benefit of fewer steps. Because of these properties the QN optimizer is the default in AMS for all kinds of optimizations with moderate and slow engines, such DFTB and ADF. It is also used as the optimizer back-end for the *PES scan task* (page 69), the *transition state search* (page 66) as well as the calculation of the *elastic tensor* (page 204).

Details of the Quasi-Newton optimizer are configured in a dedicated block:

```
GeometryOptimization
   Quasi-Newton
      MaxGDIISVectors integer
      Step
         TrustRadius float
         VaryTrustRadius Yes/No
      End
      UpdateTSVectorEveryStep Yes/No
   End
End
```

`GeometryOptimization`

`Quasi-Newton`

Type Block

Description Configures details of the Quasi-Newton geometry optimizer.

`MaxGDIISVectors`

Type Integer

Default value 0

[1] L. Versluis and T. Ziegler, *The determination of Molecular Structure by Density Functional Theory*, Journal of Chemical Physics 88, 322 (1988) (https://doi.org/10.1063/1.454603)

[2] L. Versluis, The determination of molecular structures by the HFS method, PhD thesis, University of Calgary, 1989

[3] L. Fan and T. Ziegler, *Optimization of molecular structures by self consistent and non-local density functional theory*, Journal of Chemical Physics 95, 7401 (1991) (https://doi.org/10.1063/1.461366)

[4] M. Swart and F.M. Bickelhaupt, *Optimization of strong and weak coordinates*, International Journal of Quantum Chemistry 106, 2536 (2006) (https://doi.org/10.1002/qua.21049)

Description Sets the maximum number of GDIIS vectors. Setting this to a number >0 enables the GDIIS method.

Step

Type Block

Description

TrustRadius

Type Float

Description Initial value of the trust radius.

VaryTrustRadius

Type Bool

Description Whether to allow the trust radius to change during optimization. By default True during energy minimization and False during transition state search.

UpdateTSVectorEveryStep

Type Bool

Default value Yes

GUI name Update TSRC vector every step

Description Whether to update the TS reaction coordinate at each step with the current eigenvector.

The Quasi-Newton optimizer uses the Hessian to compute the step of the geometry optimization. The Hessian is typically approximated in the beginning and then updated during the optimization. A very good initial Hessian can therefore increase the performance of the optimizer and lead to faster and more stable convergence. The choice of the initial Hessian can be configured in a dedicated block:

```
GeometryOptimization
   InitialHessian
      File string
      Type [Auto | UnitMatrix | Swart | FromFile | Calculate |␣
↪CalculateWithFastEngine]
   End
End
```

GeometryOptimization

InitialHessian

Type Block

Description Options for initial model Hessian when optimizing systems with the Quasi-Newton method.

File

Type String

GUI name Initial Hessian from

Description KF file containing the initial Hessian (or the results dir. containing it). This can be used to load a Hessian calculated in a previously with the [Properties%Hessian] keyword.

Type

Type Multiple Choice

Default value Auto

Options [Auto, UnitMatrix, Swart, FromFile, Calculate, CalculateWithFastEngine]

GUI name Initial Hessian

Description Select the type of initial Hessian. Auto: let the program pick an initial model Hessian. UnitMatrix: simplest initial model Hessian, just a unit matrix in the optimization coordinates. Swart: model Hessian from M. Swart. FromFile: load the Hessian from the results of a previous calculation (see InitialHessian%File). Calculate: compute the initial Hessian (this may be computationally expensive and it is mostly recommended for TransitionStateSearch calculations). CalculateWithFastEngine: compute the initial Hessian with a faster engine.

While there are some options for the construction of approximate model Hessians, the best initial Hessians are often those calculated explicitly at a lower level of theory, e.g. the real DFTB Hessian can be used the initial Hessian for an optimization with the more accurate BAND engine. Using the `CalculateWithFasterEngine` keyword can be used to automatically chose a fast engine at a lower level of theory. What the lower level of theory is depends on the main engine used in the calculation: DFTB with the GFN1-xTB model is used as the lower level of theory for relatively slow engines, e.g. DFT based engines. For semi-empirical engines like DFTB or MOPAC, the lower level of theory is currently UFF. If more control over the lower level engine is needed, the initial Hessian can be calculated with a user defined engine and then loaded from file, see *this example* (page 379).

FIRE

The Fast Inertial Relaxation Engine[5] based optimizer has basically no overhead per step, so that the speed of the optimization purely depends on the performance of the used compute *engine* (page 270). As such it is a good option for large systems or fast compute engines, where the overhead of the Quasi-Newton optimizer would be significant. Note that is also supports *fixed atom constraints* (page 53) and *coordinate constraints* (page 53) (as long as the value of the constrained coordinate is already satisfied in the input geometry), distance constraints, as well as lattice optimizations (with strain constraints).

FIRE is selected as the default optimizer for fast compute engines if it is compatible with all other settings of the optimization (i.e. no unsupported constraints or coordinate types).

Note: FIRE is a very robust optimizer. In case of convergence problems with the other methods, it is a good idea to see if the optimization converges with FIRE. If it does not, it is very likely that the problem is not the optimizer but the shape of the potential energy surface …

The details of the FIRE optimizer are configured in a dedicated block. It is quite easy to make the optimization numerically unstable when tweaking these settings, so we strongly recommend leaving everything at the default values.

```
GeometryOptimization
   FIRE
      AllowOverallRotation Yes/No
      AllowOverallTranslation Yes/No
      MapAtomsToUnitCell Yes/No
      NMin integer
      alphaStart float
      dtMax float
      dtStart float
      fAlpha float
      fDec float
```

(continues on next page)

[5] E. Bitzek, P. Koskinen, F. Gähler, M. Moseler and P. Gumbsch, *Structural Relaxation Made Simple*, Physical Review Letters 97, 170201 (2006) (https://doi.org/10.1103/PhysRevLett.97.170201)

(continued from previous page)

```
      fInc float
      strainMass float
   End
End
```

GeometryOptimization

FIRE

Type Block

Description This block configures the details of the FIRE optimizer. The keywords name correspond the the symbols used in the article describing the method, see PRL 97, 170201 (2006).

AllowOverallRotation

Type Bool

Default value Yes

Description Whether or not the system is allowed to freely rotate during the optimization. This is relevant when optimizing structures in the presence of external fields.

AllowOverallTranslation

Type Bool

Default value No

Description Whether or not the system is allowed to translate during the optimization. This is relevant when optimizing structures in the presence of external fields.

MapAtomsToUnitCell

Type Bool

Default value No

Description Map the atoms to the central cell at each geometry step.

NMin

Type Integer

Default value 5

Description Number of steps after stopping before increasing the time step again.

alphaStart

Type Float

Default value 0.1

Description Steering coefficient.

dtMax

Type Float

Default value 1.0

Unit Femtoseconds

Description Maximum time step used for the integration. For ReaxFF and APPLE&P, this value is reduced by 50%.

dtStart

Type Float

Default value 0.25

Unit Femtoseconds

Description Initial time step for the integration.

fAlpha

Type Float

Default value 0.99

Description Reduction factor for the steering coefficient.

fDec

Type Float

Default value 0.5

Description Reduction factor for reducing the time step in case of uphill movement.

fInc

Type Float

Default value 1.1

Description Growth factor for the integration time step.

strainMass

Type Float

Default value 0.5

Description Fictitious relative mass of the lattice degrees of freedom. This controls the stiffness of the lattice degrees of freedom relative to the atomic degrees of freedom, with smaller values resulting in a more aggressive optimization of the lattice.

Limited-memory BFGS

AMS also offers an L-BFGS based geometry optimizer. It usually converges faster than *FIRE* (page 59), but does not support constrained optimizations. For periodic systems it can be quite good for lattice optimizations. The new implementation has not been thoroughly tested yet, therefore never selected automatically. For large systems and fast engines you may want to disable symmetry: simply the detection of (non-existing) symmetry may be a huge overhead.

```
GeometryOptimization
   HessianFree
      Step
         MaxCartesianStep float
         MinRadius float
         TrialStep float
         TrustRadius float
      End
   End
End
```

GeometryOptimization

HessianFree

Type Block

Description Configures details of the Hessian-free (conjugate gradients or L-BFGS) geometry optimizer.

`Step`

Type Block

Description

`MaxCartesianStep`

Type Float

Default value 0.1

Unit Angstrom

Description Limit on a single Cartesian component of the step.

`MinRadius`

Type Float

Default value 0.0

Unit Angstrom

Description Minimum value for the trust radius.

`TrialStep`

Type Float

Default value 0.0005

Unit Angstrom

Description Length of the finite-difference step when determining curvature. Should be smaller than the step convergence criterion.

`TrustRadius`

Type Float

Default value 0.2

Unit Angstrom

Description Initial value of the trust radius.

Conjugate gradients

AMS also offers a conjugate gradients based geometry optimizer, as it was also implemented in the pre-2018 releases of the DFTB program. However, it is usually slightly slower than *FIRE* (page 59), and supports neither lattice nor constrained optimizations. It is therefore never selected automatically, and we do not recommend using it. Like L-BFGS, the conjugate gradients optimizer is also configured in the `HessianFree` block, see L-BFGS section above for details.

Dimer method for TS seach

The dimer method[6] works differently from the quasi-Newton. It is designed to always follow the lowest mode from the initial geometry without requiring the Hessian. The mode (a.k.a. the dimer vector) is defined by two close-lying points (midpoint and endpoint) on the potential energy surface. The vector's direction is found by minimizing the PES curvature (finite-difference second derivative of the energy along the vector) on the hypersphere around the midpoint. This is achieved by iteratively rotating the vector until the estimated rotation angle drops below the `AngleThreshold` value. These are called rotation iterations. After that, a translation iteration is performed that maximized the energy along the dimer vector and minimizes it in all other directions. The optimization is considered converged when the largest energy gradient component dropt below the `Convergence%Gradient` value.

Both the rotation and the translation are performed in Cartesian coordinates using the L-BFGS method as described in[7]. The L-BFGS trust radii are set by the `RotationTrustRadius` and `TranslationTrustRadius` keywords, respectively. The TS search can be restricted to a subset of atomic coordinates defined by the `Region` keyword, in which case only atoms of the selected region are moved during rotations.

Each translation iteration requires two engine evaluations: one for the midpoint and one for the endpoint. Each rotation iteration additionally requires one or two engine evaluations depending on the `ExtrapolateForces` setting. It should be noted that with the default settings the rotations are usually necessary only at the beginning of the optimization. At the later steps the dimer vector (the direction of the search) does not usually change much.

By default, the initial value of the search vector is chosen randomly. This can be changed using either a `ReactionCoordinate` or a `System final` input block described in the *Transition state search* (page 66) section.

```
GeometryOptimization
   Dimer
      AngleThreshold float
      DimerDelta float
      ExtrapolateForces Yes/No
      LBFGSMaxVectors integer
      MaxRotationIterations integer
      Region string
      RotationTrustRadius float
      TranslationTrustRadius float
   End
End
```

GeometryOptimization

Dimer

Type Block

Description Options for the Dimer method for transition state search.

AngleThreshold

Type Float

Default value 1.0

Unit Degree

[6] G. Henkelman and H. Jonsson, *A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives*, Journal of Chemical Physics 111, 7010 (1999) (https://doi.org/10.1063/1.480097)

[7] J. Kästner and P. Sherwood, *Superlinearly converging dimer method for transition state search*, Journal of Chemical Physics 128, 014106 (2008) (https://doi.org/10.1063/1.2815812)

Description The rotation is considered converged when the the rotation angle falls below the specified threshold.

`DimerDelta`

Type Float

Default value 0.01

Unit Angstrom

Description Eucledian distance between the midpoint and the endpoint.

`ExtrapolateForces`

Type Bool

Default value Yes

Description Set to false to call engine to calculate forces at the extrapolated rotation angle instead of extrapolating them.

`LBFGSMaxVectors`

Type Integer

Default value 10

Description Max number of vectors for the L-BFGS algorithm to save.

`MaxRotationIterations`

Type Integer

Default value 10

Description Maximum number of rotation iterations for a single translation step.

`Region`

Type String

Default value *

Description Include only atoms of the specified region(s) in the rotations, which allows searching for a transition state involving selected atoms only.

`RotationTrustRadius`

Type Float

Default value 0.1

Unit Angstrom

Description L-BFGS trust radius during rotation iterations.

`TranslationTrustRadius`

Type Float

Default value 0.1

Unit Angstrom

Description L-BFGS trust radius during translation iterations.

4.3.8 Troubleshooting

Failure to converge

First of all one should look how the energy changed during the latest ten or so iterations. If the energy is decreasing more or less consistently, possibly with occasional jumps, then there is probably nothing wrong with the optimization. This behavior is typical in the cases when the starting geometry was far away from the minimum and the optimization has a long way to go. Just increase the allowed number of iterations, restart from the latest geometry and see if the optimization converges.

If the energy oscillates around some value and the energy gradient hardly changes then you may need to look at the calculation setup.

The success of geometry optimization depends on the accuracy of the calculated forces. The default accuracy settings are sufficient in most cases. There are, however, cases when one has to increase the accuracy in order to get geometry optimization converged. First of all, this may be necessary if you tighten the optimization convergence criteria. In some cases it may be necessary to increase the accuracy also for the default criteria. Please refer to the *engine manuals* (page 270) for instructions on how to increase the accuracy of an engine's energies and gradients. Often this is done with the `NumericalQuality` keyword in the engine input.

A geometry optimization can also fail to converge because the underlying potential energy surface is problematic, e.g. it might be discontinuous or not have a minimum at which the gradients vanish. This often indicates real problems in the calculation setup, e.g. an electronic structure that changes fundamentally between subsequent steps in the optimization. In these cases it is advisable to run a single point calculation at the problematic geometries and carefully check if the results are physically actually sensible.

Finally it can also be a technical problem with the specific *optimization method* (page 55) used. In these cases switching to another method could help with convergence problems. We recommend first trying the *FIRE* (page 59) optimizer, as it is internally relatively simple and stable.

Converged, but did not find a minimum on the PES

If *Normal Modes* (page 207) or *PES point characterization* (page 200) were requested, the *PES character* (page 200) of the final optimized geometry is checked.

While you would generally expect the final optimized geometry to be a local minimum (i.e. no imaginary frequencies), it can happen for the optimization procedure to converge to a saddle point instead (i.e. a stationary point on the PES with one or more imaginary frequency). In that case you will get the following error message:

```
ERROR: Geometry optimization failed! (Converged, but did not find a minimum on the␣
↪PES.)
```

Depending on your application, (small) imaginary frequencies might not be a problem. But if you want to get rid of all imaginary frequencies, these are a few recommendations:

- Try using a tighter *gradient convergence threshold* (page 48) (`GeometryOptimization%Convergence%Gradient`). E.g. 1.0E-4 (instead of the default 1.0E-3).
- Try using the *MaxRestart* (page 51) option. Reasonable values for MaxRestart range from 2 to 20 (if there are many imaginary frequencies, a larger value might be needed). When using the `MaxRestart` option, you might try increasing `RestartDisplacement`.
- Open the results with the **AMSSpectra** GUI module and visually inspect the negative/imaginary vibrational modes. You can then manually perturb the input geometry along those modes and re-run the optimization.
- If the system is symmetric and *symmetry* (page 35) is enabled, the optimizer will try not to break the symmetry of the system. It might be that in order to reach the local minimum, symmetry must be broken. Try disabling

symmetry (`UseSymmetry False`) and slightly perturb the atomic coordinates in order to break the symmetry (or use the *PerturbCoordinates* (page 33) option.)

Restarting a geometry optimization

During a running optimization the system's geometry is written out to the AMS driver's output file `ams.rkf` after every step (in the `Molecule` section). This means that crashed or otherwise canceled geometry optimizations can be restarted by simply loading the last frame from there using the `LoadSystem` keyword, see *its documentation* (page 40) in the system definition section of this manual:

```
LoadSystem File=my_crashed_GO.results/ams.rkf
```

This can of course also be used to continue an optimization but e.g. with tighter convergence criteria or a different optimizer, as it essentially starts a new geometry optimization from the previous geometry, and does not propagate any information internal to the optimizer (e.g. the approximate Hessian for the Quasi-Newton optimizer or the FIRE velocities) to the new job. As such it might take a few more steps to convergence than if the original job had continued, but allows for additional flexibility.

4.4 Transition state search

A transition state (TS) search is very much like a *geometry optimization* (page 47): the purpose is to find a stationary point on the potential energy surface, primarily by monitoring the energy gradients, which should vanish. The difference between a transition state and a minimum is that at the transition state the Hessian has a negative eigenvalue: We are at a saddle point, not a minimum, with the "negative" mode connecting the two basins on the potential energy surface.

See also:

- *Examples* (page 379)
- Tutorial Transition state search and characterization of a Ziegler Natta Catalyst
- Tutorial Tips and Tricks for Transition State Searches for Click Reactions

A transition state search in AMS is performed by selecting the corresponding task:

```
Task TransitionStateSearch
```

Due to the similarities between energy minimization and transition state search, the `TransitionStateSearch` task in AMS is actually implemented as a special kind of geometry optimization using either the *quasi-Newton* (page 57) or the *dimer* (page 63) optimizer. As such most settings and keywords described on the *geometry optimization manual page* (page 47) also apply to transition state searches.

In a geometry optimization with a quasi-Newton based optimizer the Hessian is used to make a reasonably sized step in the "downhill" direction on the potential energy surface, as the goal is simply to minimize the energy. A transition state search is a bit different: In the first step a normal mode is picked along which the energy is to be *maximized*, while it is *minimized* along all other directions. Normally the mode with the lowest eigenvalue is picked, since we know that there should be exactly one negative eigenvalue at the TS geometry, but one can also choose an approximate reaction coordinate, either by setting the `ReactionCoordinate` or by adding another System block named `final`, similar to how it's done for NEB. If the initial geometry is sufficiently close to the transition state, i.e. we are close to the saddle, the lowest mode is normally the correct one to follow in order to get to the ridge of the saddle. Alternatively a different mode can also be selected manually.

```
TransitionStateSearch
   ModeToFollow integer
   ReactionCoordinate
```

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```
      Angle string
      Block string
      BlockAtoms integer_list
      Coordinate string
      Dihedral string
      Distance string
   End
End
```

TransitionStateSearch

Type Block

Description Configures some details of the transition state search.

ModeToFollow

Type Integer

Default value 1

Description In case of Transition State Search, here you can specify the index of the normal mode to follow (1 is the mode with the lowest frequency).

ReactionCoordinate

Type Block

Description Specify components of the transition state reaction coordinate (TSRC) as a linear combination of internal coordinates (distances or angles).

Angle

Type String

Recurring True

Description The TSRC contains the valence angle between the given atoms. Three atom indices followed by the weight.

Block

Type String

Recurring True

Description Name of the region. Only atoms of the region will be included in the TSRC. It is useful when computing the reaction coordinate from the initial Hessian, in which case only part of the Hessian will be analyzed.

BlockAtoms

Type Integer List

Value Range value > 0

Recurring True

Description List of atom indices. Only the listed atoms will be included in the TSRC. It is useful when computing the reaction coordinate from the initial Hessian, in which case only part of the Hessian will be analyzed.

Coordinate

Type String

Recurring True

Description The TSRC contains Cartesian displacement of an atom: atom index followed by [x|y|z] and the weight.

`Dihedral`

Type String

Recurring True

Description The TSRC contains the dihedral angle between the given atoms. Four atom indices followed by the weight.

`Distance`

Type String

Recurring True

Description The TSRC contains the distance between the given atoms. Two atom indices followed by the weight.

This selection happens only in the first step. Subsequent steps will attempt to maximize along the mode that resembles most (by overlap) the previous maximization direction.

Practice shows that a transition state are much harder to find than a minimum. For a large part this is due to the much stronger anharmonicities that usually occur near the TS, which threaten to invalidate the quasi-Newton methods to find the stationary point. For this reason it is good advice to be more cautious in the optimization strategy when approaching a transition state:

- We recommend starting the transition state search with an intial geometry that is already close to the transition state. One can use a *potential energy surface scan* (page 69) along something resembling the reaction coordinate to get a rough idea where the transition state is. This geometry can then be used as an initial geometry for the transitions state search.
- It is strongly recommended to provide a good initial Hessian for the transition state search. Otherwise the first step of the search may not be taken in the correct direction and subsequent steps may keep steering in the wrong direction. In AMS this is easily possible by loading a Hessian from a previous calculation, see the *initial Hessian section* (page 58) of this manual. A good way to obtain a reasonable Hessian is to compute it explicitly with one of the fast engines (i.e. at a lower lever of theory) and read that Hessian as the initial Hessian for the transition state search at a higher level of theory.
- When no accurate initial Hessian is available, it may be a good idea to specify an approximate normal mode vector using the `ReactionCoordinate` input block. A reaction coordinate (RC) is a linear combination of distances and/or valence and dihedral angles:

  ```
  TransitionStateSearch
    ReactionCoordinate
      Distance  i j     fac
      Distance  i j     fac
      Angle     i j k   fac
      Dihedral  i j k l fac
    End
  End
  ```

  Here, `i`, `j`, `k`, and `l` are atom indices, and the `fac` is the factor with which the internal coordinate enters the linear combination.

  One should be careful when specifying more than one bond or angle as the reaction coordinate. For example, suppose atom 2 is located between atoms 1 and 3. Then the following ReactionCoordinate block:

```
TransitionStateSearch
  ReactionCoordinate
    Distance 1 2  1.0
    Distance 2 3 -1.0
  End
End
```

means that the RC consists of two distances: R(1-2) and R(2-3). The positive direction of the RC is defined as an increase of the R(1-2) and a decrease of the R(2-3). In other words, this RC corresponds to atom 2 moving along the R(1-3) axis.

- As an alternative to `ReactionCoordinate` one can add a second System to the input and call it `final`. The difference between the initial and the `final` geometry will be used as the reaction coordinate. For non-periodic systems, the difference is computed in the internal coordinates and only coordinates that differ significantly (by more than about 0.1 Bohr or radian) are included. For this reason, the `final` geometry should not be too close to the initial. For periodic systems, the difference in the Cartesian coordinates is used. In this case, only coordinates that differ by more than 0.5 Bohr are included.
- When the method converges it is usually a good idea to verify that the found geometry is indeed a transition state. This can be done by performing a frequency analysis and checking whether the Hessian has exactly one negative eigenvalue (represented by a mode with a negative frequency). Doing so is expensive however. Since we are really only interested in the lowest two normal modes calculating the full Hessian is however not necessary and one can use the faster PES point characterization instead. This uses a Davidson-type algorithm to obtain the lowest few normal modes without constructing the full Hessian. The user is referred to the *PES point characterization* (page 200) documentation page for further details.

4.5 Linear Transit, PES scan

The PES scan task in AMS allows users to scan the potential energy surface of a system along one or multiple degrees of freedom, while relaxing all other degrees of freedom. If only one coordinate is scanned, this kind of calculation is usually just called a linear transit. However, since AMS allows scanning of multiple coordinates, and linear transit is just a special case of such a calculation, the task is always called a PES scan in AMS.

A linear transit may be used for instance to sketch an approximate path over the transition states between reactants and products. From this a reasonable guess for the Transition State can be obtained which may serve as starting point for a true transition state search for instance.

See also:

- *Examples* (page 379)
- Tutorial Transition state search and characterization of a Ziegler Natta Catalyst

The PES scan task is enabled by selecting it with the `Task` keyword:

```
Task PESScan
```

The `PESScan` block configures all details of the scan:

```
PESScan
   CalcPropertiesAtPESPoints [True | False]
   FillUnconvergedGaps [True | False]
   ScanCoordinate
      nPoints integer
      Coordinate integer [x|y|z] (float){2}
      Distance (integer){2} (float){2}
```

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```
      Angle (integer){3} (float){2}
      Dihedral (integer){4} (float){2}
      SumDist (integer){4} (float){2}
      DifDist (integer){4} (float){2}
      FromLattice
         ...
      End
      ToLattice
         ...
      End
      FromStrainVoigt (float){6}
      ToStrainVoigt (float){6}
      CellVolumeRange (float){2}
      CellVolumeScalingRange (float){2}
      LatticeARange (float){2}
      LatticeBRange (float){2}
      LatticeCRange (float){2}
   End
End
```

The `PESScan` block needs to contain at least one `ScanCoordinate` block specifying which coordinate to scan, and how many points (keyword `nPoints`) to sample along this coordinate. By default, 10 points are sampled along each scanned coordinate (including the start and end point of the scan).

4.5.1 Distance, angle, and dihedral angle coordinates

The coordinate descriptors are very similar to the *constraint descriptors* (page 52) in the `Constraints` block used by the geometry optimization task, but are followed by two values delimiting the start and end of the coordinates, instead of just a single value:

`Coordinate atomIdx [x|y|z] startValue endValue` Moves the atom with index `atomIdx` (following the order in the `System` block) along the a cartesian coordinate (`x`, `y` or `z`), starting at `startValue` and ending at `endValue` (given in Angstrom).

`Distance atomIdx1 atomIdx2 startDist endDist` Scans the distance between the atoms with index `atomIdx1` and `atomIdx2`, starting from `startDist` and ending at `endDist`, both given in Angstrom.

`Angle atomIdx1 atomIdx2 atomIdx3 startAngle endAngle` Scans the angle (1)–(2)–(3) between the atoms with indices `atomIdx1-3`, as given by their order in the `System%Atoms` block. The scanned angle starts at `startAngle` and ends at `endAngle`, given in degrees.

`Dihedral atomIdx1 atomIdx2 atomIdx3 atomIdx4 startAngle endAngle` Scans the dihedral angle (1)–(2)–(3)–(4) between the atoms with indices `atomIdx1-4`, as given by their order in the `System%Atoms` block. The scanned dihedral starts at `startAngle` and ends at `endAngle`, given in degrees.

`SumDist atomIdx1 atomIdx2 atomIdx3 atomIdx4 start end` Scans the sum of the distances R(1,2)+R(3,4) between the atoms with indices `atomIdx1-4`, as given by their order in the `System%Atoms` block. The values to be scanned start at `start` and end at `end`, given in Angstrom.

`DifDist atomIdx1 atomIdx2 atomIdx3 atomIdx4 start end` Scans the difference between the distances R(1,2)-R(3,4) of the atoms with indices `atomIdx1-4`, as given by their order in the `System%Atoms` block. The values to be scanned start at `start` and end at `end`, given in Angstrom.

4.5.2 Joint scan coordinates

Note that multiple of these coordinate descriptors can be combined within a single `ScanCoordinate` block. This combines the individual coordinates into one compound coordinate, i.e. all coordinates will transit together through their respective ranges. In this way the symmetric stretch in water could be scanned by specifying the following single `ScanCoordinate` block (assuming that the oxygen atom is the first in the `System%Atoms` block):

```
ScanCoordinate
   Distance  1 2  0.8 1.1
   Distance  1 3  0.8 1.1
End
```

4.5.3 Multidimensional PES scan

A multidimensional PES scan can be performed by specifying multiple `ScanCoordinate` blocks in the input. To scan the space spanned by the bending and symmetric stretch modes in water, one would use the following scan coordinates:

```
ScanCoordinate
   Distance  1 2  0.8 1.1
   Distance  1 3  0.8 1.1
End
ScanCoordinate
   Angle  2 1 3  90 130
End
```

In principle an arbitrary number of `ScanCoordinate` blocks can be combined to specify the scanned configuration space. However, the total number of sample points is the product of the number of points along all coordinates, and hence grows quickly with the number of dimensions. Furthermore, only 1D (linear transit) and 2D PES scans can be visualized in the GUI. We therefore suggest sticking with <=2 dimensional PES scans. (Note that it is possible to constrain additional degrees of freedom through the `Constraints` block. This could be used to sample a few points along a third dimension "manually", while still being able to see the surfaces in the GUI.)

4.5.4 Lattice scan coordinates for periodic systems

Several ways to scan lattice degrees of freedom were added to the AMS2022.1 release. **Note that for each unit cell, a geometry optimization is performed**. To keep the fractional coordinates fixed during the PES Scan, set `GeometryOptimization%MaxIterations` to `0`.

There can be only one scan coordinate for lattice degrees of freedom in a single PES scan job. Also note that scan coordinates for lattice degrees of freedom may not contain other coordinate descriptors within the same scan coordinate. Is is for example *not* possible to have a *joint scan coordinate* (page 71) for a concerted lattice and bond length stretch.

It is, however, perfectly fine to combine a lattice scan coordinate with another scan coordinate for a *two-dimensional PES scan* (page 71).

See also:

Example input files (page 420) for PES scan jobs with lattice degrees of freedom.

Important: If you use k-space sampling (e.g., with BAND or DFTB), then the k-space grid is determined for the **input structure**, which is not necessarily any of the sampled points.

Isotropic scaling of the unit cell volume or area

`CellVolumeScalingRange startValue endValue` Isotropic scaling of the unit cell. Example: `CellVolumeScalingRange 0.9 1.1` will scale the volume between 90% and 110% of the original unit cell. For 2D-periodic crystals, the area will be scaled instead.

`CellVolumeRange startValue endValue` Isotropic scaling of the unit cell. Example: `CellVolumeRange 300 500` will scale the volume between 300 Å^3 and 500 Å^3 for a 3d-periodic system. For 2D-periodic systems, the area will be scaled between 300 Å^2 and 500 Å^2.

Scaling of the lattice vector lengths

These options keep the angles between lattice vectors fixed.

`LatticeARange startValue endValue` Scans the length of the **first** lattice vector. Can be combined with the LatticeBRange and LatticeCRange keywords, but no other coordinates within the same ScanCoordinate. Unit: angstrom.

`LatticeBRange startValue endValue` Scans the length of the **second** lattice vector. Can be combined with the LatticeARange and LatticeCRange keywords, but no other coordinates within the same ScanCoordinate. Unit: angstrom.

`LatticeCRange startValue endValue` Scans the length of the **third** lattice vector. Can be combined with the LatticeARange and LatticeBRange keywords, but no other coordinates within the same ScanCoordinate. Unit: angstrom.

Strain matrix in Voigt notation

3D crystal: `FromStrainVoigt xx yy zz yz xz xy`, `ToStrainVoigt xx yy zz yz xz xy` The `FromStrainVoigt` and `ToStrainVoigt` keywords need to be applied together. Example: `FromStrainVoigt -0.1 -0.1 -0.1 -0.1 -0.1 -0.1`, `ToStrainVoigt 0.1 0.1 0.1 0.1 0.1 0.1`

2D crystal: `FromStrainVoigt xx yy xy`, `ToStrainVoigt xx yy xy` The `FromStrainVoigt` and `ToStrainVoigt` keywords need to be applied together. Example: `FromStrainVoigt -0.1 -0.1 -0.1`, `ToStrainVoigt 0.1 0.1 0.1`

1D crystal: `FromStrainVoigt xx`, `ToStrainVoigt xx` The `FromStrainVoigt` and `ToStrainVoigt` keywords need to be applied together. Example: `FromStrainVoigt -0.1`, `ToStrainVoigt 0.1`

Scan arbitrary lattices

Scan arbitrary lattices specifying the initial and final lattice vectors, using the same format as in the *System%Lattice* (page 32) block. The PES scan will then interpolate the lattice vectors linearly between these two values:

```
ScanCoordinate
   FromLattice
      ! lattice vectors as in System%Lattice
   End
   ToLattice
      ! ...
   End
End
```

4.5.5 Calculate properties for all PES points

By default the engine result files for the individual PES points are not saved on disk, as this can easily lead to huge amounts of data to be stored. This behavior can be changed with the `PESScan%CalcPropertiesAtPESPoints` keyword:

`PESScan`

`CalcPropertiesAtPESPoints`

Type Bool

Default value No

Description Whether to perform an additional calculation with properties on all the sampled points of the PES. If this option is enabled AMS will produce a separate engine output file for every sampled PES point.

Note that this performs a full single point calculation on every sampled PES point, including the calculation of any *PES point properties* (page 198) selected in `Properties` block.

4.5.6 Troubleshooting

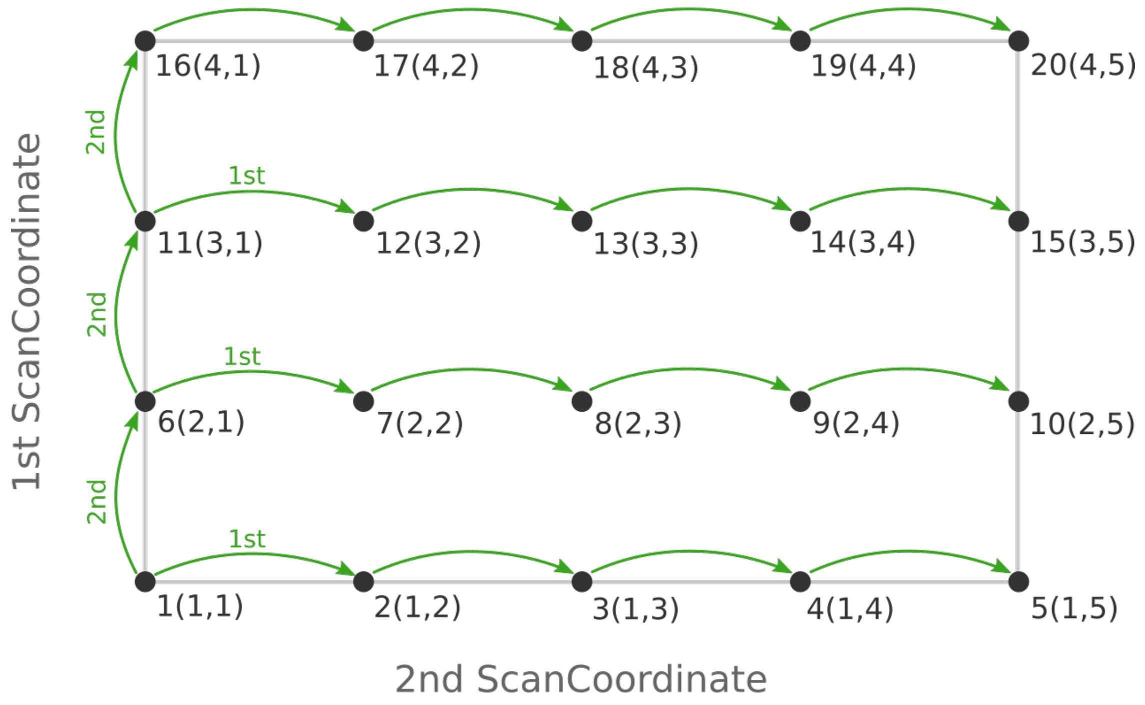
Technically all PES scan calculations are conducted as a series of geometry optimizations with constraints for the scanned coordinates, where the value of the constraint varies slowly through the scanned range. In this way every sampled point on the potential energy surface corresponds to a particular set of constraints. As with any geometry optimization, it can happen that an optimization towards a particular point on the potential energy surface does not converge. This is the most common problem encountered during PES scan calculations.

Since PES scans are implemented as a series of geometry optimizations, they are influenced by the settings used for the geometry optimizer, e.g. its convergence thresholds and the maximum number of steps before an optimization is considered to have failed. The optimizer is configured in the `GeometryOptimization` block, see the page on *geometry optimization* (page 47) in the AMS manual.

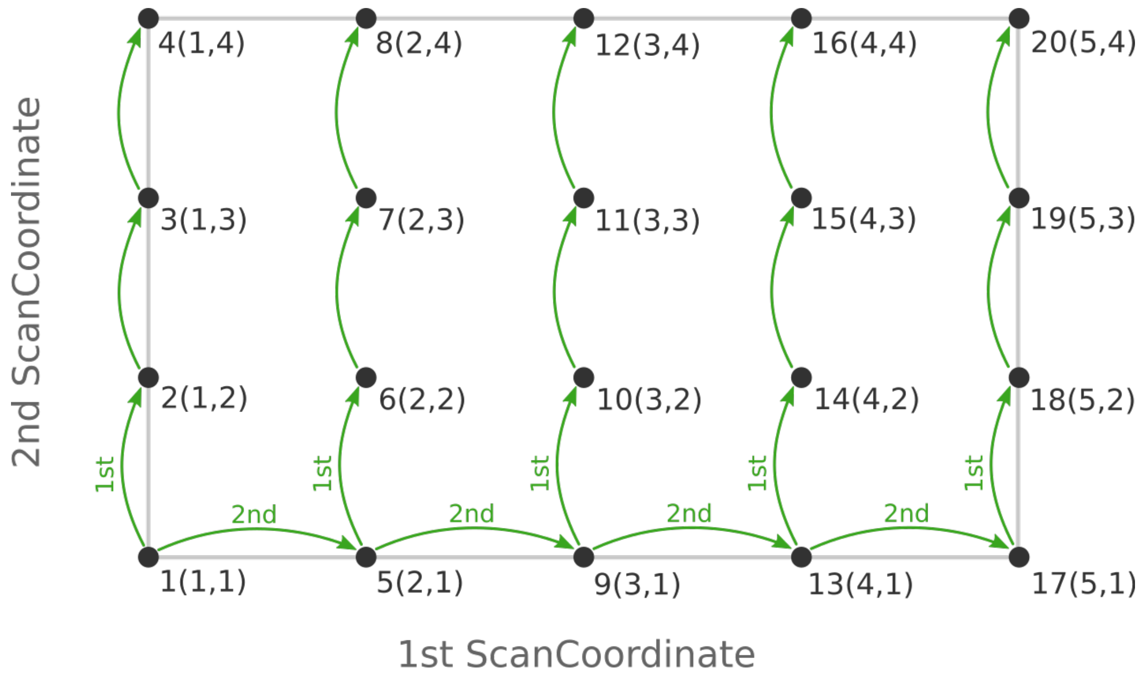
While tweaking the geometry optimizer's settings can sometimes help with convergence problems, these problems can also be easily caused by errors in the user input.

A very common problem is that the geometry in the input, i.e. the `System` block, is incompatible with the starting values of the scanned coordinates. This would for example be the case if one wants to scan a dihedral angle from 0 to 90 degrees, but the actual angle on the input geometry is close to 90 degrees. In this case it would be better to flip the scanned range from 90 to 0 degrees, so that the input geometry already close to the first sampled point on the PES. Otherwise the optimization for the first point has to cross a very long distance on the PES, making convergence much harder. AMS automatically detects this and prints a warning. We generally advise preparing the input geometry for a PES scan by first running a geometry optimization with constraints set to lower bound of the scanned coordinate intervals.

For multidimensional PES scans the order in which the PES points are visited depends on the order in which the scanned coordinates are specified, i.e. the order of the `ScanCoordinate` blocks in the input. Generally, the order in which the PES points are visited is such that the coordinate which was specified in the first `ScanCoordinate` block varies **slowest**. This is illustrated in the following figure:



Here the scan starts at point `1(1,1)` at the bottom left corner of the PES and first moves along the entire range of the 2nd scan coordinate, before taking a step along the 1st coordinate to point `6(2,1)`. The same PES points could be visited in a different order (and under different names) if the order of the two `ScanCoordinate` blocks is reversed in the AMS input:



Depending on the shape of the scanned potential energy surface a particular order of visiting the PES points might be easier or harder for the optimizer, and convergence problems can sometimes be fixed by simply changing the order of the scanned coordinates. In the example above, it might be that scanning along the “vertical” direction is “harder” than scanning along the “horizontal” direction. In this case one should use the scan order from the first picture, which has only three “vertical” steps (whereas the other scan order has 15).

Note that AMS has a little safe-guard built in to help with PES scan convergence issues: If the optimization towards a particular PES point did not succeed in the initial attempt, AMS will later try again, but starting from a different (converged) point close to unconverged one. This "PES gap filling" happens at the very end of the calculation, after the initial scan has been completed. This gap filling step is enabled by default, but can be controlled with the `PESScan%FillUnconvergedGaps` keyword:

PESScan

FillUnconvergedGaps

Type Bool

Default value Yes

Description After the initial pass over the PES, restart the unconverged points from converged neighboring points.

4.5.7 Output

Results are printed to the text output and stored in the binary result file `ams.rkf`. Most information is found in the `PESScan` section, which references the corresponding geometries from the `History` section via the `PESScan%HistoryIndices` entry.

PESScan Section content: Data related to the Potential Energy Surface (PES) Scan procedure.

PESScan%GOConverged

Type bool_array

Description Whether the (constrained) optimization at the various PES scan points converged.

Shape [nPoints]

PESScan%HistoryIndices

Type int_array

Description The indices of the frames in the History section corresponding to the PES point values.

Shape [nPoints]

PESScan%HistoryPESPoints

Type int_array

Description ?

PESScan%nPoints

Type int

Description The total number of scanned PES points. This is the product of all nPoints(#) values.

PESScan%nPoints(#)

Type int

Description Number of points along the corresponding scan coordinate.

PESScan%nScanCoord

Type int

Description Number of (independent) coordinates along which the PES scan is performed.

PESScan%PES

Type float_array

Description The total energy at each particular PES point.

Unit hartree

Shape [nPoints]

`PESScan%PESCoords`

Type float_array

Description The values of all coordinates for each particular PES point.

Shape [:, nPoints]

`PESScan%RangeEnd(#)`

Type float_array

Description The final value(s) for the corresponding scan coordinate.

`PESScan%RangeStart(#)`

Type float_array

Description The starting value(s) for the corresponding scan coordinate.

`PESScan%ScanCoord(#)`

Type string_fixed_length

Description A human readable description of the scan coordinate.

4.6 Nudged Elastic Band (NEB)

The Nudged Elastic Band (NEB) method[1] can be used to find a reaction path and the transition state between a reactant and a product state.

At the beginning of a NEB calculation, the geometry of the initial and final systems are optimized to minimize their energy (unless the *OptimizeEnds* (page 79) option is set to False).

Then, a rough approximation of the reaction path is build: a set of *images* is created by performing a linear interpolation between the **initial** and **final** systems. If there is more than two systems provided, a spline interpolation is performed between the initial, all the intermediate (in the lexicographical order) and the final system (see below).

Finally, a reaction path is found by performing a simultaneous optimization of all the images. In the NEB method the images are not independent from each other. The force on each image depend on its neighboring images: at each step the forces parallel to the reaction path are eliminated and a so-called spring force is added that tries to keep each image in the middle between its neighbors. This does not let images slide to the initial or final reaction state and ensures that they are evenly distributed along the reaction path.

During the NEB path optimization, a climbing image algorithm is used to drive the highest-energy image in the path to the transition state (unless the *Climbing* (page 79) option is set to False).

Be aware that NEB is a computationally expensive method, typically involving hundreds if not thousands of energy and gradients evaluations.

See also:

- *Nudged Elastic Band (NEB) Examples* (page 407)

[1] G. Henkelman, B.P. Uberuaga and H. Jonsson, *A climbing image nudged elastic band method for finding saddle points and minimum energy paths*, Journal of Chemical Physics 113, 9901 (2000) (https://doi.org/10.1063/1.1329672)

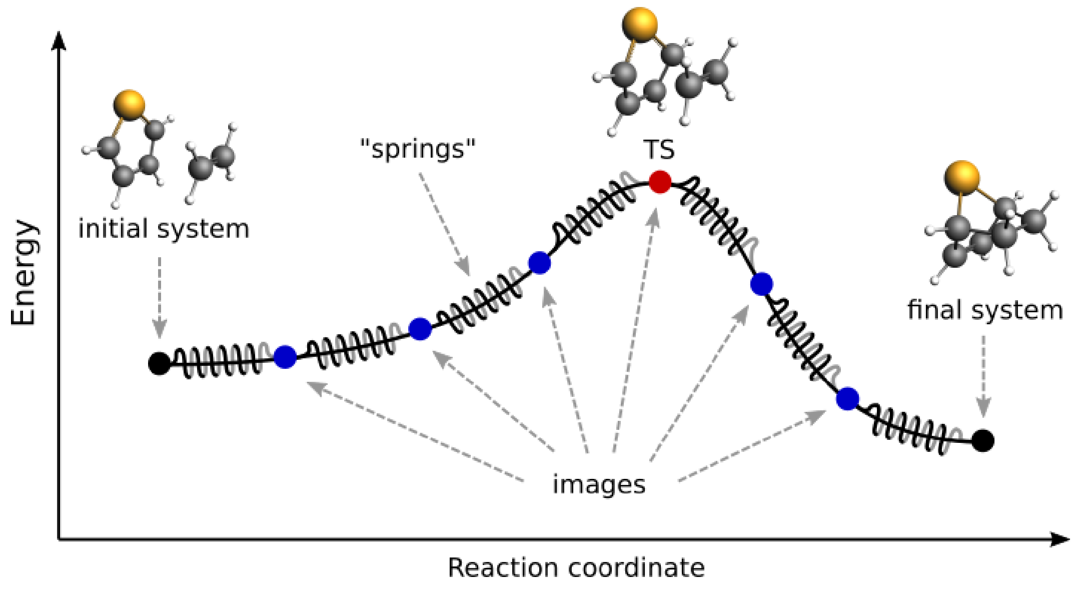


Fig. 4.1: Pictorial representation of a reaction path computed with NEB

- GUI Nudged Elastic Band tutorial

4.6.1 Input

A NEB calculation in AMS is triggered by setting the `Task` to `NEB`:

```
Task NEB
```

The NEB method requires two or more input systems. The first, unnamed system is used as the **initial system** and the system called `final` is used as a **final system**. These two systems are mandatory, unless the `LoadPath` feature is used, see below. This is an example of system-definitions for a HCN isomerization reaction:

```
Task NEB

# This is the initial system:
System
   Atoms
      C   0.0000   0.0000   0.0000
      N   1.1800   0.0000   0.0000
      H   2.1960   0.0000   0.0000
   End
End

# This is the final system (note the header 'final' in the next line):
System final
   Atoms
      C   0.0000   0.0000   0.0000
      N   1.1630   0.0000   0.0000
      H  -1.0780   0.0000   0.0000
   End
End
```

Optionally, **more systems can be used to provide a better approximation for the reaction path**. An intermediate system can have any name, but the name determines its position with respect to others. The intermediate systems are ordered lexicographically using their (case-sensitive) names and then placed evenly in that order between the initial and the final states. After that, the spline interpolation between the geometries (including lattice parameters) will be used to generate the initial images. For example, if you call the intermediate systems `a`, `b`, and `c` then the initial NEB path will be constructed by interpolating along the `initial-a-b-c-final` chain. When providing more than two input systems it may be a good idea to optimize the end points in advance and set *OptimizeEnds* (page 79) to False to prevent creating an unbalanced reaction path. The reason is that the interpolation is performed after the end points are optimized.

For molecular systems, the interpolation can be done either in the redundant internal or in the Cartesian coordinates. For periodic systems, the interpolation can only be done in the Cartesian coordinates.

When using only two systems (the initial and the final) for linear interpolation, AMS will may optionally apply a slightly modified version of the **image dependent pair potential (IDPP)** method described in[2], see `PreOptimizeWithIDPP` below. The differences with the original method are: (a) the initial structure of an image is obtained using interpolation in the redundant internal or Cartesian coordinates as described above, and (b) the weighting factor is using the target distance instead of the current one, which avoids putting too much weight on very short distances.

Note that not only the atomic coordinates, but also the lattice parameters and the charge (if non-zero) must be set for all input systems.

Important: The order in which atoms are specified in the `System%Atoms` blocks **must be the same for all systems**. The order of the atoms must be consistent because the images-interpolation algorithm maps the n-th atom of the initial system to the n-th atom of the final system.

If you have run a PESScan calculation for the system and would like to do NEB, or would like to repeat NEB for it with a different number of images then you can use the `LoadPath` feature. You need to provide the file name from which to load the path using the `File` key. The program will load the last geometries for the path points found in the file and use them for interpolation. Note that this will replace both the initial and the final point. Neither the initial nor the `final` geometry needs to be present in the input in this case because, if present, they will be replaced.

You can choose to use only part of the path, for example if the the PESScan revealed more than one barrier or if its end points do not correspond to minima on the path. In such a case, a list of point to be included in the interpolation should be specified using the `Points` key. Remember that you can specify a list of integers as `i:j`, for example to include points 13 through 25 use `Points 13:25`.

Alternatively, you can choose to use arbitrary geometries from the History section of the ams.rkf file. In this case you can specify their indices in the `Geometries` key. When using the `Geometries` key, the ams.rkf does not have to come from a PESScan or an NEB calculation. It just needs to have the History section with some geometries. It may come, for example, from molecular dynamics.

`NEB`

`LoadPath`

Type Block

Description Provide details about the trajectory to get the initial NEB path from. PESScan and NEB trajectories are supported. Only the last geometry for each point on the trajectory is considered.

`File`

Type String

[2] S. Smidstrup, A. Pedersen, K. Stokbro and H. Jonsson, *Improved initial guess for minimum energy path calculations*, Journal of Chemical Physics 140, 214106 (2014) (http://doi.org/10.1063/1.4878664)

GUI name Initial path file

Description Provide an ams.rkf file to load the initial path from. All geometries of this calculation, including initial and final, will be taken from the History section of the file.

Note that for a PESScan it should be a 1D path.

`Geometries`

Type Integer List

GUI name Raw geometry indices

Description Raw indices of the geometries from the History section. By default the last geometry of each path point is used.

`Points`

Type Integer List

GUI name Path points

Description By default the whole path is used, which may sometimes be not desirable. For example when a PESScan revealed multiple barriers. In this case one can specify indices of the path points to be used. The last geometry of the specified path point will be loaded.

All NEB-specific options are specified in the NEB input block:

```
NEB
   Climbing Yes/No
   ClimbingThreshold float
   Images integer
   InterpolateInternal Yes/No
   InterpolateShortest Yes/No
   Iterations integer
   Jacobian float
   LoadPath
      File string
      Geometries integer_list
      Points integer_list
   End
   MapAtomsToCell Yes/No
   OldTangent Yes/No
   OptimizeEnds Yes/No
   OptimizeLattice Yes/No
   Parallel
      nCoresPerGroup integer
      nGroups integer
      nNodesPerGroup integer
   End
   PreOptimizeWithIDPP Yes/No
   ReOptimizeEnds Yes/No
   Restart string
   Skewness float
   Spring float
End
```

All keys of the NEB block have reasonable defaults or are optional. Thus, in principle, the NEB block can be omitted altogether. These are the main options:

NEB

Images

Type Integer

Default value 8

GUI name Number of images

Description Number of NEB images (not counting the chain ends). Using more images will result in a smoother reaction path and can help with convergence problems, but it will also increase the computation time.

`Iterations`

Type Integer

GUI name Maximum number of iterations

Description Maximum number of NEB iterations. The default value depends on the number of degrees of freedom (number of images, atoms, periodic dimensions).

`Spring`

Type Float

Default value 1.0

Unit Hartree/Bohr^2

GUI name Spring value

Description Spring force constant in atomic units.

`Skewness`

Type Float

Default value 1.0

GUI name Skewness

Description Degree of how much images are shifted towards or away from the TS, which may help tackle problems with a long reaction path (for example involving a loose adsorption complex) without needing too many images. A value greater than 1 will make sure that images are concentrated near the transition state. The optimal value depends on the path length, the number of images (larger [Skewness] may be needed for a longer path and fewer images). Technically [Skewness] is equal to the ratio between the optimized distances to the lower and the higher neighbor image on the path.

`Climbing`

Type Bool

Default value Yes

GUI name Climb highest image to TS

Description Use the climbing image algorithm to drive the highest image to the transition state.

`ClimbingThreshold`

Type Float

Default value 0.0

Unit Hartree/Bohr

GUI name CI force threshold

Description Climbing image force threshold. If ClimbingThreshold > 0 and the max perpendicular force component is above the threshold then no climbing is performed at this step. This entry can be used to get a better approximation for the reaction path before starting the search for the transition state. A typical value is 0.01 Hartree/Bohr.

`InterpolateInternal`

Type Bool

Default value Yes

GUI name Interpolate in Internal coordinates

Description The initial NEB image geometries are calculated by interpolating between the initial and the final state. By default, for non-periodic systems the interpolation is performed in internal coordinates but the user can choose to do it in the Cartesian ones. For periodic systems the interpolation is always done in Cartesian coordinates. If PreOptimizeWithIDPP is set then the path may be further refined using the image-dependent pair potential (IDPP).

`InterpolateShortest`

Type Bool

Default value Yes

GUI name Interpolate across cell boundary

Description Allow interpolation across periodic cell boundaries. Set to false if an atom is intended to move more than half across the simulation box during reaction.

`PreOptimizeWithIDPP`

Type Bool

Default value No

GUI name Use IDPP

Description (Experimental) When there is only initial and final system available, the image-dependent pair potential (IDPP, doi: 10.1063/1.4878664) can be used to determine the initial NEB path by interpolating all interatomic distances between the two points and optimizing intermediate images towards them. The optimization starts from the geometries obtained using the selected interpolation options.

`OptimizeEnds`

Type Bool

Default value Yes

GUI name Optimize reactants/products

Description Start the NEB with optimization of the reactant and product geometries.

`Restart`

Type String

GUI name Restart from

Description Provide an ams.rkf file from a previous NEB calculation to restart from. It can be an unfinished NEB calculation or one performed with different engine parameters.

`ReOptimizeEnds`

Type Bool

Default value No

GUI name Re-optimize reactants/products

Description Re-optimize reactant and product geometries upon restart.

The following keys are related to solid-state NEB (SS-NEB):

`NEB`

`OptimizeLattice`

Type Bool

Default value No

GUI name Optimize lattice

Description Turn on the solid-state NEB (SS-NEB).

`Jacobian`

Type Float

GUI name Jacobian value

Description Scaling factor used to convert the lattice strain to a NEB coordinate value. Default value: sqrt(N)*(V/N)^(1/d), where V - lattice volume (area for 2D, length for 1D), N - number of atoms, and d - number of periodic dimensions.

`MapAtomsToCell`

Type Bool

Default value Yes

GUI name Map atoms to cell

Description Translate atoms to the [-0.5,0.5] cell before every step. This option cannot be disabled for SS-NEB.

At each iteration, the images may be computed in parallel. The parallel execution is normally configured completely automatically, but users can override the automatic parallelization using the keys in the `Parallel` block.

`NEB`

`Parallel`

Type Block

Description Options for double parallelization, which allows to split the available processor cores into groups working through all the available tasks in parallel, resulting in a better parallel performance. The keys in this block determine how to split the available processor cores into groups working in parallel.

`nCoresPerGroup`

Type Integer

GUI name Cores per group

Description Number of cores in each working group.

`nGroups`

Type Integer

GUI name Number of groups

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

nNodesPerGroup

Type Integer

GUI name Nodes per group

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

The following keys modify other aspects of the NEB and should, in principle, be left to their defaults:

NEB

OldTangent

Type Bool

Default value No

GUI name Use old tangent

Description Turn on the old central difference tangent.

4.6.2 Frozen atom constraints

It is possible to perform NEB with part of the system frozen, using any of the following keys of the Constraints block or a combination thereof:

Constraints

Atom

Type Integer

Recurring True

Description Fix the position of an atom. Just one integer referring to the index of the atom in the [System%Atoms] block.

AtomList

Type Integer List

Recurring True

Description Fix positions of the specified atoms. A list of integers referring to indices of atoms in the [System%Atoms] block.

FixedRegion

Type String

Recurring True

Description Fix positions of all atoms in a region.

Note: the frozen atom constraints will be enforced both during the geometry optimizations of the initial and final systems and during the NEB optimization.

4.6.3 Optimizations and convergence criteria

The NEB path is optimized using a limited-memory BFGS (l-BFGS) method where the system being optimized is a union of all NEB images with their respective molecular and spring forces.

The NEB convergence thresholds are defined in the *GeometryOptimization%Convergence block* (page 48). NEB is considered converged when the following criteria are satisfied:

- the change in the highest image energy must be less than [GeometryOptimization%Convergence%Energy]
- the max atomic force component for the highest image must be less than [GeometryOptimization%Convergence%Gradients]
- the max atomic force component for all other images must be less than ten times the [GeometryOptimization%Convergence%Gradients] value.

If the optimization of the initial NEB end point fails to converge, you can try using the *FIRE optimization method* (page 55).

4.6.4 Output

Results are printed to the text output and stored in the binary result file 'ams.rkf'. In the 'ams.rkf' file, NEB calculation results are stored in the History section just like in a normal geometry optimization. The NEB section of the RKF file contains additional, NEB-specific, information.

The NEB reaction path can be visualized using the **AMSmovie GUI module**.

4.6.5 Troubleshooting

- In case the geometry optimization of the initial and final systems fails: try using the *FIRE optimization method* (page 55)
- In case the optimization of the NEB path does not converge:
  - make sure that the order in which the atoms are defined is consistent between the initial and final systems (see the *important* note in the *NEB input section* (page 77));
  - try increasing the number of *NEB images* (page 79);
  - try tweaking the *TrustRadius* (page 61) or *TrialStep* (page 61) options (see *Limited-memory BFGS* (page 61)) ;
  - try specifying one or more **intermediate** systems.

4.7 Intrinsic Reaction Coordinate (IRC)

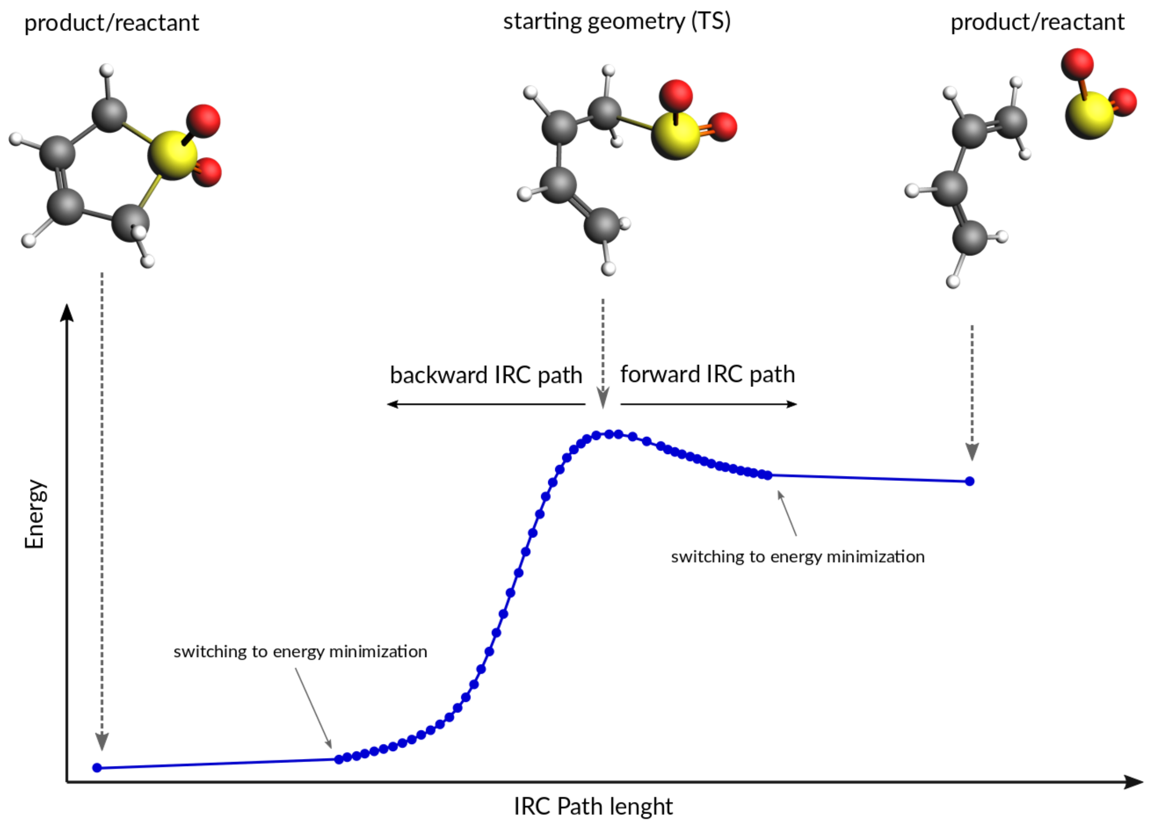
The path of a chemical reaction can be traced from the transition state (TS) to the products and/or reactants using the Intrinsic Reaction Coordinate (IRC) method[1] [2]. **The method assumes that the starting geometry is a fair approximation of the TS**. A minimum energy profile (MEP) is defined as the steepest-descent path on the potential energy surface from the transition state down towards a local minimum. An IRC path is defined similarly but in the mass-weighted coordinates[3], which means that instead of the steepest descent direction it follows that of the maximum instantaneous

[1] L. Deng, T. Ziegler and L. Fan, *A combined density functional and intrinsic reaction coordinate study on the ground state energy surface of H_2 CO*, Journal of Chemical Physics 99, 3823 (1993) (https://doi.org/10.1063/1.466129)

[2] L. Deng and T. Ziegler, *The determination of Intrinsic Reaction Coordinates by density functional theory*, International Journal of Quantum Chemistry 52, 731 (1994) (https://doi.org/10.1002/qua.560520406)

[3] C. Gonzalez and H.B. Schlegel, *Reaction Path Following In Mass-Weighted Internal Coordinates* J. Phys. Chem. 94, 5523-5527 (1990) (https://doi.org/10.1021/j100377a021)

acceleration. This makes IRC somewhat related to the Molecular Dynamics method. The energy profile is obtained as well as the length and curvature properties of the path, providing the basic quantities for an analysis of the reaction path.



See also:

Examples (page 379) and the PES exploration for hydrohalogenation tutorial

4.7.1 Method details

Calculation of an IRC path consists of two nested loops, the so-called outer and inner loops. The outer loop runs over IRC points and the inner loop is over geometry optimization steps for the given IRC point. The first IRC point starts from the transition state geometry, which is a saddle point, in one of the two possible downhill directions. Each IRC point after that starts from the optimized geometry of the previous point. At the start of every step, the pivot point is determined, which is a point at the Step/2 distance in the direction opposite to the gradient. When working in the mass-weighted coordinates, this direction corresponds to the acceleration of the corresponding atom. The final point of the given IRC step corresponds to the energy minimum point at the same distance (Step/2) from the pivot point further downhill. More precisely, the coordinates of the target point are optimized during the inner loop to minimize projection of the gradient on the hypersphere of radius Step/2 around the pivot point. The angle between the (pivot-start) and (pivot-final) vectors determines the curvature of the reaction path. If this angle becomes smaller than 90 degrees then the IRC scan is considered to have reached vicinity of an endpoint and the program switches to energy minimization (options for this energy minimization can be specified in the *Geometry Optimization* (page 48) block.). If the angle is between 90 and 120 degrees then the current IRC step is canceled and a new one is started from the same starting point with half the initial Step parameter. In all other cases the optimized geometry becomes a starting point for the next IRC step. By default, when the forward path is completed the backward one is started from the same TS geometry. When both forward and backward paths are complete, a summary of the whole reaction path is printed to the output.

4.7.2 Input

The IRC scan in AMS is triggered by setting the `Task` to `IRC`:

```
Task IRC
```

All IRC-related options are specified in the IRC input block:

```
IRC
   Convergence
      Gradients float
      Step float
   End
   CoordinateType [Cartesian | Delocalized]
   Direction [Both | Forward | Backward]
   InitialHessian
      File string
      Type [Calculate | FromFile]
   End
   KeepConvergedResults Yes/No
   MaxIRCSteps integer
   MaxIterations integer
   MaxPoints integer
   MinEnergyProfile Yes/No
   MinPathLength float
   Restart
      File string
      RedoBackward integer
      RedoForward integer
   End
   Step float
End
```

All keys of the IRC block have reasonable defaults or are optional. Thus, in principle, the IRC block can be omitted altogether. These are some of the main options:

IRC

Direction

Type Multiple Choice

Default value Both

Options [Both, Forward, Backward]

Description Select direction of the IRC path. The difference between the Forward and the Backward directions is determined by the sign of the largest component of the vibrational normal mode corresponding to the reaction coordinate at the transition state geometry. The Forward path correspond to the positive sign of the component. If Both is selected then first the Forward path is computed followed by the Backward one.

Step

Type Float

Default value 0.2

GUI name Step size

Description IRC step size in mass-weighted coordinates, sqrt(amu)*bohr. One may have to increase this value when heavy atoms are involved in the reaction, or decrease it if the reactant or products are very close to the transition state.

`InitialHessian`

Type Block

Description Options for initial Hessian at the transition state. The first eigenvalue of the initial Hessian defines direction of the first forward or backward step. This block is ignored when restarting from a previous IRC calculation because the initial Hessian found in the restart file is used.

`File`

Type String

GUI name File

Description If 'Type' is set to 'FromFile' then in this key you should specify the RKF file containing the initial Hessian (or the ams results dir. containing it). This can be used to load a Hessian calculated previously with the 'Properties%Hessian' keyword. If you want to also use this file for the initial geometry then also specify it in a 'LoadSystem' block.

`Type`

Type Multiple Choice

Default value Calculate

Options [Calculate, FromFile]

GUI name Initial Hessian

Description Calculate the exact Hessian for the input geometry or load it from the results of a previous calculation.

The following keys set limits on the number of steps for the inner and outer IRC loops and, related to that, the geometry optimization criteria. Note that tighter criteria may require a greater MaxIterations limit. Please also note that the outer loop limits are valid for each half of the path (forward and backward) separately. That is, if all settings are left at their defaults then up to 200 IRC points may be calculated, each of them may require up to 300 energy evaluations.

`IRC`

`MaxIRCSteps`

Type Integer

GUI name Maximum IRC steps

Description Soft limit on the number of IRC points to compute in each direction. After the specified number of IRC steps the program will switch to energy minimization and complete the path. This option should be used when you are interested only in the reaction path area near the transition state. Note that even if the soft limit has been hit and the calculation has completed, the IRC can still be restarted with a 'RedoBackward' or 'RedoForward' option.

`MaxPoints`

Type Integer

Default value 100

GUI name Maximum points

Description Hard limit on the number of IRC points to compute in each direction. After the specified number of IRC steps the program will stop with the current direction and switch to the next one. If both 'MaxPoints' and 'MaxIRCSteps' are set to the same value then 'MaxPoints' takes precedence, therefore this option should be used to set a limit on the number of IRC steps if you intend to use the results later for a restart.

`MaxIterations`

Type Integer

Default value 300

GUI name Maximum iterations

Description The maximum number of geometry iterations allowed to converge the inner IRC loop. If optimization does not converge within the specified number of steps, the calculation is aborted.

`Convergence`

Type Block

Description Convergence at each given point is monitored for two items: the Cartesian gradient and the calculated step size. Convergence criteria can be specified separately for each of these items. The same criteria are used both in the inner IRC loop and when performing energy minimization at the path ends.

`Gradients`

Type Float

Default value 0.001

Unit Hartree/Angstrom

GUI name Gradient convergence

Description Convergence criterion for the max component of the residual energy gradient.

`Step`

Type Float

Default value 0.001

Unit Angstrom

GUI name Step convergence

Description Convergence criterion for the max component of the step in the optimization coordinates.

`MinPathLength`

Type Float

Default value 0.1

Unit Angstrom

Description Minimum length of the path required before switching to energy minimization. Use this to overcome a small kink or a shoulder on the path.

The following keys modify other aspects of the IRC scan:

`IRC`

`CoordinateType`

Type Multiple Choice

Default value Cartesian

Options [Cartesian, Delocalized]

GUI name Coordinates used for optimization

Description Select the type of coordinates in which to perform the optimization. Note that the Delocalized option should be considered experimental.

`MinEnergyProfile`

Type Bool

Default value No

GUI name Minimum energy profile

Description Calculate minimum energy profile (i.e. no mass-weighting) instead of the IRC.

`KeepConvergedResults`

Type Bool

Default value Yes

Description Keep the binary RKF result file for every converged IRC point. These files may contain more information than the main ams.rkf result file.

It is possible to restart an IRC calculation that crashed, has been killed or exceeded the MaxPoints limit, or to re-compute the path starting from a certain point, using the Restart key:

`IRC`

`Restart`

Type Block

Description Restart options. Upon restart, the information about the IRC input parameters and the initial system (atomic coordinates, lattice, charge, etc.) is read from the restart file. The IRC input parameters can be modified from input. Except for 'MaxPoints' and 'Direction' all parameters not specified in the input will use their values from the restart file. The 'MaxPoints' and 'Direction' will be reset to their respective default values if not specified in the input. By default, the IRC calculation will continue from the point where it left off. However, the 'RedoForward' and/or 'RedoBackward' option can be used to enforce recalculation of a part of the reaction path, for example, using a different 'Step' value.

`File`

Type String

GUI name Restart

Description Name of an RKF restart file generated by a previous IRC calculation. Do not use this key to provide an RKF file generated by a TransitionStateSearch or a SinglePoint calculation, use the 'LoadSystem' block instead.

`RedoBackward`

Type Integer

Default value 0

Description IRC step number to start recalculating the backward path from. By default, if the backward path has not been completed then start after the last completed step. If the backward path has been completed and the 'RedoBackward' is omitted then no point on the backward path will be recomputed.

`RedoForward`

Type Integer

Default value 0

Description IRC step number to start recalculating the forward path from. By default, if the forward path has not been completed then start after the last completed step. If the forward path has been completed and the 'RedoForward' is omitted then no point on the forward path will be recomputed.

4.7.3 Output

A summary of reaction path is printed to the output file at the end of the IRC calculation.

The IRC reaction path can be visualized using the AMSmovie GUI module.

Results of an IRC calculation are also stored in the History section of the 'ams.rkf' file, just like in a normal geometry optimization. In addition to the standard KF variables such as "Coords" and "Energy", the following IRC-specific variables are also created:

- *IRCDirection* - IRC direction to which this point belongs: 1 - forward, 2 - backward.
- *IRCIteration* - the IRC (a.k.a. the outer loop) iteration number.
- *OptIteration* - the geometry optimization (a.k.a. the inner loop) iteration number (0 means the results correspond to the converged geometry at this IRC step).
- *IRCGradMax* - value of the max component of the IRC gradient that determines convergence of the inner loop.
- *IRCGradRms* - the RMS value of the IRC gradient that determines convergence of the inner loop. Both the ircGradRms and the ircGradMax are given in the mass-weighted atomic units for IRC steps and in the atomic units for the final minimization loop.
- *ArcLength* - length, in Angstrom, of the arc that connects the initial and the final point of this IRC step. The corresponding pivot point is located near the the middle point of the arc.
- *Angle* - value of the angle (in degrees) between lines connecting the pivot point with the initial and final points. A value of 180 degrees means the path is passing straight through the pivot point, while a smaller value means the path makes a bend at this point.
- *PathLength* - sum of the *ArcLength* values from the transition state up to this point, in Angstrom.
- *Converged* - a Fortran logical value containing the convergence status of the given geometry.

The IRC section of the RKF file contains all the data needed for a successful restart procedure.

4.8 Excited state optimizations

It depends on the engine if it is possible to do an electronically excited state optimization, like an electronically excited state *geometry optimization* (page 47), *transition state search* (page 66), *linear transit, PES scan* (page 69), or *IRC* (page 84). Required is that the engine should be able to calculate the nuclear gradient for a particular electronically excited state. ADF and DFTB are engines that can do such calculation. If the excited state gradient is available one can also calculate an *IR spectrum* (page 209) of the excited state, and one could calculate a *vibrationally resolved electronic spectrum* (page 244).

One should look in the documentation of the engine how to set up the calculation of the excited state gradient.

4.9 Molecular dynamics

Molecular dynamics (MD) can be used to simulate the evolution of a system in time.

See also:

- *Examples* (page 379)
- AMS GUI Tutorial
- *MD trajectory analysis tool* (page 348)

To perform a MD simulation, first select the corresponding `Task`:

```
Task MolecularDynamics
```

All aspects of the simulation can then be configured using the `MolecularDynamics` block.

```
MolecularDynamics
   AddMolecules
      AtomTemperature float
      ContactDistance float
      Coords float_list
      CoordsBox float_list
      CoordsSigma float_list
      DeviationAngle float
      Energy float
      EnergySigma float
      FractionalCoords float_list
      FractionalCoordsBox float_list
      FractionalCoordsSigma float_list
      Frequency integer
      MinDistance float
      MoleFraction float
      NumAttempts integer
      Rotate Yes/No
      StartStep integer
      StopStep integer
      System string
      Temperature float
      TemperatureSigma float
      Velocity float
      VelocityDirection float_list
      VelocitySigma float
   End
   ApplyForce
      Force float_list
      PerAtom Yes/No
      Region string
   End
   ApplyVelocity
      Components [X | Y | Z | XY | YZ | XZ | XYZ]
      Region string
      Velocity float_list
   End
   Barostat
      BulkModulus float
      ConstantVolume Yes/No
      Duration integer_list
```

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```
      Equal [None | XYZ | XY | YZ | XZ]
      Pressure float_list
      Scale [XYZ | Shape | X | Y | Z | XY | YZ | XZ]
      Tau float
      Type [None | Berendsen | MTK]
   End
   BinLog
      BiasEnergy Yes/No
      BoostFactor Yes/No
      ConservedEnergy Yes/No
      Density Yes/No
      DipoleMoment Yes/No
      Hypertime Yes/No
      KineticEnergy Yes/No
      MaxBiasEnergy Yes/No
      MaxBoostFactor Yes/No
      PotentialEnergy Yes/No
      Pressure Yes/No
      PressureTensor Yes/No
      Step Yes/No
      Temperature Yes/No
      Time Yes/No
      TotalEnergy Yes/No
      Volume Yes/No
   End
   BondBoost
      Chain
         AtomNames string
         MaxDistances float_list
         MinDistances float_list
      End
      DistanceRestraint string
      Moving Yes/No
      NSteps integer
      NumInstances integer
      Units [Default | MD]
   End
   CRESTMTD
      AddEnergy Yes/No
      GaussianScaling
         ScaleGaussians Yes/No
         ScalingSlope float
      End
      Height float
      NGaussiansMax integer
      NSteps integer
      Region string
      RestartFile string
      Width float
   End
   CVHD
      Bias
         DampingTemp float
         Delta float
         Height float
      End
      ColVarBB
```

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```
            at1
               region string
               symbol string
            End
            at2
               region string
               symbol string
            End
            cutoff float
            p integer
            rmax float
            rmin float
         End
         ColVarBM
            at1
               region string
               symbol string
            End
            at2
               region string
               symbol string
            End
            cutoff float
            p integer
            rmax float
            rmin float
         End
         Frequency integer
         MaxEvents integer
         StartStep integer
         StopStep integer
         WaitSteps integer
      End
      CalcPressure Yes/No
      Checkpoint
         Frequency integer
         WriteProperties Yes/No
      End
      CopyRestartTrajectory Yes/No
      CosineShear
         Acceleration float
         Enabled Yes/No
         FlowDirection float_list
         ProfileAxis [X | Y | Z]
      End
      Deformation
         LatticeVelocity # Non-standard block. See details.
            ...
         End
         LengthRate float_list
         LengthVelocity float_list
         Period float
         ScaleAtoms Yes/No
         StartStep integer
         StopStep integer
         StrainRate # Non-standard block. See details.
            ...
```

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```
      End
      TargetLattice # Non-standard block. See details.
         ...
      End
      TargetLength float_list
      Type [Linear | Exponential | Sine | Cosine]
   End
   Gravity
      Acceleration float
   End
   HeatExchange
      HeatingRate float
      Method [Simple | HEX | eHEX]
      Sink
         AtomList integer_list
         Box
            Amax float
            Amin float
            Bmax float
            Bmin float
            Cmax float
            Cmin float
         End
         Region string
      End
      Source
         AtomList integer_list
         Box
            Amax float
            Amin float
            Bmax float
            Bmin float
            Cmax float
            Cmin float
         End
         Region string
      End
      StartStep integer
      StopStep integer
   End
   InitialVelocities
      File string
      RandomVelocitiesMethod [Exact | Boltzmann | Gromacs]
      Temperature float
      Type [Zero | Random | FromFile | Input]
      Values # Non-standard block. See details.
         ...
      End
   End
   MovingRestraints
      Change [Linear | Sine | Cosine]
      Distance
         Atom1 integer
         Atom2 integer
         EndValue float
         StartValue float
      End
```

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```
      Erf
         ForceConstant float
         MaxForce float
      End
      GaussianWell
         Sigma float
         WellDepth float
      End
      Harmonic
         ForceConstant float
      End
      Hyperbolic
         ForceConstant float
         MaxForce float
      End
      Name string
      Period float
      RestraintType [None | Harmonic | Hyperbolic | Erf | GaussianWell]
      StartStep integer
      StopStep integer
   End
   NSteps integer
   Plumed
      Input # Non-standard block. See details.
         ...
      End
      Parallel
         nCoresPerGroup integer
         nGroups integer
         nNodesPerGroup integer
      End
   End
   Preserve
      AngularMomentum Yes/No
      CenterOfMass Yes/No
      Momentum Yes/No
   End
   Print
      System Yes/No
      Velocities Yes/No
   End
   ReactionBoost
      BondBreakingRestraints
         Erf
            ForceConstant float
            MaxForce float
         End
         GaussianWell
            Sigma float
            WellDepth float
         End
         Harmonic
            ForceConstant float
         End
         Hyperbolic
            ForceConstant float
            MaxForce float
```

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```
         End
         Taper
            Enabled Yes/No
            MaxDistance float
            MinDistance float
         End
         Type [None | Harmonic | Hyperbolic | Erf | GaussianWell]
      End
      BondMakingRestraints
         Erf
            ForceConstant float
            MaxForce float
         End
         GaussianWell
            Sigma float
            WellDepth float
         End
         Harmonic
            ForceConstant float
         End
         Hyperbolic
            ForceConstant float
            MaxForce float
         End
         Type [None | Harmonic | Hyperbolic | Erf | GaussianWell]
      End
      BondedRestraints
         Harmonic
            ForceConstant float
         End
         Type [None | Harmonic]
      End
      Change [TargetCoordinate | Force | LogForce]
      InitialFraction float
      InterEquilibrationSteps integer
      MinBondChange float
      MinBondStrength float
      NSteps integer
      NonBondedRestraints
         Exponential
            Epsilon float
            Sigma float
         End
         Type [None | Exponential]
      End
      PreEquilibrationSteps integer
      RMSDRestraint
         Erf
            ForceConstant float
            MaxForce float
         End
         GaussianWell
            Sigma float
            WellDepth float
         End
         Harmonic
            ForceConstant float
```

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```
      End
      Hyperbolic
         ForceConstant float
         MaxForce float
      End
      Type [None | Harmonic | Hyperbolic | Erf | GaussianWell]
   End
   Region string
   TargetSystem string
   Type [None | Pair | RMSD]
End
Reactor
   ForceConstant float
   MassScaled Yes/No
   NSteps integer
   Radius float
End
ReflectiveWall
   Axis float_list
   Region string
   Threshold float
End
Remap
   Type [None | Atoms]
End
RemoveMolecules
   Formula string
   Frequency integer
   SafeBox
      Amax float
      Amin float
      Bmax float
      Bmin float
      Cmax float
      Cmin float
      FractionalCoordsBox float_list
   End
   SinkBox
      Amax float
      Amin float
      Bmax float
      Bmin float
      Cmax float
      Cmin float
      FractionalCoordsBox float_list
   End
   StartStep integer
   StopStep integer
End
ReplicaExchange
   AllowWrongResults Yes/No
   EWMALength integer
   SwapFrequency integer
   TemperatureFactors float_list
   Temperatures float_list
   nReplicas integer
End
```

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```
   Restart string
   Shake
      All string
      ConvergeR2 float
      ConvergeRV float
      Iterations integer
      ShakeInitialCoordinates Yes/No
   End
   Thermostat
      BerendsenApply [Local | Global]
      ChainLength integer
      Duration integer_list
      Region string
      Tau float
      Temperature float_list
      Type [None | Berendsen | NHC]
   End
   TimeStep float
   Trajectory
      ExitConditionFreq integer
      PrintFreq integer
      SamplingFreq integer
      TProfileGridPoints integer
      WriteBonds Yes/No
      WriteCharges Yes/No
      WriteCoordinates Yes/No
      WriteEngineGradients Yes/No
      WriteMolecules Yes/No
      WriteVelocities Yes/No
   End
   fbMC
      Frequency integer
      MassRoot float
      MolecularMoves
         Enabled Yes/No
         RotationStepAngle float
         TranslationStepLength float
      End
      NSteps integer
      PrintFreq integer
      StartStep integer
      StepLength float
      StopStep integer
      Temperature float
   End
End
```

4.9.1 General

The time evolution of the system is simulated by numerically integrating the equations of motion. A velocity Verlet integrator is used with a time step set by the `TimeStep` key. The MD driver will perform `NSteps` timesteps in total.

Because the overall computational cost depends on `NSteps` but not on `TimeStep`, it is desirable to set the timestep as large as possible to maximize the sampled timescale with a given computational budget. However, numerical integration errors grow rapidly as the timestep increases. These errors will cause a loss of energy conservation, crashes, and other artifacts. It is thus important to set the `TimeStep` value carefully, as its optimal value strongly depends on the studied system and simulated conditions.

As a rule of thumb, reasonable timesteps for systems not undergoing chemical reactions are 10-20 times lower than the period of the fastest vibration mode. Systems containing hydrogen atoms at room temperature can thus be accurately simulated using a 1 fs timestep. Longer timesteps can be safely used for systems containing only heavy atoms (vibration periods scale with the square root of the atomic mass). Conversely, the timestep needs to be made shorter for high-temperature simulations. The same also applies to simulations of chemical reactions, which are usually accompanied by significant transient local heating. The default timestep of 0.25 fs should work for most of these cases.

MolecularDynamics

NSteps

Type Integer

Default value 1000

GUI name Number of steps

Description The number of steps to be taken in the MD simulation.

TimeStep

Type Float

Default value 0.25

Unit Femtoseconds

Description The time difference per step.

During a long simulation, numerical integration errors will cause some system-wide quantities to drift from their exact values. For example, the system may develop a nonzero net linear velocity, causing an overall translation or flow. Non-periodic (molecular) and 1D-periodic systems may also develop nonzero angular momentum (overall rotation) and a Brownian motion of their center of mass through space. These problems are corrected by periodically removing any accumulated drift. This feature can be controlled using the `Preserve` key.

MolecularDynamics

Preserve

Type Block

Description Periodically remove numerical drift accumulated during the simulation to preserve different whole-system parameters.

AngularMomentum

Type Bool

Default value Yes

GUI name : Angular momentum

Description Remove overall angular momentum of the system. This option is ignored for 2D and 3D-periodic systems, and disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

CenterOfMass

Type Bool

Default value No

GUI name : Center of mass

Description Translate the system to keep its center of mass at the coordinate origin. This option is not very useful for 3D-periodic systems.

Momentum

Type Bool

Default value Yes

GUI name Preserve: Total momentum

Description Remove overall (linear) momentum of the system. This is disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

4.9.2 Constrained molecular dynamics

There are two types of constraint available for MD: frozen atoms and Shake/Rattle. Atoms can be kept frozen using the `Atom`, `AtomList` and `FixedRegion` keys of the `Constraints` top-level input block.

Constraints

Atom

Type Integer

Recurring True

Description Fix the position of an atom. Just one integer referring to the index of the atom in the [System%Atoms] block.

AtomList

Type Integer List

Recurring True

Description Fix positions of the specified atoms. A list of integers referring to indices of atoms in the [System%Atoms] block.

FixedRegion

Type String

Recurring True

Description Fix positions of all atoms in a region.

The Shake/Rattle constraints are implemented following H.C. Andersen, J Comp. Phys., 52 (1983) 24 (https://doi.org/10.1016/0021-9991(83)90014-1). The procedure consists of two steps: update of the coordinates to satisfy the constraints (the Shake part) and orthogonalization of atomic velocities to them (the Rattle part). The Shake part is implemented as an additional correcting force that brings each bond length exactly to its constrained value upon the subsequent velocity Verlet integration step. Application of the constraints is an iterative procedure and the convergence greatly depends on how intertwined the constraints are. For diatomic molecules, usually no more than two iterations are necessary, while tens of iterations may be required for rings (a triangle constraint is treated as a 3-membered ring).

Note: During simulations with a changing simulation box (NpT, NpH), the absolute Cartesian coordinates of the frozen atoms cannot be kept fixed. In this case, their fractional cell coordinates are maintained at the original values. Also the Shake constraints cannot be satisfied exactly during such simulations but the difference is usually small enough.

The Shake/Rattle constraints are specified using the Shake input block:

`MolecularDynamics`

`Shake`

Type Block

Description Parameters of the Shake/Rattle algorithm.

`All`

Type String

Recurring True

GUI name Constrain all

Description Constraint description in one the following formats: All [bondOrder] bonds at1 at2 [to distance] All triangles at1 at2 at3

The first option constrains all bonds between atoms at1 at2 to a certain length, while the second - bonds at1-at2 and at2-at3 and the angle between them.

The [bondOrder] can be a number or a string such as single, double, triple or aromatic. If it's omitted then all bonds between specified atoms will be constrained. Atom names are case-sensitive and they must be as they are in the Atoms block, or an asterisk '*' denoting any atom. The distance, if present, must be in Angstrom. If it is omitted then the bond length from the initial geometry is used.

Important: only the bonds present in the system at certain points of the simulation (at the start or right after adding/removing atoms) can be constrained, which means that the bonds may need to be specified in the System block.

Warning: the triangles constraint should be used with care because each constrained bond or angle means removing one degree of freedom from the dynamics. When there are too many constraints (for example, "All triangles H C H" in methane) some of them may be linearly dependent, which will lead to an error in the temperature computation.

Valid examples: All single bonds C C to 1.4 All bonds O H to 0.98 All bonds O H All bonds H * All triangles H * H

`ConvergeR2`

Type Float

Default value 1e-08

Description Convergence criterion on the max squared difference, in atomic units.

`ConvergeRV`

Type Float

Default value 1e-08

Description Convergence criterion on the orthogonality of the constraint and the relative atomic velocity, in atomic units.

Iterations

Type Integer

Default value 100

Description Number of iterations.

ShakeInitialCoordinates

Type Bool

Default value Yes

Description Apply constraints before computing the first energy and gradients.

Note: The list of constrained bonds is built by matching the input against the *bonds as specified* (page 37) in the *System block* (page 31). This means that bonds not specified in the System block will *not* be constrained.

4.9.3 (Re-)Starting a simulation

The state of a system at the beginning of a simulation is defined by the positions and momenta of all atoms. The positions can be set in the input or loaded from a file as described under *Geometry, System definition* (page 31). Initial velocities are then supplied using the `InitialVelocities` block.

Probably the most common way to start up a simulation is to draw the initial velocities from a Maxwell-Boltzmann distribution by setting `Type=Random` and `Temperature` to a suitable value. Alternatively, velocities can be loaded from an `ams.rkf` file produced by an earlier simulation using `Type=FromFile` and `File`. This is the recommended way to start a production simulation from the results of a short preparation/equilibration run.

Velocities of all atoms in units of Å/fs can also be explicitly defined in the `Values` block after setting `Type=Input`. This is mainly useful to repeat or extend simulations done by other programs. For example, velocities can be extracted from the `vels` or `moldyn.vel` files used by the standalone ReaxFF program. A simple AWK script is supplied in `scripting/standalone/reaxff-ams/vels2ams.awk` to help with the conversion.

MolecularDynamics

InitialVelocities

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

File

Type String

Description AMS RKF file containing the initial velocities.

RandomVelocitiesMethod

Type Multiple Choice

Default value Exact

Options [Exact, Boltzmann, Gromacs]

GUI name Velocity randomization method

Description Specifies how are random velocities generated. Three methods are available.

Exact: Velocities are scaled to exactly match set random velocities temperature.

Boltzmann: Velocities are not scaled and sample Maxwell-Boltzmann distribution. However, the distribution is not corrected for constraints.

Gromacs: Velocities are scaled to match set random velocities temperature, but removal of net momentum is performed only after the scaling. Resulting kinetic energy is lower based on how much net momentum the system had.

`Temperature`

Type Float

Unit Kelvin

GUI name Initial temperature

Description Sets the temperature for the Maxwell-Boltzmann distribution when the type of the initial velocities is set to random, in which case specifying this key is mandatory.

AMSinput will use the first temperature of the first thermostat as default.

`Type`

Type Multiple Choice

Default value Random

Options [Zero, Random, FromFile, Input]

GUI name Initial velocities

Description Specifies the initial velocities to assign to the atoms. Three methods to assign velocities are available.

Zero: All atom are at rest at the beginning of the calculation.

Random: Initial atom velocities follow a Maxwell-Boltzmann distribution for the temperature given by the [MolecularDynamics%InitialVelocities%Temperature] keyword.

FromFile: Load the velocities from a previous ams result file.

Input: Atom's velocities are set to the values specified in the [MolecularDynamics%InitialVelocities%Values] block, which can be accessed via the Expert AMS panel in AMSinput.

`Values`

Type Non-standard block

Description This block specifies the velocity of each atom, in Angstrom/fs, when [MolecularDynamics%InitialVelocities%Type] is set to Input. Each row must contain three floating point values (corresponding to the x,y,z component of the velocity vector) and a number of rows equal to the number of atoms must be present, given in the same order as the [System%Atoms] block.

The MD module also supports exact restarts of interrupted simulations by pointing the `Restart` key to an `ams.rkf` file. This will restore the entire state of the MD module from the last available checkpoint (if the previous simulation was interrupted) or from the final state (if the previous simulation ended after `NSteps`). An earlier trajectory can thus be seamlessly extended by increasing `NSteps` and using `Restart`.

Note: `Restart` should be combined with `LoadSystem` from the same `ams.rkf` to restore the atomic positions.

Warning: The `Restart` feature is only intended for exact restarts, so the rest of the `MolecularDynamics` settings should be the same as in the original run. Only `NSteps` and engine settings (contents of the `Engine` block) can always be changed safely across restarts.

Although some MD settings (such as the trajectory sampling options) can in practice be changed without problems, changing others (such as thermostat or barostat settings) will cause the restart to fail or produce physically incorrect results. It is thus strongly recommended to only use `Restart` for exact continuation and `InitialVelocities Type=FromFile` together with `LoadSystem` otherwise.

`MolecularDynamics`

`Restart`

Type String

GUI name Restart from

Description The path to the ams.rkf file from which to restart the simulation.

4.9.4 Thermostats and barostats

By default, the MD simulation samples the microcanonical (NVE) ensemble. Although this is useful to check energy conservation and other basic physical properties, it does not directly map to common experimental conditions. The canonical (NVT) ensemble can be sampled instead by applying a `Thermostat`, which serves as a simulated heat bath around the system, keeping its average temperature at a set value.

AMS offers two thermostats with drastically different properties, mode of operation, and applicability, selected using the `Type` key:

Berendsen The Berendsen friction thermostat drives the system to a particular target temperature by rescaling the velocities of all atoms in each step. This ensures rapid (exponential) convergence of the temperature with a time constant `Tau`. However, this thermostat produces an incorrect velocity distribution and should thus be avoided in all situations where correct energy fluctuations are important. Additionally, using a too short time constant `Tau` tends to cause incorrect equipartition of energy between different degrees of freedom in the system, leading to the “flying ice cube” phenomenon. The time constant `Tau` should thus be set as large as possible to limit these artifacts while still providing sufficient temperature control. Common values of `Tau` for condensed-phase systems lie between 100 fs (strong damping, rapid convergence) and 10 ps (weak coupling with minimal artifacts).

This thermostat is mainly useful for systems far from equilibrium, for example during the initial preparation and equilibration phase of a simulation. The `NHC` thermostat should be preferred where possible.

NHC This enables a chain of coupled Nosé-Hoover thermostats. This method introduces artificial degrees of freedom representing the heat bath and ensures correct sampling of the canonical ensemble. The combined total energy of the system and the heat bath is conserved and shown in the GUI as `Conserved Energy`. Checking this quantity for drift and artifacts thus offers a valuable test of the correctness of the simulation. This thermostat exhibits oscillatory relaxation with a period of `Tau`. It is thus not well suited for systems starting far from equilibrium, because the oscillations may take long to settle. The time constant `Tau` should be at least comparable to the period of some natural oscillation of the system to ensure efficient energy transfer. It is commonly on the order of hundreds of femtoseconds, although higher values may be used if weak coupling is desired.

Multiple independent thermostats can be used to separately control different non-overlapping regions of the system at the same time. This is done by first defining appropriate *Regions* (page 36) in the `System` block and then specifying the `Thermostat` block multiple times with the `Region` key of each thermostat set to an appropriate region expression.

`MolecularDynamics`

`Thermostat`

Type Block

Recurring True

Description This block allows to specify the use of a thermostat during the simulation. Depending on the selected thermostat type, different additional options may be needed to characterize the specific thermostat' behavior.

`BerendsenApply`

Type Multiple Choice

Default value Global

Options [Local, Global]

GUI name Apply Berendsen

Description Select how to apply the scaling correction for the Berendsen thermostat:

- per-atom-velocity (Local) - on the molecular system as a whole (Global).

`ChainLength`

Type Integer

Default value 10

GUI name NHC chain length

Description Number of individual thermostats forming the NHC thermostat

`Duration`

Type Integer List

GUI name Duration(s)

Description Specifies how many steps should a transition from a particular temperature to the next one in sequence take.

`Region`

Type String

Default value *

Description The identifier of the region to thermostat. The default '*' applies the thermostat to the entire system. The value can by a plain region name, or a region expression, e.g. '*-myregion' to thermostat all atoms that are not in myregion, or 'regionA+regionB' to thermostat the union of the 'regionA' and 'regionB'. Note that if multiple thermostats are used, their regions may not overlap.

`Tau`

Type Float

Unit Femtoseconds

GUI name Damping constant

Description The time constant of the thermostat.

`Temperature`

Type Float List

Unit Kelvin

GUI name Temperature(s)

Description The target temperature of the thermostat.

You can specify multiple temperatures (separated by spaces). In that case the Duration field specifies how many steps to use for the transition from one T to the next T (using a linear ramp). For NHC thermostat, the temperature may not be zero.

`Type`

Type Multiple Choice

Default value None

Options [None, Berendsen, NHC]

GUI name Thermostat

Description Selects the type of the thermostat.

Just like using a `Thermostat` to control the temperature of the system, a `Barostat` can be applied to keep the pressure constant by adjusting the volume. This enables sampling the isenthalpic-isobaric (NpH) ensemble by using only a barostat or the isothermal-isobaric (NpT) ensemble by combining a barostat and a thermostat. Unlike thermostats, a barostat always applies to the entire system and there can thus be at most one barostat defined.

AMS offers two barostats with similar properties to the related thermostats:

Berendsen The Berendsen friction-like isobaric ensemble method rescales the system in each step to drive the pressure towards a target value. Similarly to the `Berendsen` thermostat, the relaxation is exponential with a time constant `Tau`. Similar considerations for the choice of `Tau` apply as in the case of the thermostat, but the value of `Tau` for the barostat is usually at least several times higher than the corresponding `Tau` used for the thermostat. This barostat does not have any conserved quantity.

MTK This enables the Martyna-Tobias-Klein extended Lagrangian barostat, which generates a true isobaric ensemble by integrating the cell parameters as additional degrees of freedom. This barostat is derived from the Andersen-Hoover isotropic barostat and the Parrinello-Rahman-Hoover anisotropic barostat. Like the `NHC` thermostat, it exhibits oscillatory relaxation unsuitable for systems far from equilibrium. This barostat must always be combined with a `NHC` thermostat. One instance of such thermostat coupled to the atoms as usual, while a second instance is created internally and coupled to the cell degrees of freedom.

`MolecularDynamics`

`Barostat`

Type Block

Description This block allows to specify the use of a barostat during the simulation.

`BulkModulus`

Type Float

Default value 2200000000.0

Unit Pascal

Description An estimate of the bulk modulus (inverse compressibility) of the system for the Berendsen barostat.

This is only used to make Tau correspond to the true observed relaxation time constant. Values are commonly on the order of 10-100 GPa (1e10 to 1e11) for solids and 1 GPa (1e9) for liquids (2.2e9 for water). Use 1e9 to match the behavior of standalone ReaxFF.

`ConstantVolume`

Type Bool

Default value No

Description Keep the volume constant while allowing the box shape to change.

This is currently supported only by the MTK barostat.

`Duration`

Type Integer List

Description Specifies how many steps should a transition from a particular pressure to the next one in sequence take.

`Equal`

Type Multiple Choice

Default value None

Options [None, XYZ, XY, YZ, XZ]

Description Enforce equal scaling of the selected set of dimensions. They will be barostatted as one dimension according to the average pressure over the components.

`Pressure`

Type Float List

Unit Pascal

Description Specifies the target pressure.

You can specify multiple pressures (separated by spaces). In that case the Duration field specifies how many steps to use for the transition from one p to the next p (using a linear ramp).

`Scale`

Type Multiple Choice

Default value XYZ

Options [XYZ, Shape, X, Y, Z, XY, YZ, XZ]

Description Dimensions that should be scaled by the barostat to maintain pressure. Selecting Shape means that all three dimensions and also all the cell angles are allowed to change.

`Tau`

Type Float

Unit Femtoseconds

GUI name Damping constant

Description Specifies the time constant of the barostat.

`Type`

Type Multiple Choice

Default value None

Options [None, Berendsen, MTK]

GUI name Barostat

Description Selects the type of the barostat.

Temperature and pressure regimes

Arbitrary temperature and pressure regimes can be generated by setting `Temperature` or `Pressure` to a list of values, corresponding to the successive set points. This needs to be accompanied by a `Duration` key specifying the length of each regime segment in steps:

```
Thermostat
   Temperature 0      300      300      500      500      300
   Duration       100      200      100      200      100
End
```

Note that there is always N-1 `Duration` values for N `Temperature` values. The target temperature of the thermostat in this example will evolve as follows:

1. Increase linearly from 0 to 300 K over 100 steps.
2. Stay constant at 300 K for 200 steps.
3. Increase linearly from 300 to 500 K over 100 steps.
4. Stay constant at 500 K for 200 steps.
5. Decrease linearly from 500 to 300 K over 100 steps.
6. Stay constant at 300 K for the rest of the simulation.

4.9.5 Trajectory sampling and output

A basic principle of the numerical integration of motion in MD is that the changes in the state of the system between successive time steps are small. This means that storing the results of every step is not useful, because all the data is strongly correlated. Instead, a snapshot of the system is taken every N steps, where N is set low enough to still capture the fastest motion of interest but high enough to avoid wasting space due to correlations. The resulting sequence of snapshots is then commonly called the trajectory.

AMS writes the trajectory to the `History` and `MDHistory` sections of `ams.rkf`, according to the settings in the `Trajectory` block. A snapshot of the system and various MD variables is stored every `SamplingFreq` timesteps. By default, this frequency is also used to print basic thermodynamic parameters of the simulation to the output and log file. Set `PrintFreq` to override this.

Frequently sampling a long trajectory can generate large volumes of data. If the space usage becomes a concern, one can selectively disable storing some parts of the trajectory to save space using the `Write*` keys. Note however that this will make it impossible to use some analysis methods on the resulting trajectory:

- `WriteBonds` is necessary for reaction network analysis (ChemTraYzer). Disabling `WriteBonds` also makes AMSmovie show only guessed bonds instead of those calculated by the engine.
- `WriteMolecules` is required by the Molecule Fractions panel in AMSmovie.
- `WriteVelocities` is required to calculate the velocity autocorrelation functions needed for diffusivity and IR spectra.

The trajectory itself contains only the data needed for subsequent analysis of the dynamics of the system. However, much more data is usually generated on every integration step. This includes, for example, the internal data used by an engine when evaluating the energies and forces. This information is normally discarded after each step, because it is often very large. However, a `Checkpoint` containing the complete internal state of the MD driver together with a result file generated by the engine is stored every `Frequency` steps. An interrupted simulation can then be restarted from this checkpoint using the `Restart` keyword. Additionally, the engine result files called `MDStep*.rkf` can also be used to extract various engine-specific details about the system, such as the orbitals for QM engines.

`MolecularDynamics`

`Trajectory`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`ExitConditionFreq`

Type Integer

GUI name Exit condition frequency

Description Check the exit conditions every N steps. By default this is done every SamplingFreq steps.

`PrintFreq`

Type Integer

GUI name Printing frequency

Description Print current thermodynamic properties to the output every N steps. By default this is done every SamplingFreq steps.

`SamplingFreq`

Type Integer

Default value 100

GUI name Sample frequency

Description Write the the molecular geometry (and possibly other properties) to the .rkf file once every N steps.

`TProfileGridPoints`

Type Integer

Default value 0

Description Number of points in the temperature profile. If TProfileGridPoints > 0, a temperature profile along each of the three lattice axes will be written to the .rkf file. The temperature at a given profile point is calculated as the total temperature of all atoms inside the corresponding slice of the simulation box, time-averaged over all MD steps since the previous snapshot. By default, no profile is generated.

`WriteBonds`

Type Bool

Default value Yes

Description Write detected bonds to the .rkf file.

`WriteCharges`

Type Bool

Default value Yes

Description Write current atomic point charges (if available) to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze charges.

`WriteCoordinates`

Type Bool

Default value Yes

Description Write atomic coordinates to the .rkf file.

`WriteEngineGradients`

Type Bool

Default value No

Description Write atomic gradients (negative of the atomic forces, as calculated by the engine) to the History section of ams.rkf.

`WriteMolecules`

Type Bool

Default value Yes

Description Write the results of molecule analysis to the .rkf file.

`WriteVelocities`

Type Bool

Default value Yes

Description Write velocities to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze the velocities.

`Checkpoint`

Type Block

Description Sets the frequency for storing the entire MD state necessary for restarting the calculation.

`Frequency`

Type Integer

Default value 1000

GUI name Checkpoint frequency

Description Write the MD state and engine-specific data to the respective .rkf files once every N steps.

`WriteProperties`

Type Bool

Default value No

Description Write the properties from the properties section to the ChecoPoint file once every N steps.

`CalcPressure`

Type Bool

Default value No

GUI name Calculate pressure

Description Calculate the pressure in periodic systems.

This may be computationally expensive for some engines that require numerical differentiation.

Some other engines can calculate the pressure for negligible additional cost and will always do so, even if this option is disabled.

Print

Type Block

Description This block controls the printing of additional information to stdout.

System

Type Bool

Default value No

Description Print the chemical system before and after the simulation.

Velocities

Type Bool

Default value No

Description Print the atomic velocities before and after the simulation.

In rare cases, one may require some properties from every MD step, for example, the pressure tensor for the Green-Kubo viscosity calculation. In this case one can use the `BinLog` (binary log) feature. When enabled, the selected MD variables will be stored in the `BinLog` section of `ams.rkf` in the format similar to that of the `MDHistory` section with a few differences: the blocking factor is larger (1000 instead of 100) and the pressure tensor is stored per component, for example, P_{xx} is stored in `PressureTensor_xx`, and so on. Note that none of the atomic properties (coordinates, velocities) are included in the binlog.

MolecularDynamics

BinLog

Type Block

Description This block controls writing the BinLog section in ams.rkf, which contains the selected MD state scalars and tensors from every MD step. No per-atom data is written. If you need the per-atom data then you can set the sampling frequency to 1 and get the required data from the MDHistory section. The tensors are written per component, that is, the pressure tensor is written as six variables: PressureTensor_xx, PressureTensor_yy, etc.. To reduce the file size, all data is written in blocks.

BiasEnergy

Type Bool

Default value No

Description Write the CVDH bias energy.

BoostFactor

Type Bool

Default value No

Description Write the CVDH boost factor.

ConservedEnergy

Type Bool

Default value No

Description Write the conserved energy value.

`Density`

Type Bool

Default value No

Description Write the density.

`DipoleMoment`

Type Bool

Default value No

Description Write the dipole moment. Each component of the tensor is written in its own variable.

`Hypertime`

Type Bool

Default value No

Description Write the CVDH hypertime.

`KineticEnergy`

Type Bool

Default value No

Description Write the kinetic energy value.

`MaxBiasEnergy`

Type Bool

Default value No

Description Write the max CVDH bias energy.

`MaxBoostFactor`

Type Bool

Default value No

Description Write the max CVDH boost factor.

`PotentialEnergy`

Type Bool

Default value No

Description Write the potential energy value.

`Pressure`

Type Bool

Default value No

Description Write the pressure.

`PressureTensor`

Type Bool

Default value No

Description Write the pressure tensor in Voigt notation. Each component of the tensor is written in its own variable.

Step

Type Bool

Default value No

Description Write the step index during the simulation.

Temperature

Type Bool

Default value No

Description Write the temperature.

Time

Type Bool

Default value No

Description Write the simulation time (fs).

TotalEnergy

Type Bool

Default value No

Description Write the total energy value.

Volume

Type Bool

Default value No

Description Write the simulation cell volume, area or length, depending on the system periodicity.

4.9.6 Lattice deformations (volume regimes)

The `Deformation` block can be used to gradually deform the periodic lattice of the system during a MD simulation. This block can be repeated to define multiple deformations, which will be applied on every MD step in the order in which they are listed in the input.

See also:

- *Example demonstrating various lattice deformations* (page 434)
- The ReactionsDiscovery workflow uses lattice deformations to predict chemical reactions

Warning: While a `Deformation` and a `Barostat` can be used at the same time, remember to set the `Scale` parameter of the barostat so that no dimension is simultaneously being deformed and barostatted.

Each `Deformation` block will be active on MD steps between `StartStep` and `StopStep`.

The time dependence of the lattice parameters is defined by the `Type` key:

Linear This deformation type adds the same constant amount to the selected lattice parameters on every simulation step. When used with `TargetLattice`, `LatticeVelocity`, or `StrainRate`, the lattice matrix H evolves as $H(t) = H_0 + \Delta H \cdot t$, where H_0 is the lattice at `StartStep`.

Exponential When used with `StrainRate`, this type strains the lattice by the given strain matrix `\epsilon` on every step, so that the lattice matrix H evolves as $H(t) = H_0(1 + \epsilon)^t$. When used with `LengthRate`, the length of each lattice vector evolves as $l(t) = l_0(1 + r)^t$.

Sine This is a periodic deformation going from the starting value of the selected lattice parameters to a set target, and then with the same amplitude to the opposite direction from the starting lattice.

Cosine This periodic deformation oscillates between the starting lattice and a defined target.

The period of the oscillation for the `Sine` and `Cosine` types must be set using the `Period` key.

The extent of the deformation is defined by setting one of the six mutually exclusive input keys. These belong to two groups, depending on whether they operate on the lattice matrix as a whole, or just on the lengths of the individual lattice vectors:

TargetLattice, Velocity, and Rate These input keys expect a "lattice-like" matrix of numbers, consisting of up to three rows containing up to three values each. Each row contains the components of a single lattice vector and corresponds to a row of the *Lattice block* (page 32). For systems with 1D or 2D periodicity the matrix may be padded to 3x3 with zeros.

TargetLength, LengthVelocity, and LengthRate These input keys expect a list of up to three values, defining the desired length of each lattice vector or the (absolute or relative) rate of its change.

`MolecularDynamics`

`Deformation`

Type Block

Recurring True

Description Deform the periodic lattice of the system during the simulation.

`LatticeVelocity`

Type Non-standard block

Description Velocity of individual lattice vector components in Angstrom/fs. The format is identical to the System%Lattice block. For Type Sine and Cosine, this defines the maximum velocity (at the inflection point).

`LengthRate`

Type Float List

Default value [0.0, 0.0, 0.0]

Description Relative rate of change of each lattice vector per step.

`LengthVelocity`

Type Float List

Default value [0.0, 0.0, 0.0]

Unit Angstrom/fs

Description Change the length of each lattice vector with this velocity. With Type=Exponential, LengthVelocity is divided by the current lattice vector lengths on StartStep to determine a LengthRate, which is then applied on all subsequent steps. For Type Sine and Cosine, this defines the maximum velocity (at the inflection point).

Period

Type Float

Unit Femtoseconds

Description Period of oscillation for Type Sine and Cosine.

ScaleAtoms

Type Bool

Default value Yes

Description Scale the atomic positions together with the lattice vectors. Disable this to deform only the lattice, keeping the coordinates of atoms unchanged.

StartStep

Type Integer

Default value 1

Description First step at which the deformation will be applied.

StopStep

Type Integer

Default value 0

Description Last step at which the deformation will be applied. If unset or zero, nSteps will be used instead.

StrainRate

Type Non-standard block

Description Strain rate matrix to be applied on every step. The format is identical to the System%Lattice block.

TargetLattice

Type Non-standard block

Description Target lattice vectors to be achieved by StopStep. The format is identical to the System%Lattice block.

TargetLength

Type Float List

Default value [0.0, 0.0, 0.0]

Unit Angstrom

Description Target lengths of each lattice vector to be achieved by StopStep. The number of values should equal the periodicity of the system. If a value is zero, the corresponding lattice vector will not be modified.

Type

Type Multiple Choice

Default value Linear

Options [Linear, Exponential, Sine, Cosine]

Description Function defining the time dependence of the deformed lattice parameters.

Linear increments the lattice parameters by the same absolute amount every timestep. Exponential multiplies the lattice parameters by the same factor every timestep. Only StrainRate, LengthRate, and LengthVelocity are supported for Type=Exponential. Sine deforms the system from the starting lattice to TargetLattice/TargetLength and then by the same amount to the opposite direction, while Cosine deforms the system from the starting lattice to the target and back.

Example: Transition from the initial lattice to a 10 Å cube over 1000 steps:

```
MolecularDynamics
   Deformation
      StopStep 1000
      TargetLattice
         10.0  0.0  0.0
          0.0 10.0  0.0
          0.0  0.0 10.0
      End
   End
End
```

Example: Oscillate the length of the *c* lattice vector between the initial value and 20 Å, leaving the *a* and *b* vectors unchanged:

```
MolecularDynamics
   Deformation
      Type Cosine
      Period 100
      TargetLength 0 0 20
   End
End
```

Example: Stretch the box in the “z” direction by a true exponential strain of 10 ppm per timestep while barostatting the remaining dimensions:

```
MolecularDynamics
   Barostat Type=MTK Pressure=1e5 Tau=1000 Scale=XY
   Deformation
      Type Exponential
      StrainRate
          0.0  0.0  0.0
          0.0  0.0  0.0
          0.0  0.0 1e-5
      End
   End
End
```

4.9.7 Molecule Gun: adding molecules during simulation

The molecule gun allows you to "shoot" (add with velocity) a molecule into the simulation box.

See also:

The GUI tutorial on the molecule gun.

Molecules can be continuously added to the simulation or only once. The initial position can be pre-set or be random within the simulation box or a part thereof. It can be defined either in the Cartesian or fractional coordinates. The initial velocity can be specified either directly (in Angstrom per femtosecond) or as translational temperature or kinetic energy. Possible applications of the molecule gun include e.g. the simulation of enforced collisions or deposition processes on surfaces.

`MolecularDynamics`

`AddMolecules`

Type Block

Recurring True

GUI name Add molecules

Description This block controls adding molecules to the system (a.k.a. the Molecule Gun). Multiple occurrences of this block are possible.

By default, molecules are added at random positions in the simulation box with velocity matching the current system temperature. The initial position can be modified using one of the following keywords: Coords, CoordsBox, FractionalCoords, FractionalCoordsBox. The Coords and FractionalCoords keys can optionally be accompanied by CoordsSigma or FractionalCoordsSigma, respectively.

`AtomTemperature`

Type Float

Default value 0.0

Unit Kelvin

Description Add random velocity corresponding to the specified temperature to individual atoms of the molecule. This only affects rotational and internal degrees of freedom, not the net translational velocity of the inserted molecule as set by the other options.

`ContactDistance`

Type Float

Default value 0.0

Unit Angstrom

Description Translate the bullet along the velocity vector until it comes within ContactDistance of any other atom.

`Coords`

Type Float List

Unit Angstrom

Description Place molecules at or around the specified Cartesian coordinates.

This setting takes precedence over other ways to specify initial coordinates of the molecule: [CoordsBox], [FractionalCoords], and [FractionalCoordsBox].

`CoordsBox`

Type Float List

Unit Angstrom

Description Place molecules at random locations inside the specified box in Cartesian coordinates.

Coordinates of the box corners are specified as: Xmin, Xmax, Ymin, Ymax, Zmin, Zmax. This setting is ignored if Coords is used.

In AMSinput, if this field is not empty it will be used instead of the default Coords.

`CoordsSigma`

Type Float List

Unit Angstrom

Description Sigma values (one per Cartesian axis) for a Gauss distribution of the initial coordinates. Can only be used together with Coords.

`DeviationAngle`

Type Float

Default value 0.0

Unit Degree

Description Randomly tilt the shooting direction up to this angle away from the VelocityDirection vector.

`Energy`

Type Float

Unit Hartree

Description Initial kinetic energy of the molecule in the shooting direction.

`EnergySigma`

Type Float

Default value 0.0

Unit Hartree

Description Sigma value for the Gauss distribution of the initial kinetic energy around the specified value. Should only be used together with Energy.

`FractionalCoords`

Type Float List

Description Place molecules at or around the specified fractional coordinates in the main system's lattice. For non-periodic dimensions a Cartesian value in Angstrom is expected. This setting is ignored if [Coords] or [CoordsBox] is used.

`FractionalCoordsBox`

Type Float List

Description Place molecules at random locations inside the box specified as fractional coordinates in the main system's lattice.

Coordinates of the box corners are specified as: Xmin, Xmax, Ymin, Ymax, Zmin, Zmax.

For non-periodic dimensions the Cartesian value in Angstrom is expected.

This setting is ignored if [Coords], [CoordsBox], or [FractionalCoords] is used.

`FractionalCoordsSigma`

Type Float List

Description Sigma values (one per axis) for a Gauss distribution of the initial coordinates. For non-periodic dimensions the Cartesian value in Angstrom is expected. Can only be used together with FractionalCoords.

`Frequency`

Type Integer

Default value 0

Description A molecule is added every [Frequency] steps after the StartStep.

There is never a molecule added at step 0.

`MinDistance`

Type Float

Default value 0.0

Unit Angstrom

Description Keep the minimal distance to other atoms of the system when adding the molecule.

`MoleFraction`

Type Float

Description Defines a mixture to be deposited using one AddMolecules block per component.

AMS will randomly alternate between any guns that have MoleFraction set. These need to all have the same settings for StartStep, StopStep and Frequency. Any additional AddMolecules blocks without MoleFraction will remain completely independent.

`NumAttempts`

Type Integer

Default value 10

Description Try adding the molecule up to the specified number of times or until the MinDistance constraint is satisfied. If all attempts fail a message will be printed and the simulation will continue normally.

`Rotate`

Type Bool

Default value No

Description Rotate the molecule randomly before adding it to the system.

`StartStep`

Type Integer

Default value 0

Description Step number when the first molecule should be added. After that, molecules are added every Frequency steps.

For example, ff StartStep=99 and Frequency=100 then a molecule will be added at steps 99, 199, 299, etc…

No molecule will be added at step 0, so if StartStep=0 the first molecule is added at the step number equal to [Frequency].

`StopStep`

Type Integer

Description Do not add this molecule after the specified step.

`System`

Type String

Description String ID of the [System] that will be added with this 'gun'.

The lattice specified with this System is ignored and the main system's lattice is used instead.

AMSinput adds the system at the coordinates of the System (thus setting Coords to the center of the System).

`Temperature`

Type Float

Unit Kelvin

Description Initial energy of the molecule in the shooting direction will correspond to the given temperature.

`TemperatureSigma`

Type Float

Default value 0.0

Unit Kelvin

Description Sigma value for the Gauss distribution of the initial temperature the specified value. Should only be used together with Temperature.

`Velocity`

Type Float

Unit Angstrom/fs

Description Initial velocity of the molecule in the shooting direction.

`VelocityDirection`

Type Float List

Description Velocity direction vector for aimed shooting. It will be random if not specified.

In AMSinput add one or two atoms (which may be dummies).

One atom: use vector from center of the system to add to that atom.

Two atoms: use vector from the first to the second atom.

`VelocitySigma`

Type Float

Default value 0.0

Unit Angstrom/fs

Description Sigma value for the Gauss distribution of the initial velocity around the specified value. Should only be used together with Velocity.

Since the 2022 release of the AMS driver, it is possible to generate molecule mixtures by using multiple guns that each have the `MoleFraction` keyword set: AMS will then randomly alternate between any of these guns. The cooperating guns need to all have the same settings for `StartStep`, `StopStep` and `Frequency`. (Any additional AddMolecules blocks without MoleFraction will remain completely independent.) The following example shows the generation of a 80:20 mixture of `molA` and `molB`:

```
MolecularDynamics
   AddMolecules
       System molA
       MoleFraction 0.8
       Frequency 2000
       StartStep 1
   End
   AddMolecules
       System molB
       MoleFraction 0.2
       Frequency 2000
       StartStep 1
   End
End

System anthracene
   ...
End

System benzene
   ...
End
```

Note that the exact number of inserted molecules of each type is not deterministic: running the same job twice may give you slightly different ratios. However, when running the job many times, the relative ratios averaged over the different runs should approach the fractions as requested in the input.

4.9.8 Removing molecules during simulation

Molecules *detected* (page 266) by the AMS driver can also be removed from the system. This feature can, for example, be used to remove reaction products.

MolecularDynamics

RemoveMolecules

Type Block

Recurring True

GUI name Remove molecules

Description This block controls removal of molecules from the system. Multiple occurrences of this block are possible.

Formula

Type String

Description Molecular formula of the molecules that should be removed from the system.

The order of elements in the formula is very important and the correct order is: C, H, all other elements in the strictly alphabetic order. Element names are case-sensitive, spaces in the formula are not allowed. Digit '1' must be omitted.

Valid formula examples: C2H6O, H2O, O2S. Invalid formula examples: C2H5OH, H2O1, OH, SO2. Invalid formulas are silently ignored.

Use * to remove any molecule, which must be combined with SinkBox or SafeBox.

`Frequency`

Type Integer

Default value 0

Description The specified molecules are removed every so many steps after the StartStep. There is never a molecule removed at step 0.

`SafeBox`

Type Block

Description Part of the simulation box where molecules may not be removed. Only one of the SinkBox or SafeBox blocks may be present. If this block is present the molecule will not be removed if any of its atoms is within the box. For a periodic dimension it is given as a fraction of the simulation box (the full 0 to 1 range by default). For a non-periodic dimension it represents absolute Cartesian coordinates in Angstrom.

`Amax`

Type Float

Description Coordinate of the upper bound along the first axis.

`Amin`

Type Float

Description Coordinate of the lower bound along the first axis.

`Bmax`

Type Float

Description Coordinate of the upper bound along the second axis.

`Bmin`

Type Float

Description Coordinate of the lower bound along the second axis.

`Cmax`

Type Float

Description Coordinate of the upper bound along the third axis.

`Cmin`

Type Float

Description Coordinate of the lower bound along the third axis.

`FractionalCoordsBox`

Type Float List

GUI name Safe box

Description Do not remove molecules that are (partly) inside the safe box.

Borders of the safe box specified as: Amin, Amax, Bmin, Bmax, Cmin, Cmax.

For periodic dimensions fractional coordinates between 0 and 1 and for non-periodic dimensions Cartesian values in Angstrom are expected.

`SinkBox`

Type Block

Description Part of the simulation box where matching molecules will be removed. By default, molecules matching the formula will be removed regardless of their location. If this block is present then such a molecule will only be removed if any of its atoms is within the box. For a periodic dimension it is given as a fraction of the simulation box (the full 0 to 1 range by default). For a non-periodic dimension it represents absolute Cartesian coordinates in Angstrom.

`Amax`

Type Float

Description Coordinate of the upper bound along the first axis.

`Amin`

Type Float

Description Coordinate of the lower bound along the first axis.

`Bmax`

Type Float

Description Coordinate of the upper bound along the second axis.

`Bmin`

Type Float

Description Coordinate of the lower bound along the second axis.

`Cmax`

Type Float

Description Coordinate of the upper bound along the third axis.

`Cmin`

Type Float

Description Coordinate of the lower bound along the third axis.

`FractionalCoordsBox`

Type Float List

GUI name Sink box

Description Remove molecules that are (partly) inside the sink box.

Borders of the sink box specified as: Amin, Amax, Bmin, Bmax, Cmin, Cmax.

For periodic dimensions fractional coordinates between 0 and 1 and for non-periodic dimensions Cartesian values in Angstrom are expected.

`StartStep`

Type Integer

Default value 0

Description Step number when molecules are removed for the first time. After that, molecules are removed every [Frequency] steps.

For example, if StartStep=99 and Frequency=100 then molecules will be removed at steps 99, 199, 299, etc…

No molecule will be removed at step 0, so if StartStep=0 the first molecules are removed at the step number equal to [Frequency].

`StopStep`

Type Integer

Description Do not remove the specified molecules after this step.

Warning: When there is a Molecules%AdsorptionSupportRegion defined, the molecule formulas depend on whether the molecule is adsorbed or not.

4.9.9 Accelerated dynamics

The PLUMED library support in AMS

PLUMED (http://www.plumed.org/) is a plugin that works with various MD programs and is also available in AMS. It can be used for on-the-fly analysis of the dynamics, or to perform a wide variety of free energy methods. The interface with the plugin is really simple: you just need to specify the PLUMED input in the MolecularDynamics%Plumed%Input block and it will be passed to the library "as is". At each MD step, the current state of the system will be passed to the plugin to be updated according to the PLUMED input.

`MolecularDynamics`

`Plumed`

Type Block

Description Input for PLUMED. The parallel option is still experimental.

`Input`

Type Non-standard block

Description Input for PLUMED. Contents of this block is passed to PLUMED as is.

`Parallel`

Type Block

Description Options for double parallelization, which allows to split the available processor cores into groups working through all the available tasks in parallel, resulting in a better parallel performance. The keys in this block determine how to split the available processor cores into groups working in parallel.

`nCoresPerGroup`

Type Integer

GUI name Cores per group

Description Number of cores in each working group.

nGroups

Type Integer

GUI name Number of groups

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

nNodesPerGroup

Type Integer

GUI name Nodes per group

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

Metadynamics for Conformer-Rotamer Ensemble Sampling (CREST-MTD)

This is a very specific implementation of metadynamics that is only meant for exploration of conformer space, as used in the Conformer-Rotamer Ensemble Sampling (CREST) approach. It is an RMSD-based metadynamics that places a new 1-dimensional Gaussian on the potential energy surface every `NSteps` steps. The Gaussian is a function of the RMSD from the current geometry, which will always be zero at the moment of placement. All Gaussians have the same maximum height (`Height`) and the same width (`Width`). There is an upper limit of `NGaussiansMax` to the number of Gaussians present in the system, and when this is exceeded the oldest Gaussian is removed. By default the Gaussians are gradually introduced, using a scaling function that increases exponentially from 0 to 1 with the simulation time. The keyword `ScalingSlope` in the input block `GaussianScaling` determines the slope of the scaling function with respect to time. The default value of 0.03 $steps^{-1}$ yields a scaling factor of nearly 1 after 100 steps. The keyword `ScaleGaussians` in the inputblock `GaussianScaling` determines whether the Gaussians are scaled at all.

By default, all atoms are included in the RMSD calculation. However, the selection can be restricted to specific regions using the `Region` keyword. This can be a single region or a combination thereof using region expressions (for example, `reg1+reg2` for a union).

MolecularDynamics

CRESTMTD

Type Block

GUI name CREST_MTD

Description Input for CREST metadynamics simulation.

AddEnergy

Type Bool

Default value No

Description Add the bias energy to the potential energy (to match the gradients)

GaussianScaling

Type Block

Description Options for gradual introduction of the Gaussians

ScaleGaussians

Type Bool

Default value Yes

Description Introduce the Gaussians gradually, using a scaling function

`ScalingSlope`

Type Float

Default value 0.03

Description Slope of the scaling function for the Gaussians with respect to time

`Height`

Type Float

Unit Hartree

Description The height of the Gaussians added

`NGaussiansMax`

Type Integer

Description Maximum number of Gaussians stored

`NSteps`

Type Integer

Description Interval of Gaussian placement

`Region`

Type String

Default value *

Description Restrict the range of atoms for RMSD calculation to the specified region.

`RestartFile`

Type String

Description Filename for file from which to read data on Gaussians placed previously.

`Width`

Type Float

Unit Bohr

Description The width of the Gaussians added in terms of the RMSD

By default, the gradients of the Gaussians with respect to the atom coordinates are added to the state gradients, but the value of the Gaussians is not added to the energy, which is common in metadynamics. For testing purposes it can be useful to add the Gaussian value to the energy, and this can be done with the keyword `AddEnergy`. Irrespective of this choice, the energy value of the Gaussian at each geometry is printed in the ams.rkf file in the section CrestMTDHistory. It is also possible to use Gaussians from an earlier CREST-MTD simulation, using the keyword `RestartFile`.

Collective Variable-driven HyperDynamics (CVHD)

The Collective Variable-driven HyperDynamics is a molecular dynamics acceleration method that allows observation of rare events by filling energy minima with a bias potential. In this sense it is similar to metadynamics. The difference of the hyperdynamics is that it ensures that the bias disappears in the transition state region. This difference allows hyperdynamics to calculate the rate of slow processes, for example the ignition phase of combustion.

See also:

The GUI tutorial on CVHD.

The CVHD implementation in AMS follows the algorithm described in K.M. Bal, E.C. Neyts, JCTC, 11 (2015) (https://doi.org/10.1021/acs.jctc.5b00597)

The StartStep, Frequency, StopStep, and WaitSteps keys define when and how often the bias potential is added, and when it is removed. The Bias block defines parameters of the bias potential peaks and the ColVarBB block describes parameters of the bond-breaking collective variable.

`MolecularDynamics`

`CVHD`

Type Block

Recurring True

GUI name CVHD

Description Input for the Collective Variable-driven HyperDynamics (CVHD).

`Bias`

Type Block

Description The bias is built from a series of Gaussian peaks deposited on the collective variable axis every [Frequency] steps during MD. Each peak is characterized by its (possibly damped) height and the RMS width (standard deviation).

`DampingTemp`

Type Float

Default value 0.0

Unit Kelvin

GUI name Bias damping T

Description During well-tempered hyperdynamics the height of the added bias is scaled down with an exp(-E/kT) factor [PhysRevLett 100, 020603 (2008)], where E is the current value of the bias at the given CV value and T is the damping temperature DampingTemp. If DampingTemp is zero then no damping is applied.

`Delta`

Type Float

Description Standard deviation parameter of the Gaussian bias peak.

`Height`

Type Float

Unit Hartree

Description Height of the Gaussian bias peak.

ColVarBB

Type Block

Recurring True

GUI name Collective Variable

Description Description of a bond-breaking collective variable (CV) as described in [Bal & Neyts, JCTC, 11 (2015)]. A collective variable may consist of multiple ColVar blocks.

at1

Type Block

Description Specifies the first bonded atom in the collective variable.

region

Type String

Default value *

Description Restrict the selection of bonded atoms to a specific region. If this is not set, atoms anywhere in the system will be selected.

symbol

Type String

Description Atom type name of the first atom of the bond. The name must be as it appears in the System block. That is, if the atom name contains an extension (e.g C.1) then the full name including the extension must be used here.

at2

Type Block

Description Specifies the second bonded atom in the collective variable.

region

Type String

Default value *

Description Restrict the selection of bonded atoms to a specific region. If this is not set, atoms anywhere in the system will be selected.

symbol

Type String

Description Atom type name of the second atom of the bond. The value is allowed to be the same as [at1], in which case bonds between atoms of the same type will be included.

cutoff

Type Float

Default value 0.3

GUI name Bond order cutoff

Description Bond order cutoff. Bonds with BO below this value are ignored when creating the initial bond list for the CV. The bond list does not change during lifetime of the variable even if some bond orders drop below the cutoff.

p

Type Integer

Default value 6

GUI name Exponent p

Description Exponent value p used to calculate the p-norm for this CV.

`rmax`

Type Float

Unit Angstrom

GUI name R max

Description Max bond distance parameter Rmax used for calculating the CV. It should be close to the transition-state distance for the corresponding bond.

`rmin`

Type Float

Unit Angstrom

GUI name R min

Description Min bond distance parameter Rmin used for calculating the CV. It should be close to equilibrium distance for the corresponding bond.

`ColVarBM`

Type Block

Recurring True

GUI name Collective Variable

Description Description of a bond-making collective variable (CV). A collective variable may consist of multiple ColVar blocks.

`at1`

Type Block

Description Specifies selection criteria for the first atom of a pair in the collective variable.

`region`

Type String

Default value *

Description Restrict the selection to a specific region. If this is not set, atoms anywhere in the system will be selected.

`symbol`

Type String

Description Atom type name of the first atom of the pair. The name must be as it appears in the System block. That is, if the atom name contains an extension (e.g C.1) then the full name including the extension must be used here.

`at2`

Type Block

Description Specifies selection criteria for the second atom of a pair in the collective variable.

`region`

Type String

Default value *

Description Restrict the selection to a specific region. If this is not set, atoms anywhere in the system will be selected.

`symbol`

Type String

Description Atom type name of the second atom of the pair. The value is allowed to be the same as [at1], in which case pairs of atoms of the same type will be included.

`cutoff`

Type Float

Default value 0.3

GUI name Bond order cutoff

Description Bond order cutoff. Bonds with BO above this value are ignored when creating the initial atom-pair list for the CV. The list does not change during lifetime of the variable even if some bond orders rise above the cutoff.

`p`

Type Integer

Default value 6

GUI name Exponent p

Description Exponent value p used to calculate the p-norm for this CV.

`rmax`

Type Float

Unit Angstrom

GUI name R max

Description Max bond distance parameter Rmax used for calculating the CV. It should be much larger than the corresponding Rmin.

`rmin`

Type Float

Unit Angstrom

GUI name R min

Description Min bond distance parameter Rmin used for calculating the CV. It should be close to the transition-state distance for the corresponding bond.

`Frequency`

Type Integer

Description Frequency of adding a new bias peak, in steps. New bias is deposited every [Frequency] steps after [StartStep] if the following conditions are satisfied: the current CV value is less than 0.9 (to avoid creating barriers at the transition state), the step number is greater than or equal to [StartStep], and the step number is less than or equal to [StopStep].

MaxEvents

Type Integer

Default value 0

Description Max number of events to allow during dynamics. When this number is reached no new bias will be added for this input block.

StartStep

Type Integer

Description If this key is specified, the first bias will be deposited at this step. Otherwise, the first bias peak is added at the step number equal to the Frequency parameter. The bias is never deposited at step 0.

StopStep

Type Integer

Description No bias will be deposited after the specified step. The already deposited bias will continue to be applied until the reaction event occurs. After that no new CVHD will be started. By default, the CVHD runs for the whole duration of the MD calculation.

WaitSteps

Type Integer

Description If the CV value becomes equal to 1 and remains at this value for this many steps then the reaction event is considered having taken place. After this, the collective variable will be reset and the bias will be removed.

During a CVHD calculation, the following variables are saved to the MDHistory section of the RKF file, in addition to other MD properties:

- *BiasEnergy* - value the bias energy at the current MD step, in Hartree.
- *MaxBiasEnergy* - max BiasEnergy since the last sampling step.
- *BoostFactor* - the boost factor at the given MD step. The boost factor is calculated at each MD step as $boost = e^{E_{bias}/kT}$, where T is the MD ensemble temperature.
- *MaxBoostFactor* - max BoostFactor value since the last sampling step.
- *HyperTime* - boosted MD time, in femtoseconds, which is a sum of the hyper-time steps calculated from the current boost factor and the MD time step as $\Delta t_{boost} = boost * \Delta t$. In hyperdynamics, the hyper-time value is directly related to the rate of the process boosted by the corresponding collective variable.

Temperature Replica Exchange

Sampling of rare events can be accelerated using the Replica Exchange Molecular Dynamics (REMD) method, also known as Parallel Tempering. This method runs multiple replicas (copies) of the simulated system in parallel, each in a different ensemble. In the case of Temperature REMD, these ensembles are all NVT or NpT, each at a different temperature. Periodically, Monte Carlo swaps are attempted between neighboring ensembles. If the current configuration of replica A has a sufficient Boltzmann probability in the ensemble of replica B (and vice versa), the two configurations will be swapped. This causes high-energy configuration to migrate into the high-temperature replicas while low-energy configurations eventually end up in the coldest ensemble. This facilitates the crossing of energy barriers in the high-temperature ensembles while keeping the coldest replica at a given temperature of interest. Because each replica always samples an unbiased ensemble, any property can be calculated using standard MD analysis methods without special preparation.

The method is controlled using the ReplicaExchange block:

MolecularDynamics

ReplicaExchange

Type Block

Description This block is used for (temperature) Replica Exchange MD (Parallel Tempering) simulations.

AllowWrongResults

Type Bool

Default value No

Description Allow combining Replica Exchange with other features when the combination is known to produce physically incorrect results.

EWMALength

Type Integer

Default value 10

Description Length of the exponentially weighted moving average used to smooth swap probabilities for monitoring.

This value is equal to the inverse of the EWMA mixing factor.

SwapFrequency

Type Integer

Default value 100

Description Attempt an exchange every N steps.

TemperatureFactors

Type Float List

Description This is the ratio of the temperatures of two successive replicas.

The first value sets the temperature of the second replica with respect to the first replica, the second value sets the temperature of the third replica with respect to the second one, and so on. If there are fewer values than nReplicas, the last value of TemperatureFactor is used for all the remaining replicas.

Temperatures

Type Float List

Description List of temperatures for all replicas except for the first one.

This is mutually exclusive with TemperatureFactors. Exactly nReplicas-1 temperature values need to be specified, in increasing order. The temperature of the first replica is given by [Thermostat%Temperature].

nReplicas

Type Integer

Default value 1

GUI name Number of replicas

Description Number of replicas to run in parallel.

The number of replicas set by `nReplicas` must never exceed the total number of processors used for the simulation. If possible, the total number of processors should be an integer multiple of `nReplicas` to ensure good load balancing.

The temperature of the base (coldest) replica is determined by the `Thermostat` input block, just like in an ordinary MD simulation. There are two ways to set the temperatures of the remaining replicas, either using `Temperatures` or `TemperatureFactors`. The latter is typically more convenient, as it makes it easy to set up the optimal geometric progression of temperatures. In the simplest case, it is enough to supply just a single value in `TemperatureFactors`, setting the common ratio of temperatures of any two adjacent replicas.

`SwapFrequency` should be set as low as practical for maximum efficiency. The value of this parameter isn't critical because it doesn't affect the validity of the results. However, setting it too high will decrease overall acceleration by missing some opportunities to exchange. Conversely, using a value that is too low will increase the communication overhead and lead to useless back-and-forth swaps between adjacent replicas. Ideally, `SwapFrequency` should be comparable to the correlation time of the system to ensure that individual exchange attempts are uncorrelated.

The trajectory of each replica is written to a separate RKF file: *ams.rkf* for the base replica and *replicaX.rkf* for the other replicas. One can easily switch between these files in the GUI using *File → Related Files*. In addition to data present in any MD trajectory, these files also contain an extra section *ReplicaExchangeHistory* with the following data items written every `SwapFrequency` steps:

- *AvgSwapProbability* – Average swap acceptance for each pair of replicas, smoothed using an exponentially weighted moving average with a mixing factor equal to the inverse of `EWMALength`.
- *{Min,Max,Mean,StdDev}PotentialEnergy* – Statistics of the potential energy for each ensemble over the last `SwapFrequency` steps.
- *SystemInEnsemble i* – Identifies the system (continuous trajectory) currently running in ensemble (replica) *i*.
- *EnsembleOfSystem i* – Inverse mapping of *SystemInEnsemble*, giving the current replica number in which the system number *i* runs.
- *TemperatureOfSystem i* – Equivalent to *EnsembleOfSystem* using temperatures instead of integer numbers to identify ensembles.

These data items can be plotted using the `MD Replica Exchange` menu in AMSmovie. For example, plotting *TemperatureOfSystem* or *EnsembleOfSystem* is useful to visualize the migration of each system through the space of ensembles, where each curve represents one continuous trajectory. Plotting potential energy statistics or average acceptances facilitates tuning the number of replicas and their temperatures to achieve efficient acceleration. The replica exchange method can only work when the potential energy distributions of adjacent ensembles have a sufficient overlap. This can be easily seen by comparing *MaxPotentialEnergy* of ensemble *i* with *MinPotentialEnergy* of ensemble *i+1*. The optimal degree of overlap is such that leads to approximately 20 % of swap attempts getting accepted. The acceptance of swaps can be monitored by plotting *AvgSwapProbability* and the corresponding `TemperatureFactors` can then be adjusted to keep it near the optimal value.

Bond Boost Method

The bond boost method implemented here is described in[3]. In this method, the distances between atoms that are relevant to the reaction of interest are calculated to determine the orientation of the reactant molecules. If a suitable initial configuration is recognized, an additional restraint energy (possibly consisting of more than one term) is added to the system that is intended to stretch or compress bonds at a pre-defined rate such that this additional energy can help achieve the energy to cross the reaction barrier. A single term of the restraint energy is depends on the restraints type and its parameters, see *restraint definitions* (page 284) for details. If more than one suitable configuration is found then the one with the smallest sum of distances is used to create the restraints.

[3] A. Vashisth, C. Ashraf, W. Zhang, C.E. Bakis, and A.C.T. van Duin, *Accelerated ReaxFF simulations for describing the reactive cross-linking of polymers*, J. Phys. Chem. A, 122, 6633-6642 (2018) (https://doi.org/10.1021/acs.jpca.8b03826)

See also:

The GUI tutorial on the Bond Boost Method.

`MolecularDynamics`

`BondBoost`

Type Block

Recurring True

Description Forced reaction (bond boost) definitions. Multiple BondBoost blocks may be specified, which will be treated independently.

`Chain`

Type Block

Description Specifications of a chain of atoms. When a chain is detected the distance restraints will be activated. No other chain of this type will be detected while any restraints for this chain is active.

`AtomNames`

Type String

Description Atom names specifying the chain. An atom name can optionally be followed by '@' and a region name, in this case only atoms of this type from the given region will be matched. A leading '@' followed by a number indicates that this position in the chain must be occupied by the atom found earlier at the specified position in the chain. For example "O H N C @1" indicates that the last atom in the chain of the five atoms must be the first oxygen, thus defining a 4-membered ring. This is the only way to define a ring because implicit rings will not be detected. For example, "O H N C O" does not include rings.

`MaxDistances`

Type Float List

Unit Angstrom

Description Maximum distances for each pair of atoms in the chain. The number of distances must be one less than the number of AtomNames.

`MinDistances`

Type Float List

Unit Angstrom

Description Minimum distances for each pair of atoms in the chain. The number of distances must be one less than the number of AtomNames.

`DistanceRestraint`

Type String

Recurring True

Description Specify two atom indices followed by the optimum distance in Angstrom, the first parameter and, optionally, the profile type and the second parameter.

This restraint will try to keep the distance between the two specified atoms at the given value. For periodic systems this restraint follows the minimum image convention.

Each atom index indicates a position of the corresponding atom in the AtomNames key. Currently recognized restraint profile types: Harmonic (default), Hyperbolic, Erf, GaussianWell.

The first parameter is the force constant for the Harmonic, Hyperbolic, and Erf profiles, or well depth for GaussianWell. The second parameter is the asymptotic force value F(Inf) for Hyperbolic and Erf profiles, or the factor before x^2 in the exponent for GaussianWell.

Note: the GaussianWell restraint should be used with the Moving flag.

Moving

Type Bool

Default value No

GUI name Move restraint

Description Move the restraints created with this BondBoost. The restraint value will start at the currect coordinate's value and will move towards the optimum during the restraint's lifetime. The increment is calculated from the initial deviation and the [NSteps] parameter.

This feature should be used with the GaussianWell restraint types.

NSteps

Type Integer

GUI name Boost lifetime

Description Number of steps the restraints will remain active until removed. Atoms participating in one reaction are not available for the given number of steps.

NumInstances

Type Integer

Default value 1

GUI name Number of instances

Description Number of reactions of this type taking place simultaneously.

Units

Type Multiple Choice

Default value Default

Options [Default, MD]

GUI name Restr. parameter units

Description Change energy, force and force constant units in the DistanceRestraint key from the default (atomic units) to those often used in the MD community (based on kcal/mol and Angstrom). Units for the optimum distances are not affected.

For example:

```
MolecularDynamics
   BondBoost
      NSteps 10000
      Chain
         AtomNames     N.1   C.t    O     H     @1
         MinDistances     3.0   1.2   1.5   0.8
         MaxDistances     3.8   3.0   2.5   1.5
      End
#     Restraints          i  j   R_0    FC
      DistanceRestraint  1  2   1.5   0.05   Hyperbolic   0.7
      DistanceRestraint  2  3   3.5   0.03   Hyperbolic   0.5
```

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```
      DistanceRestraint  3  4   1.0   0.03   Hyperbolic   0.5
   End
End
```

The `AtomNames`, `MinDistances`, and `MaxDistances` keys constitute the atom chain definitions for the initial configuration. Thus, the example above defines a chain of atoms N.1-C.t-O-H-N.1 with R(N.1-C) in the (3.0,3.8) range, R(C.t-O) in the (1.2,3.0) range, etc.. In this example, the last atoms in the chain is required to be the same as the fist one, thus defining a ring. The specified restraints will push pairs of atoms C-N and O-H close together, which will hopefully let them form a bond, and pull atoms C.t and O away from each other, thus breaking the C-O bond. The restraint type is set to `Hyperbolic` to avoid very large forces that would otherwise result from a harmonic potential at a large deviation.

Note: When detecting coordinates, the program uses the full atom name and not just the element name. An atom name consists of the element name optionally followed by a period and a suffix, just like `N.1` and `C.t` in the example above. Using extended names for some atoms one may allow only a subset of bonds to be boosted.

Reaction boost (Targeted MD)

The principle of targeted (or steered) MD is simple: during molecular dynamics, the system is pushed towards a certain known configuration in small steps. The steering can be in the form of holonomic constraints, then it is the standard Targeted MD (TMD). When restraints instead of constraints are used, then some authors call it steered MD[6].

The ReactionBoost feature uses restraints to push the system towards the target configuration. The restraints can be one of the following two types: atom-pair or (mass-weighted) RMSD. In both cases, the user can select a region to which the steering will be limited. AMS will then apply the restraints only to the atoms of the region(s). The RMSD type of restraints is suitable for very large systems or regions while the pair restraints can be used for small to moderately-sized ones. The atom-pair restraints can be further sub-divided into the following types, depending on the mutual bonding situation of the two atoms in the initial and the final state: bonded, non-bonded, bond-breaking and bond-making. The type is determined automatically at the time the steering is started based on the interatomic distances and the covalent radii of the atoms. A non-bonded restraint is a static repulsive potential, it is intended to keep atoms from forming a bond. The other three are moving: the restraint's target distance changes between its initial and final values as the MD progresses. Setting the profile to `None` disables the corresponding pair restraint type.

The following keys define parameters of the method:

`MolecularDynamics`

`ReactionBoost`

Type Block

GUI name Reaction Boost

Description Define a series of transitions between different states of the system.

Each transition is defined by a TargetSystem and by a set of restraints that force the transition.

`BondBreakingRestraints`

Type Block

Description Define parameters for moving restraints that are added for pairs of atoms that become disconnected during the transition.

[6] He Huang, E. Ozkirimli, C.B. Post, *A Comparison of Three Perturbation Molecular Dynamics Methods for Modeling Conformational Transitions*, J Chem Theory Comput. 5 (2009) 1301–1314 (https://doi.org/10.1021/ct9000153)

It is intended to make sure the corresponding bonds get broken, although this may not always be required because forming other bonds will likely get these bonds broken.

Erf

Type Block

Description Define parameters for the Int(erf) potential V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI)). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce.

ForceConstant

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

MaxForce

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

GaussianWell

Type Block

Description Define parameters in the Gaussian well potential V=-WellDepth*exp(-Sigma*(r-r0)^2).

Sigma

Type Float

Default value 1.0

Unit 1/Bohr^2

Description Sigma parameter in the potential expression.

WellDepth

Type Float

Default value 1.0

Unit Hartree

Description WellDepth parameter in the potential expression.

Harmonic

Type Block

Description Define parameters for the harmonic potential V=0.5*FC*(r-r0)^2.

ForceConstant

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The FC parameter of the harmonic potential.

`Hyperbolic`

Type Block

Description Define parameters for the hyperbolic potential V=alpha*(sqrt(1 + beta*x^2) - 1). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce: beta=ForceConstant/MaxForce, alpha=MaxForce/beta

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

`MaxForce`

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

`Taper`

Type Block

Description

`Enabled`

Type Bool

Default value No

GUI name Tapering

Description Enable tapering of the restraint potential and force between the given range of bond distances. A 7-th order tapering function on the actual (not target!) distance will be used. The MaxDistance must be greater than MinDistance.

`MaxDistance`

Type Float

Default value 0.0

Unit Angstrom

GUI name End tapering at

Description Bond length at which the restraint potential and force decays to zero.

`MinDistance`

Type Float

Default value 0.0

Unit Angstrom

GUI name Start tapering at

Description Bond length at which the restraint potential and force will start decaying to zero.

`Type`

Type Multiple Choice

Default value Erf

Options [None, Harmonic, Hyperbolic, Erf, GaussianWell]

GUI name Bond breaking restraints

Description Select type of the moving restraint profile.

Harmonic: V=0.5*FC*(r-r0)^2

Hyperbolic: V=alpha*(sqrt(1 + beta*x^2) - 1)

Erf: V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI))

GaussianWell: V=-WellDepth*exp(-Sigma*(r-r0)^2)

Here beta=ForceConstant/MaxForce, alpha=MaxForce/beta.

The force for Hyperbolic and Erf is bounded by a user-defined value, the latter converging to it faster than the former. The GaussianWell has a finite depth so it is suitable for cases when crossing a high reaction barrier is not desirable.

Moving restraints are added for pairs of atoms that become disconnected during the transition.

It is intended to make sure the corresponding bonds get broken, although this may not always be required because forming other bonds will likely get these bonds broken.

`BondMakingRestraints`

Type Block

Description Define parameters for moving restraints that are added for pairs of atoms that become connected during the transition.

It is intended to make sure the bonds are created as required.

`Erf`

Type Block

Description Define parameters for the Int(erf) potential V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI)). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

`MaxForce`

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

`GaussianWell`

Type Block

Description Define parameters in the Gaussian well potential V=-WellDepth*exp(-Sigma*(r-r0)^2).

`Sigma`

Type Float

Default value 1.0

Unit 1/Bohr^2

Description Sigma parameter in the potential expression.

`WellDepth`

Type Float

Default value 1.0

Unit Hartree

Description WellDepth parameter in the potential expression.

`Harmonic`

Type Block

Description Define parameters for the harmonic potential V=0.5*FC*(r-r0)^2.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The FC parameter of the harmonic potential.

`Hyperbolic`

Type Block

Description Define parameters for the hyperbolic potential V=alpha*(sqrt(1 + beta*x^2) - 1). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce: beta=ForceConstant/MaxForce, alpha=MaxForce/beta

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

`MaxForce`

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

`Type`

Type Multiple Choice

Default value Erf

Options [None, Harmonic, Hyperbolic, Erf, GaussianWell]

GUI name Bond making restraints

Description Select type of the moving restraint profile.

Harmonic: V=0.5*FC*(r-r0)^2

Hyperbolic: V=alpha*(sqrt(1 + beta*x^2) - 1)

Erf: V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI))

GaussianWell: V=-WellDepth*exp(-Sigma*(r-r0)^2)

Here beta=ForceConstant/MaxForce, alpha=MaxForce/beta.

The force for Hyperbolic and Erf is bounded by a user-defined value. The GaussianWell has a finite depth so it is suitable for cases when crossing a high reaction barrier is not desirable.

Moving restraints are added for pairs of atoms that become connected during the transition.

It is intended to make sure the bonds are created as required.

`BondedRestraints`

Type Block

Description Define parameters for bonded restraints. A bonded restraint is added for each pair of atoms that are bonded both in the current and in the final state.

It is intended to make sure they remain bonded during simulation.

`Harmonic`

Type Block

Description Define parameters for the harmonic potential V=0.5*FC*(r-r0)^2.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The FC parameter of the harmonic potential.

`Type`

Type Multiple Choice

Default value None

Options [None, Harmonic]

GUI name Bonded restraints

Description Select type of the bonded restraints:

Harmonic: V=0.5*FC*(r-r0)^2

A bonded restraint is added for each pair of atoms that are bonded both in the current and in the final state.

It is intended to make sure they remain bonded during simulation.

`Change`

Type Multiple Choice

Default value TargetCoordinate

Options [TargetCoordinate, Force, LogForce]

GUI name Move type

Description Select what to change during dynamics.

By default, once the restraints are switched on, AMS will change the restraint's target coordinate towards its final value.

If the [Force] or [LogForce] option is selected then the target coordinate is set to its final value immediately and instead the restraint force is gradually scaled from 0 to 1. The scaling is either linear (Force) or logarithmic (LogForce).

`InitialFraction`

Type Float

Default value 0.0

Description Initial fraction of the boost variable.

At the first boosting step, the restraint's target value (or force or log(force)) is equal to InitialFraction + 1/NSteps.

`InterEquilibrationSteps`

Type Integer

Default value 0

Description Number of equilibration steps after reaching a target before setting up restraints for the next one.

`MinBondChange`

Type Float

Default value 1.0

Unit Bohr

Description Minimal change in the distance for an individual restraint to be considered bond-breaking/making vs bonded.

`MinBondStrength`

Type Float

Default value 0.5

Description Minimum strength (usually ranges from 0 to 1) for a bond to be considered.

`NSteps`

Type Integer

Default value 500

GUI name Steps per target

Description Number of steps per target the restraints should be active for.

`NonBondedRestraints`

Type Block

Description Define parameters for non-bonded restraints. A non-bonded restraint is added for each pair of atoms that are bonded neither in the current nor in the final state.

It is intended to keep them from forming a bond unintentionally. They are represented by a repulsive potential

`Exponential`

Type Block

Description Define parameters for the repulsive potential V=Epsilon*exp(-Sigma*r).

`Epsilon`

Type Float

Default value 1.0

Unit Hartree

Description Epsilon parameter in the repulsive potential expression.

`Sigma`

Type Float

Default value 1.0

Unit 1/Bohr

Description Sigma parameter in the repulsive potential expression.

`Type`

Type Multiple Choice

Default value None

Options [None, Exponential]

GUI name Non-bonded restraints

Description Select type of the non-bonded restraints:

Exponential: V=Epsilon*exp(-Sigma*r)

A non-bonded restraint is added for each pair of atoms that are bonded neither in the current nor in the final state.

It is intended to keep them from forming a bond unintentionally. They are represented by a repulsive potential.

`PreEquilibrationSteps`

Type Integer

Default value 0

Description Number of steps before enabling the first set of restraints.

`RMSDRestraint`

Type Block

GUI name RMSD restraint

Description Define a static restraint that pulls each atom to its position in the target system, but in contrast to the individual restraints, the force for this one depends on the total mass-weighted root-mean-squared distance (RMSD) between the two structures.

`Erf`

Type Block

Description Define parameters for the Int(erf) potential V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI)). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

`MaxForce`

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

`GaussianWell`

Type Block

Description Define parameters in the Gaussian well potential V=-WellDepth*exp(-Sigma*(r-r0)^2).

`Sigma`

Type Float

Default value 1.0

Unit 1/Bohr^2

Description Sigma parameter in the potential expression.

`WellDepth`

Type Float

Default value 1.0

Unit Hartree

Description WellDepth parameter in the potential expression.

`Harmonic`

Type Block

Description Define parameters for the harmonic potential V=0.5*FC*(r-r0)^2.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The FC parameter of the harmonic potential.

`Hyperbolic`

Type Block

Description Define parameters for the hyperbolic potential V=alpha*(sqrt(1 + beta*x^2) - 1). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce: beta=ForceConstant/MaxForce, alpha=MaxForce/beta

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

`MaxForce`

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

`Type`

Type Multiple Choice

Default value None

Options [None, Harmonic, Hyperbolic, Erf, GaussianWell]

GUI name Type

Description Select type of the RMSD restraint profile:

Harmonic: V=0.5*FC*(r-r0)^2

Hyperbolic: V=alpha*(sqrt(1 + beta*x^2) - 1)

Erf: V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI),

GaussianWell: V=-WellDepth*exp(-Sigma*(r-r0)^2)

Here beta=ForceConstant/MaxForce, alpha=MaxForce/beta.

The Harmonic profile can be problematic at large deviations as it may result in large forces. The force for Hyperbolic and Erf is bounded by a user-defined value. The GaussianWell has a finite depth so it is suitable for cases when crossing a high reaction barrier is not desirable.

`Region`

Type String

Default value *

GUI name Region

Description Region to which the restraints should be limited.

`TargetSystem`

Type String

Recurring True

GUI name Target system

Description The target system's name for this transition. Multiple targets can be specified to request multiple transitions in one simulation.

Note that only the lattice and the atomic coordinates of the target system are used and other properties (bonds, charge, etc.) are ignored. The target system's lattice is used only to determine connections and it cannot be restrainted.

`Type`

Type Multiple Choice

Default value None

Options [None, Pair, RMSD]

GUI name Restraint set type

Description Reaction Boost uses a series of transitions between different states of the system. Each transition is defined by a TargetSystem and by a set of restraints that force the transition.

Select the type of the restraint set: -None: no Reaction Boost - Pair: use pair restraints - RMSD: use RMSD restraints.

Pair restraints are defined per atom pair while the RMSD defines one collective restraint for all atoms and is thus suitable for very large systems.

The pair restraints are further divided into four sub-types: bonding, non-bonding, bond-breaking and bond-making. The sub-type of restraints for each pair is determined automatically depending on whether the two atoms are bonded in the initial/final state.

Parameters of the pair restraints are defined by [NonBondedRestraints], [BondedRestraints], [BondBreakingRestraints] and [BondMakingRestraints] blocks, while those of the RMSD restraint by the [RMSDRestraint] block.

Force bias Monte Carlo (fbMC)

Configurational sampling and structural relaxation can be accelerated by the Force bias Monte Carlo method. Unlike molecular dynamics, this approach does not use the equations of motion or atomic velocities. Instead, all atoms are randomly displaced in each fbMC steps. AMS uses an uniform-acceptance force bias Monte Carlo flavour of fbMC called tfMC, as published by Mees et al.[4] Unlike other well-known Monte Carlo methods such as the Metropolis algorithm, fbMC does not generate completely random moves and then test whether these should be accepted or rejected. Instead, the atomic displacements are generated so that atoms preferably move in the direction of the forces acting on them. This special biasing enables fbMC to accept every move, sampling the correct canonical ensemble with high efficiency.

In AMS the fbMC method is implemented as an add-on to molecular dynamics, enabling mixed MC-MD simulations. After every `Frequency` MD steps, the MD procedure is stopped and fbMC takes over, executing `NSteps` Monte

[4] M.J. Mees, G. Pourtois, E. C. Neyts, B. J. Thijsse, and André Stesmans, *Uniform-acceptance force-bias Monte Carlo method with time scale to study solid-state diffusion*, Phys. Rev. B 85, 134301 (2012) (https://doi.org/10.1103/PhysRevB.85.134301)

Carlo steps. Once the fbMC procedure completes, the MD simulation continues from the new geometry generated by fbMC while reusing atomic velocities from before the start of fbMC.

The fbMC module requires three main input settings. Apart from the `NSteps` and `Frequency` defining the mix of molecular dynamics and Monte Carlo, `Temperature` needs to be set as desired to sample a particular canonical (NVT) ensemble. Although the fbMC procedure always runs in constant temperature mode, the rest of the MD simulation can in principle use any ensemble (with or without a thermostat or barostat).

Note: To run a pure fbMC simulation with no molecular dynamics component, leave `Frequency` set to 1 (the default), set the MD `TimeStep` and `InitialVelocities` to zero, and do not use other MD features such as a thermostat or a barostat.

Note: AMS currently cannot write sampled geometries to the trajectory during the fbMC procedure. To see the evolution of the system during a long fbMC run, split it into multiple shorter fbMC passes to let the MD driver sample the current state between them. To do this, set the `NSteps` for fbMC to the desired trajectory sampling interval, keep `Frequency` set to 1 and set `Trajectory SamplingFreq` to 1.

The amount of acceleration provided by fbMC depends on the `StepLength` parameter, which defines the maximum displacement of the lightest atom in the system. The default value of 0.1 Å is relatively conservative. Increasing `StepLength` leads to faster evolution of the system, but setting it too high can lead to inaccurate sampling or cause crashes by generating geometries that are too distorted.

An estimate of the timescale associated with fbMC (tfMC) steps will be printed to the output.

`MolecularDynamics`

`fbMC`

Type Block

Recurring True

GUI name fbMC

Description This block sets up force bias Monte Carlo interleaved with the molecular dynamics simulation.

`Frequency`

Type Integer

Default value 1

Description Run the fbMC procedure every Frequency MD steps.

`MassRoot`

Type Float

Default value 2.0

Description Inverse of the exponent used to mass-weight fbMC steps.

`MolecularMoves`

Type Block

Description Move molecules as rigid bodies in addition to normal atomic moves.

`Enabled`

Type Bool

Default value No

GUI name Enable molecular moves

Description Enable moving molecules as rigid bodies based on net forces and torques. Ordinary per-atom displacements will then be based on residual atomic forces.

`RotationStepAngle`

Type Float

Default value 0.1

Unit Radian

Description Maximum allowed angle of rotation of each molecule in one fbMC step.

`TranslationStepLength`

Type Float

Default value 0.1

Unit Angstrom

Description Maximum allowed displacement of each molecule in each Cartesian coordinate in one fbMC step.

`NSteps`

Type Integer

GUI name Number of steps

Description Number of fbMC steps to perform on every invocation of the procedure.

`PrintFreq`

Type Integer

GUI name Printing frequency

Description Print current thermodynamic properties to the output every N fbMC steps. This defaults to the PrintFreq set in the Trajectory block. Setting this to zero disables printing fbMC steps.

`StartStep`

Type Integer

Default value 1

Description First step at which the fbMC procedure may run.

`StepLength`

Type Float

Default value 0.1

Unit Angstrom

Description Maximum allowed displacement of the lightest atom in the system in each Cartesian coordinate in one fbMC step.

`StopStep`

Type Integer

Default value 0

Description Last step at which the fbMC procedure may run. If unset or zero, there is no limit.

`Temperature`

Type Float

Unit Kelvin

Description Temperature used for fbMC.

Nanoreactor

See also:

The ReactionsDiscovery workflow uses the nanoreactor to predict chemical reactions.

Nanoreactor is implemented following the article by L.-P. Wang et al.[5]. The nanoreactor is a spherical region of space centered at the origin and surrounded by an elastic wall (represented by a harmonic potential), its size changing over time. The idea of the nanoreactor is to have two phases: reaction and relaxation. In the following, each nanoreactor phase is referred to as a *reactor*. During the relaxation phase, the reactor is large and if the temperature is high enough the reactants are distributed more or less evenly throughout its volume. In the reaction phase, the reactor shrinks and the atoms that now fall outside the reactor's sphere accelerate towards its center. During this phase, high-energy collisions may lead to reactions. After the reaction phase is over, the relaxation phase begins again and the reactor is expanded. This cycle is repeated indefinitely.

Each phase is specified by its own `Reactor` input block. There should be at least two of them but there can be more. The `NSteps` key specifies the duration of the phase in MD steps. The radius of the reactor and the force constant of its wall are set by the `Radius` and `ForceConstant` keys, respectively. To minimize additional strain on internal degrees of freedom of the affected molecules, the force applied by the wall on an atom is proportional to the atom's mass by default. This means that atoms situated at the same distance from the center of the reactor will receive the same acceleration irrespective of their mass. This should be taken into account when choosing a value for the ForceConstant. Alternatively, this feature can be disabled using the `MassScaled` key.

`MolecularDynamics`

`Reactor`

Type Block

Recurring True

Description Define one phase of the nanoreactor. A reactor is a region of space surrounded by an elastic wall. Atoms inside the region are not affected. Atoms outside it will be pushed back with force depending on the [ForceConstant] and the [MassScaled] flag.

`ForceConstant`

Type Float

GUI name Reactor force constant

Description Force constant of the reactor wall in Hartree/Bohr^2 (or Hartree/Bohr^2/Dalton if [MassScaled] is true).

`MassScaled`

Type Bool

Default value Yes

GUI name Scale force by mass

[5] L.-P. Wang, A. Titov, R. McGibbon, F. Liu, V.S. Pande and T.J. Martínez, *Discovering chemistry with an ab initio nanoreactor*, Nature Chemistry 6, 1044 (2014) (https://doi.org/10.1038/NCHEM.2099)

Description If this flag is disabled the force on an atom outside of the reactor depends only on the atomic coordinates and the force constant. Otherwise, the force is also multiplied by the mass of the atom. This means that atoms at the same distance from the wall will receive the same accelerate due to the wall potential.

`NSteps`

Type Integer

GUI name Reactor lifetime

Description Number of steps for which the reactor will remain active until disabled. The next reactor will be activated immediately after this. After the last reactor is disabled the cycle will repeat.

`Radius`

Type Float

Unit Angstrom

GUI name Reactor radius

Description Radius of the reactor sphere.

4.9.10 Non-equilibrium MD (NEMD)

T-NEMD for thermoconductivity: heat exchange

There are different methods to study thermal conductivity using non-equilibrium molecular dynamics (NEMD). A common feature of these methods is that they require the system to be divided into three or more zones, each with its own thermostat and other properties. One method maintains the temperature of the heat source and the heat sink zones at the given temperature using two different thermostats and measures the amount of heat transferred. These method does not require any special features besides a standard thermostat and a possibility to calculate the amount of heat accumulated by the thermostat per unit of time. The accumulated thermostat energies are available in the MDHistory section of ams.rkf file, in variables called 'XXXXstat#Energy', where XXXX is a 4-letter abbreviation of the thermo-/barostat ('BerT' for a Berendsen thermostat, 'NHCT' for an NHC thermostat, 'NHTB' for an MTK barostat, etc.) and '#' is a 1-digit index of the thermo-/barostat.

In the other method, the heat flow is constant and the induced temperature gradient is measured. This method is implemented in AMS in three variants: a simple heat exchange, HEX[1] and eHEX[2]. In the simple heat exchange method the atom velocities are scaled up (or down) by a factor corresponding to the amount of heat deposited to the heat source (or withdrawn from the heat sink) without paying attention to the conservation of the total momentum of the heat source (or sink). In the HEX method the velocities are scaled in such a way that the total momentum is conserved. This, however, introduces a small but measurable drift in the total energy. The eHEX algorithm improves upon the HEX by adding a third-order time-integration correction to remove the drift.

This method is controlled by the HeatExchange sub-block of the MolecularDynamics block:

`MolecularDynamics`

`HeatExchange`

Type Block

Recurring True

[1] T. Ikeshoji and B. Hafskjold, *Non-equilibrium molecular dynamics calculation of heat conduction in liquid and through liquid-gas interface* Molecular Physics 81, 251-261 (1994) (https://doi.org/10.1080/00268979400100171)

[2] P. Wirnsberger, D. Frenkel, and C. Dellago, *An enhanced version of the heat exchange algorithm with excellent energy conservation properties* Journal of Chemical Physics 143, 124104 (2015) (http://dx.doi.org/10.1063/1.4931597)

GUI name Heat exchange

Description Input for the heat-exchange non-equilibrium MD (T-NEMD).

`HeatingRate`

Type Float

Unit Hartree/fs

Description Rate at which the energy is added to the Source and removed from the Sink. A heating rate of 1 Hartree/fs equals to about 0.00436 Watt of power being transferred through the system.

`Method`

Type Multiple Choice

Default value Simple

Options [Simple, HEX, eHEX]

Description Heat exchange method used.

Simple: kinetic energy of the atoms of the source and sink regions is modified irrespective of that of the center of mass (CoM) of the region (recommended for solids).

HEX: kinetic energy of the atoms of these regions is modified keeping that of the corresponding CoM constant.

eHEX: an enhanced version of HEX that conserves the total energy better (recommended for gases and liquids).

`Sink`

Type Block

Description Defines the heat sink region (where the heat will be removed).

`AtomList`

Type Integer List

GUI name Sink region

Description The atoms that are part of the sink.

This key is ignored if the [Box] block or [Region] key is present.

`Box`

Type Block

Description Part of the simulation box (in fractional cell coordinates) defining the heat sink. If this block is specified, then by default, the whole box in each of the three dimensions is used, which usually does not make much sense. Normally, you will want to set the bounds along one of the axes.

`Amax`

Type Float

Default value 1.0

Description Coordinate of the upper bound along the first axis.

`Amin`

Type Float

Default value 0.0

Description Coordinate of the lower bound along the first axis.

`Bmax`

Type Float

Default value 1.0

Description Coordinate of the upper bound along the second axis.

`Bmin`

Type Float

Default value 0.0

Description Coordinate of the lower bound along the second axis.

`Cmax`

Type Float

Default value 1.0

Description Coordinate of the upper bound along the third axis.

`Cmin`

Type Float

Default value 0.0

Description Coordinate of the lower bound along the third axis.

`Region`

Type String

GUI name Sink region

Description The region that is the sink.

This key is ignored if the [Box] block is present.

`Source`

Type Block

Description Defines the heat source region (where the heat will be added).

`AtomList`

Type Integer List

GUI name Source region

Description The atoms that are part of the source.

This key is ignored if the [Box] block or [Region] key is present.

`Box`

Type Block

Description Part of the simulation box (in fractional cell coordinates) defining the heat source. If this block is specified, then by default, the whole box in each of the three dimensions is used, which usually does not make much sense. Normally, you will want to set the bounds along one of the axes. This block is mutually exclusive with the FirstAtom/LastAtom setting.

Amax

Type Float

Default value 1.0

Description Coordinate of the upper bound along the first axis.

Amin

Type Float

Default value 0.0

Description Coordinate of the lower bound along the first axis.

Bmax

Type Float

Default value 1.0

Description Coordinate of the upper bound along the second axis.

Bmin

Type Float

Default value 0.0

Description Coordinate of the lower bound along the second axis.

Cmax

Type Float

Default value 1.0

Description Coordinate of the upper bound along the third axis.

Cmin

Type Float

Default value 0.0

Description Coordinate of the lower bound along the third axis.

Region

Type String

GUI name Source region

Description The region that is the source.

This key is ignored if the [Box] block is present.

StartStep

Type Integer

Default value 0

Description Index of the MD step at which the heat exchange will start.

StopStep

Type Integer

Description Index of the MD step at which the heat exchange will stop.

One should be careful when choosing a value for the HeatingRate because a too large value may lead to pyrolysis of the heat source or to an abnormal termination when all the kinetic energy of the heat sink has been drained. The optimal value depends on the size of the system, its heat conductivity and the desired temperature gradient value. The thermal conductivity k can be calculated by dividing the heat flow rate W by the temperature gradient *grad(T)* and by the flow cross-section area S: $k = W/(S \cdot grad(T))$. See the *trajectory sampling* (page 108) section above on how to obtain the temperature profile from which the *grad(T)* can be computed.

NEMD for tribology: Applying velocities / forces

Non-equilibrium Molecular Dynamics (NEMD) is a commonly used tool to study phenomena like friction & wear in tribochemical systems. In these MD simulations, an constant external force or velocity is applied to a specific subgroup of atoms. For example, when studying sliding solid surfaces, the `ApplyForce` feature can be used to exert a compressive normal force in the -Z direction on one of the solid slabs while the `ApplyVelocity` block simultaneously slides the same group of atoms along the X or Y axis.

In the case of `ApplyVelocity`, the specified group of atoms (defined as a Region) will move with the specified constant net `Velocity`. The imposed velocity is automatically excluded from thermostatting and system-wide momentum removal. The `Components` input key can be used to select just a subset of Cartesian components of the net velocity of the group to be controlled, so that other components can be left to evolve freely. In the sliding example in the previous paragraph, one would use `Components=XY` to let the Z motion of the sliding slab to freely follow the applied normal force.

In the case of `ApplyForce`, the selected Region (group of atoms) will experience an additional specified constant `Force` on each timestep of the simulation. By default, the `Force` parameter defines the total (net) force acting on the whole Region. This can be changed by setting the `PerAtom` option to apply the `Force` to each atom in the Region separately.

See also:

Example demonstrating a NEMD friction simulation (page 453)

`MolecularDynamics`

`ApplyVelocity`

Type Block

Recurring True

Description The ApplyVelocity keyword can be used to move an arbitrary group of atoms in the system with a constant net velocity

`Components`

Type Multiple Choice

Default value XY

Options [X, Y, Z, XY, YZ, XZ, XYZ]

Description Select which components of the Velocity vector are used to set the corresponding components of the net velocity of the specified set of atoms. Any other components of Velocity are ignored and the motion of the selected atoms in those directions is unaffected by ApplyVelocity.

`Region`

Type String

Recurring True

Description Applies the defined velocity to all atoms in this region.

`Velocity`

Type Float List

Unit Angstrom/fs

Recurring False

Description The constant velocity that will be applied to the specified atoms.

`MolecularDynamics`

`ApplyForce`

Type Block

Recurring True

Description The ApplyForce keyword can be used to apply an arbitrary constant force to a certain (subgroups of) atoms in the system

`Force`

Type Float List

Unit Hartree/Bohr

Description Defines the constant force vector

`PerAtom`

Type Bool

Default value No

Description If enabled, the Force vector is applied separately to every atom in the selected Region, so that the total net force on the Region equals the value of Force times the number of atoms in Region. This was the behaviour of ApplyForce in AMS2022. By default, with PerAtom disabled, the Force vector defines the total net force on the Region, so the force applied to each atom equals the value of Force divided by the number of atoms in Region.

`Region`

Type String

Recurring True

Description Apply the constant force to all atoms in this region.

When the `ApplyVelocity` block is used to slide a region, the measured net force experienced by that region is written to the MDHistory section on the trajectory. This force is calculated directly from the gradients returned by an Engine and thus excludes the effect of any `ApplyForce` blocks. The ratio of the tangential (sliding) and normal (compression) component of the mean force is thus equal to the friction coefficient. Three variables will be written by any `ApplyVelocity` block:

- *EngXFrcRgnA*: instantaneous engine force on region *A*, Cartesian component *X*
- *MeanEngXFrcRgnA*: average of *EngXFrcRgnA* over all timesteps since the previous trajectory frame
- *StdevEngXFrcRgnA*: standard deviation of *EngXFrcRgnA* over all timesteps since the previous trajectory frame

Note: Only the first eight characters of the region name are used to construct the *EngXFrcRgn* variables. When using multiple `ApplyVelocity` instances with different regions, make sure their names are not ambiguous after shortening to eight characters.

NEMD viscosity via cosine shear perturbation

In order to calculate the viscosity using NEMD, apply a periodic perturbation to the system using the `CosineShear` input block. This will add an amount of acceleration to the atoms in the system according to a cosine function running along the specified Cartesian `ProfileAxis`. The acceleration applied to each atom will have the direction of `FlowDirection` and magnitude equal to $a_x(z) = A\cos(\frac{2\pi z}{L_z})$, where A is the amplitude defined by the `Acceleration` input key and L_z is the length of the periodic box in the Z axis (assuming `ProfileAxis=Z` and `FlowDirection="1 0 0"`. It is typically the most efficient to use a box roughly three times taller in the `ProfileAxis` direction than in the other two axes. AMS currently requires the `ProfileAxis` to be aligned with one of the lattice vectors and perpendicular to the remaining lattice vectors.

See also:

Example demonstrating a NEMD viscosity simulation (page 457)

Warning: `CosineShear` simulations are typically performed in the NVT ensemble. While using a `Barostat` is theoretically possible, such a combination has not been physically validated by SCM.

MolecularDynamics

CosineShear

Type Block

Description Apply an external acceleration to all atoms of a fluid using a periodic (cosine) function along a selected coordinate axis. This induces a periodic shear flow profile which can be used to determine the viscosity.

Acceleration

Type Float

Default value 5e-06

Unit Angstrom/fs^2

Description Amplitude of the applied cosine shear acceleration profile. The default value should be a rough first guess for water and it needs to be adjusted by experimentation for other systems.

Enabled

Type Bool

Default value No

GUI name Enable cosine shear

Description Apply a cosine shear acceleration profile for a NEMD calculation of viscosity.

FlowDirection

Type Float List

Default value [1.0, 0.0, 0.0]

Description The direction in which to apply the shear acceleration, in Cartesian coordinates. The magnitude of this vector is ignored (AMS will normalize it internally). FlowDirection has to be perpendicular to ProfileAxis.

ProfileAxis

Type Multiple Choice

Default value Z

Options [X, Y, Z]

Description The Cartesian coordinate axis along which the cosine wave runs

This generates a velocity profile in the steady state that looks like: $v_x(z) = V\cos(\frac{2\pi z}{L_z})$. After the system reaches a steady state, the velocity amplitude V will be approximately constant, although typically relatively noisy. Averaging V over a long enough trajectory yields a reasonable estimate of the steady-state flow velocity, which can then be used to calculate the viscosity as $\eta = \frac{A\rho L_z^2}{4\pi^2}$. The measured value of V averaged over every `Trajectory SamplingFreq` timesteps is written to the trajectory as *MeanCosineShearVelocity* in the units of Bohr/fs.

The calculated viscosity value will be different from the equilibrium viscosity of the studied liquid due to shear thinning and heating caused by the applied acceleration A. It is thus necessary to measure the viscosity at several different values of A and extrapolate the obtained values to the zero-shear limit $A = 0$. To do this, it is useful to calculate the "shear parameter" $S = \frac{A^2 m\rho L_z^2}{8\pi^2 N_f k_B}$, where *m* is the total mass of the system and *N_f* is the number of degrees of freedom. The measured viscosity η is then approximately a linear function of *S*, enabling a straightforward extrapolation to zero *S*. Typical values of the shear parameter *S* in SI units are on the order of 10^9 - 10^{10} kg m s^{-2} K.

4.9.11 Applying reflective walls

Note: This feature is still experimental. It may contain bugs and some input keys are still subject to change in future releases of AMS. If you are interested in trying it out, monitor the bug fix changelog (https://www.scm.com/support/downloads/changelog/) for updates and feel free to get in touch with us at support@scm.com if you run into any issues.

The ReflectiveWall keyword can be used to define impenetrable planes in space, causing molecules to bounce off by an elastic collision. Therefore, the main usage of reflective walls is to make sure that molecules will stay within a certain area in space.

The reflective wall is defined by a normal vector (`Axis`) and a `Threshold`. The plane of the wall is perpendicular to `Axis` and passes through a point given by multiplying `Axis` by `Threshold`. Any atom moving in the direction of `Axis` will be reflected back, but the opposite does not apply. Particles moving in the direction opposite to `Axis` will not be affected (the wall works like a one-way mirror). The `Axis` vector does not need to be normalized to unity, AMS will normalize it internally and adjust `Threshold` accordingly.

`MolecularDynamics`

`ReflectiveWall`

Type Block

Recurring True

Description Apply a reflective wall in space

`Axis`

Type Float List

Unit Angstrom

Description Defines the normal vector perpendicular to the plane of the reflective wall. Any particle moving in this direction will be reflected back.

`Region`

Type String

Recurring True

Description Apply the reflective wall to all atoms in this region.

Threshold

Type Float

Unit Angstrom

Description Defines the threshold value determining the position of the reflective wall. If the dot product of a position of a particle with Axis exceeds Threshold, the particle will be reflected. This means that the plane of the wall passes through a point given by Axis times Threshold.

4.9.12 Exit Conditions

It is possible to define exit conditions to end a molecular dynamics calculations before all timesteps have been performed. If an exit condition is met, the variable `History%ExitConditionMsg` is populated with a message describing why the moleculard dynamics task was stopped. When an exit condition is met, its status is considered to be `NORMAL TERMINATION`.

```
ExitCondition
   AtomsTooClose
      MinimumDistance float
      PairCalculation [NeighborList | DistanceMatrix]
   End
   EngineEnergyUncertainty
      MaxUncertainty float
      Normalization float
   End
   EngineGradientsUncertainty
      MaxUncertainty float
   End
   Type [AtomsTooClose | EngineEnergyUncertainty | EngineGradientsUncertainty]
End
```

ExitCondition

Type Block

Recurring True

Description If any of the specified exitconditions are met, the AMS driver will exit cleanly.

AtomsTooClose

Type Block

Description If any pair of atoms is closer than the specified minimum value, the program will exit cleanly.

MinimumDistance

Type Float

Default value 0.7

Unit Angstrom

Description Two atoms closer than this threshold value are considered too close.

PairCalculation

Type Multiple Choice

Default value NeighborList

Options [NeighborList, DistanceMatrix]

Description Two atoms closer than this threshold value are considered too close.

`EngineEnergyUncertainty`

Type Block

Description If the engine reports an uncertainty that is too high, the program will exit cleanly.

`MaxUncertainty`

Type Float

Default value 0.001

Unit Hartree

Description Threshold for Engine Energy Uncertainty divided by Normalization (by default the number of atoms)

`Normalization`

Type Float

Value Range value >= 0.0

Description Divide the reported Engine Energy Uncertainty by this normalization. Will divide by the number of atoms if unset.

`EngineGradientsUncertainty`

Type Block

Description If the engine reports an uncertainty in the magnitude of the nuclear gradient of any atom that is too high, the program will exit cleanly.

`MaxUncertainty`

Type Float

Default value 0.01580221

Unit Hartree/Angstrom

Description Threshold for Engine Gradients Uncertainty.

`Type`

Type Multiple Choice

Default value AtomsTooClose

Options [AtomsTooClose, EngineEnergyUncertainty, EngineGradientsUncertainty]

Description The type of exitcondition specified

4.10 Trajectory replay

For some applications it is necessary to run calculations on all (or a subset of) frames from a trajectory obtained in another job. Often this is done with a different engine in order to learn something about the differences in the potential energy surface between the engines. This could easily be scripted with *PLAMS* (page 25), but since the 2022.1 release the AMS driver itself also implements a convenient "Replay" task to do this.

The input for the replay task is quite minimal. The following input file would replay every tenth of the first 1000 frames on the trajectory of `oldjob` with the DFTB engine to calculate nuclear gradients:

```
Task Replay

Replay
   File oldjob.results
   Frames 1:1000:10
End

Properties
   Gradients True
End

Engine DFTB
EndEngine
```

See also:

Example input files (page 461) for replaying PES scans, NEB and MD calculations.

Note that it is not necessary to specify a *System block* (page 31) in the input of a replay job, as the system will just be loaded from the job to be replayed. What properties are evaluated for each frame in the trajectory can be configured in the `Properties` block of the input file. For a list of available properties, see for example the the manual pages on *Gradients, Hessian, Stress tensor, Elasticity* (page 198) and *Dipole moment, Polarizability, Bond orders* (page 264).

Depending on the kind of job that is being replayed, you will get a slightly different default behavior for the selection of frames to be replayed:

- For *PES scans* (page 69) only the frames corresponding to the converged PES points will be replayed. The resulting `ams.rkf` output file will contain the `PESScan` section, as if it had been produced by running a PES scan job.
- For *Nudged Elastic Band (NEB)* (page 76) jobs only the frames corresponding to the converged images are replayed. The resulting `ams.rkf` file will have an `NEB` section that looks like it is from a NEB job that converged immediately.
- All other job types (such as *Molecular Dynamics* (page 91)) will just replay whatever is on the `History` section on the `ams.rkf` file. By default all frames are replayed, but a subset can be chosen with the `Replay%Frames` keyword.

Note that the replay task does not use *driver level parallelism* (page 21). The engine is called on each frame in turn, always restarting from the previously calculated frame. (The restarting should not cause problems, but it can be disabled with the `EngineDebugging%IgnorePreviousResults` option, see *developer options* (page 487)).

Details of the Replay task can be configure in the `Replay` block in the input.

```
Replay
   File string
   Frames integer_list
   StoreAllResultFiles Yes/No
End
```

`Replay`

Type Block

Description Configures the details of the Replay task.

`File`

Type String

GUI name Restart from

Description Provide an ams.rkf file (or a .results folder) from a previously run job to replay. The file needs to contain a History section.

`Frames`

Type Integer List

Description List of frames from the History section to recompute.

If not specified the recomputed frames are determined automatically based on the task of the job that is being replayed: PES scans and NEB calculations will only have the converged points replayed, while all other tasks will have all frames recomputed.

Specifying the frames to recompute in the input is probably only useful when replaying trajectories from MolecularDynamics calculations.

`StoreAllResultFiles`

Type Bool

Default value No

Description If this option is enabled AMS will produce a separate engine output file for every replayed frame.

While basic properties like energy, gradients, stress tensor, etc. are stored anyway on the History section in the AMS driver output file (if they were requested in the Properties block), engine specific properties (e.g. excitations energies from ADF) will only be available if the full result files are stored.

4.11 Grand Canonical Monte Carlo (GCMC)

Tip: Take a look at the GCMC tutorial and learn how to setup a GCMC calculation.

4.11.1 General info

About Monte Carlo / the Grand Canonical Ensemble

It is best to read a bit about Monte Carlo and ensembles before working with the GCMC code. Almost every book or review text on molecular simulations will do, for example: Frenkel D, Smit B. Understanding molecular simulation: from algorithms to applications. Academic Press; 2002. 672 p.

Wikipedia also has some pages of interest:

- http://en.wikipedia.org/wiki/Monte_Carlo_method
- http://en.wikipedia.org/wiki/Grand_canonical_ensemble

It is important to note that this method heavily relies on random numbers, and simulations are thus non-repeatable in detail, but should converge to the same answer.

About the AMS GCMC code

The GCMC code was originally developed for standalone Reaxff by Thomas Senftle, working as a Graduate Student at Penn State University under the supervision of Dr. Adri van Duin[1][2]. The original version was a wrapper code that called an external executable to perform the reaxff minimization step and energy calculation, and relied on file modification and parsing to steer the reaxff code and get the results back.

The code was later rewritten by Hans van Schoot (SCM), in close collaboration with Thomas Senftle, to integrate it directly into the ADF-ReaxFF code. The current version is an AMS re-implementation so the method can be used with almost any engine supported by AMS (support for 3D periodic boundary conditions by the engine is currently a requirement).

4.11.2 Method Details

Overview

The GCMC method will perform a number of Grand Canonical Monte Carlo trial moves (set by the `Iterations` option of the `GCMC` input block), and accept or reject them based on the energy produced by the geometry optimization of the trial geometry for the given engine. The Monte Carlo algorithm will always accept a step if it results in a decrease of the energy, and accept steps that go up in energy with a probability. This section will give some details about how the method works.

MC Moves (Insert/Delete/Displace/ChangeVolume)

The GCMC method currently supports 4 types of MC Moves: Insert, Delete, Displace (sometimes also called Move), and ChangeVolume. The first three MC moves are always available and the ChangeVolume becomes available only `ChangeVolume` option is set to True. The first three move types change coordinates of atoms in the system, while the ChangeVolume move changes the lattice only.

On every MC iteration, the method first selects one of the molecules defined by the `Molecule` input blocks at random and then selects an applicable MC move type. If there are no molecules of this type in the system then no Delete or Displace is attempted. If the selected molecule has the `NoAddRemove` option set then the Insert and Delete moves will not be attempted. If no MC move is possible with the selected molecule type then another one is selected or a VolumeChange is attempted, if allowed. If no moves with any of the provided molecules is possible (i.e. if all molecules have `NoAddRemove` set to True, there is nothing to displace and the volume is fixed) then the program will stop.

The Insert and Displace MC move will rotate the molecule randomly and put it at a random position, and then check if the minimum interatomic distance between the molecule and the rest of the system is within the `MinDistance` and `MaxDistance` boundaries. If the condition is not satisfied, a new set of coordinates is generated and the check is performed again. This is repeated up to `NumAttempts` times before stopping with an error.

The volume change is controlled by the `VolumeChangeMax` keyword. This sets the volume change limit, and it should be a value between between 0 and 1. The new volume will be calculated as: V_{new} = exp(random(-1:1)*VolumeChangeMax)*V_{old}.

Calculating the chemical potential

The chemical potential of the molecule (or atom) reservoir is used when calculating the Boltzmann accept/reject criteria after a MC move is executed. This value can be derived from first principles using statistical mechanics, or equivalently, it can be determined from thermochemical tables available in literature sources.

For example, the proper chemical potential for a GCMC simulation in which single oxygen atoms are exchanged with a reservoir of O2 gas, should be equal to 1/2 the chemical potential of O2 at the temperature and pressure of the reservoir[?]:

[1] T.P. Senftle, R.J. Meyer, M.J. Janik, A.C.T. van Duin, *Development of a ReaxFF potential for Pd/O and application to palladium oxide formation*, J. Chem. Phys. 139, 044109 (2013) (https://doi.org/10.1063/1.4815820)

[2] T.P. Senftle, A.C.T. van Duin, M.J. Janik, *Determining in situ phases of a nanoparticle catalyst via grand canonical Monte Carlo simulations with the ReaxFF potential*, Catalysis Communications 52, 72–77 (https://doi.org/10.1016/j.catcom.2013.12.001)

$\mu_O^{MC}(T,P) = \frac{1}{2}\mu_{O2}^{MC}(T,P) = \frac{1}{2}\left[\mu_{O2}^{ref}(T,P_{ref}) + kTln\left(\frac{P}{P_{ref}}\right) - E_{O2}^{diss}\right]$

where the reference chemical potential $\mu_{O2}^{ref}(T,P_{ref})$ is the experimentally determined chemical potential of O2 at T and P_{ref}, $kTln\left(\frac{P}{P_{ref}}\right)$ is the pressure correction to the free energy, and E_{O2}^{diss} is the dissociation energy of the O_2 molecule.

Calculating energies

Because the GCMC simulation adds and deletes atoms or molecules during the runtime, it cannot directly compare the AMS energies for the MC acceptance criteria: inserting a molecule will usually lower the total energy of the system, causing the MC to always accept it, and always reject a deletion. To compensate this, the GCMC method calculates a "corrected" MC energy to compare the trial energy with, consisting of the previously accepted AMS energy and a correction depending on the move:

$E_{old}^{MC} = E_{old}^{AMS} + \mu^{MC}$ for an Insert move;

$E_{old}^{MC} = E_{old}^{AMS} - \mu^{MC}$ for a Delete move;

$E_{old}^{MC} = E_{old}^{AMS}$ for a Displace move;

$E_{old}^{MC} = E_{old}^{AMS} - P(V_{new} - V_{old}) + N_{inserted}ln\left(\frac{V_{new}^{avail}}{V_{old}^{avail}}\right)kT$ for a ChangeVolume move.

Here, μ^{MC} is the chemical potential of the inserted/deleted molecule, P is the pressure, V is the volume, and $N_{inserted}$ is the total number of MC molecules. The "new" and "old" subscripts refer to the current and the last accepted values. The V^{avail} values are calculated from the MC-available volume as described below.

Calculating volumes

The available volume can be calculated in a few different ways, depending on the `VolumeOption` setting:

- *Free*: volume = total volume - occupied volume - specified vacuum volume (`NonAccessibleVolume`)
- *Total*: volume = total cell volume
- *Accessible*: volume = specified accessible volume (`AccessibleVolume`)
- *FreeAccessible*: volume = specified accessible volume (`AccessibleVolume`) - occupied volume

Here, the occupied volume is calculated as a sum of volumes of atoms that do not belong to the MC part of the system (i.e. that were not inserted during calculation and are not `Removables`). The volume of an atom is calculated using the average of the covalent and the Van der Waals radii of the atom defined in the atominfo module used throughout AMS.

The `AccessibleVolume` and `NonAccessibleVolume` keywords can be used to get a more accurate available volume.

Acceptance criteria

An MC move is always accepted if the AMS energy is lower than the corrected MC energy of the last accepted MC move, or if the energy increase is small enough. If the new energy is higher, the code generates a random number between 0 and 1, and accepts the move if the random number is greater than:

```
prob = preFactor * exp(-Beta*deltaE)
```

The prefactor is calculated (for insert and delete moves) using the deBroglie wavelength of the inserted molecules, the number of inserted molecules and the available MC volume of the system.

4.11.3 Input

The GCMC functionality in AMS is triggered using the following Task key:

```
Task GCMC
```

```
GCMC
   AccessibleVolume float
   Box
      Amax float
      Amin float
      Bmax float
      Bmin float
      Cmax float
      Cmin float
   End
   Ensemble [Mu-VT | Mu-PT]
   Iterations integer
   MapAtomsToOriginalCell Yes/No
   MaxDistance float
   MinDistance float
   Molecule
      ChemicalPotential float
      NoAddRemove Yes/No
      SystemName string
   End
   NonAccessibleVolume float
   NumAttempts integer
   Pressure float
   Removables # Non-standard block. See details.
      ...
   End
   Restart string
   SwapAtoms
      Probability float
      Regions string
   End
   Temperature float
   UseGCPreFactor Yes/No
   VolumeChangeMax float
   VolumeOption [Free | Total | Accessible | FreeAccessible]
End
```

The following keys are common for all GCMC calculations and should always be specified. The ChemicalPotential value should correspond to the μ^{MC} expression above, and not to the experimental chemical potential μ^{ref}, which means it should include the (engine-dependent) free molecule's energy.

GCMC

Molecule

Type Block

Recurring True

GUI name Molecules

Description This block defines the molecule (or atom) that can be inserted/moved/deleted with the MC method. The coordinates should form a reasonable structure. The MC code uses these coordinates during the insertion step by giving them a random rotation, followed by a random translation to generate a random position of the molecule inside the box. Currently, there is no check to make sure all atoms of the molecule stay inside the simulation box. The program does check that the MaxDistance/MinDistance conditions are satisfied.

ChemicalPotential

Type Float

Unit Hartree

Description Chemical potential of the molecule (or atom) reservoir.

It is used when calculating the Boltzmann accept/reject criteria after a MC move is executed. This value can be derived from first principles using statistical mechanics, or equivalently, it can be determined from thermochemical tables available in literature sources. For example, the proper chemical potential for a GCMC simulation in which single oxygen atoms are exchanged with a reservoir of O2 gas, should equal 1/2 the chemical potential of O2 at the temperature and pressure of the reservoir:

cmpot = Mu_O(T,P) = 1/2*Mu_O2(T,P) = 1/2 * [Mu_ref(T,P_ref) + kT*Log(P/Pref) - E_diss]

where the reference chemical potential [Mu_ref(T,P_ref)] is the experimentally determined chemical potential of O2 at T and Pref; kT*Log(P/Pref) is the pressure correction to the free energy, and E_diss is the dissociation energy of the O2 molecule.

NoAddRemove

Type Bool

Default value No

GUI name Fix molecule

Description Set to True to tell the GCMC code to keep the number of molecules/atoms of this type fixed.

It will thus disable Insert/Delete moves on this type, meaning it can only do a displacement move, or volume change move (for an NPT ensemble).

SystemName

Type String

GUI name Molecule

Description String ID of a named [System] to be inserted. The lattice specified with this System, if any, is ignored and the main system's lattice is used instead.

Iterations

Type Integer

GUI name Number of GCMC iterations

Description Number of GCMC moves.

Temperature

Type Float

Default value 300.0

Unit Kelvin

Description Temperature of the simulation. Increase the temperature to improve the chance of accepting steps that result in a higher energy.

The following keys are related to Insert and Displace moves.

GCMC

NumAttempts

Type Integer

Default value 1000

GUI name Max tries

Description Try inserting/moving the selected molecule up to the specified number of times or until all constraints are satisfied. If all attempts fail a message will be printed and the simulation will stop. If the MaxDistance-MinDistance interval is small this number may have to be large.

MinDistance

Type Float

Default value 0.3

Unit Angstrom

GUI name Add molecules not closer than

Description Keep the minimal distance to other atoms of the system when adding the molecule.

MaxDistance

Type Float

Default value 3.0

Unit Angstrom

GUI name Add molecules within

Description The max distance to other atoms of the system when adding the molecule.

The following keys influence computation of the acceptance probability and of the MC energy correction.

GCMC

UseGCPreFactor

Type Bool

Default value Yes

GUI name Use GC prefactor

Description Use the GC pre-exponential factor for probability.

VolumeOption

Type Multiple Choice

Default value Free

Options [Free, Total, Accessible, FreeAccessible]

GUI name Volume method

Description Specifies the method to calculate the volume used to calculate the GC pre-exponential factor and the energy correction in the Mu-PT ensemble: Free: V = totalVolume - occupiedVolume - NonAccessibleVolume; Total: V = totalVolume; Accessible: V = AccessibleVolume; FreeAccessible: V = AccessibleVolume - occupiedVolume. The AccessibleVolume and

NonAccessibleVolume are specified in the input, the occupiedVolume is calculated as a sum of atomic volumes.

AccessibleVolume

Type Float

Default value 0.0

Description Volume available to GCMC, in cubic Angstroms. AccessibleVolume should be specified for "Accessible" and "FreeAccessible" [VolumeOption].

NonAccessibleVolume

Type Float

Default value 0.0

GUI name Non-accessible volume

Description Volume not available to GCMC, in cubic Angstroms. NonAccessibleVolume may be specified for the "Free" [VolumeOption] to reduce the accessible volume.

The following keys apply to the ensemble choice and options for the Mu-PT ensemble.

GCMC

Ensemble

Type Multiple Choice

Default value Mu-VT

Options [Mu-VT, Mu-PT]

Description Select the MC ensemble: Mu-VT for fixed volume or Mu-PT for variable volume. When the Mu-PT ensemble is selected the [Pressure] and [VolumeChangeMax] should also be specified.

VolumeChangeMax

Type Float

Default value 0.05

Description Fractional value by which logarithm of the volume is allowed to change at each step. The new volume is then calculated as Vnew = exp(random(-1:1)*VolumeChangeMax)*Vold

Pressure

Type Float

Default value 0.0

Unit Pascal

Description Pressure used to calculate the energy correction in the Mu-PT ensemble. Set it to zero for incompressible solid systems unless at very high pressures.

The GCMC code can insert multiple atom/molecule types in a single simulation, so it needs to keep track of what atom belongs to which insert. This information is automatically stored and updated when insertion/deletion/moving of atoms or molecules during the simulation, but is by default unknown for the atoms of the starting geometry. The GCMC code will therefore by default not modify the atoms in the original input in the MC trial moves. The `Restart` key and the `Removables` block are two ways to provide information about Deletable/Movable atoms/molecules in the input structure. If the `Restart` key is present the `Removables` block will be ignored.

GCMC

Restart

Type String

Description Name of an RKF restart file. Upon restart, the information about the GCMC input parameters, the initial system (atomic coordinates, lattice, charge, etc.) and the MC molecules (both already inserted and to be inserted) are read from the restart file. The global GCMC input parameters and the MC Molecules can be modified from input. Any parameter not specified in the input will use its value from the restart file (i.e. not the default value). Molecules found in the restart file do not have to be present as named Systems in the input, however if there is a System present that matches the name of a molecule from restart then the System's geometry will replace that found in the restart file. It is also possible to specify new Molecules in the input, which will be added to the pool of the MC molecules from restart.

Removables

Type Non-standard block

Description The Removables can be used to specify a list of molecules that can be removed or moved during this GCMC calculation. Molecules are specified one per line in the format following format: MoleculeName atom1 atom2 … The MoleculeName must match a name specified in one of the [Molecule] blocks. The atom indices refer to the whole input System and the number of atoms must match that in the specified Molecule. A suitable Removables block is written to the standard output after each accepted MC move. If you do so then you should also replace the initial atomic coordinates with the ones found in the same file. If a [Restart] key is present then the Removables block is ignored.

An example of the Removables block:

```
Removables
  Oatom 41
  O2   44 45
  Oatom 42
  Oatom 43
End
```

This example specifies that 5 atoms belong to 4 different GCMC molecules of two different types, `Oatom` and `O2`. Thus in addition to the main input `System` there should be at least two additional Systems defined, one called "Oatom" (containing one atom) and the other "O2" (containing two atoms). The first one was inserted three times (atoms 41, 42, and 43) and the second one was inserted once.

Finally there are more technical keywords:

GCMC

MapAtomsToOriginalCell

Type Bool

Default value Yes

Description Keeps the atom (mostly) in the original cell by mapping them back before the geometry optimizations.

Note that the `GeometryOptimization` block is also read by the GCMC task, and the settings used for the individual optimizations. The documentation for these keywords can be found in the *Geometry Optimization* (page 47) section of this manual.

4.11.4 Output

In addition to the standard KF variables in the "History" section on `ams.rkf` such as "Coords" and "Energy", the following GCMC-specific variables are also created for each accepted MC step:

- *MCMove* - integer index of the MC move.
- *MCMoveType* - string containing the type of the MC move.
- *MCMolecule* - string containing the name of the inserted/displaced/removed molecule.
- *Converged* - a Fortran logical value containing the convergence status of the given geometry.

Results of a GCMC calculation are stored in the GCMC section of the RKF file, in a number of variables. The following variables contain a summary of the MC statistics up to and including the latest step:

- *NIterMCtried* - the latest iteration number.
- *NIterMCaccept* - the number of accepted MC moves.
- *NIterMCreject* - the number of rejected MC moves.
- *NMCacceptAdd* - the number of accepted MC molecule insertions.
- *NMCacceptRemove* - the number of accepted MC molecule removals.
- *NMCacceptMove* - the number of accepted MC molecule moves.
- *NMCacceptVolume* - the number of accepted volume changes.
- *NMCrejectAdd* - the number of rejected MC molecule insertions.
- *NMCrejectRemove* - the number of rejected MC molecule removals.
- *NMCrejectMove* - the number of rejected MC molecule moves.
- *NMCrejectVolume* - the number of rejected volume changes.

The following variables (actually arrays of the size `Iterations`) in the GCMC section contain the detailed information about all MC moves in the current simulation. Only the first *NIterMCtried* elements of each array contain valid data.

- *HistoryAccepted* - MC move status value (1 - accepted, 0 - rejected, -1 - not done yet).
- *HistoryAMSEnergy* - the AMS energy (the E^{AMS} above).
- *HistoryMCEnergy* - the corrected MC energy ($E^{MC} = E^{AMS} - \Sigma\mu_i^{MC}$, where $\Sigma\mu_i^{MC}$ is the total chemical potential of all inserted molecules).
- *HistoryVolume* - the simulation box volume.
- *HistoryMoveType* - the MC move type index (0 - insert, 1 - delete, 2 - displace, 3 - change volume). The name of the move type with index *i* can be found in the *MoveType(i)* variable.
- *HistoryMoleculeType* - the inserted/deleted/displaced molecule type index. The name of the molecule type with index *i* can be found in the *MoleculeName(i)* variable.
- *HistoryMoleculeIndex* - the inserted/deleted/displaced molecule index within its type.

4.12 Automated PES Exploration

In chemistry and materials science, two types of Potential Energy Surface (PES) critical points are of particular interest: local minima and (first-order) saddle points.

The `PESExploration` task consists of a set of algorithms (which we will refer to as *jobs*) that will automatically explore the PES of a given system, looking for local minima and saddle points.

The available PES exploration jobs are:

***Process Search* (page 178)** A composite method for finding escape mechanisms from a state. This will find both local minima and saddle points.

***Basin Hopping* (page 183)** A Monte Carlo method for finding local minima.

***Saddle Search* (page 180)** A single-ended method for finding nearby saddle points.

***Landscape Refinement* (page 187)** Given a pre-calculated Energy Landscape, re-optimize local minima and saddle points using a different computational engine/settings.

***Binding Sites* (page 193)** Given a pre-calculated Energy Landscape, compute the binding sites.

The AMS driver links to the client program of the EON software package (http://theory.cm.utexas.edu/eon/index.html)[1] and uses its implementation of the dimer method. EON is developed by the University of Texas at Austin and the University of Iceland. See also the *Required citations* (page 493) section.

See also:

- PES Exploration GUI tutorials:
  - Automated reaction pathway discovery for hydrohalogenation
  - Cluster Growth: Cobalt Clusters
  - Water dissociation on an oxide surface
- Examples:
  - *Example: Basin Hopping for Ar 13 cluster* (page 425)
  - *Example: PES Exploration, Process Search for alanine with PLAMS* (page 427)
  - *Example: PES Exploration, Binding Sites for O on Pt 111* (page 427)

Tip: There is a separate tool specifically for the generation of conformers, see this *manual page* (page 295). While the PES exploration can in principle also be used to find conformers, using the dedicated *Conformers tool* (page 295) is usually easier and faster. Note that the set of minima found by the Conformers tool can be used as input for a PES exploration, see *this example* (page 430).

[1] Samuel T Chill, Matthew Welborn, Rye Terrell, Liang Zhang, Jean-Claude Berthet, Andreas Pedersen, Hannes Jónsson and Graeme Henkelman *EON: software for long time simulations of atomic scale systems*, Modelling Simul. Mater. Sci. Eng. 22 055002 (2014) (https://doi.org/10.1088/0965-0393/22/5/055002)

4.12.1 Overview

While many details of a PES exploration calculation depend on the specific *job* (page 172) selected, some aspects are common to all PES explorations jobs. Here we give a brief overview of a typical PES exploration, using a Process Search job as example.

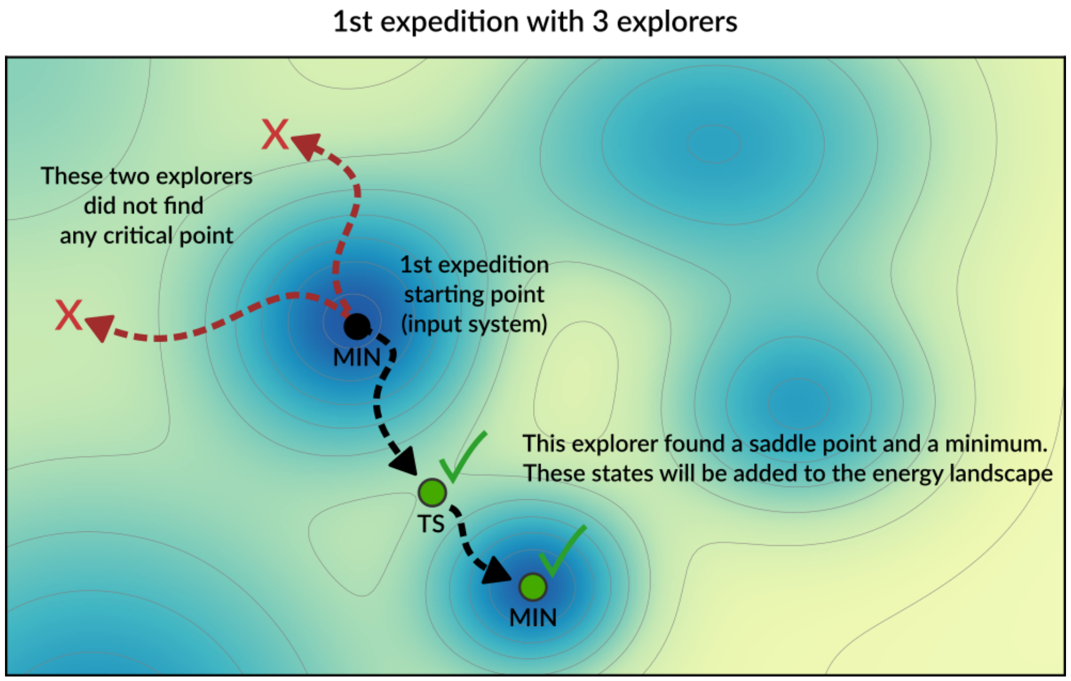
A PES exploration calculation generally consists of multiple *expeditions*, each with several *explorers*.

Explorers are given an initial structure, and their goal is to find a nearby critical point (a local minimum, a saddle point or both). The explorer moves around the PES by modifying the atomic positions of the system and by using the specified *Engine* (page 270) to compute energy and gradients.

An *expedition* is a collection of *explorers* all starting from the same point on the PES.

Before setting off for the first expedition, the input structure is optimized and added to the *Energy Landscape*, which is the database of all interesting points found during the exploration (see the section *Results: the "Energy Landscape"* (page 174) for more details).

Starting from this initial structure, a number of PES explorers (3 in the diagram below) will set off in random directions exploring the potential energy surface and looking for nearby critical points.

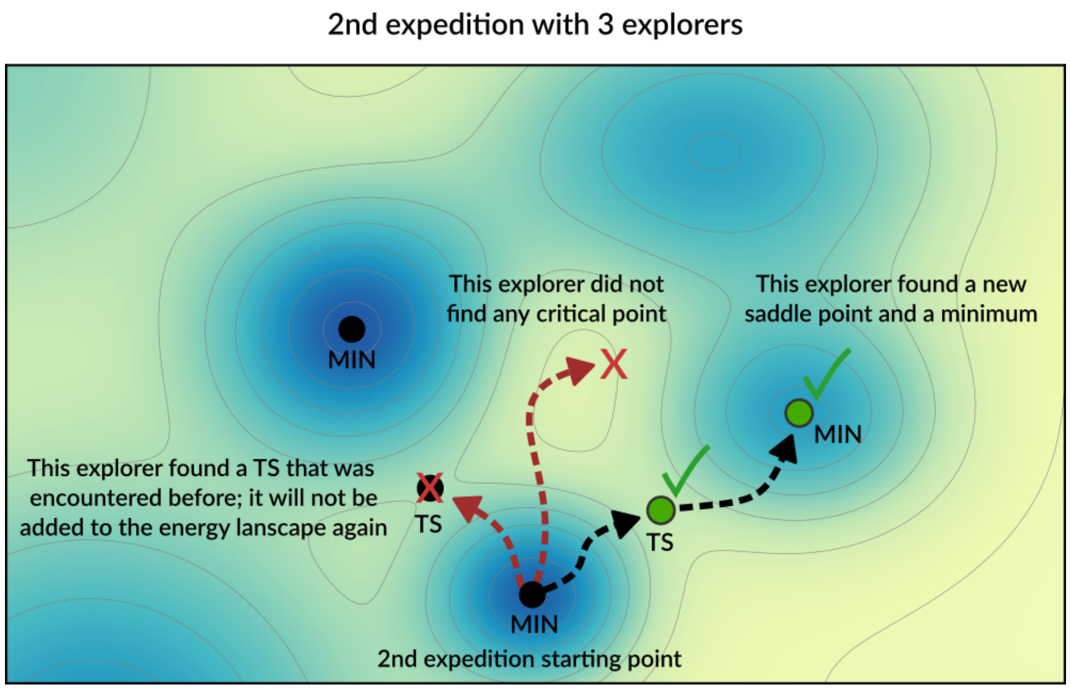

1st expedition with 3 explorers
These two explorers did not find any critical point
X
X
1st expedition starting point (input system)
MIN
This explorer found a saddle point and a minimum. These states will be added to the energy landscape
TS
MIN

Explorers have "stop conditions" (e.g. a maximum number of steps or a maximum energy above the starting point) so in general not all explorers will successfully find a critical point. In this case, only one of the explorers found relevant critical points: a saddle point and a local minimum. These newly found critical points are added to the Energy Landscape.

After the first expedition is over, the program will start with the second expedition. The starting point for the next expedition will be a randomly chosen local minimum from the list of minima present in the Energy Landscape (the possible starting points for an exploration are called *seed states*. See also the *DynamicSeedStates* (page 172) option).

In this example, the starting point of the second expedition is the new local minimum found during the first expedition. A new set of explorers will set off in random directions from this point.

In the diagram above, one of the explorer found a saddle point that was already found in a previous exploration. This structure will not be added to Energy Landscape since it was already *seen* before (see the *Structure comparison* (page 177) section for more details). The newly found critical points are added to the Energy Landscape.


2nd expedition with 3 explorers
This explorer did not find any critical point
This explorer found a new saddle point and a minimum
MIN
MIN
This explorer found a TS that was encountered before; it will not be added to the energy lanscape again
TS
TS
MIN
2nd expedition starting point

Usually, many expeditions and/or many explorers are needed to map the PES, but you should keep in mind that the computation time of the calculation will roughly be proportional to the product `NumExpeditions x NumExplorers`.

By having many explorers you will have a higher chance of comprehensively mapping the PES near the starting point of each expedition. By having many expeditions, you will have a higher chance of traveling further away from the initial structure.

It should be emphasized that the PES exploration task is stochastic in nature, as it uses random numbers to perform initial-displacements. This means that if you run the same calculation twice you might find different critical points.

4.12.2 Job selection and main options

To use one of the PES Exploration procedures you should set the *Task* (page 10) to `PESExploration` and specify one of the jobs in the `PESExploration%Job` key:

```
Task PESExploration

PESExploration
   Job [ProcessSearch | BasinHopping | SaddleSearch | LandscapeRefinement |␣
↪BindingSites]
End
```

The input options for the various jobs are described in the corresponding sections: *Process Search* (page 178), *Basin Hopping* (page 183), *Saddle Search* (page 180), *Landscape Refinement* (page 187), *Binding Sites* (page 193).

It is then important pick an appropriate number of expeditions and explorers. Having many expeditions and explorers will result in a more comprehensive PES exploration, but since the computation time will roughly be proportional to the product `NumExpeditions x NumExplorers` you'll need to find an appropriate balance.

```
PESExploration
   NumExpeditions integer
   NumExplorers integer
```

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```
   DynamicSeedStates Yes/No
End
```

PESExploration

Type Block

Description Configures details of the automated PES exploration methods.

NumExpeditions

Type Integer

Default value 1

Description Sets the number of subsequent expeditions our job will consist of. Larger values result in a more comprehensive exploration of the potential energy surface, but will take more computational time.

NumExplorers

Type Integer

Default value 1

Description Sets the number of independent PES explorers dispatched as part of each expedition. Larger values will result in a more comprehensive exploration of the potential energy surface, but will take more computational time. By default an appropriate number of explorers are executed in parallel.

DynamicSeedStates

Type Bool

Default value Yes

Description Whether subsequent expeditions may start from states discovered by previous expeditions. This should lead to a more comprehensive exploration of the potential energy surface. Disabling this will focus the PES exploration around the initial seed states.

The following miscellaneous input option generally apply to most PES exploration calculations:

```
PESExploration
   WriteHistory [None | Converged | All]
   Temperature float
   FiniteDifference float
End
```

PESExploration

Type Block

Description Configures details of the automated PES exploration methods.

WriteHistory

Type Multiple Choice

Default value Converged

Options [None, Converged, All]

Description When to write the molecular geometry (and possibly other properties) to the history on the ams.rkf file. The default is to only write the converged geometries to the history. Can be changed to write no frames at all to the history, or write all frames (should only be used when testing because of the performance impact). Note that for parallel calculations, only the first group of processes writes to ams.rkf.

`Temperature`

Type Float

Default value 300.0

Unit Kelvin

Description The temperature that the job will run at. This may be used in different ways depending on the job, e.g. acceptance probabilities for Monte-Carlo based jobs, thermostatting for dynamics based jobs, kinetic prefactors for jobs that find transition states. Some jobs may not use this temperature at all.

`FiniteDifference`

Type Float

Default value 0.0026458861

Unit Angstrom

Description The finite difference distance to use for Dimer, Hessian, Lanczos, and optimization methods.

4.12.3 Results: the "Energy Landscape"

The results of a PES Exploration are the structures and energies of the critical points found. There are multiple ways for you to inspect the results:

- The energy landscape can be visualized using the `AMSMovie` GUI module (In AMSMovie: `File → Open` and select the `ams.rkf` file of your calculation). See the GUI tutorials (e.g. Automated reaction pathway discovery for hydrohalogenation) for more details.
- The results are printed to the text output under the header `Final Energy Landscape`, see *below* (page 174).
- The results are stored on the `ams.rkf` binary results file in the section `EnergyLandscape`
- In PLAMS, you can use the get_energy_landscape method of the `AMSResults` object to conveniently extract the results.

Results on the text output

These are printed at the end of the text output under the header `Final Energy Landscape`. Here is an output example for a ProcessSearch job for the simple HCN molecule (computed with the DFTB engine):

```
----------------------
Final Energy Landscape
----------------------


      Id        Energy(a.u.)         RE(eV)   RE(kcal/mol)     Counts     Crit. point
   --------------------------------------------------------------------------------
       1           -5.782789        0.00000         0.0000          4             Min
       2           -5.748792        0.92510        21.3334          4             Min
       3           -5.689025        2.55143        58.8375          4              TS ␣
↪1 <--> 2
```

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```
Number of configurations                              3
Number of local minima                                2
Number of transition states                           1
Energy range (a.u.)                            0.093763
Energy range (eV)                               2.55143
Energy range (kcal/mol)                         58.8375

Configurations
--------------
3
Id 1 Energy(hartree)     -5.78278852 isTS=False
H       -5.05604362312999       1.04394551246415       0.36836337958238
C       -4.06812264817497       0.95005534859126      -0.01533183100739
N       -3.00601476684712       0.84907755770632      -0.42810754191928
3
Id 2 Energy(hartree)     -5.74879169 isTS=False
H       -4.01886309319822       1.09046314142766       1.01610923624838
C       -4.06910389782095       0.79751242545583      -1.12016730790896
N       -4.04221404713293       0.95510285187825       0.02898207831626
3
Id 3 Energy(hartree)     -5.68902502 isTS=True
H       -4.51488871821561       1.04261603660424       0.52096081259126
C       -4.32990923520194       0.88203060069718      -0.58636688911847
N       -3.28538308473452       0.91843178146029      -0.00966991681712
```

From this you can see that 3 critical points were found: 2 minima (`Id 1` and `Id 2`) and 1 transition state (`Id 3`) connecting the first two states (indicated by `1 <--> 2`).

Under `Counts` you can see how many times each state was encountered during the exploration (often the same state is found multiple times) See the *Structure comparison* (page 177) section for more details on how states are compared.

`RE` is the "relative energy" with respect to the lowest-energy state found.

Under the header `Configurations` you will find the XYZ geometries (in Angstrom) corresponding to the various critical points.

4.12.4 Continue a PES exploration from a previous calculation

You can load an Energy Landscape obtained from a PES exploration calculation (or by the *Conformers utility* (page 295)) and use it as starting point for a new PES exploration. In this way you can extend your Energy Landscape, and potentially use different PES exploration algorithms.

To load a previously computed energy landscape, use the `PESExploration%LoadEnergyLandscape%Path` option (note: you should still provide an input system in the *System* (page 31) block even if you are loading a previous Energy Landscape. The input system will be optimized and added to the energy landscape as a minimum).

It is often convenient to load only some of the states from a previous calculation; this can be done via the `Remove` or `KeepOnly` input options. Specify the seed states with the `SeedStates` option.

These are all the input options related to the loading an Energy Landscape:

```
PESExploration
   LoadEnergyLandscape
      GenerateSymmetryImages Yes/No
      KeepOnly integer_list
      Path string
```

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```
      Remove integer_list
      RemoveWithNoBindingSites Yes/No
      SeedStates integer_list
   End
End
```

PESExploration

LoadEnergyLandscape

Type Block

Description Options related to the loading of an Energy Landscape from a previous calculation.

GenerateSymmetryImages

Type Bool

Default value No

Description By activating this option, after loading the energy landscape, it will create the complete set of symmetry-related copies by using the symmetry operators of the reference structure. Be aware that rkf result files of the generated symmetry images are copies from the parent structures but only atomic coordinates are updated.

KeepOnly

Type Integer List

GUI name List of states to keep

Description Upon loading the Energy Landscape, only keep the states specified here. The states should be specified via a list of integers referring to the indices of the states you want to keep.

Path

Type String

GUI name Load energy landscape from

Description AMS results folder to load an energy landscape from. In the text input file, you may alternatively specify a `.con` file in the native EON format.

Remove

Type Integer List

GUI name List of states to remove

Description Upon loading the Energy Landscape, remove (i.e. do not load) the states specified here. The states should be specified via a list of integers referring to the indices of the states you want to remove (i.e. the states you don't want to load).

RemoveWithNoBindingSites

Type Bool

Default value No

Description Upon loading the Energy Landscape, it removes states with no associated binding sites. Associated transition states are also removed. This is an advantageous option to remove physisorbed states automatically. Notice that it requires that the previous calculation was executed, enabling the option [BindingSites%Calculate].

SeedStates

Type Integer List

GUI name List of seed states

Description By default when you start a new PES Exploration from a loaded Energy Landscape, expeditions can start from any of the loaded minima. By using this input option, you can instruct the program to only use some of the states as 'expedition starting point'. The states that serve as 'expedition starting points' should be specified via a list of integers referring to the indices of the states.

4.12.5 Troubleshooting

The PES exploration in AMS is quite sensitive to noise on the potential energy surface. A too noisy PES may result in bad convergence of the individual explorers, or states being rejected because their *PES point character* (page 200) is not the expected one.

In case of problems we therefore advise to set engine options that result in a smoother PES. Often this can be accomplished by setting the `NumericalQuality` keyword in the engine input.

Especially the ReaxFF engine has a rather noisy PES by default, which may cause problems in a PES exploration job. Please refer to the ReaxFF manual for advice on how to smoothen the ReaxFF potential energy surface:

- ReaxFF manual: Smoothened potential energy surface
- ReaxFF manual: Geometry optimization issues

4.12.6 Structure comparison

During a PES exploration some critical points will most likely be encountered more than once.

Whenever a critical point is found, the program will ask itself: is this a new structure, or have I already encountered this before? If the structure was not seen before (i.e. it's a novel configuration), it will be added to the list of structures found during the exploration. If the structure was already found before, the program will simply increase a counter keeping track of how many times a specific structure was found during the PES exploration.

When deciding if two structures are the same or not, the program will compare both the geometry and the energy of the two configurations. Several parameters and thresholds can be tweaked in the `PESExploration%StructureComparison` block to tell AMS under which conditions two systems should be considered equal.

```
PESExploration
   StructureComparison
      CheckRotation Yes/No
      CheckSymmetry Yes/No
      DistanceDifference float
      EnergyDifference float
      IndistinguishableAtoms Yes/No
      NeighborCutoff float
      RemoveTranslation Yes/No
   End
End
```

PESExploration

StructureComparison

Type Block

Description Settings for structure comparison.

`CheckRotation`

Type Bool

Description Rotates the system optimally before comparing structures. The default is to do this only for molecular systems when there are no fixed atom constraints.

`CheckSymmetry`

Type Bool

Default value No

Description Considers that two systems are equal if they are equivalent by symmetry.

`DistanceDifference`

Type Float

Default value 0.1

Unit Angstrom

Description If the distance between two mapped atoms is larger than this threshold, the two configurations are considered different structures.

`EnergyDifference`

Type Float

Default value 0.01

Unit eV

Description If the energy difference between two configurations is larger than this threshold, the two configurations are considered to be different structures.

`IndistinguishableAtoms`

Type Bool

Default value Yes

Description If yes, the order of the atoms does not affect the structural comparison. Atoms of the same element are then indistinguishable.

`NeighborCutoff`

Type Float

Default value 3.3

Unit Angstrom

Description Atoms within this distance of each other are considered neighbors.

`RemoveTranslation`

Type Bool

Description Translates the system optimally before comparing structures. The default is to do this only when there are no fixed atom constraints.

4.12.7 Process Search job

Overview

Process Search is a composite method for finding escape mechanisms from a state. Each PES explorer will perform the following steps:

- Starting from a minimum, a *SaddleSearch* (page 180) calculation is performed to find a nearby saddle point
- If a saddle point is found, two images are placed on either side of the saddle along the min mode.
- The two images are then minimized; one of the images is expected to fall back into the original minimum, while the other image is expected to end up in the product state on the other side of the saddle. If this is case, the product, TS and reactant states are added to the energy landscape.

The Process Search procedure will therefore not only find minima and saddle points, but it will also keep track of which minima each saddle point is connecting.

See also:

- GUI tutorials Automated reaction pathway discovery for hydrohalogenation and Water dissociation on an oxide surface.

Input options

To perform a Process Search calculation you should specify:

```
Task PESExploration

PESExploration
   Job ProcessSearch

   ProcessSearch
      # Options for the Process Search procedure. See description below.
   End

   SaddleSearch
      # Options for the Saddle Search part of the Process Search procedure.
   End
End
```

The options for the saddle search part of a Process Search job are described in the *SaddleSearch* (page 180) section.

Options specific to the Process Search procedure can be specified in the `PESExploration%ProcessSearch` block:

```
PESExploration
   ProcessSearch
      MinimizationOffset float
   End
End
```

`PESExploration`

`ProcessSearch`

Type Block

Description Input options specific to the process search procedure.

`MinimizationOffset`

Type Float

Default value 0.2

Description After a saddle is found, images are placed on either side of the saddle along the mode and minimized to ensure that the saddle is connected to the original minimum and to locate the product state. MinimizationOffset is the distance those images are displaced from the saddle.

4.12.8 Saddle Search job

Overview

Saddle Search is a single-ended method for finding nearby saddle points.

In a Saddle Search calculation, each PES explorer starts by performing a random displacement from the initial geometry (or seed state). Then, starting from this point, the explorer searches for a nearby saddle point using a minimum-mode following method (the available min-mode following methods are dimer[3][4][5] and Lanczos[6]).

If you already know which atoms are likely to be involved in the reactions, you can use the `DisplaceAtomsInRegion` option to nudge the Saddle Search procedure towards the right part of the PES (*regions* (page 36) can be specified in the *system input block* (page 31), or via the "Model → Regions" panel in AMSinput).

Input options

To perform a Saddle Search calculation you should specify:

```
Task PESExploration

PESExploration
   Job SaddleSearch

   SaddleSearch
      # Options for the Saddle Search procedure. See description below.
   End
End
```

Options for the Saddle Search procedure can be specified in the `PESExploration%SaddleSearch` block.

Note: these options also affect the Saddle Search part of *Process Search Jobs* (page 178).

```
PESExploration
   SaddleSearch
      ConvergedForce float
      DisplaceAlongNormalModesActiveModes string
      DisplaceAlongNormalModesWeight float
      DisplaceAtomsInRegion string
      DisplaceAtomsInRegionWeight float
```

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[3] G. Henkelman and H. Jónsson, *A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives*, J. Chem. Phys. 111, 7010-7022 (1999) (http://dx.doi.org/10.1063/1.480097)

[4] A. Heyden, A.T. Bell, and F.J. Keil *Efficient methods for finding transition states in chemical reactions: Comparison of improved dimer method and partitioned rational function optimization method*, J. Chem. Phys. 123, 224101 (2005) (http://dx.doi.org/10.1063/1.2104507)

[5] J. Kästner and P. Sherwood *Superlinearly converging dimer method for transition state search*, J. Chem. Phys. 128, 014106 (2008) (http://dx.doi.org/10.1063/1.2815812)

[6] R. Malek and N. Mousseau, *Dynamics of Lennard-Jones clusters: A characterization of the activation-relaxation technique*, Phys. Rev. E 62, 7723 (2000) (http://dx.doi.org/10.1103/PhysRevE.62.7723)

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```
      DisplaceListedAtoms string
      DisplaceListedTypes string
      DisplaceMagnitude float
      DisplaceRadius float
      MaxEnergy float
      MaxIterations integer
      MinEnergyBarrier float
      MinModeMethod [dimer | lanczos]
      RelaxFromSaddlePoint Yes/No
      ZeroModeAbortCurvature float
   End
End
```

PESExploration

SaddleSearch

Type Block

Description Configuration for the Saddle Search procedure (used in SaddleSearch and ProcessSearch Jobs).

ConvergedForce

Type Float

Default value -1.0

Unit eV/Angstrom

Description Convergence threshold for nuclear gradients. Note: Special value of -1.0 means using the same convergence criterion as the PES explorer's geometry optimizer.

DisplaceAlongNormalModesActiveModes

Type String

Default value

Description Sets the active modes to be used when the option [SaddleSearch%DisplaceAlongNormalModesWeight] is enabled. e.g. 1,2,3,5. By default, all normal modes are considered active.

DisplaceAlongNormalModesWeight

Type Float

Default value 0.0

Description The probability of generating a displacement resulting in a random linear combination of the normal modes specified in [SaddleSearch%DisplaceAlongNormalModesActiveModes]. This parameter is a numeric value that should fall within the interval [0.0, 1.0].

DisplaceAtomsInRegion

Type String

Default value

Description A string corresponding to the name of a region. When performing the initial random displacement, only displace atoms in the specified region.

DisplaceAtomsInRegionWeight

Type Float

Default value 0.0

Description The probability of generating a displacement involving only atoms from the region specified in [SaddleSearch%DisplaceAtomsInRegion]. This parameter is a numeric value that should fall within the interval [0.0, 1.0].

`DisplaceListedAtoms`

Type String

Default value

Description Sets the active atoms to be used when the option [SaddleSearch%DisplaceAlongNormalModesWeight] is enabled. e.g. 1,2,3,5. By default, all normal modes are considered active.

`DisplaceListedTypes`

Type String

Default value

Description ???.

`DisplaceMagnitude`

Type Float

Default value 0.1

Unit Angstrom

Description The standard deviation of the Gaussian displacement in each degree of freedom for the selected atoms.

`DisplaceRadius`

Type Float

Default value 4.0

Unit Angstrom

Description Atoms within this distance of the epicenter will be displaced.

`MaxEnergy`

Type Float

Default value 20.0

Unit eV

Description The energy (relative to the starting point of the saddle search) at which a saddle search explorer considers the search bad and terminates it.

`MaxIterations`

Type Integer

Default value 400

Description Maximum number of iterations for each saddle search run.

`MinEnergyBarrier`

Type Float

Default value 0.001

Unit eV

Description Minimum energy barrier to accept a new transition state.

`MinModeMethod`

Type Multiple Choice

Default value dimer

Options [dimer, lanczos]

Description The minimum-mode following method to use.

`RelaxFromSaddlePoint`

Type Bool

Default value No

Description Relaxes the saddle point geometries following the imaginary mode to get both reactants and products.

`ZeroModeAbortCurvature`

Type Float

Default value 0.01

Unit eV/Angstrom^2

Description The threshold in the frequency below which the minimum mode is considered zero. The calculation is aborted if the negative mode becomes zero.

4.12.9 Basin Hopping job

Overview

Basin hopping[2] is an iterative Monte Carlo method for PES exploration and global minimization.

An "iteration" in basin hopping consists of the following steps:

1. The atomic coordinates of the system are randomly perturbed (the details of this random perturbation can be configured via the keywords `Displacement`, `DisplacementDistribution`, `SingleAtomDisplace`, `SwapProbability`. See *below* (page 184) for more details).
2. A local optimization of the randomly perturbed structure is performed (see also the *Optimizer* (page 192) section)
3. The new optimized structure is accepted or rejected based of its energy (if the energy of the newly optimized structure lower than the lowest energy so far, the new structure is readily accepted. Otherwise it is accepted with probability $e^{(-\Delta E/kT)}$ where ΔE is the difference between the energy at the previous iteration and the current energy, T is temperature specified in the `PESExploration%Temperature` keyword, see *Job selection and main options* (page 172)).

By iteratively performing these steps, the basin hopping procedure explores the highly-dimensional configuration space of the system, looking for the global minimum and finding local minima along the way. The number of iteration can be specified via the `Steps` keywords (see *below* (page 184) for more details).

[2] David J. Wales and Jonathan P. K. Doye *Global Optimization by Basin-Hopping and the Lowest Energy Structures of Lennard-Jones Clusters Containing up to 110 Atoms*, J. Phys. Chem. A 1997, 101, 28, 5111–5116 (https://doi.org/10.1021/jp970984n)

For a more comprehensive PES exploration, AMS can perform several expeditions (potentially with several explorers for each expedition) in a single calculation. See the `NumExpeditions` and `NumExplorers` keywords in the *Job selection and main options* (page 172) section for more details.

See also:

- *Example: Basin Hopping for Ar 13 cluster* (page 425)
- GUI tutorials Cluster Growth: Cobalt Clusters and Water dissociation on an oxide surface.

Input options

To perform a Basin Hopping calculation you should specify:

```
Task PESExploration

PESExploration
   Job BasinHopping

   Temperature float

   BasinHopping
      # Options for the Basin Hopping procedure. See description below.
   End
End
```

The `PESExploration%Temperature` keyword is described in the *Job selection and main options* (page 172) section.

The following input keywords are specific to Basin Hopping procedure:

```
PESExploration
   BasinHopping
      DisplaceAtomsInRegion string
      Displacement float
      MainSystemAsSeed Yes/No
      PESPointCharacterization Yes/No
      PushApartDistance float
      Steps integer
   End
End
```

PESExploration

BasinHopping

Type Block

Description Configures the details of the Basin Hopping subtask.

DisplaceAtomsInRegion

Type String

Default value

Description If you specify a region name here, only the atoms belonging to this region will be displaced during the basin hopping procedure. For more details on regions, see the documentation on the System definition.

Displacement

Type Float

Default value 0.5

Unit Angstrom

Description Displacement in each degree of freedom.

`MainSystemAsSeed`

Type Bool

Default value No

Description If true, only the main system will be used as a seed state. The main system is not added to the database.

`PESPointCharacterization`

Type Bool

Default value Yes

Description If true, a PES point characterization based on a vibrational analysis is carried out to confirm each detected state is an actual local minimum (no imaginary frequencies). Conversely, if this option is false, the PES point characterization is avoided, which will assume that all located states are local minima (zero gradients). Enabling this option is very useful for large systems. It circumvents the need for computing and diagonalizing the Hessian matrix, a typically expensive computational process.

`PushApartDistance`

Type Float

Default value 0.4

Unit Angstrom

Description Push atoms apart until no atoms are closer than this distance. This criterion is enforced for the initial structure and all those generated by random displacements.

`Steps`

Type Integer

Default value 20

Description Number of displace & optimize Monte-Carlo steps to take.

4.12.10 Fragmented states

When studying adsorption processes, it is required to review those situations where a transition state (TS) does not mediate the adsorption process. They are formally known as **non-activated exothermic adsorption** processes. These processes are not discovered naturally in the PES exploration. Since the AMS2022 release, there is a systematic way of including those processes. To this aim, we defined the **fragmented states**, where the adsorbate and adsorbent are infinitely far away from each other.

The fragmented states can be included in the *Energy Landscape* (page 174) through the use of the `CalculateFragments` keyword:

```
PESExploration
   CalculateFragments Yes/No
End
```

PESExploration

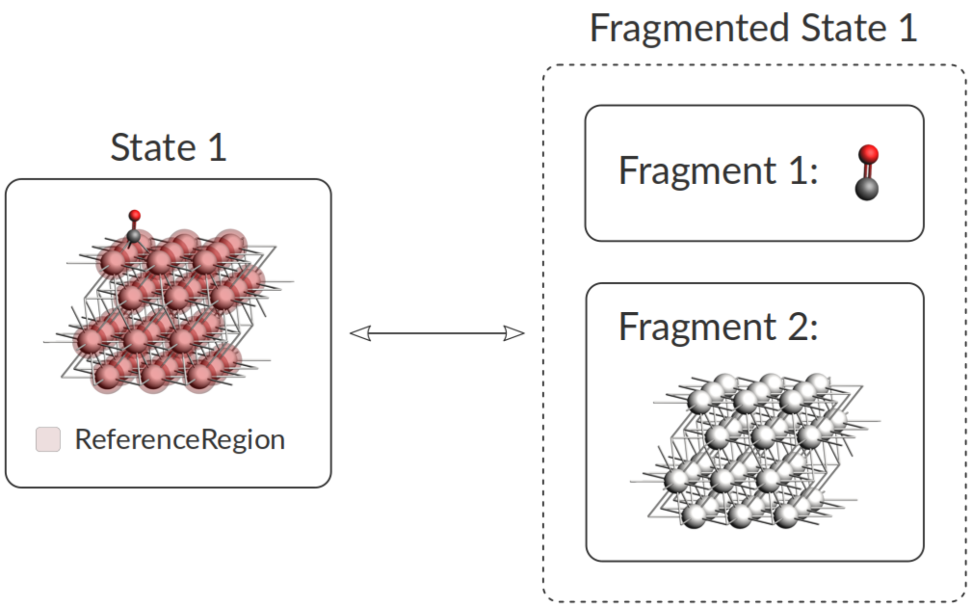
CalculateFragments

Type Bool

Default value No

Description Must be used together with an adsorbent set as the StatesAlignment%ReferenceRegion. Runs a final calculation of the adsorbate and adsorbent (marked by the ReferenceRegion) individually. The fragmented state is included in the energy landscape.

The keyword has to be used together with a *reference region* (page 197) set via the `StatesAlignment%ReferenceRegion` keyword. The calculation of the fragmented states will happen at the very end of a PES exploration. For every minimum in the energy landscape, two geometry optimizations will be performed: one with only the atoms belonging to the reference region (the adsorbent), the other with only the atoms outside of the reference region (the adsorbate). This relaxes the structure of the adsorbent in the *absence* of the adsorbate, and vice versa.



The total energy of the fragmented state is then simply taken as the sum of the energies of both fragments, and the adsorption energy is the difference between the adsorbed and fragmented state.

$$E(\text{fragmented state } 1) = E(\text{fragment } 1) + E(\text{fragment } 2)$$
$$E_{ad} = E(\text{state } 1) - E(\text{fragmented state } 1)$$

You will find fragmented states and the fragments in the *text output* (page 174) following the `Final Energy Landscape` section. The example shown above would look like this:

```
----------------------
Final Energy Landscape
----------------------

       Id        Energy(a.u.)         RE(eV)   RE(kcal/mol)     Counts     Crit. point
     ------------------------------------------------------------------------------
        1           -7.651642        0.00000         0.0000          1             Min
        2           -7.651572        0.00191         0.0441          1             Min
        3           -7.623820        0.75709        17.4589          1             Min
```

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```
        4          -7.622548        0.79170        18.2571          7             TS␣
↪2<-->3
        5          -7.622430        0.79491        18.3310          5             TS␣
↪3<-->1

Number of configurations                             5
Number of local minima                               3
Number of transition states                          2
Energy range (a.u.)                           0.029212
Energy range (eV)                              0.79491
Energy range (kcal/mol)                        18.3310

Fragments
---------

Number of fragments                                  2

        Id              Formula        Energy(a.u.)              Region
     ----------------------------------------------------------------
        1                    CO           -0.424454              active
        2                  Pt36           -7.154286             surface

Fragmented States
-----------------

Number of fragmented states                          1

        Id            Fragments        Energy(a.u.)          RE(eV)    RE(kcal/mol)
     --------------------------------------------------------------------------
        1                   1,2           -7.578740         1.98377         45.7467 -->1
                                                                                    -->2
                                                                                    -->3
```

Notice the following: 1) one fragment may be included in multiple fragmented states, and 2) multiple states may be connected to the same fragmented state. The latter happens when the individual optimizations of adsorbate and adsorbent yield the same results for multiple states. By definition, these states are considered connected if the difference in energy is lower than `PESExploration%SaddleSearch%MaxEnergy`, which by default is `20.0 eV`. Interestingly, you may find, for example, that an adsorbed fragment is in multiple fragmented states together with different surface defects. In other words: the adsorbed fragment is always the same when you remove it from the surface, but the surface may look different, depending on the geometry from which the adsorbent is removed.

The following figure shows a graphical representation of the energy landscape of the example above (made with **amsmovie**). The blue line represents the fragmented state.

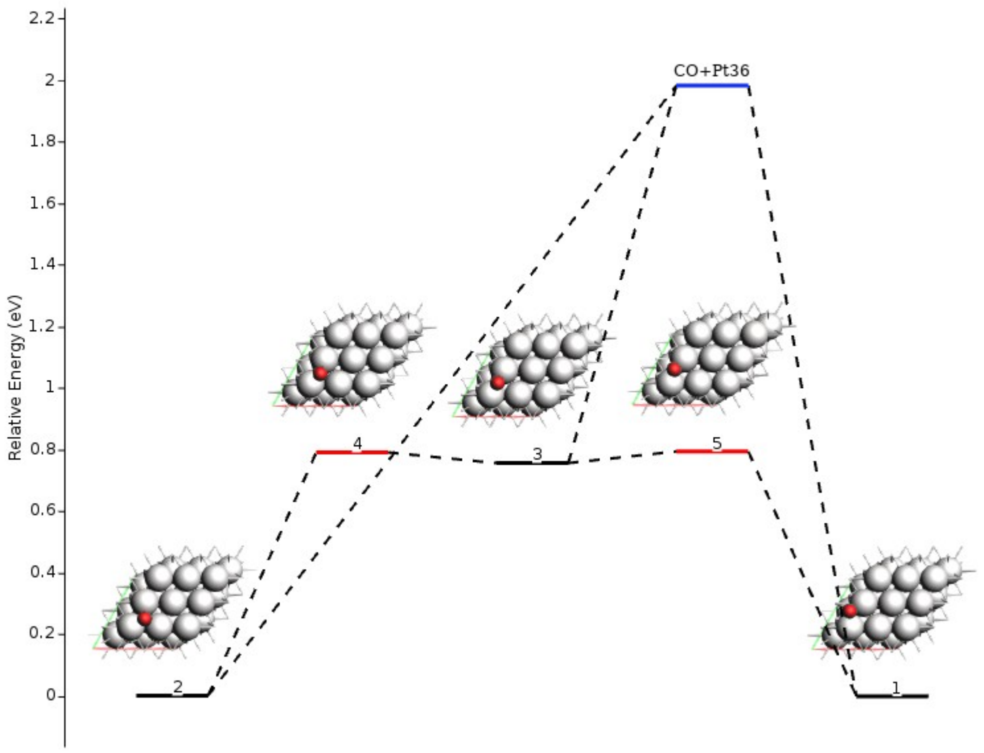
4.12.11 Landscape Refinement

The `LandscapeRefinement` Job can be used to re-optimize the critical points (local minima and saddle points) found in a previous PES exploration calculation using a different engine or different engine settings.

Since PES exploration calculations can be computationally demanding, a possible strategy is to first perform a PES exploration using either a fast engine or computationally cheap settings for the engine of choice, and then to *refine* the energy landscape obtained using a more accurate (and computationally more expensive) method.

See also:

Check the tutorial on automated reaction pathway discovery for hydrohalogenation. There the landscape refinement is



used to go from the DFTB level of theory to DFT.

The `LandscapeRefinement` job needs a previously computed Energy Landscape. See the section *Continue a PES exploration from a previous calculation* (page 175) for more details.

To perform a Landscape Refinement calculation you should specify:

```
Task LandscapeRefinement

PESExploration
   Job LandscapeRefinement

   LoadEnergyLandscape
     Path path/to/previous/calculation/ams.results
   End
End
```

Warning: If you perform a LandscapeRefinement of an Energy Landscapes obtained with *ProcessSearch* (page 178) job, the connections between TS and minima are **NOT** recomputed by default unless the parameter `LandscapeRefinement%RelaxFromSaddlePoint` is activated. By turning on `LandscapeRefinement%RelaxFromSaddlePoint`, both reactants and products can be reconstructed for each transition state using a geometry optimization that follows the imaginary vibrational mode.

Lets say, for example, that after a ProcessSearch calculation using DFTB we found a TS connecting minima with `Id` `3` and `4`. After a LandscapeRefinement using a different engine (for example ADF) it is no longer assured that the refined TS will still connect the same two minima.

When you visualize a refined energy landscape using AMSmovie, be aware that some of the connections might be incorrect.

4.12.12 Creating and/or Extending an Energy Landscape from the Input File

It is pretty common to have a set of structures or geometries from the literature or previous calculations that you want to use to continue an energy exploration or an energy landscape refinement. In this case, you can use `System` blocks in your input file to create and/or extend an energy landscape.

The header of the *System* (page 31) block is extended using the following syntax:

```
System label ts=Yes/No reactant=string/int product=string/int
   Atoms header
      ...
   End
   ...
End
```

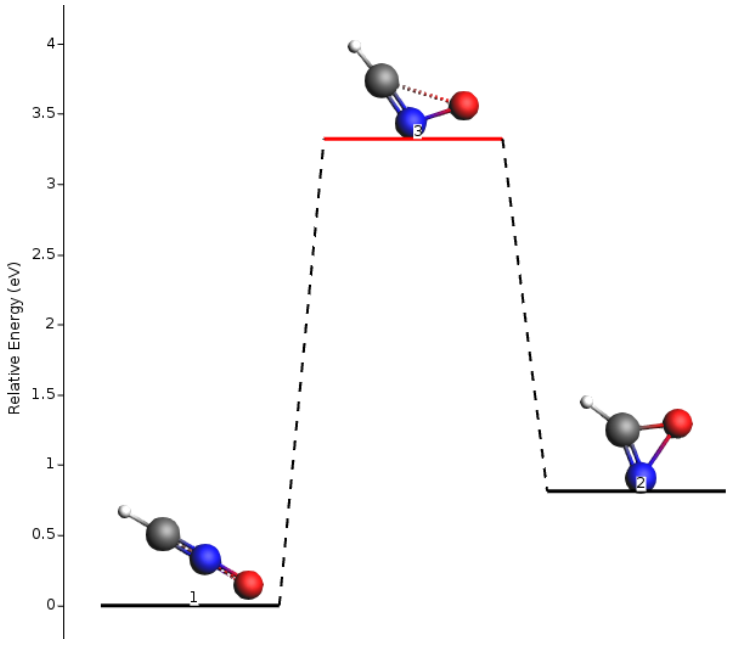
The label `label` is a string. It is required and unequivocally identifies each `System` block defined by the user. The parameters `ts`, `reactant`, and `product` are optional. The latter two, however, can be specified only if `ts` is set to `Yes`. They are otherwise ignored. Notice that it is possible to have transition states with no reactants, or products, or none of them.

The example below illustrates how to use this feature:

```
PESExploration
   Job LandscapeRefinement
End

Task PESExploration

System state1
   Atoms
      H      -1.08012803       1.17268451       0.09177647
      O       1.82672244      -0.54837752       0.33538717
      N       0.81411565       0.05127399       0.25048411
      C      -0.17673006       0.63776902       0.16748225
   End
End

System state2
   Atoms
      H      -0.71003072       1.06490526       0.04975824
      O       1.41363000       0.55626133       0.07710644
      N       0.55490964      -0.71415530       0.51752525
      C       0.12547108       0.40633871       0.20074007
   End
End

System state3 ts=Yes reactant=state1 product=state2
   Atoms
      H      -0.78063395       1.32905463      -0.01879702
      O       1.78011528      -0.06505936       0.19126583
      N       0.53076199      -0.47128241       0.41047761
      C      -0.14626334       0.52063714       0.26218359
   End
End

Engine DFTB
EndEngine
```

This example executes an Energy Landscape Refinement calculation at the DFTB level of theory for the energy landscape loaded from the `System` blocks. It loads the coordinates of two local minima (`state1`, and `state2`) and one transition state (`state3`). The transition state is connected with both minima, being `state1`, the reactant, and `state2`, the product. Below you can see the output text lines and a graphical representation of the obtained energy landscape:

```
   Id         Energy(a.u.)          RE(eV)    RE(kcal/mol)     Counts     Crit. point
--------------------------------------------------------------------------------
   1           -10.424825         0.00000          0.0000          1            Min
   2           -10.394956         0.81277         18.7428          1            Min
   3           -10.302822         3.31986         76.5577          1              TS 1<-->2
```



To add states to an existing Energy Landscape, use the keyword `PESExploration%LoadEnergyLandscape%Path` to specify the KF file to load. Then, define new links to its states using their ids. The following example shows how to use this feature:

```
PESExploration
   Job LandscapeRefinement
   LoadEnergyLandscape
      Path previous.results
   End
End

Task PESExploration

System state3
   Atoms
      H       0.51485007       1.62340128      -0.20665749
      O       1.05880703       0.84482125      -0.00604063
      N       0.23989165      -0.13660458       0.36835485
      C      -0.42956874      -1.01826795       0.68947328
   End
End

System state4 ts=Yes reactant=2 product=state3
   Atoms
      H      -0.10604142       1.11162691       0.00025950
```

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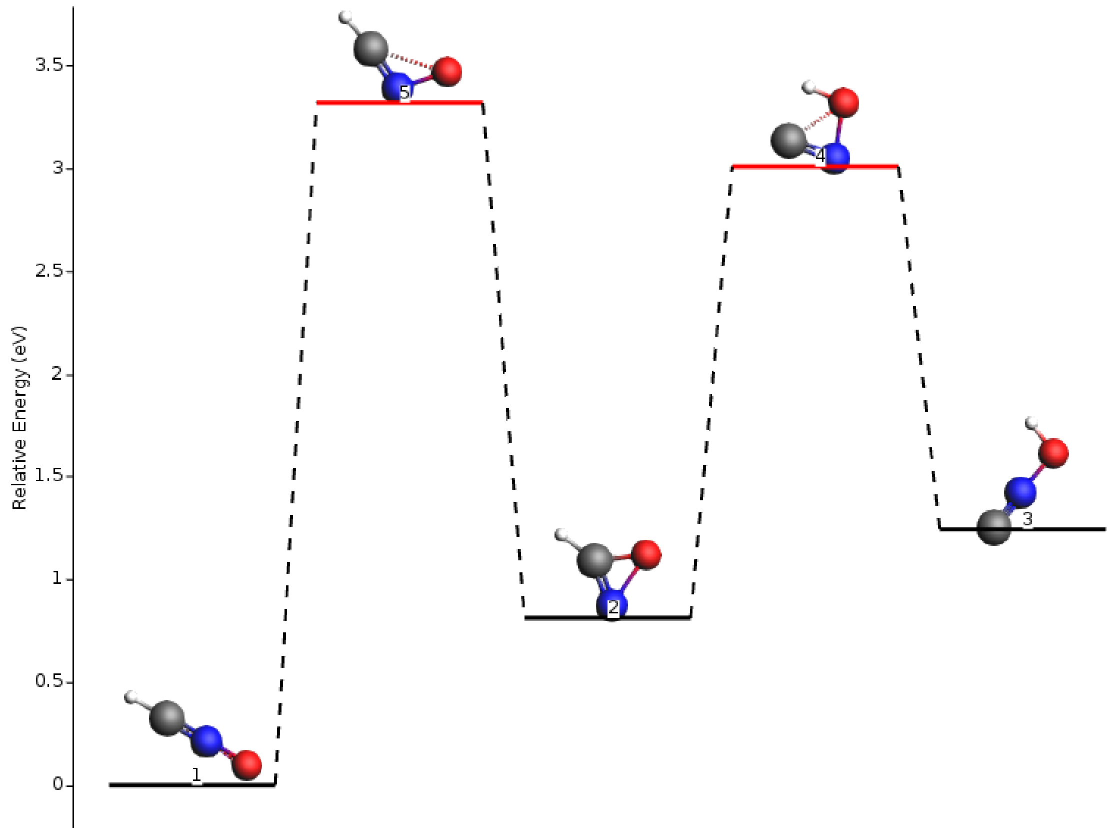
```
      O       1.08875440       0.73993713       0.03512861
      N       0.74116588      -0.56372211       0.45954036
      C      -0.33989886       0.02550806       0.35020153
   End
End

Engine DFTB
EndEngine
```

This example performs an Energy Landscape Refinement calculation at the DFTB level of theory on the energy landscape loaded from the previous calculation's directory results (`previous.results`). It also loads the coordinates of an additional local minimum (`state3`) and one transition state (`state4`) from the input file using the `System` blocks. The latter transition state is linked to the product `state3` (defined in the same input file) and the reactant state with `id=2` from the loaded energy landscape (see image above). The output text lines and the graphical representation of the obtained energy landscape are shown below. Notice that the states have been rearranged according to energy.

```
   Id          Energy(a.u.)          RE(eV)    RE(kcal/mol)     Counts     Crit. point
--------------------------------------------------------------------------------
   1           -10.424825        0.00000          0.0000           1            Min
   2           -10.394956        0.81277         18.7428           1            Min
   3           -10.379113        1.24388         28.6845           1            Min
   4           -10.314160        3.01134         69.4432           1              TS  2<-->3
   5           -10.302822        3.31986         76.5577           1              TS  1<-->2
```



Note: If you want to combine this feature of creating and/or extending an energy landscape with any other job (`PESExploration%Job`) other than `LandscapeRefinement`. Don't forget to include a `System` block with no header (or label) to define the main chemical system.

4.12.13 Optimizer

Geometry optimizations are performed for most PES Explorations job types. In the `PESExploration%Optimizer` block you may configure some of the parameters for these geometry optimizations:

```
PESExploration
   Optimizer
      ConvergedForce float
      MaxIterations integer
      Method [CG | QM | LBFGS | FIRE | SD]
   End
End
```

PESExploration

Optimizer

Type Block

Description Configures the details of the geometry optimizers used by the PES explorers.

ConvergedForce

Type Float

Default value 0.005

Unit eV/Angstrom

Description Convergence threshold for nuclear gradients.

MaxIterations

Type Integer

Default value 400

Description Maximum number of iterations allowed for optimizations.

Method

Type Multiple Choice

Default value CG

Options [CG, QM, LBFGS, FIRE, SD]

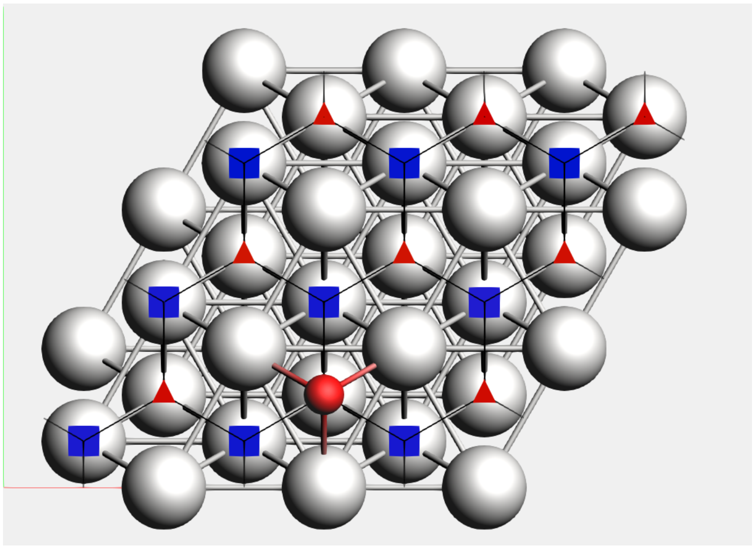
Description Select the method for geometry optimizations.

4.12.14 Binding Sites

Binding sites can be determined from an Energy Landscape.

When computing binding sites you will first need to define a **reference region**, which typically will be a surface or a cluster (*regions* (page 36) can be specified in the *system input block* (page 31), or via the "Model → Regions" panel in AMSinput). AMS will then go though all the local minima of Energy Landscape and mark as 'binding sites' the positions where an atom of an adsorbed molecule is neighboring atoms in the reference region.

For instance, in *Example: PES Exploration, Binding Sites for O on Pt 111* (page 427), the platinum surface is the reference region, while the oxygen atom is the adsorbate. In the picture below, you can see the oxygen binding sites on the platinum 111 surface (the two different types of binding sites are marked by a blue square and a red triangle respectively).



Lines connecting the the binding sites will be drawn if 1) there is a transition state connecting two local minima associated to these binding-sites (notice that may there are multiple local minima associated with the same binding site), and 2) there is at least an atom (from the adsorbate region) that changes its position from the first binding site to the second one mediated by the same transition state described above. In this process, AMS will align as much as possible all local minima and transition states to the input's file structure but ignoring the atoms in the region adsorbate trying to establish a common reference frame (see also the `StatesAlignment` input block below).

See also:

- *Example: PES Exploration, Binding Sites for O on Pt 111* (page 427)
- Cluster Growth: Cobalt Clusters

Binding sites are labeled according to the number of neighbors they have on each of their coordination shells. It has the format `N<int><int>...`. For example, the label `N334` denotes three neighbors in the first shell, three in the second, and four in the third. The parameter `PESExploration%BindingSites%MaxCoordinationShellsForLabels` or the largest shell contained in the unit cell, determines the maximum number of coordination shells to consider. For labeling purposes, the center of the binding site is taken to be `1.5 Å` from the center of the atoms in the first shell in the direction of the adsorbed atom position. `PESExploration%BindingSites%DistanceDifference` is an important parameter to remember. It is critical because it specifies the tolerance for determining whether or not two atoms are in the same coordination shell based on their distances from the binding site.

The figure below depicts the four types of binding sites observed on a Pt(111) surface. There, you can see the AMS label (e.g., `N33`, `N34`, ...) as well as the traditional one (e.g., `fcc`, `hcp`, ...). The distances between the binding site and the highlighted atoms on that coordination shell (or neighborhood) are listed below each geometry. If two numbers are listed, it is because two different distances are involved, but they are considered in the same coordination shell because their difference is less than `PESExploration%BindingSites%DistanceDifference`.

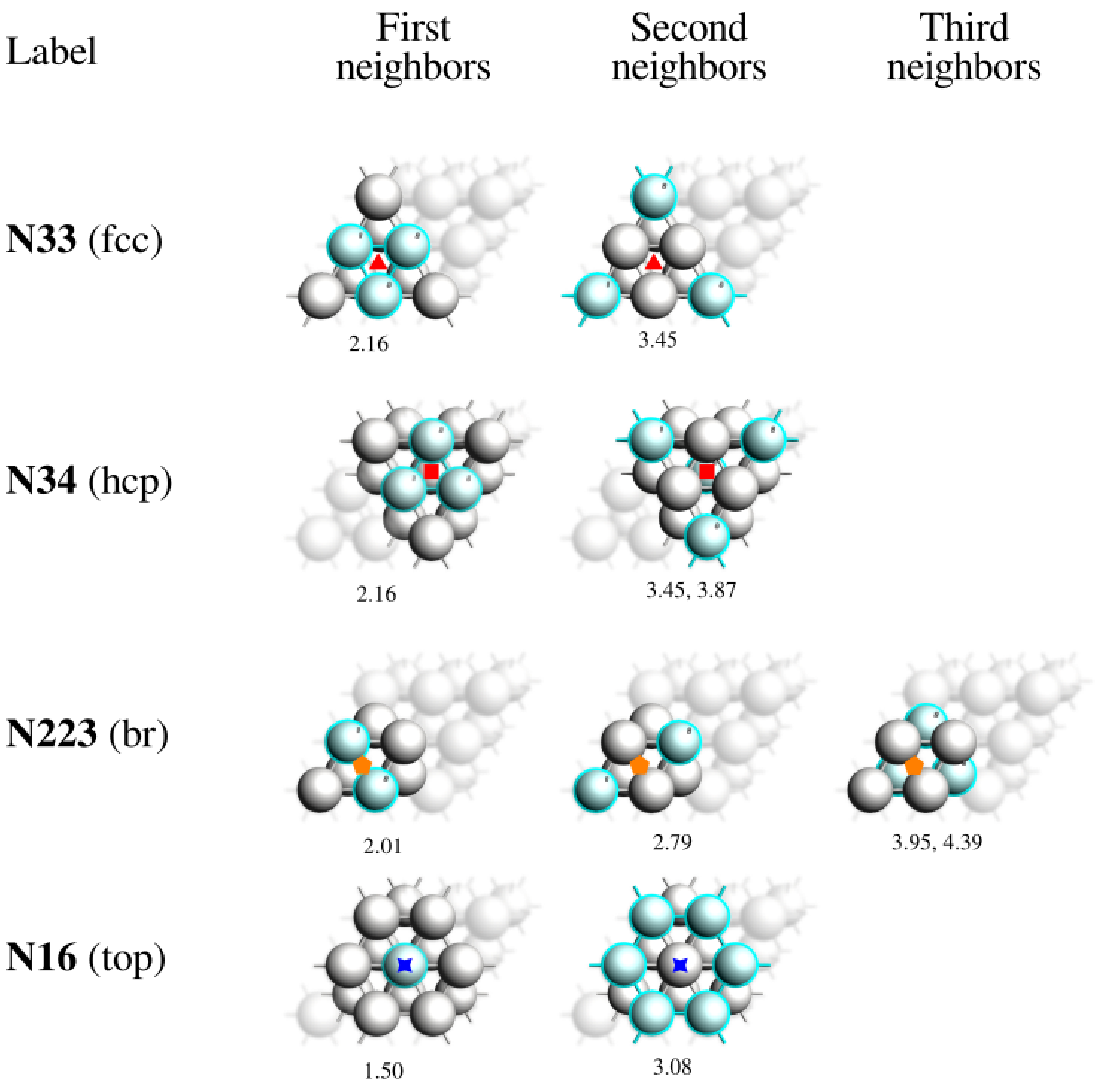


Fig. 4.2: Binding sites obtained for a CO molecule adsorbed on a Pt(111) surface using `PESExploration%BindingSites%DistanceDifference = 0.5 Å`.

The following is an example of the section in the output file describing the obtained binding sites. In particular, you can find the above details regarding distances involved in calculating their labels.

```
-------------
Binding Sites
-------------


Number of binding sites:                                 4
Number of connections:                                   3
```

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```
Binding sites:

  id   Label   Aver.E(a.u.)  Stdev.E(a.u.)          x         y         z      Parents
   1     N34      -3.773094       0.000000     3.59065   2.09219   3.88471      1(1)
   2     N33      -3.772967       0.000000     4.93783   2.86841   3.88471      2(1)
   3    N223      -3.746180       0.000000     4.25120   2.47351   3.88462      3(1)
   4     N16      -3.683784       0.000000     3.60490   3.59820   3.88382      6(1)

Labels details:

   Label            Center example(A)      Radius(A)
     N33         4.94     2.87     3.88     2.16 - 2.66
                                            3.45 - 3.95
     N34         3.59     2.09     3.88     2.16 - 2.66
                                            3.45 - 3.95
    N223         4.25     2.47     3.88     2.02 - 2.52
                                            2.76 - 3.26
                                            3.86 - 4.36
     N16         3.60     3.60     3.88     1.50 - 2.00
                                            3.04 - 3.54
```

Input options

There are two distinct ways of triggering the computation of binding sites. You can either:

compute the binding sites at the end of a *Process Search* (page 178), *Basin Hopping* (page 183) or *Landscape Refinement* (page 187) calculation by setting the `PESExploration%BindingSites%Calculate` option to `yes`:

```
PESExploration
  Job [ProcessSearch | BasinHopping | LandscapeRefinement]

  BindingSites
    Calculate Yes
  End

  StatesAlignment
    ReferenceRegion reference_region_name
  End
End
```

or

compute the binding sites by setting the `PESExploration%Job` to `BindingSites` and load a previously computed Energy Landscape (see *Example: PES Exploration, Binding Sites for O on Pt 111* (page 427)):

```
PESExploration
  Job BindingSites

  LoadEnergyLandscape
    Path path/to/previous/calculation/ams.results
  End

  StatesAlignment
    ReferenceRegion reference_region_name
```

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```
  End
End
```

The following input options are related to the calculation of binding sites:

```
PESExploration
   BindingSites
      Calculate Yes/No
      DistanceDifference float
      MaxCoordinationShellsForLabels integer
      NeighborCutoff float
      ReferenceRegion string
   End
End
```

PESExploration

BindingSites

Type Block

Description Options related to the calculation of binding sites.

Calculate

Type Bool

Default value No

Description Calculate binding sites at the end of a job. Not needed for Binding Sites job.

DistanceDifference

Type Float

Default value -1.0

Unit Angstrom

Description If the distance between two mapped binding-sites is larger than this threshold, the binding-sites are considered different. If not specified, its value will set equal to [PESExploration%StructureComparison%DistanceDifference]

MaxCoordinationShellsForLabels

Type Integer

Default value 3

Description The binding site labels are given based on the coordination numbers of shells in the reference region, using the following format: N<int><int>…, e.g., the label 'N334' means 3 atoms in the first coordination shell, 3 in the second one, and 4 in the third one. This parameter controls the maximum number of shells to include.

NeighborCutoff

Type Float

Default value -1.0

Unit Angstrom

Description Atoms within this distance of each other are considered neighbors for the calculation of the binding sites. If not specified, its value will set equal to [PESExploration%StructureComparison%NeighborCutoff]

`ReferenceRegion`

Type String

Default value

Description Defines the region that is considered as the reference for binding sites detection. Binding sites are projected on this region using the geometry from the reference system. If not specified, its value will set equal to [PESExploration%StatesAlignment%ReferenceRegion]

The following input options are related to the definition of the reference region and alignment thereof:

```
PESExploration
   StatesAlignment
      DistanceDifference float
      ReferenceRegion string
   End
End
```

`PESExploration`

`StatesAlignment`

Type Block

Description Configures details of how the energy landscape configurations are aligned respect to the main chemical system [System].

`DistanceDifference`

Type Float

Default value -1.0

Unit Angstrom

Description If the distance between two mapped atoms is larger than this threshold, the configuration is considered not aligned. If not specified, its value will set equal to [PESExploration%StructureComparison%DistanceDifference]

`ReferenceRegion`

Type String

Default value

Description Defines the region that is considered as the reference for alignments. Atoms outside this region are ignored in the alignments.

4.12.15 References

CHAPTER

FIVE

GRADIENTS, HESSIAN, STRESS TENSOR, ELASTICITY

No matter what application the AMS driver is used for, in one way or another it always explores the potential energy surface (PES) of the system. One can furthermore ask AMS to calculate additional properties of the PES in the points that are visited. These are mostly (but not exclusively) derivatives of the energy, e.g. we can ask AMS to calculate the gradients or the Hessian in the visited points. In general all these PES point properties are requested through the `Properties` block in the AMS input:

```
Properties
   Gradients Yes/No
   StressTensor Yes/No
   Hessian Yes/No
   SelectedRegionForHessian string
   PESPointCharacter Yes/No
   ElasticTensor Yes/No
End
```

This properties described on this page in the AMS manual are all related to derivatives of the energy.

Note that because these properties are tied to a particular point on the potential energy surface, they are found on the *engine output files* (page 19). Note also that the properties are not always calculated in every PES point that the AMS driver visits during a calculation. By default they are only calculated in *special* PES points, where the definition of special depends on the *task* (page 45) AMS is performing: For a *geometry optimization* (page 47) properties would for example only be calculated at the final, converged geometry. This behavior can often be modified by keywords special to the particular running task.

5.1 Nuclear gradients

The first derivative with respect to the nuclear coordinates can be requested as follows:

```
Properties
   Gradients Yes/No
End
```

`Properties`

`Gradients`

Type Bool

Default value No

GUI name Nuclear gradients

Description Calculate the nuclear gradients.

Note that these are gradients, not forces, the difference being the sign. The gradients are printed in the output and written to the *engine result file* (page 19) belonging to the particular point on the PES in the `AMSResults%Gradients` variable as a $3 \times n_{\text{atoms}}$ array in atomic units (Hartree/Bohr).

5.2 Hessian

The calculation of the second derivative of the total energy with respect to the nuclear coordinates is enabled by:

```
Properties
   Hessian Yes/No
   SelectedRegionForHessian string
End
```

`Properties`

`Hessian`

Type Bool

Default value No

Description Whether or not to calculate the Hessian.

`SelectedRegionForHessian`

Type String

GUI name Hessian only for

Description Compute the Hessian matrix elements only for the atoms in a particular region. If not specified, the Hessian will be computed for all atoms.

The Hessian is not printed to the text output, but is saved in the engine result file as variable `AMSResults%Hessian`. Note that this is just the plain partial second derivatives (no mass-weighting) of the total energy. The $3 \times N_{\text{atoms}}$ columns/rows of the matrix are grouped by atom: the first three rows/columns correspond to the first atom, etc..

Note that the AMS driver also supports the *Mobile Block Hessian* (page 213) (MBH) method, which allows treating parts of the system as rigid blocks.

Often one is not interested in the Hessian matrix itself, but just in using it for the calculation of IR frequencies or to characterize a PES point (as e.g. a local minimum or a saddle point). For these application, see the following pages in the manual:

- *IR frequencies* (page 209)
- *PES point character* (page 200)

5.3 PES point character

A PES point can according to the slope and curvature of the PES at that point be classified in the following categories:

- A local minimum on the PES with vanishing nuclear gradients and no negative frequencies.
- A transition state with vanishing nuclear gradients and exactly one negative frequency, i.e. a first order saddle point on the PES.
- A higher order saddle point, i.e. a stationary point on the PES with vanishing nuclear gradients but more than one imaginary frequency.

- A non-stationary point on the PES. Here the gradients are non-zero.

This classification can easily be done if both the gradients and the normal modes have already been calculated. However, calculating the full Hessian needed for the entire set of normal modes is very expensive and undesirable if one only wants to know the character of a PES point. The AMS driver can quickly, and without calculating the full Hessian, characterize a PES point into one of the above categories. This can be used to confirm the success of e.g. a *transition state search* (page 66) or *geometry optimization* (page 47). A PES point can be characterized by requesting `PESPointCharacter` as a property:

```
Properties
   PESPointCharacter Yes/No
End
```

Properties

PESPointCharacter

Type Bool

Default value No

GUI name Characterize PES point

Description Determine whether the sampled PES point is a minimum or saddle point. Note that for large systems this does not entail the calculation of the full Hessian and can therefore be used to quickly confirm the success of a geometry optimization or transition state search.

This will calculate the few lowest normal modes using an iterative diagonalization of the Hessian[1] based on a Davidson algorithm implemented in the PRIMME library[2]. The procedure has been optimized for finding a small number of low-lying eigenvalues in as few matrix-vector multiplications (and thus single point calculations) as possible. This is facilitated by performing the iterative method using a pre-conditioning matrix based on an approximation of the Hessian. The approximate Hessian is obtained from the full Hessian at a lower level of theory. This calculation also provides the initial guesses for the desired normal modes. What the lower level of theory is depends on the main engine used in the calculation: DFTB with the GFN1-xTB model is used as the lower level of theory for relatively slow engines, e.g. DFT based engines. For semi-empirical engines like DFTB or MOPAC, the lower level of theory is currently UFF. It is currently not possible to change the engine used to obtain the preconditioning Hessian and the approximate modes.

- Note that the iterative calculation of the normal modes is skipped when …
  1. … the nuclear gradients are so large that the PES point is considered non-stationary. The calculation of the modes is then just not necessary for classifying it.
  2. … the full normal modes or Hessian have also been requested. The iterative calculation is then not necessary, as all modes are already known.
  3. … the molecule is very small. (For small systems the iterative calculation of the few lowest normal modes is not faster than the full calculation of all modes, so all modes are calculated instead.)
- The classification as a stationary or non-stationary point uses the gradient convergence criterion from the geometry optimizer as the tolerance, see *geometry optimization* (page 47). This makes sure that the criterion for what is considered converged/stationary is always in sync between the optimizer and the PES point characterization.
- For periodic systems the PES point characterization does not take the lattice degrees of freedom into account. A PES point where the nuclear gradients are small enough would for example be classified as a stationary point, even if the system is under stress.

Details of the iterative procedure can be configured in the `PESPointCharacter` block:

[1] P. Deglmann and F. Furche, *Efficient characterization of stationary points on potential energy surfaces*, J. Chem. Phys. 117, 9535 (2002) (https://doi.org/10.1063/1.1523393)

[2] A. Stathopoulos and J. R. McCombs, *PRIMME: PReconditioned Iterative MultiMethod Eigensolver: Methods and software description*, ACM Transactions on Mathematical Software, Vol. 37, No. 2, (2010), 21:1–21:30. (https://doi.org/10.1145/1731022.1731031)

```
PESPointCharacter
   Displacement float
   NegativeEigenvalueTolerance float
   NumberOfModes integer
   Tolerance float
End
```

PESPointCharacter

Type Block

Description Options for the characterization of PES points.

Displacement

Type Float

Default value 0.04

Description Controls the size of the displacements used for numerical differentiation: The displaced geometries are calculated by taking the original coordinates and adding the mass-weighted mode times the reduced mass of the mode times the value of this keyword.

NegativeEigenvalueTolerance

Type Float

Default value -0.0001

Unit Hartree/Bohr^2

Description The threshold in Hessian eigenvalue below which a mode is considered imaginary, i.e. indicating a transition state. This is a small negative number, as very small negative eigenvalues may be due to numerical noise on an essentially flat PES and do not indicate true transition states.

NumberOfModes

Type Integer

Default value 2

Description The number of (lowest) eigenvalues that should be checked.

Tolerance

Type Float

Default value 0.016

Description Convergence tolerance for residual in iterative Davidson diagonalization.

- Note that the residual tolerance that can be achieved is limited by the numerical differentiation that is performed. The default values should apply in most cases, but if convergence becomes a problem one may choose to increase the tolerance or to increase the step size (slightly). Note that the default residual tolerance is lower than for the other mode selective methods. This is because PRIMME uses a different convergence criteria than mode tracking/refinement. The higher value used as a default will therefore not result in decreased levels of accuracy. The method will bail if the number of iterations exceeds the number of normal modes as at this point still achieving convergence becomes unlikely, in part due to the next point.
- In order to avoid producing the known and irrelevant rigid modes, the method searches for normal modes orthogonal to six (or five) rigid modes. Imperfections due to the numerical differentiation may mean that the translational and rotational rigid modes are not exact eigenmodes of the Hessian that is constructed. As a result, some part of the lowest vibrational normal mode may lie in the span of the theoretical rigid modes and therefore be inaccessible to

the Davidson method. This places a lower bound on the residual tolerance that can be achieved, which is directly related to the numerical differentiation accuracy. The take-away: do not set the tolerance too low, the default usually suffices.

- Behind the scenes, the method actually computes a few more modes than requested. In the case of multiplicities, eigenvalues may still converge out of order. These additional eigenvalues essentially guarantee that the obtained modes are indeed the lowest ones.

5.4 Thermodynamics, gas phase Gibbs free energy

At the end of a completed IR Frequencies (normal modes) calculation, a survey is given of thermodynamic properties: entropy, internal energy, constant volume heat capacity, enthalpy and Gibbs free energy, see:

- *IR frequencies* (page 209)
  - *Thermodynamics* (page 229)
  - *Gibbs free energy change for a gas phase reaction* (page 232)

5.5 Stress tensor

For periodic systems (chains, slabs, bulk) one can also request the clamped-ion stress tensor (note: the clamped-ion stress is only part of the *true* stress tensor):

```
Properties
   StressTensor Yes/No
End
```

Properties

StressTensor

Type Bool

Default value No

GUI name Stress tensor

Description Calculate the stress tensor.

The clamped-ion stress tensor σ_α (Voigt notation) is computed via numerical differentiation of the energy E WRT a strain deformations ϵ_α keeping the atomic fractional coordinates constant:

$$\sigma_\alpha = \frac{1}{V_0} \frac{\partial E}{\partial \epsilon_\alpha}\Big|_{\text{constant atomic fractional coordinates}}$$

where V_0 is the volume of the unit cell (for 2D periodic system V_0 is the area of the unit cell, and for 1D periodic system V_0 is the length of the unit cell).

The clamped-ion stress tensor (in Cartesian notation) is written to the engine result file in `AMSResults%StressTensor`.

5.6 Elastic tensor

The elastic tensor $c_{\alpha,\beta}$ (Voigt notation) is computed via second order numerical differentiation of the energy E WRT strain deformations ϵ_α and ϵ_β:

$$c_{\alpha,\beta} = \frac{1}{V_0} \frac{\partial^2 E}{\partial \epsilon_\alpha \partial \epsilon_\beta}$$

where V_0 is the volume of the unit cell (for 2D periodic system V_0 is the area of the unit cell, and for 1D periodic system V_0 is the length of the unit cell).

For each strain deformation $\epsilon_\alpha \epsilon_\beta$, the atomic positions will be optimized. The elastic tensor can be computed for any periodicity, i.e. 1D, 2D and 3D. Computing the elastic tensor will also calculate the bulk modulus, Young's modulus, and shear modulus, as well as the Poisson ratio.

See also:

Example: Elastic tensor (page 479)

To compute the elastic tensor, request it in the `Properties` input block of AMS:

```
Properties
   ElasticTensor Yes/No
End
```

Note: The elastic tensor should be computed at the fully optimized geometry. One should therefore perform a geometry optimization of all degrees of freedom, **including the lattice vectors**. It is recommended to use a tight gradient convergence threshold for the geometry optimization (e.g. Quality "Good"). Note that all this can be done in one job by combining the *geometry optimization task* (page 47) with the elastic tensor calculation.

The elastic tensor (in Voigt notation) is printed to the output file and stored in the *engine result file* (page 19) in the `AMSResults` section (for 3D system, the elastic tensor in Voigt notation is a 6x6 matrix; for 2D systems is a 3x3 matrix; for 1D systems is just one number).

Options for the numerical differentiation procedure can be specified in the `ElasticTensor` input block:

```
ElasticTensor
   ConvergenceQuality [Normal | Good | VeryGood]
   StrainStepSize float
End
```

`ElasticTensor`

Type Block

Description Options for numerical evaluation of the elastic tensor.

`ConvergenceQuality`

Type Multiple Choice

Default value Good

Options [Normal, Good, VeryGood]

GUI name Convergence

Description The tightness of the convergence of the geometry optimizations for each strain deformation. This should not be set higher than the overall convergence quality of the preceeding geometry optimization configured by the `GeometryOptimization%Convergence%Quality` keyword.

StrainStepSize

Type Float

Default value 0.001

Description Step size (relative) of strain deformations used for computing the elastic tensor numerically.

Pressure (page 282) or *non-isotropic external stress* (page 282) can be included in your simulation via the corresponding *engine addons* (page 278).

The elastic tensor calculation supports AMS' *double parallelization* (page 21), which can perform the calculations for the individual displacements in parallel. This is configured automatically, but can be further tweaked using the keys in the `NumericalDifferentiation%Parallel` block:

```
ElasticTensor
   Parallel
      nCoresPerGroup integer
      nGroups integer
      nNodesPerGroup integer
   End
End
```

ElasticTensor

Parallel

Type Block

Description Options for double parallelization, which allows to split the available processor cores into groups working through all the available tasks in parallel, resulting in a better parallel performance. The keys in this block determine how to split the available processor cores into groups working in parallel.

nCoresPerGroup

Type Integer

GUI name Cores per group

Description Number of cores in each working group.

nGroups

Type Integer

GUI name Number of groups

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

nNodesPerGroup

Type Integer

GUI name Nodes per group

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

5.7 Numerical differentiation options

The following options apply whenever AMS computes gradients, Hessians or stress tensors via numerical differentiation.

```
NumericalDifferentiation
   NuclearStepSize float
   StrainStepSize float
End
```

NumericalDifferentiation

Type Block

Description Define options for numerical differentiations, that is the numerical calculation of gradients, Hessian and the stress tensor for periodic systems.

NuclearStepSize

Type Float

Default value 0.005

Unit Bohr

Description Step size for numerical nuclear gradient calculation.

StrainStepSize

Type Float

Default value 0.001

Description Step size (relative) for numerical stress tensor calculation.

AMS may use symmetry (key `NumericalDifferentiation%UseSymmetry`) in case of numerical differentiation calculations. If symmetry is used only symmetry unique atoms are displaced. Symmetry is only recognized if the starting geometry has symmetry. Symmetry is only used for molecules if the molecule has a specific orientation in space, like that the z-axis is the main rotation axis. If the GUI is used one can click the Symmetrize button (the star), such that the GUI will (try to) symmetrize and reorient the molecule. There are some cases that even after such symmetrization, the orientation of the molecule is not what is needed for the symmetry to be used in case of numerical differentiation calculations. If that is the case or if key `NumericalDifferentiation%UseSymmetry` is set to 'False', then no symmetry will be used.

The numerical differentiation calculation supports AMS' *double parallelization* (page 21), which can perform the calculations for the individual displacements in parallel. This is configured automatically, but can be further tweaked using the keys in the `NumericalDifferentiation%Parallel` block:

```
NumericalDifferentiation
   Parallel
      nCoresPerGroup integer
      nGroups integer
      nNodesPerGroup integer
   End
End
```

NumericalDifferentiation

Parallel

Type Block

Description Options for double parallelization, which allows to split the available processor cores into groups working through all the available tasks in parallel, resulting in a better parallel performance. The keys in this block determine how to split the available processor cores into groups working in parallel.

`nCoresPerGroup`

Type Integer

GUI name Cores per group

Description Number of cores in each working group.

`nGroups`

Type Integer

GUI name Number of groups

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

`nNodesPerGroup`

Type Integer

GUI name Nodes per group

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

CHAPTER

SIX

VIBRATIONAL SPECTROSCOPY

6.1 General

The starting point is the Hessian of the system, being the second derivative of the energy with respect to the atomic coordinates.

The eigenvalues of the Hessian are the frequencies and the eigen vectors are the normal modes.

As the calculation of the full Hessian is very expensive there are several ways to avoid it, so that you only get a part of the full spectrum, or only modes for a region of the system, see *IR frequencies and normal modes* (page 209) section.

A full, partial, or approximate Hessian in itself can be useful for a (Hessian-based) geometry optimization or a transition state search.

Vibrational spectra are obtained by differentiating a property along the normal modes at a (local) minimum of the PES. So for spectra you need to optimize the geometry first, otherwise you get negative frequencies.

The Normal modes and or vibrational spectra can be requested via the `Properties` block

```
Properties
   NormalModes Yes/No
   Raman Yes/No
   VROA Yes/No
   VCD Yes/No
   Phonons Yes/No
End
```

When requesting the normal modes, the IR intensities are calculated, as they are very cheap.

See also:

Tutorials on Vibrational Spectroscopy

6.1.1 Where are the results?

Because the results of a vibrational spectroscopy calculation are tied to a particular point on the potential energy surface, they are found on the *engine output files* (page 19). Note also that the properties are not always calculated in every PES point that the AMS driver visits during a calculation. By default they are only calculated in *special* PES points, where the definition of special depends on the *task* (page 45) AMS is performing: For a *geometry optimization* (page 47) properties would for example only be calculated at the final, converged geometry. This behavior can often be modified by keywords special to the particular running task.

6.2 IR frequencies and normal modes

6.2.1 All vibrational Modes

The calculation of the normal modes of vibration can be requested with:

```
Properties
   NormalModes Yes/No
End
```

Typically used icw with *Task SinglePoint* (page 45), *Task GeometryOptimization* (page 47), or *Task TransitionStateSearch* (page 66). In case of geometry optimization or transition state search the normal modes will only be calculated at the final, converged geometry.

Properties

NormalModes

Type Bool

Default value No

GUI name Frequencies

Description Calculate the frequencies and normal modes of vibration, and for molecules also the corresponding IR intensities if the engine supports the calculation of dipole moments.

The molecular normal modes are normally calculated within the harmonic oscillation model. If the molecule is in its equilibrium conformation, it sits in the lowest point (at least locally) on the PES. The cross-section of the PES profile close to this point can then be assumed to be approximately parabolic, such that the second derivative of the energy w.r.t a nuclear coordinate can be interpreted as a force constant for the harmonic oscillation of an atom along this coordinate. Since molecular vibrations in polyatomics involve the simultaneous displacement of multiple atoms, this harmonic oscillator model can be generalized to multiple nuclear coordinates. The normal modes and their frequencies then become eigenvectors and eigenvalues of a force constant matrix, the Hessian:

$$H_{ij} = \frac{\partial^2 E}{\partial R_i \partial R_j}$$

The (non-mass-weighted) Hessian is saved in the engine result file as variable `AMSResults%Hessian`. It is not printed to the text output. The column/row indices are ordered as: x-component of atom 1, y-component of atom 1, z-component of atom 1, x-component of atom 2, etc.

Most *engines* (page 270) cannot calculate the Hessian analytically. Only the ADF engine can calculate the Hessian analytically, however, only for a limited number of XC functionals, see the ADF manual. In case the Hessian is not calculated analytically the Hessian is constructed column-wise through numerical differentiation of the energy gradients w.r.t. each nuclear coordinate. AMS will set up 2 single-point calculations (1 for the positive displacement, 1 for the negative displacement), and the requested engine will return the energy gradients at these displacements. These gradients are calculated analytically for most engines.

Note: Numerical calculation of the full Hessian requires 6N single points calculation, which can take a considerable amount of time for large systems. A mode selective method can be a fast alternative, see *mode scanning* (page 215), *mode refinement* (page 216), and *mode tracking* (page 219).

When requesting the normal modes calculation, integrated IR intensities are simultaneously calculated during the finite differentiation steps when constructing the Hessian (as long as dipole moments are supported by the engine). These IR intensities are calculated from the numerical dipole gradients:

$$I_{IR} = \frac{N\pi}{3c^2} \sum_{\alpha} \left(\sum_{j} \frac{\partial \mu_\alpha}{\partial R_j^m} Q_j^m \right)^2$$

Where α denotes the x-,y- and z-components of the dipole moment μ, and Q^m is the mass-weighted vibrational normal mode.

The resulting IR spectrum can be visualized by opening the engine result file with AMSspectra. The normal modes of vibration and the IR intensities are saved to the *engine result file* (page 19) in the `Vibrations` section.

Note: The calculation of the normal modes of vibration needs to be done the system's equilibrium geometry. So one should either run the normal modes calculation using an already optimized geometry, or combine both steps into one job by using the *geometry optimization task* (page 47) together with the `Properties%NormalModes` keyword.

Symmetry labels of the normal modes may be calculated if AMS uses symmetry in the calculation (key `UseSymmetry`). If symmetry is used, the normal modes are projected against symmetric displacements for each irrep. If that is not successful the symmetry label is 'MIX'. Symmetry is only recognized if the geometry is (almost) perfectly symmetric and has a specific orientation in space. You can use the `Symmetrize` key in the *System block* (page 31) to symmetrize and reorient the molecule. If the AMSinput GUI module is used, one can click the Symmetrize button (the star) and the GUI will try to symmetrize and reorient the molecule. Unless one is an expert user, best is not to specify an explicit symmetry in any part of the input.

Rescanning Imaginary modes

The `ReScanModes` keyword can be used to calculate more accurately frequencies of specific modes after a normal modes calculation. It is identical to the `ScanFreq` option that was available for older versions of ADF and BAND. Primarily used to identify spurious imaginary modes, and is on by default for this purpose. See also the *Mode Scanning* (page 215) task, which is an extension of this method, but which is not on by default. One should not specify an explicit symmetry in any part of the input, otherwise the rescanning of the normal modes might fail.

```
NormalModes
   ReScanModes Yes/No
   ReScanFreqRange float_list
End
```

`NormalModes`

`ReScanModes`

Type Bool

Default value Yes

GUI name Re-scan modes

Description Whether or not to scan imaginary modes after normal modes calculation has concluded.

`ReScanFreqRange`

Type Float List

Default value [-10000000.0, 10.0]

Unit cm-1

Recurring True

GUI name Re-scan range

Description Specifies a frequency range within which all modes will be scanned. 2 numbers: an upper and a lower bound.

6.2.2 Symmetric Displacements

```
NormalModes
   Displacements Symmetric
End
```

Specify `Displacements Symmetric` to calculate the energy Hessian using finite differences in symmetry-adapted displacements, and the corresponding normal modes.

```
NormalModes
   SymmetricDisplacements
      Type [All | Infrared | Raman | InfraredAndRaman]
   End
End
```

If `Type InfraRed` or `Type Raman` is specified then only irreps that result in non-zero intensities for the corresponding spectroscopy will be included in the calculation. Using this feature may save a lot of time for large symmetric molecules by skipping calculation of normal modes that would not contribute to the spectrum anyway. If `Type InfraRedAndRaman` is specified then vibrations that have a non-zero IR or Raman intensity will be calculated. If `Type All` is specified then all vibrations will be calculated. For multi-dimensional irreps (such as E and T) only the first component will be computed. For any component beyond the first, the frequencies and intensities will be copied from the first one.

NormalModes

SymmetricDisplacements

Type Block

Description Configures details of the calculation of the frequencies and normal modes of vibration in symmetric displacements.

Type

Type Multiple Choice

Default value All

Options [All, Infrared, Raman, InfraredAndRaman]

GUI name Symm Frequencies

Description For symmetric molecules it is possible to choose only the modes that have non-zero IR or Raman intensity (or either of them) by symmetry.

In order to calculate the Raman intensities the Raman property must be requested.

Warning: Specifying `Type Raman` alone does not trigger calculation of the Raman intensities. In order to calculate the Raman spectrum one should also specify `Raman True`.

Note: `Displacements Symmetric` will also produce a *3N*-by-*3N* Hessian matrix but if the Type key's argument is not `All` then this matrix will likely have many zero eigenvalues.

6.2.3 Mobile Block Hessian (MBH)

```
NormalModes
   Displacements Block
End
```

Specify `Displacements Block` for the Block Normal Modes option (also known as **Mobile Block Hessian**, or **MBH**[1][2]). MBH is useful when calculating vibrational frequencies of a small part of a very large system (molecule or cluster). Calculation of the full spectrum of such a system may be inefficient and is unnecessary if one is interested in one particular part. Besides, it may be difficult to extract normal modes related to the interesting sub-system out of the whole spectrum. Using Block Normal Modes it is possible to treat parts of the system as rigid blocks. Each block will usually have only six frequencies related to its rigid motions compared to 3*N for when each atom of the block is treated separately.

MBH is suitable to calculate frequencies in partially optimized structures. Assume a geometry optimization is performed with the Block key in the Constraints input block [see constrained geometry optimizations]. During the geometry optimization, the shape of the block is not changed. The internal geometry of the block is kept fixed, but the block as a whole can still translate or rotate.

At the end of such a partial geometry optimization, the position and orientation of the block is optimized, thus the total force on the block is zero. However, there might be still some residual forces within a block, since those degrees of freedom were not optimized. A traditional frequency calculation performed on this partially optimized structure might result in non-physical imaginary frequencies without a clear interpretation. Therefore one should use an adapted formulation of normal mode analysis: the Mobile Block Hessian method. MBH does not consider the internal degrees of freedom of the block (on which residual forces) apply, but instead uses the position/orientation of the block as coordinates. In the resulting normal mode eigenvectors, all atoms within the same block move collectively.

Of course, MBH can also be applied on a fully optimized structure.

Accuracy

```
NormalModes
   BlockDisplacements
      AngularDisplacement float
      BlockAtoms integer_list
      BlockRegion string
      Parallel
         nCoresPerGroup integer
         nGroups integer
         nNodesPerGroup integer
      End
      RadialDisplacement float
   End
End
```

`NormalModes`

`BlockDisplacements`

[1] A. Ghysels, D. Van Neck, V. Van Speybroeck, T. Verstraelen and M. Waroquier, *Vibrational Modes in partially optimized molecular systems*, Journal of Chemical Physics 126, 224102 (2007) (https://doi.org/10.1063/1.2737444)

[2] A. Ghysels, D. Van Neck and M. Waroquier, *Cartesian formulation of the Mobile Block Hessian Approach to vibrational analysis in partially optimized systems*, Journal of Chemical Physics 127, 164108 (2007) (https://doi.org/10.1063/1.2789429)

Type Block

Description Configures details of a Block Normal Modes (a.k.a. Mobile Block Hessian, or MBH) calculation.

`AngularDisplacement`

Type Float

Default value 0.5

Unit Degree

Description Relative step size for rotational degrees of freedom during Block Normal Modes finite difference calculations. It will be scaled with the characteristic block size.

`BlockAtoms`

Type Integer List

Recurring True

Description List of atoms belonging to a block. You can have multiple BlockAtoms.

`BlockRegion`

Type String

Recurring True

Description The region to to be considered a block. You can have multiple BlockRegions, also in combination with BlockAtoms.

`Parallel`

Type Block

Description Configuration for how the individual displacements are calculated in parallel.

`nCoresPerGroup`

Type Integer

Description Number of cores in each working group.

`nGroups`

Type Integer

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

`nNodesPerGroup`

Type Integer

GUI name Cores per task

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

`RadialDisplacement`

Type Float

Default value 0.005

Unit Angstrom

Description Step size for translational degrees of freedom during Block Normal Modes finite difference calculations.

The second derivatives of the energy with respect to Cartesian displacements of the free atoms and those with respect to block motions (3 translation plus 3 rotations) are calculated by numerical differentiation of the gradient. The accuracy of the second derivatives is determined by the accuracy of the gradient evaluation and the step size in the numerical differentiation. The `RadialDisplacement` and `AngularDisplacement` parameters can be specified to set the step size for Cartesian displacements (translations) and block rotations respectively. The step size for angles is automatically scaled with the block size.

Note: Blocks should consist of at least 3 atoms (i.e. block of 1 or 2 atoms are not supported).

6.2.4 Mode Scanning

Mode Scanning can be used to obtain more accurate approximations for properties obtained by numerical differentiation along the vibrational normal modes (frequencies, intensities, Raman, etc.), without changing the modes themselves. Mode Scanning is an extension of the frequency scanning options (`ScanFreq`) that were part of ADF and BAND in earlier versions of the Amsterdam Modeling Suite. These latter options are still available as the `ReScanModes` keyword in the `NormalModes` block, if these are requested during a calculation.

- Primarily used to identify spurious imaginary modes.
- Improve numerical accuracy of normal mode properties.
- Rescanning modes using a different level of theory.

Theory

Vibrational normal modes are usually obtained as eigenvectors of the Hessian matrix. A common problem with this scheme however, is that due to numerical errors in constructing this Hessian, low-frequency vibrations may be reported to have imaginary frequencies instead. The Mode Scanning task allows for re-calculation of the frequency of these modes. The Mode Scanning task does not change the normal modes itself, only its properties. This Mode Scanning task allows you to confirm whether reported imaginary frequencies are attributed to transition states or whether they are simply due to numerical errors.

Given a user-supplied mode Q, the frequency is calculated from the force constant:

$$k = \frac{\partial^2 E}{\partial^2 Q}$$

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu_r}}$$

This is again done by numerical differentiation of the energy gradients, requiring AMS to set up 2 single point calculations per selected normal mode. Integrated IR intensities are also calculated simultaneously (if dipole moments are supported by the *engine* (page 270)):

$$I_{IR} = \frac{N\pi}{3c^2}\sum_{\alpha}\left(\frac{\partial\mu_\alpha}{\partial Q^m}\right)^2$$

Where the derivative is with respect to the mass-weighted normal mode.

It is also possible to use this method to selectively re-calculate the normal mode properties for different engine settings. This has two distinct uses:

- If the modes were originally generated using a finite difference method, a different stepsize can be used. For strong vibrations (high frequencies), large stepsizes may cause inaccuracies due to increasing anharmonic contributions. For weak vibrations (low frequencies) on the other hand, stepsizes can often be too small. The displacements associated with these vibrations are small, which can give incorrect sampling of the PES profile. This should be compensated for by choosing a larger stepsize. The stepsize can be set using the `Displacement` key.
- Users can also recalculate modes using higher levels of theory. Modes generated from a full frequency analysis using e.g. DFTB can be recalculated using e.g. LDA DFT to obtain more realistic integrated IR intensities. The method used for the single point calculations can be set in the *Engine block* (page 270).

Input

A numerical frequency calculation is performed by requesting the `VibrationalAnalysis` task with `Type ModeScanning`:

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type ModeScanning
   Displacement 0.001
   NormalModes
     ModeFile adf.rkf
     # select all modes with imaginary frequencies
     ModeSelect
        ImFreq true
     End
   End
End
```

The Mode Scanning tasks uses only the `NormalModes` block for its input handling. Here, `ModeFile` specifies the AMS output file containing the normal modes for which you want to calculate the frequencies. The `ModeSelect` block is used to specify which of the modes in this file should be recalculated, since we are often only interested in a select few of them. A more detailed overview of this block is given in the section *Selecting Modes* on the *main page* (page 227). Finally, `Displacement` can be used to specify the stepsize (in Bohr) for the finite differences. The stepsize is provided for displacements along the Cartesian normal modes.

The Mode Scanning module is the main driving force for the *Mode Tracking* (page 219) and *Vibrational Mode Refinement* (page 216) tasks, which provide more advanced options for refining not only the properties of the modes, but also the modes themselves. Consult the relevant pages for more information. Alternatively, a simplified version of Mode Scanning is available which follows the old implementation in ADF and BAND (as the `ScanFreq` option). This version can be enabled when doing a full frequency analysis by enabling the `Properties%NormalModes` keyword. See the *Full Analysis* (page 210) page for further details.

6.2.5 Mode Refinement

With this option you can improve the normal modes, by importing previously calculated modes and then applying a more accurate engine, or more accurate settings, typically for only part of the spectrum. The vibrational Mode Refinement method not only refines frequencies from a previous calculation, but also tries to correct the vibrational modes themselves.

- Refinement of spectral regions requires a sufficient number of modes in the basis to be accurate.
- 1-step refinement. No iterative improvement possible. (Unless followed by a separate Mode Tracking calculation.)
- Quality of the results depends on accuracy of the selected guess modes.

If we start from e.g. a semi-empirical method such as in MOPAC, we can get approximations for the vibrational modes. Mode Refinement then re-calculates part of the Hessian for a subset of these modes using a more accurate method such as GGA DFT, and updates the normal modes themselves to fit this more accurate method. It is intended to circumvent the expensive calculation of the Hessian if you are only interested in a (small) part of the full spectrum. This is based on the method in reference[3].

Because the Mode Refinement method uses linear combinations of the guess modes, its accuracy depends on the set of modes that is supplied.

- If we want to e.g. obtain a mode which includes a C=O stretch, then the initial set must contain a mode which has this C=O stretch, otherwise this cannot be included in the refined modes.
- If we are refining a region containing many similar modes, e.g. vibrations of aromatic ring backbones, and we only use part of this spectral region for the initial set, the set of refined modes will "drift" towards the centre of the spectral region as a results of mode-mixing. This is again an artefact of missing character in the modes.
- This mode-mixing may result in reduced accuracy for some of the modes, as this procedure minimizes the total error for all of the modes. Instead of having a couple of modes with large errors, mode-mixing tends to spread out the error across multiple normal modes. Adding 1 "bad" mode to the basis can then negatively affect your results.
- The advantage of Mode Refinement over Mode Tracking is the ability to refine entire spectral regions at once. If we have a good basis, Mode Refinement can be less computationally expensive than Mode Tracking. If you want to refine larger sections of the spectrum, Mode Refinement is therefore recommended. If you only want to calculate a select few modes, use Mode Tracking to avoid basis dependence and to assure accuracy of the obtained modes.
- For characteristic peaks, Mode Tracking shows very good convergence, and will thus be cheaper to use than Mode Refinement. For (semi-)degenerate modes however, Mode Refinement works better due to the poor tracking performance for these modes.

See also:

The GUI tutorial on Mode Refinement.

Theory

We are going to start from a set of normal modes b, obtained from e.g. a semi-empirical or force-field method. First, this task runs the *numerical frequency* (page 215) calculation for all selected normal modes, but this time using an ab initio method such as DFT. During the finite difference steps, we also calculate the projection of the Hessian onto the normal modes:

$$\sigma_i = H^m \cdot b_i^m = \frac{\partial^2 E}{\partial R_i^m \partial b^m}$$

This term is calculated through finite differences on the analytical gradients of the electronic energy along the mass-weighted normal modes b^m. The index i denotes the $3N$ nuclear coordinates. These projections are then used to construct a Rayleigh matrix:

$$\tilde{H}^m = B^{mT} \cdot H^m \cdot B^m = B^{mT} \cdot \Sigma$$

Here, B^m and Σ are matrices containing the b^m and σ vectors. The eigenvectors of $\tilde{H}^m$ give us the coefficient series for linear combinations of the normal modes b^m such that we obtain a new set of modes q:

$$q^m = \sum_k c_k \cdot b_k^m$$

These modes q are the closest approximation to the DFT-modes that we could obtain from a linear combination of the approximate modes b. In other words: the approximate modes b are used as a basis for finding the modes from a more sophisticated theory.

[3] T.Q. Teodoro, M.A.J. Koenis, S.E. Galembeck, V.P. Nicu, W.J. Buma, L. Visscher, *A frequency range selection method for vibrational spectra*, J. Phys. Chem. Lett., 9 (23), 6878 (2018) (https://doi.org/10.1021/acs.jpclett.8b02963)

Input

This method inherently features a trade-off:

- The computational benefit comes from only performing the finite difference calculations for the selected modes. By only selecting a small set of modes that we are interested in, we minimize computational expense.
- The more modes we select, the larger the basis for constructing the refined modes. Running for a larger number of modes yields better results. (In the extreme case, running for all 3N modes equates to constructing the full Hessian.)

In practice, Mode Refinement requires you to select a reasonable portion of the spectrum to get accurate results. Specifically, you should select all modes in a region of the spectrum which look similar. Ring structures for instance often feature broad frequency regions with many ring distortions. Even if you are only interested in a couple of these, you should still select all modes in this region, to assure sufficient basis size. Vibrational modes involving ring substituents can however be omitted, which is where we save computation time.

If you are interested only in IR-active vibrations, you could further minimize the basis by only selecting the approximate modes which are IR-active (since adding the non-active modes to the linear expansion does not affect the IR-intensity of the refined modes). Do note that if the semi-empirical method used for calculating the approximate modes yields poor approximations for the dipole gradients, it may be safer to include also modes with very low IR intensity. This is because their low IR-activity may have only been due to the low accuracy of the approximate method.

See also:

A tutorial showing this basis representability.

A Mode Refinement calculation is set up by requesting the `VibrationalAnalysis` task with the Type `ModeRefinement`:

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type ModeRefinement
   Displacement 0.001
   NormalModes
     ModeSelect adf.rkf
     ModeSelect
        ...
     End
     ScanModes true
   End
End
```

The details of the calculation are specified in the `NormalModes` block. Here, `ModeFile` specifies the AMS output file containing the normal modes for which you want to calculate the frequencies. The `ModeSelect` block is used to specify which of the modes in this file will be selected for refinement. A more detailed overview of this block is given in the section *Selecting modes* on the *main page* (page 227). Finally, `Displacement` can be used to specify the stepsize (in Bohr) for the finite differences. The stepsize is provided for displacements along the Cartesian normal modes.

The `ScanModes` key in the `NormalModes` block can be used to automatically run a *numerical frequencies* (page 215) calculation on the new modes q. Mode Refinement uses a linear combination of modes and properties, all obtained through finite differences. These results may still contain some minor errors due to the accumulation of numerical errors from the linear expansion, or stepsize issues in the numerical frequency calculations. While commonly not necessary, it is possible to run an additional numerical refinement calculation on the new modes to minimize these errors. Only in exceptional cases will these errors be significant. Running this additional refinement step is therefore only necessary if you need complete certainty that the results are accurate.

6.2.6 Mode Tracking

The Mode Tracking task is an interface for mode- and intensity-tracking methods, adapted from the MoViPac suite[4]-[5]. These methods can be used to obtain select normal modes, without having to calculate the entire vibrational spectrum. It does this through an iterative procedure.

- Calculations are conducted for each mode separately. Converges fastest for characteristic (non-highly degenerate) modes.
- Iterative approximation to the true modes. Guaranteed to give the correct normal modes if the procedure converges.
- Will not necessarily reproduce the entire spectrum as multiple guess modes can converge to the same normal mode.

Mode Tracking uses information about the known parts of the Hessian to expand its basis iteratively:

- Missing C-O stretch character can thus be recovered in this procedure, and there is no basis dependency.
- For large regions with similar modes however, it is possible that multiple guess modes converge to the same normal mode. Running mode tracking for all modes in this region might not reproduce all unique normal modes.
- The advantage of Mode Refinement over Mode Tracking is the ability to refine entire spectral regions at once. If we have a good basis, Mode Refinement can be less computationally expensive than Mode Tracking. If you want to refine larger sections of the spectrum, Mode Refinement is therefore recommended. If you only want to calculate a select few modes, use Mode Tracking to avoid basis dependence and to assure accuracy of the obtained modes.
- For characteristic peaks, Mode Tracking shows very good convergence, and will thus be cheaper to use than Mode Refinement. For (semi-)degenerate modes however, Mode Refinement works better due to the poor tracking performance for these modes.

Mode Tracking starts with a *numerical frequency* (page 215) calculation, which refines the initial guess b^m for the selected mode. The error of this mode with respect to the true Hessian eigenvector is calculated. This error is used in a (Jacobi-)Davidson algorithm to generate an additional mode. In subsequent iterations, we use these modes as approximations to the true normal modes. In this way, the error of the mode is minimized iteratively, yielding a closer approximation to true normal modes. This is how Mode Tracking differs from the Mode Refinement methods, in that it guarantees that the obtained modes are correct (assuming the procedure has converged).

See also:

The GUI tutorial on Mode Tracking.

Theory

During the numerical frequency calculation, we obtain also the projection of the Hessian onto this mode:

$$\sigma_i = H^m \cdot b_i^m = \frac{\partial^2 E}{\partial R_i^m \partial b^m}$$

This term is calculated through finite differences on the analytical gradients of the electronic energy along the mass-weighted normal modes q^m. The index i denotes the $3N$ nuclear coordinates. From this projection a Rayleigh matrix is generated:

$$\tilde{H}^m = B^{mT} \cdot \Sigma$$

Here, B^m and Σ are matrices containing the b^m and σ vectors for all foregoing iterations. During each iteration k, if we have not converged, we generate an updated guess vector b_k^m, and so the number of vectors in the matrices above is equal

[4] T. Weymuth, M.P. Haag, K. Kiewisch, S. Luber, S. Schenk, C.R. Jacob, C. Herrmann, J. Neugebauer, M. Reiher, *MoViPac: Vibrational Spectroscopy with a Robust Meta-Program for Massively Parallel Standard Inverse Calculations*, Journal of Computational Chemistry 33, 2186 (2012) (https://doi.org/10.1002/jcc.23036)

[5] S. Luber, J.Neugebauer, M. Reiher, *Intensity tracking for theoretical infrared spectroscopy of large molecules*, Journal of Chemical Physics 130, 064105 (2009) (https://doi.org/10.1063/1.3069834)

to the number of iterations k. The eigenvectors of $\tilde{H}^m$ give us the coefficient series for linear combinations of the guess modes b^m such that we obtain approximations for the true normal modes:

$$Q^m = \sum_k c_k \cdot b_k^m$$

Each iteration, we expand the vector basis B^m, which allows this series expansion to come closer to the true normal modes each time. We can also calculate the error of this mode with respect to how close it is to being an eigenvalue of the real Hessian:

$$r = \sum_k c_k \cdot \left[\sigma_k - \lambda \cdot b_k\right]$$

Here, λ is the corresponding eigenvalue of $\tilde{H}^m$. r is the residual vector, giving the error for each vector element. It should be zero if the mode is an exact eigenvector of the true Hessian.

Since $\tilde{H}^m$ may give multiple eigenvectors, several approximate modes will be generated during those iterations. Out of these, 1 mode is identified as the mode of interest according to the specified *tracking method* (page 223). If the residual of this mode has been minimized sufficiently, the procedure has converged. If not, we generate a new guess vector b_k^m. There are 2 algorithms for generating this new guess, set by `UpdateMethod` in the `ModeTracking` block:

Davidson method

The Davidson method uses a pre-conditioner D to generate a new guess mode from the residual vector of the mode selected by the tracking method:

$$b_k^m = D^{-1} \cdot r$$

This preconditioner is constructed from an approximation of the Hessian:

$$D = H_A - \lambda \cdot I$$

The Davidson method works reasonably well, but can have trouble converging if the approximate modes or the Hessian are too accurate. This results as the new vectors that are generated do not necessarily extend the span of the basis.[6]

vdVorst-Sleijpen-Jacobi-Davidson

This variant of the Jacobi-Davidson scheme from Sleijpen & vdVorst[?] automatically makes the new guess vector orthogonal to the normal mode selected by the tracking method:

$$b_k^m = \left(\frac{Q^m D^{-1} r}{Q^m D^{-1} Q^m}\right) D^{-1} Q^m - D^{-1} r$$

The new vector is therefore guaranteed to extend the span of the basis as much as possible, and thus also eliminates the aforementioned issue with the Davidson method. In general, it is therefore recommended to use this Jacobi-Davidson method since it is found to converge faster, and be more reliable, as a result of yielding better guess modes.

[6] G.L.G. Sleijpen, H.A. van der Vorst, *A Jacobi-Davidson Iteration Method for Linear Eigenvalue Problems*, SIAM Journal on Matrix Analysis and Applications 17, 401 (1996) (https://doi.org/10.1137/S0895479894270427)

Input

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type ModeTracking
   ...
   ModeTracking
      HessianGuess [Unit | File | UFF | Inline]
      HessianInline # Non-standard block. See details.
         ...
      End
      HessianPath string
      UpdateMethod [JD | D | I]
      MaxIterations integer
      ...
      GramSchmidt [True | False]
      GramSchmidtIterations integer
      GramSchmidtTolerance float
   End
End
```

There are 4 methods to obtain the approximate Hessian H_A, used by both update methods. They are set by `HessianGuess`:

`HessianGuess [Unit | File | UFF | Inline]`

`UFF` is the default, which generates the approximate Hessian using UFF. While this Hessian may not yield the correct modes by itself, it produces good results as a preconditioner since it correctly represents the molecular structure.

`File` will read the Hessian from an AMS output file, which can be specified in `HessianPath`. Using a Hessian from a more advanced method will generally yield better results for the Jacobi-Davidson method. The Davidson method will however experience difficulties with convergence as the Hessian becomes too accurate.?

`Inline` will read a Hessian specified in the input file, in the `HessianInline` block. This allows you to use Hessians generated in external programs:

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type ModeTracking
   ModeTracking
     HessianGuess Inline
     # Approximate Hessian for H2O: 3 x nAtoms = 9 so 9x9 Hessian
     HessianInline
         0.62088786   0.00000000   0.00000000  -0.31044393   0.00000000  -0.
↪21902068  -0.31044393   0.00000000   0.21902068
         0.00000000   0.00000000   0.00000000   0.00000000   0.00000000   0.
↪00000000   0.00000000   0.00000000   0.00000000
         0.00000000   0.00000000   0.32143213  -0.15284008   0.00000000  -0.
↪16071607   0.15284008   0.00000000  -0.16071607
        -0.31044393   0.00000000  -0.15284008   0.33598889   0.00000000   0.
↪18593038  -0.02554496   0.00000000  -0.03309030
         0.00000000   0.00000000   0.00000000   0.00000000   0.00000000   0.
↪00000000   0.00000000   0.00000000   0.00000000
        -0.21902068   0.00000000  -0.16071607   0.18593038   0.00000000   0.
↪15761846   0.03309030   0.00000000   0.00309761
        -0.31044393   0.00000000   0.15284008  -0.02554496   0.00000000   0.
↪03309030   0.33598889   0.00000000  -0.18593038
```

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```
        0.00000000   0.00000000   0.00000000   0.00000000   0.00000000   0.
↪00000000   0.00000000   0.00000000   0.00000000
        0.21902068   0.00000000  -0.16071607  -0.03309030   0.00000000   0.
↪00309761  -0.18593038   0.00000000   0.15761846
      End
    End
End
```

Unit uses the unit matrix. This is evidently not a good approximation for the Hessian, and is not intended to be used for proper Mode Tracking runs. However: using a poor approximation for the Hessian can result in basis vectors being generated that we would not obtain otherwise. Running Mode Tracking with this option can allow you to "probe" the vector space to obtain guesses for normal modes, which can be used as starting points for proper Mode Tracking calculations. It is however generally recommended to instead do e.g. a DFTB or UFF run if your goal is to obtain guess modes.

UpdateMethod [JD | D | I]

JD vdVorst-Sleijpen variant of Jacobi-Davidson (Mode tracking default).

D Davidson

I No preconditioner (VST default). This is not recommended for typical mode tracking applications, but is useful for a variation of mode tracking, *Vibronic-Structure Tracking* (page 256).

In later iterations, the basis B^m will become larger. In order to improve the guess modes even further, an iterative Gram-Schmidt procedure is used to orthogonalize the new guess mode to the existing basis. An iterative procedure is necessary to account for numerical noise.

GramSchmidt [True | False] Expert key. Sets whether to perform this Gram-Schmidt orthogonalization step. It is `True` by default.

GramSchmidtTolerance float Expert key. Sets the absolute tolerance for orthogonality of the basis. It is evaluated with respect to the norm of the overlap vector between the new guess mode and the basis of the previous iteration $||b_k^{mT} B^m||$.

GramSchmidtIterations Expert key. Sets the maximum number of allowed iterations during the Gram-Schmidt procedure.

The default settings for the Gram-Schmidt procedure should work for almost all systems.

MaxIterations integer Finally, the Mode Tracking input block contains the `MaxIterations` key. It sets the maximum allowed number of iterations that the Mode Tracking calculation may go through. If this number is reached, the calculation will stop even if convergence was not achieved. If no value is supplied, a default of $3N/2$ will be used. This is approximately the maximum number of iterations where the procedure remains computationally competitive with the construction of the full Hessian.

Additional input parameters

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type ModeTracking
   Displacement float
   ...
   NormalModes
      ScanModes [True | False]
      ...
```

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```
   End
End
```

Displacement float is the displacement stepsize (in Bohr) that is used for calculating frequencies, IR intensities and the Hessian projections through finite differences. The stepsize is provided for displacements along the Cartesian normal modes.

ScanModes [True | False] key (False by default) in the `NormalModes` vibrational analysis sub-block can be used to automatically run a *numerical frequencies* (page 215) calculation on the new modes Q after the Mode Tracking calculation has finished. Ritz vectors are obtained here as linear combinations of the guess modes, which in turn follow from finite difference calculations. This makes it possible for numerical errors to accumulate in the normal modes. Only in exceptional cases will these errors be significant, and running this additional refinement step is therefore only necessary if you need complete certainty that the results are accurate.

Input: Tracking methods

The `TrackingMethod` parameter allows you to select what property of the normal modes you want to track. At the end of each iteration, we obtain a set of approximate normal modes. The tracking method identifies which of these modes fits best for some criterion, and either returns this mode as the calculation result, or, if convergence was not achieved, uses it to generating a new basis mode for the next iteration. In general these methods are distinguished in 3 categories:

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type ModeTracking
   ModeTracking
      TrackingMethod [OverlapInitial, DifferenceInitial, FreqInitial, IRInitial,
                      OverlapPrevious, DifferencePrevious, FreqPrevious, IRPrevious,
                      HighestFreq, HighestIR, LowestFreq, LowestResidual]
      ...
   End
End
```

Mode Tracking

The original tracking methods focus on obtaining as accurate as possible a normal mode for the system. This class of tracking methods focuses either on accuracy of the mode, or obtaining modes with particular vibrational character:

TrackingMethod [OverlapInitial, DifferenceInitial, FreqInitial, OverlapPrevious, Difference

OverlapInitial is the default tracking method. Here, we choose the mode which resembles most closely the guess mode that was initially supplied b_1^m. This is done by choosing the mode which has the greatest overlap with the initial guess vector. This method allows us to direct the optimization towards modes that e.g. involve particular atoms or include particular bending/stretching vibrations.

OverlapPrevious instead chooses the mode which resembles closest the approximate mode of the previous iteration Q_k^m. This procedure allows a bit more flexibility in the optimization. Since we essentially “forget” about earlier iterations, this procedure allows the optimization to correct errors in the initial guess. (It is possible for instance that the initial guess included 2 different bond stretches which do not mutually occur in the true modes. This method will then converge quicker to a mode involving only 1 of these stretches, whereas `OverlapInitial` will take a much larger number of iterations to achieve this, if it does so at all.) Do note that this means that the final mode that you obtain does not necessarily represent the mode you initially supplied.

`DifferenceInitial` works the same as `OverlapInitial`, except that it chooses the mode which has the smallest norm for the difference vector between the initial mode and the approximate normal modes of this iteration. The use of the difference vector prioritizes deviations in the dominant parts of the vibrational character. E.g. if a mode consists primarily of a CO stretch, plus some minor vibrations in a carbon backbone, it may be desired to prioritize getting the correct force constant for the dominant CO stretch. This is achieved using these difference vector methods. In general, overlap methods still work well in these situations, and the use of difference methods should only be necessary in extreme cases.

`DifferencePrevious` is also the same as `DifferenceInitial` except for the use of the difference vector norm as the selection criterion.

`FreqInitial` chooses the mode with the frequency closest to that of the initial guess. This allows us to direct the tracking towards modes in a particular frequency region of the spectrum. Note that convergence for these frequency-based methods is slightly slower since the character of the mode itself is not included in the selection criteria, allowing for larger differences in the modes between iterations.

`FreqPrevious` is similar to `FreqInitial` except that we choose the mode with the frequency closest to that of the previous iteration. This allows the optimization more freedom to move away from the frequency region of the initial guess, and thus allows to correct somewhat for poor initial guesses.

`HighestFreq` chooses the mode with the highest frequency. This method can be used if it is desired to track particular characteristic high-frequency vibrations.

`LowestResidual` chooses the mode which has the smallest norm for the residual vector (see the 'Convergence' section below.) This method only focuses on obtain the most accurate mode, regardless of vibrational character or where it lies in the spectrum. This method should generally only be used as a pre-conditioner if you have very little information on what the normal modes should look like. (Since it is basically a non-directed optimization.) This method will then try and find the normal mode closest to your guess. The approximate normal mode obtained this way will most likely not have converged yet, but should give you an indication of what the normal modes may look like. You can use these modes to refine your initial guess, and then do a new Mode Tracking run using any of the other tracking parameters to obtain the desired mode. Although this strategy is possible, it is generally recommended to use an approximate method to get an initial guess for the normal modes instead (as shown in the *examples* (page 379)).

Intensity Tracking

This class of methods focuses on tracking modes based on their intensity in e.g. the infrared spectrum, rather than focusing on getting a mode with a particular type of vibration.

`TrackingMethod [IRInitial, IRPrevious, HighestIR]` `IRInitial` chooses the mode with the IR intensity closest to that of the initial guess. This constrains the optimization to modes which are IR active, a property that may be lost when using mode tracking update methods.

`IRPrevious` similarly chooses the mode with the IR intensity closest to that of the previous iteration. This allows the method some more flexibility in varying the intensity of the vibration, and thus works better if the initial guess is not that good.

`HighestIR` chooses the mode with the highest IR intensity. This option can be used to find the modes associated with sharp peaks in the IR spectrum.

With Intensity Tracking, we essentially add an additional requirement to the modes: they must have a particular IR intensity. This constrained search has different convergence characteristics than conventional mode tracking, which you should take into account when setting up the mode tracking calculations.

- The majority of modes will have near-zero IR intensity. If we use a near-zero IR intensity mode as our initial guess, and request `IRIntitial` or `IRPrevious`, then we could be tracking any of one of these. Conversely, convergence behavior will be poor since the generated basis modes are essentially random. If you are trying to obtain a high IR-intensity mode, use an IR-susceptible mode.

Note: In our conventional work-flow, we recommend starting mode tracking or refinement calculations from a set of approximate normal modes obtained from a semi-empirical or force-field method. Note however, that these method often do not produce accurate IR intensities. When selecting the initial guess mode, do **not** use the `IRRange` or related options in the `ModeSelect` block. This will cause you to miss vibrations which were incorrectly labeled with low IR intensity, or vice versa. Instead, rely on chemical intuition to identify the modes which contain commonly IR active vibrational components (such as C-O or N-H stretches). You can use AMSspectra in the GUI to visualize the vibrational modes, to help you in this process.

- To allow the intensity tracking procedure to converge faster, it is recommended to use the `IRPrevious` tag instead of the `IRInitial` tag. As discussed earlier, the former allows more flexibility in the optimization procedure, which counters the rigidity imposed by the intensity constraint. Intensity tracking methods often need this additional flexibility in generating guess modes to converge to the desired modes.
- **Poor Initial Guesses:** During each iteration, we still use the mode tracking methods to generate new basis modes. These basis modes try to expand the span of the basis with respect to the vibrational character of the modes. Note that this expansion does not guarantee that we will expand the basis specifically in the sub-span of IR-susceptible vibrations. If the initial guess for intensity tracking is correct, we already start our search in the sub-span vicinity of the normal modes. Basis expansion is then more efficient and there is a high chance that new guess modes sample the IR characteristic vibrations. For intensity tracking it is therefore discouraged to use poor initial guess modes.
- `HighestIR` is considered a "pure" intensity tracking method, in that it is used specifically to target characteristics of the IR spectrum irrespective of the underlying vibrational character. Consequently, the normal mode character can vary a lot between iterations. In order to assure that the procedure converges to the desired modes, it is recommended to use sufficiently strict tolerances (see the *Convergence* section). If the tolerances are too lax, the program may consider the modes to be "good enough" based on residual minimization, even though there may be another mode with a higher IR intensity. For this reason it is generally recommended to use `ToleranceForNorm` values 1 order of magnitude lower than the default, or around `0.00005`.

Input: Selecting modes

It is possible to track multiple modes in a single Mode Tracking calculation. The Mode Tracking task will then run the Mode Tracking algorithm for each mode in order.

The initial guess for the mode which will be tracked can be supplied in several ways. This is governed by `ModeInput-Format`:

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type ModeTracking
   NormalModes
      ModeInputFormat [File | Inline | Hessian]
      ModeFile string
      ModeInline # Non-standard block. See details.
         ...
      End
      ModeSelect
         ...
      End
      MassWeighInlineMode [True | False]
  End
End
```

`ModeInputFormat [File | Inline | Hessian]`

Inline will make the module read the mode from the input file. If this option is selected, you can supply the mode in the `ModeInline` block. It is possible to supply multiple modes by adding additional `ModeInline` blocks. The modes are given with one line for the x,y,z-displacement per atom, and in the same order, as the `Atoms` block in `System`:

```
ModeTracking
   TrackedMode Inline
   ModeInline
       0.00000000   0.00000000   -0.03815965
      -0.18888544   0.00000000    0.30281066
       0.18888544   0.00000000    0.30281066
   End
   ModeInline
       0.00000000   0.00000000   -0.02243153
       0.32132452   0.00000000    0.17800237
      -0.32132452   0.00000000    0.17800237
   End
   ...
End
```

File will make the module read modes from an AMS or engine output file, specified by `ModePath`. Modes generated using DFTB can be read from the `dftb.rkf` file and optimised using Mode Tracking for example. When this option is selected, all the vibrational modes present in the file are read first. The `ModeSelect` block then specifies for which of these modes you want to perform the Mode Tracking calculation.

Hessian will generate modes as the eigenvectors of the approximate Hessian selected for the preconditioner in `HessianGuess`. This also allows modes to be generated for Hessians obtained from external programs. `ModeSelect` specifies which of the generated vibrational modes are selected for Mode Tracking.

- Settings for the `ModeSelect` block are discussed on the *main page* (page 227).

MassWeighInlineMode [True | False] decides whether the initial guess modes need to be mass-weighted (default True). As discussed above, Mode Tracking uses mass-weighted normal modes. In most cases, the normal modes are given in regular Cartesian coordinates however. By setting `MassWeighInlineMode true`, these Cartesian modes are converted into mass-weighted modes by the program. If you supply a mass-weighted mode through the `ModeInline` block however, you do not need the program to do the mass-weighing, and you should set `MassWeighInlineMode false`.

Input: Convergence

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type ModeTracking
   ModeTracking
      ToleranceForNorm float
      ToleranceForResidual float
      ToleranceForBasis float
   End
End
```

In order to guide the Mode Tracking procedure, several convergence criteria are used:

ToleranceForNorm float is the absolute tolerance for convergence of the norm of the residual vector. The residual vector is a vector containing the error for each element of the normal mode, and we use the norm as a measure for the total error. If the total error is smaller than this threshold, we consider the mode to be a true normal mode and we stop iterating. Since the value of this norm depends on the length of the residual vector hence the number of atoms in the system, this tolerance is scaled internally to the number of atoms. `0.0005` is used as a default value for which most systems will converge to reasonably accurate modes in not too many iterations. If you want a more accurate approximation, you can decrease this value by e.g. 1 order of magnitude. (Consider running using the default settings, and reading the norm at convergence from the logfile. The new norm can be chosen to be lower than this value to 'force' the method into another iteration.)

ToleranceForResidual float is the absolute tolerance for the maximum component of the residual vector. Particularly in larger systems, where the vibration may be dominated by a small number of atoms, the error associated with the vibration of the majority of atoms may be small (the scaled residual norm will be small). The error for the atoms involved in the vibration may be comparatively large then, which is why we also check convergence for the maximum component of the error. Note that both the norm and this max. error are checked simultaneously. By varying strictness of the criteria for the norm and the max. error separately, you can prioritize either the total vibration or more localized character.

ToleranceForBasis float checks that the basis mode generated in the previous iteration, through the (Jacobi-)Davidson method, contributes to the approximate normal mode. Since the approximate mode is taken as a linear combination of the basis modes, its linear expansion coefficient must be larger than this tolerance.

The iterative procedure is stopped in one of two cases. Either both the residual criteria are achieved, in which case the mode is deemed to be converged and the program exits normally. Alternatively, the basis criterion is met in which case a warning is broadcast indicating that the desired level of accuracy of the mode may not have been reachd yet, but the basis has stopped expanding. The default values for these parameters should be applicable for most cases, but can be adjusted if needed. If stricter criteria are required, it is recommended to adjust both `ToleranceForNorm` and `ToleranceForResidual`.

6.2.7 Selecting modes

Mode Scanning, Mode Refinement and Mode Tracking as well as VG-FC Vibronic-Structure, VG-FC Vibronic-Structure Refinement and VG-FC resonance Raman all require a set of normal modes to operate on. For Mode Scanning these are the modes that you want to calculate the properties of, for Mode Refinement these modes form the basis modes, and for Mode Tracking these are the initial guess modes. For the VG-FC based methods these modes are the modes responsible for the vibronic coupling to the electronic excitation (in VG-FC Vibronic-Structure Refinement they are refined first).

Note: VG-FC Vibronic-Structure Tracking does not require any normal modes and as such does not support the `ModeSelect` (nor does it support the `NormalModes` block for that matter).

These methods provide options to load a large set of modes, after which the program will filter out the modes of interest. This is done according to the keys set in the `ModeSelect` block.

Note: The `ModeSelect` block is part of the `NormalModes` block of the Vibrational Analysis input. All Vibrational Analysis methods share this block, with the exception of VG-FC Vibronic-Structure Tracking. The methods for obtaining the set of modes that we will filter can differ per method. Particularly Mode Tracking features a lot of additional options, and the vibronic variants feature more specialized options.

Below is an overview of all the available options for the `ModeSelect` block as they appear in the basic vibrational analysis tools. The vibronic variants are discussed in more detail on their respective documentation pages.

The options below are not mutually exclusive.

```
ModeSelect
   DisplacementBound float
   FreqAndIRRange float_list
   FreqRange float_list
   Full Yes/No
```

(continues on next page)

(continued from previous page)

```
   HighFreq integer
   HighIR integer
   IRRange float_list
   ImFreq Yes/No
   LargestDisplacement integer
   LowFreq integer
   LowFreqNoIm integer
   LowIR integer
   ModeNumber integer_list
End
```

ModeSelect

DisplacementBound

Type Float

Description Vibronic Structure (Refinement), Resonance Raman: Select all modes with a dimensionless oscillator displacement greater than the specified value.

FreqAndIRRange

Type Float List

Recurring True

Description Specifies a combined frequency and IR intensity range within which all modes will be selected. First 2 numbers are the frequency range in cm-1, last 2 numbers are the IR intensity range in km/mol.

FreqRange

Type Float List

Unit cm-1

Recurring True

Description Specifies a frequency range within which all modes will be selected. 2 numbers: an upper and a lower bound. Calculating all modes higher than some frequency can be achieved by making the upper bound very large.

Full

Type Bool

Default value No

GUI name All modes

Description Select all modes. This only make sense for Mode Scanning calculations.

HighFreq

Type Integer

GUI name # High frequencies

Description Select the N modes with the highest frequencies.

HighIR

Type Integer

GUI name # High IR

Description Select the N modes with the largest IR intensities.

`IRRange`

Type Float List

Unit km/mol

Recurring True

Description Specifies an IR intensity range within which all modes will be selected. 2 numbers: an upper and a lower bound.

`ImFreq`

Type Bool

Default value No

GUI name All imaginary frequencies

Description Select all modes with imaginary frequencies.

`LargestDisplacement`

Type Integer

Description Vibronic Structure (Refinement), Resonance Raman: Select the N modes with the largest VG-FC displacement.

`LowFreq`

Type Integer

GUI name # Low frequencies

Description Select the N modes with the lowest frequencies. Includes imaginary modes which are recorded with negative frequencies.

`LowFreqNoIm`

Type Integer

GUI name # Low positive frequencies

Description Select the N modes with the lowest non-negative frequencies. Imaginary modes have negative frequencies and are thus omitted here.

`LowIR`

Type Integer

GUI name # Low IR

Description Select the N modes with the smallest IR intensities.

`ModeNumber`

Type Integer List

GUI name Mode numbers

Description Indices of the modes to select.

6.2.8 Thermodynamics (ideal gas)

The following thermodynamic properties are calculated by default whenever normal modes are computed: entropy, internal energy, constant volume heat capacity, enthalpy and Gibbs free energy. Translational, rotational and vibrational contributions are calculated for entropy, internal energy and constant volume heat capacity.

The results are written to the output file (section: "Statistical Thermal Analysis") and to the engine binary results file (section: "Thermodynamics").

The thermodynamic properties are computed assuming an ideal gas, and electronic contributions are ignored. The latter is a serious omission if the electronic configuration is (almost) degenerate, but the effect is small whenever the energy difference with the next state is large compared to the vibrational frequencies. The thermal analysis is based on the temperature dependent partition function. The energy of a (non-linear) molecule is (if the energy is measured from the zero-point energy)

$$\frac{E}{NkT} = \frac{3}{2} + \frac{3}{2} + \sum_{j}^{3N-6} \left(\frac{h\nu_j}{2kT} + \frac{h\nu_j}{kT(e^{h\nu_j/(kT)} - 1)} \right) - \frac{D}{kT}$$

The summation is over all harmonic ν_j, h is Planck's constant and D is the dissociation energy

$$D = D_0 + \sum_j \frac{h\nu_j}{2}$$

Contributions from low (less than 20 1/cm) frequencies to entropy, heat capacity and internal energy are excluded from the total values, but they are listed separately (so the user can add them if they wish).

As an alternative to outright excluding low-frequency contributions, a correction scheme is available that is based on interpolating between harmonic oscillator and free rotor values[7][8] (Li/Head-Gordon and Grimme). It can greatly reduce the impact of the inaccuracies of the harmonic oscillator model on thermodynamic properties at these low frequencies. The scheme corrects vibrational contributions to entropies, internal energies and constant volume heat capacities. This correction is applied automatically and its results are printed separately (in the text output, the corrected terms are marked with the symbol `(c)`). When applied, the correction considers all real frequencies, including those less than 20 1/cm.

The interpolation for a corrected thermodynamic property f at pressure p and temperature T in terms of harmonic oscillator terms f_{HO}, free rotor terms f_{FR}, and interpolator terms x for each harmonic oscillator frequency ν_j is:

$$f\left(p,T\right) = \sum_j x\left(\nu_j\right) \cdot f_{HO}\left(p,T,\nu_j\right) + \left(1 - x\left(\nu_j\right)\right) \cdot f_{FR}\left(p,T,\nu_j\right)$$

$$x\left(\nu_j\right) = \frac{1}{1 + \left(\frac{\nu_0}{\nu_j}\right)^{\alpha}}$$

Where α is an arbitrary exponent and ν_0 is the harmonic oscillator frequency around which x interpolates, with $x = 0.5$ when $\nu_j = \nu_0$ and $x \approx 1.0$ when $\nu_j \gg \nu_0$.

While the free rotor terms used for internal energies and heat capacities are the standard ones, the terms used for entropies have to use the rotors' moments of inertia μ_{FR} and symmetry σ, which formally cannot be calculated from harmonic frequencies alone. The correction scheme instead estimates each moment of inertia as being of a $\sigma = 1$ free rotor whose first excited state has an energy equal to the given $h\nu_j$. After this, each obtained moment of inertia μ_{FR} is modified by an averaging moment of inertia μ_{av} to avoid grossly overestimating entropies at very small frequencies (less than around 1 1/cm):

$$\mu = \frac{\mu_{FR} \cdot \mu_{av}}{\mu_{FR} + \mu_{av}}$$

Input options

[7] Yi-Pei Li, Joseph Gomes, Shaama Mallikarjun Sharada, Alexis T. Bell, Martin Head-Gordon, *Improved Force-Field Parameters for QM/MM Simulations of the Energies of Adsorption for Molecules in Zeolites and a Free Rotor Correction to the Rigid Rotor Harmonic Oscillator Model for Adsorption Enthalpies*, J. Phys. Chem. C 2015, 119, 4, 1840-1850 (https://doi.org/10.1021/jp509921r)

[8] Stefan Grimme, *Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory*, Chem. Eur. J., 18: 9955-9964 (https://doi.org/10.1002/chem.201200497)

```
Thermo
   Temperatures float_list
   Pressure float
   LowFrequencyCorrector
      Alpha float
      Frequency float
      MomentOfInertia float
   End
End
```

Thermo

Type Block

Description Options for thermodynamic properties (assuming an ideal gas). The properties are computed for all specified temperatures.

Temperatures

Type Float List

Default value [298.15]

Unit Kelvin

Value Range value >= 0

Description List of temperatures at which the thermodynamic properties will be calculated.

Pressure

Type Float

Default value 1.0

Unit atm

Description The pressure at which the thermodynamic properties are computed.

LowFrequencyCorrector

Type Block

Description Options for the dampener-powered free rotor interpolator that corrects thermodynamic quantities for low frequencies. See DOI:10.1021/jp509921r and DOI:10.1002/chem.201200497.

Alpha

Type Float

Default value 4.0

Description The exponent term used in the dampener.

Frequency

Type Float

Default value 100.0

Unit cm-1

Description The frequency around which the dampener interpolates between harmonic oscillator and free rotor quantities.

MomentOfInertia

Type Float

Default value 1e-44

Unit kg m^2

GUI name Averaging Moment of Inertia

Description The moment of inertia used to restrict entropy results for very small frequencies (generally around less than 1 cm-1).

Gibbs free energy change for a gas phase reaction

Here an example is given how to calculate the free energy change for a reaction. In the AMS output of a normal modes calculation you can find the electronic bonding energy and nuclear kinetic energies, at room temperature. Example part of the AMS output of a nonlinear molecule:

```
Zero-point energy (Hartree):     0.0333

...
...

Temp                                                        Transl      Rotat     ␣
↪Vibrat     Total
----                                                        ------      -----      ----
↪--     -----

298.15   Entropy (cal/mol-K):                              34.441     11.474      0.
↪137     46.052
         Nuclear Internal Energy (kcal/mol):                0.889      0.889     20.
↪941     22.718
         Constant Volume Heat Capacity (cal/mol-K):         2.981      2.981      0.
↪565      6.526

 Summary of energy terms
                                                  hartree             eV          kcal/
↪mol           kJ/mol
                                 --------------------     -----------      ----------
↪      -----------
 Energy from Engine:               -0.743995039793930        -20.2451            -466.
↪86         -1953.36
 Nuclear Internal Energy:           0.036203917534227          0.9852              22.
↪72            95.05
 Internal Energy U:                -0.707791122259703        -19.2599            -444.
↪14         -1858.31
 pV/n = RT:                         0.000944186013486          0.0257               0.
↪59             2.48
 Enthalpy H:                       -0.706846936246217        -19.2343            -443.
↪55         -1855.83
 -T*S:                             -0.021880868282982         -0.5954             -13.
↪73           -57.45
 Gibbs free energy:                -0.728727804529199        -19.8297            -457.
↪28         -1913.27
```

The Energy from Engine = -466.86 kcal/mol. It depends on the engine how this energy is calculated. In the ADF and BAND engines the energy is normally calculated with respect to (artificial) spherical averaged neutral atoms.

The Nuclear Internal Energy = zero point energy + 3 kT + small correction term = 22.72 kcal/mol. 3 kT = 3/2 kT for rotation, and 3/2 kT for translation (i.e. 1/2 kT for each degree of freedom). The small correction term is a term due to the vibration partition function, depending on the temperature not only the ground state vibrational levels are occupied, see also the previous discussion.

The Internal Energy U = Energy from Engine + Nuclear Internal Energy = -466.86 + 22.72 = -444.14 kcal/mol. Gas phase pV/n = RT = 8.314472 * 298.15 / 4184 = 0.59 kcal/mol. The enthalpy H = U + pV = -444.14 + 0.59 = -443.55 kcal/mol. The Gibbs free energy G = H - TS = -443.55 - 298.15*46.052/1000 = -457.28 kcal/mol.

For a calculation of the free energy change for reaction (Δ G), you will have to do this for the reactant and product molecules, and add and subtract these energies, for each molecule proportional to the number of molecules that take place in the reaction. Application of ADF for obtaining enthalpy, entropy and Gibbs free energy can for instance be obtained in Refs.[9][10].

6.2.9 Moments of inertia

In case normal modes are computed in AMS, AMS also reports the moments of inertia of the molecule in units of amu bohr^2 (amu = atomic mass unit) and its corresponding principal axes.

6.2.10 Partial Vibrational Spectra (PVDOS)

The Partial Vibrational Spectra (also known as PVDOS) is computed by default whenever normal modes are requested. The PVDOS $P_{I,n}$ for atom I and normal mode n is defined as:

$$P_{I,n} = \frac{m_I |\vec{\eta}_{I,n}|^2}{\sum_J m_J |\vec{\eta}_{J,n}|^2}$$

where m_I is the nuclear weight of atom I, and $\vec{\eta}_{I,n}$ is the displacement vector for atom I in normal normal mode n.

Tip: The Partial Vibrational Spectra (PVDOS) can be visualized using the **AMSspectra** GUI module (**Vibrations → Partial Vibrational Spectra (PVDOS)**). When plotting a partial vibrational spectrum, the IR intensity of normal modes is scaled by the corresponding PVDOS of the selected atoms.

The PVDOS matrix is not printed to the text output, but only saved to the engine binary output (.rkf) in the variable `Vibrations%PVDOS`.

6.3 Phonons

Collective oscillations of atoms around theirs equilibrium positions, giving rise to lattice vibrations, are called phonons. AMS can calculate phonon dispersion curves within standard harmonic theory, implemented with a finite difference method. Within the harmonic approximation we can calculate the partition function and therefore thermodynamic properties, such as the specific heat and the free energy.

See also:

Example: Phonons for graphene (page 475), *Example: Phonons with isotopes* (page 476), *Example: User-defined Brillouin zone for phonon dispersion* (page 478) and silicon lattice optimization and phonons tutorial

The calculation of phonons is enabled in the `Properties` block.

[9] M. Swart, E. Rösler, and F. M. Bickelhaupt, *Proton affinities of maingroup-element hydrides and noble gases: Trends across the periodic table, structural effects, and DFT validation*, Journal of Computational Chemistry 27, 1486 (2006) (https://doi.org/10.1002/jcc.20431)

[10] M. Swart, and F. M. Bickelhaupt, *Proton Affinities of Anionic Bases: Trends Across the Periodic Table, Structural Effects, and DFT Validation*, Journal of Chemical Theory and Computation 2, 281 (2006) (https://doi.org/10.1021/ct0502460).

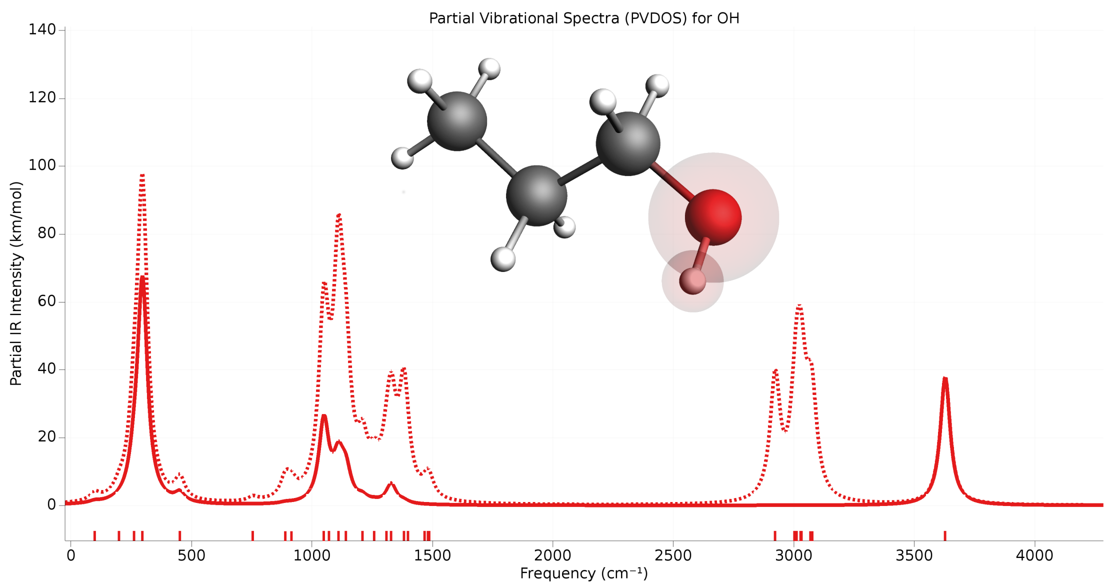

Fig. 6.1: Example of partial vibrational spectrum (PVDOS). The dotted line is the full IR spectrum of 1-propanol. The solid line is the PVDOS-scaled IR spectrum of the OH group (IR spectrum computed using GFN1-xTB).

```
Properties
   Phonons Yes/No
End
```

Note: Phonon calculations should be performed on optimized geometries, **including the lattice vectors**. This can be done by either using an already optimized system as input, or by combining the phonon calculation with the *geometry optimization task* (page 47) (you should set the `GeometryOptimization%OptimizeLattice` input option to `True`).

The details of the phonon calculations are configured in the `NumericalPhonons` block:

```
NumericalPhonons
   SuperCell # Non-standard block. See details.
      ...
   End
   StepSize float
   DoubleSided Yes/No
   Interpolation integer
   NDosEnergies integer
   AutomaticBZPath Yes/No
   BZPath
      Path # Non-standard block. See details.
         ...
      End
   End
   Parallel
      nCoresPerGroup integer
      nGroups integer
      nNodesPerGroup integer
   End
```

(continues on next page)

(continued from previous page)

```
End
```

NumericalPhonons

SuperCell

Type Non-standard block

Description Used for the phonon run. The super lattice is expressed in the lattice vectors. Most people will find a diagonal matrix easiest to understand.

The most important setting here is the super cell transformation. In principle this should be as large as possible, as the phonon bandstructure converges with the size of the super cell. In practice one may want to start with a 2x2x2 cell and increase the size of the super cell until the phonon band structure converges:

```
NumericalPhonons
   SuperCell
      2 0 0
      0 2 0
      0 0 2
   End
End
```

By default the phonon dispersion curves are computed for the standard path though the Brillouin zone (see https://doi.org/10.1016/j.commatsci.2010.05.010). One can request the a different path using the following keywords (for an example of how to specify a user-defined path see *Example: User-defined Brillouin zone for phonon dispersion* (page 478)):

```
NumericalPhonons
   AutomaticBZPath Yes/No
   BZPath
      Path # Non-standard block. See details.
         ...
      End
   End
End
```

NumericalPhonons

AutomaticBZPath

Type Bool

Default value Yes

GUI name Automatic BZ path

Description If True, compute the phonon dispersion curve for the standard path through the Brillouin zone. If False, you must specify your custom path in the [BZPath] block.

BZPath

Type Block

Description If [NumericalPhonons%AutomaticBZPath] is false, the phonon dispersion curve will be computed for the user-defined path in the [BZPath] block. You should define the vertices of your path in fractional coordinates (with respect to the reciprocal lattice vectors) in the [Path] sub-block. If you want to make a jump in your path (i.e. have a discontinuous path), you need to specify a new [Path] sub-block.

Path

Type Non-standard block

Recurring True

Description A section of a k space path. This block should contain multiple lines, and in each line you should specify one vertex of the path in fractional coordinates. Optionally, you can add text labels for your vertices at the end of each line.

Other keywords in the `NumericalPhonons` block modify the details of the numerical differentiation procedure and the accuracy of the results:

`NumericalPhonons`

`StepSize`

Type Float

Default value 0.04

Unit Angstrom

Description Step size to be taken to obtain the force constants (second derivative) from the analytical gradients numerically.

`DoubleSided`

Type Bool

Default value Yes

Description By default a two-sided (or quadratic) numerical differentiation of the nuclear gradients is used. Using a single-sided (or linear) numerical differentiation is computationally faster but much less accurate. Note: In older versions of the program only the single-sided option was available.

`Interpolation`

Type Integer

Default value 100

Description Use interpolation to generate smooth phonon plots.

`NDosEnergies`

Type Integer

Default value 1000

Description Nr. of energies used to calculate the phonon DOS used to integrate thermodynamic properties. For fast compute engines this may become time limiting and smaller values can be tried.

The numerical phonon calculation supports AMS' *double parallelization* (page 21), which can perform the calculations for the individual displacements in parallel. This is configured automatically, but can be further tweaked using the keys in the `NumericalPhonons%Parallel` block:

```
NumericalPhonons
   Parallel
      nCoresPerGroup integer
      nGroups integer
      nNodesPerGroup integer
   End
End
```

`NumericalPhonons`

Parallel

Type Block

Description Options for double parallelization, which allows to split the available processor cores into groups working through all the available tasks in parallel, resulting in a better parallel performance. The keys in this block determine how to split the available processor cores into groups working in parallel.

nCoresPerGroup

Type Integer

GUI name Cores per group

Description Number of cores in each working group.

nGroups

Type Integer

GUI name Number of groups

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

nNodesPerGroup

Type Integer

GUI name Nodes per group

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

6.4 (Resonance) Raman

6.4.1 Raman

In this method the Raman scattering spectrum is calculated from the geometrical derivatives of the frequency-dependent polarizability. Engine ADF is required. Raman scattering intensities and depolarization ratios for all or a selected number of molecular vibrations at a certain laser frequency can be calculated. The Raman scattering calculation is very similar to an IR intensity calculation. In fact, all IR output is automatically generated as well. At all distorted geometries the dipole polarizability tensor is calculated. This is time-consuming and is only feasible for small molecules.

```
Properties
   Raman Yes/No
End
```

```
Raman
   IncidentFrequency float
   FreqRange float_list
End
```

If a `FreqRange` is included the Raman intensities are calculated for a range of vibrational frequencies only. Using this option is a fast alternative for calculating all Raman intensities.

Note that in order to change the nuclear step size that is used in calculating the numerical derivative of the polarizability in case of `FreqRange` one should use `VibrationalAnalysis%Displacement` and `NumericalDiffer-`

`entiation%NuclearStepSize` otherwise. A larger value for the nuclear step size may be needed since it is harder to calculate the polarizability with enough precision than, for example, the dipole moment.

Properties

Raman

Type Bool

Default value No

Description Requests calculation of Raman intensities for vibrational normal modes.

Raman

IncidentFrequency

Type Float

Default value 0.0

Unit eV

Description Frequency of incident light.

FreqRange

Type Float List

Unit cm-1

Recurring True

GUI name Frequency range

Description Specifies a frequency range within which all modes will be scanned. 2 numbers: an upper and a lower bound.

6.4.2 Resonance Raman: excited-state finite lifetime

Resonance Raman spectroscopy uses incident light with a wavelength close to that of an electronic transition. In this method (Ref.[11]) the resonance Raman-scattering (RRS) spectra is calculated from the geometrical derivatives of the frequency-dependent polarizability. Engine ADF is required. The polarizability derivatives are calculated from resonance polarizabilities by including a finite lifetime (phenomenological parameter) of the electronic excited states.

```
Raman
   FreqRange float_list
   IncidentFrequency float
   LifeTime float
End
```

Raman

FreqRange

Type Float List

Unit cm-1

Recurring True

GUI name Frequency range

[11] L. Jensen, L. Zhao, J. Autschbach and G.C. Schatz, *Theory and method for calculating resonance Raman scattering from resonance polarizability derivatives*, Journal of Chemical Physics 123, 174110 (2005) (https://doi.org/10.1063/1.2046670)

Description Specifies a frequency range within which all modes will be scanned. 2 numbers: an upper and a lower bound.

`IncidentFrequency`

Type Float

Default value 0.0

Unit eV

Description Frequency of incident light.

`LifeTime`

Type Float

Default value 0.0

Unit hartree

Description Specify the resonance peak width (damping) in Hartree units. Typically the lifetime of the excited states is approximated with a common phenomenological damping parameter. Values are best obtained by fitting absorption data for the molecule, however, the values do not vary a lot between similar molecules, so it is not hard to estimate values. A typical value is 0.004 Hartree.

It is similar to the simple excited-state gradient approximation method (see next section) if only one electronic excited state is important, however, it is not restricted to only one electronic excited state. In the limit that there is only one possible state in resonance the two methods should give more or less the same results. However, for many states and high-energy states and to get resonance Raman profiles (i.e., Raman intensities as a function of the energy of the incident light beam) this approach might be more suitable. The resonance Raman profiles in this approach are averaged profiles since vibronic coupling effects are not accounted for.

6.4.3 Resonance Raman: VG-FC

According to a the time-dependent picture of resonance-Raman (RR) scattering the relative intensities of RR scattering cross sections are, under certain assumptions, proportional to the square of the excited-state energy gradients projected onto the ground-state normal modes of the molecule (see Ref.[12]). For an alternative implementation of RR scattering using a finite lifetime of the excited states, and a discussion of some of the differences, see the previous section. Engine ADF or DFTB is required.

The vertical gradient Franck-Condon (VG-FC) method, also called the Independent Mode Displaced Harmonic Oscillator (IMDHO) model, we use to calculate vibrationally resolved absorption spectra can also be applied to the calculation of resonance Raman spectra. In resonance Raman spectroscopy a molecule is excited from its ground state to some electronically excited state. After a short period of time, the molecule then relaxes back to its electronic ground state. However, when doing so, it might end up in a different vibrational state than it started off in. The result is an energy difference between the incident and emmitted photon. One can then plot the intensity for different energy differences to produce what is known as a Raman spectra. Resonance Raman spectroscopy uses incident light with a wavelength close to that of an electronic transition.

AMS supports the calculation of such spectra by modeling the vibronic coupling of electronic transitions using the VG-FC model. This model is discussed also on the *Vibronic-Structure* (page 254) documentation page. Here we will discuss the modifications necessary to use the VG-FC model for resonance Raman spectroscopy. It is worth noting that this VG-FC resonance Raman application does not support the mode selective options. As a result the VG-FC Resonance Raman application will always first perform a full frequency analysis to obtain its normal modes.

[12] J. Neugebauer, E.J. Baerends, E. Efremov, F. Ariese and C. Gooijer, *Combined Theoretical and Experimental Deep-UV Resonance Raman Studies of Substituted Pyrenes*, Journal of Physical Chemistry A 109, 2100 (2005) (https://doi.org/10.1021/jp045360d)

Theory

While the basic theory behind the VG-FC model is explained in detail on the *Vibronic-Structure* (page 254) documentation page, we will briefly summarize the most important points here, as well as the modifications necessary for its application to resonance Raman spectroscopy. It applies the harmonic approximation to both the ground state and excited state PES and then goes on to assume that neither frequency changes nor normal mode rotations occur. Thus the excited state PES is a shifted version of the ground state PES. We do not include temperature effects (so all initial states will be ground states) and work at the Franck-Condon point. Under these assumptions, the Raman polarizability of a particular excited state n, for a transition between initial and final vibrational states I and F can be written as:

$$(\alpha_{n,ij})_{F\leftarrow I} = \mu_{n,i}\mu_{n,j}\int_0^\infty \langle F|I_n(t)\rangle e^{i[\omega-(E_{n,0}-E_{m,0})]t}\cdot e^{-\Gamma t}dt$$

Here, i, j label the components of the polarizability tensor and $\langle F|I_n(t)\rangle$ denotes the overlap of the initial state I, propagated along the excited state PES with the final state F. Under the *assumptions of the VG-FC model* (page 244), this overlap is equal to:

$$\langle F|I_n(t)\rangle = \prod_{j=1}^{N_{modes}}\left\{\frac{(-1)^{m_j}\Delta^{m_j}}{2^{m_j/2}m_j!}(1-e^{-i\omega_j t})^{m_j}\right\}\exp\left[-\frac{\Delta_{n,j}^2}{2}(1-e^{-i\omega_j t})\right]$$

Where the m_j denote the excitation number of mode j in final state F. For a more detailed discussion, we refer to[13]. The only parameters that appear in our expression are the dimensionless oscillator displacements $\Delta_{n,j}$ that represent displacement of the excited state PES along normal mode j. Under the simplifying assumptions of the VG-FC, these can be obtained from the ground state normal modes and a single excited state gradient. The Raman intensity is then proportional to the square of the polarizabilities:

$$\sigma(\omega)_{F\leftarrow I}\propto\sum_{i,j}|\sum_n(\alpha_{n,ij})_{F\leftarrow I}|^2$$

A spectrum is then generated by including various different final states F, which are defined by different combinations of normal mode excitation numbers, and assigning a relative intensity to each transition equal to the above expression. AMS only supports spectra which display relative intensities so the results are plotted in arbitrary units and are normalized such that the largest peak reaches an intensity of 1.

Input

The calculation setup for resonance Raman spectra largely proceeds as it does for *Absorption Spectra* (page 254). We need a set of ground state normal modes as well as an excited state gradient. The former are calculated at the start using the selected AMS engine, or, in case the user has a pre-calculated set of normal modes, these can be read from a .rkf file using the `ModeFile` key in the `NormalModes` sub-block. In this latter case, the engine is not used. The `ModeSelect` block can be used to select specific modes from the full set of normal modes for which the spectrum should be calculated. For details see the *Mode Select* (page 227) documentation on the main page. If one simply wants the spectrum for the full set of normal modes, the `Full` key in the `ModeSelect` block can be set to `True`. The excited state information is passed to the application via the `ExcitationSettings` block.

Another point to note is that since our states are labeled by discrete indices we will be calculating stick spectra (which can be homogeneously broadened in amsspectra). By contrast, the absorption spectra produced by `VibronicStructure` are raw x,y data. Due to this difference in nature of the Raman spectrum compared to the absorption spectrum, this method uses the `ResonanceRaman` block for input options related to its spectrum (as opposed to the `Absorption-Spectrum` block).

The `ExcitationSettings` block is discussed on the *Vibronic-Structure* (page 261) page. One important difference with the latter is that Resonance Raman calculations are supported for more than one excitation at once. This is more

[13] T. Petrenko and F. Neese, *Analysis and prediction of absorption band shapes, fluorescence band shapes, resonance Raman intensities, and excitation profiles using the time-dependent theory of electronic spectroscopy* The Journal of Chemical Physics 127, 164319 (2007) (https://doi.org/10.1063/1.2770706)

important for the case of Raman spectra as the intensity associated with a set of transitions is not equal to the sum of their individual intensities (we sum over electronic states n before we square the polarizabilities). Here we will address settings specific to the Raman spectrum, all of which can be found in the `ResonanceRaman` block. A short example of how a typical input file might look is included at the end of this section.

```
Task VibrationalAnalysis
VibrationalAnalysis
   Task ResonanceRaman
   ResonanceRaman
      IncidentFrequency float
      LifeTime float
      RamanOrder integer
      RamanRange float_list
      MaximumStates integer
   End
   ...
End
```

IncidentFrequency float Frequency of incident light.

LifeTime float sets the value of Γ (in Hartree) that controls the exponential damping in our integral. This phenomenological parameter can be interpreted as the (inverse) life time of the Raman excited state and can be used to help the results agree with experiment. The default value of 4.5e-4 is on the low end of reasonable values but should provide a good starting point for most cases.

RamanOrder integer determines the set of final states and overtones to be included in the spectrum. It is an integer and the application considers only final states such that the sum of excitation numbers of all normal modes is less than or equal to this number. Setting this to 1 means we only include the fundamental band.

RamanRange float_list this keyword specifies the frequency range (in cm^{-1}) the Raman shift is restricted to lie in. This prevents us from including excessively many states and overtones for high frequency modes. The default is [0, 2000] cm^{-1} but this can be changed to whatever is desired.

MaximumStates integer Expert key. Due to the combinatorial explosion of included final states that occurs for combinations of large values of the raman order, large molecules and wide spectrum ranges, there is a maximum number of final states that can be included in the spectrum. This is to prevent the program from using excessive amounts of memory/computation times. The user can set this number using the `MaximumStates` key but this should be done with caution.

Finally we give an example of a typical `VibrationalAnalysis` block for a resonance Raman calculation. This also gives an idea of how the settings that were not explicitly mentioned above work:

```
VibrationalAnalysis
   Type ResonanceRaman
   NormalModes
     ModeSelect
       Full True
     End
   End
   ExcitationSettings
     ExcitationInfo File
     ExcitationFile ./your_excitation/dftb.rkf
     Singlet
       A 1 2 4
     End
   End
   ResonanceRaman
     RamanOrder 3
```

(continues on next page)

(continued from previous page)

```
     RamanRange 0.0 3000.0
   End
End
```

6.5 VROA: (Resonance) vibrational Raman optical activity

The normal and resonance VROA spectra are calculated from geometric derivatives of the different generalized polarizabilities obtained using linear response theory which may include a damping term to account for the finite lifetime. Engine ADF is required. These polarizabilities are the electric dipole - electric dipole polarizability, the electric dipole - magnetic dipole polarizability, and the the electric dipole - electric quadrupole polarizability. For resonance VROA one should include a finite lifetime.

```
Properties
   VROA Yes/No
End
```

```
Raman
   FreqRange float_list
   IncidentFrequency float
   LifeTime float
End
```

Properties

VROA

Type Bool

Default value No

Description Requests calculation of VROA for vibrational normal modes.

Raman

FreqRange

Type Float List

Unit cm-1

Recurring True

GUI name Frequency range

Description Specifies a frequency range within which all modes will be scanned. 2 numbers: an upper and a lower bound.

IncidentFrequency

Type Float

Default value 0.0

Unit eV

Description Frequency of incident light.

LifeTime

Type Float

Default value 0.0

Unit hartree

Description Specify the resonance peak width (damping) in Hartree units. Typically the lifetime of the excited states is approximated with a common phenomenological damping parameter. Values are best obtained by fitting absorption data for the molecule, however, the values do not vary a lot between similar molecules, so it is not hard to estimate values. A typical value is 0.004 Hartree.

6.5.1 Engine ADF

In the ADF engine a method is implemented to calculate both on- and off-resonance vibrational Raman optical activities (VROAs) of molecules using time-dependent density functional theory, see Ref.[14]. This is an extension of a method to calculate the normal VROA by including a finite lifetime of the electronic excited states in all calculated properties. The method is based on a short-time approximation to Raman scattering and is, in the off-resonance case, identical to the standard theory of Placzek. The normal and resonance VROA spectra are calculated from geometric derivatives of the different generalized polarizabilities obtained using linear response theory which includes a damping term to account for the finite lifetime. Gauge-origin independent results for normal VROA have been ensured using either the modified-velocity gauge or gauge-included atomic orbitals. In ADF2016 the velocity gauge tensors required for the calculation of VROA are now correctly calculated with the life time damping parameter. With these complex tensors fixed, resonance VROA intensities are now origin invariant in the velocity gauge, see also Ref.[15].

6.6 VCD: Vibrational Circular Dichroism

Vibrational circular dichroism (VCD) is the differential absorption of left and right circularly polarized infrared light by vibrating molecules. Most engines can be used to calculate VCD with the approximate Atomic polar tensor (APT) model. Engine ADF is required for the more accurate analytical VCD.

```
Properties
   VCD Yes/No
End
```

`Properties`

`VCD`

Type Bool

Default value No

Description Requests calculation of VCD for vibrational normal modes.

VCDtools (page 376) is a program that can be used to do an analysis of the VCD spectrum. *VCDtools* (page 376) can be used with the AMS-GUI module AMSspectra.

[14] L. Jensen, J. Autschbach, M. Krykunov, and G.C. Schatz, *Resonance vibrational Raman optical activity: A time-dependent density functional theory approach*, Journal of Chemical Physics 127, 134101 (2007) (https://doi.org/10.1063/1.2768533)

[15] D.V. Chulhai and L. Jensen, *Simulating Surface-Enhanced Raman Optical Activity Using Atomistic Electrodynamics-Quantum Mechanical Models*, Journal of Physical Chemistry A 118, 9069 (2014) (https://doi.org/10.1021/jp502107f)

6.6.1 Atomic polar tensor (APT) model

In the so-called atomic polar tensor (APT) model the atomic axial tensors (AATs) can be calculated from electric dipole gradients. Note that the APT model may not be very reliable for predicting VCD bands and its implementation should not be blindly applied beyond a quick assessment. Results using the engine DFTB can be found in[16].

For the engines BAND and DFTB only the APT model can be used. In case of the engine ADF the default is to calculate the VCD analytically, see next section. One can calculate VCD using the APT model with the ADF engine if one includes:

```
NormalModes
  Hessian Numerical
End
```

6.6.2 Analytical VCD in ADF

In the ADF engine the VCD intensities are calculated using Stephens' equations for VCD. For the calculation of the atomic axial tensors (AATs), analytical derivatives techniques and London atomic orbitals (the so called GIAO) are employed. As a result the calculated rotational strengths are origin independent, and therefore the common origin gauge is used[17].

New in AMS2020 is that one can calculate analytical VCD also for open-shell systems in a spin-unrestricted calculation.

Calculation of the AATs requires an analytical frequencies calculation. This limits the choice of functionals that can be used for VCD calculations.

The accuracy of the vibrational rotational strengths are determined by the accuracy of the harmonic force field, atomic polar tensors (APTs) and AATs. The most critical parameter being the harmonic force field. Thus, for a fair comparison with experimental data, accurate geometries and functionals that yield accurate force fields (e.g. BP86, OLYP, etc) should be used. Our tests showed that the BP86 functional in combination with TZP basis sets is always a safe choice. For a comparison of VCD spectra calculated with various functionals (e.g BP86, OLYP, BLYP, B3PW91 and B3LYP) see[?]. Regarding the geometries, we recommend the following strict settings, 10^{-4} for the geometry convergence of the gradients, and BeckeGrid quality good. The default settings should be used for the calculation of the frequencies.

By default, only the vibrational rotational strengths are printed in the AMS output file. For a deeper insight regarding the origin of the VCD intensity of a given normal mode one can use the auxiliary program *VCDtools* (page 376). *VCDtools* (page 376) can be used with the ADF-GUI module ADFspectra.

6.7 Vibrational Polarizabilities

If IR intensities are available it is possible to calculate the pure vibrational component for static electric polarizabilities[18] of the system. The tensor can be expressed as a sum-over-state that runs over all normal vibrational modes j :

$$\alpha^{vib}_{\alpha,\beta} = \frac{2}{\hbar} \sum_j \frac{1}{\omega_j} \langle 0|\mu_\alpha|j\rangle\langle j|\mu_\beta|0\rangle$$

Where Q_j are the normal mode coordinates, ω_j are the normal modes angular frequencies, and the bracket notation is used for the system's vibrational states. The full polarizability tensor is printed in atomic units along with the isotropic average of the tensor.

[16] T.Q. Teodoro, M.A.J. Koenis, R. Rüger, S.E. Galembeck, W.J. Buma, V.P. Nicu, L. Visscher, *Use of Density Functional Based Tight Binding Methods in Vibrational Circular Dichroism*, Journal of Physical Chemistry A 122, 9435 (2018) (https://doi.org/10.1021/acs.jpca.8b08218)

[17] V.P. Nicu, J. Neugebauer, S.K. Wolff, and E.J. Baerends, *A vibrational circular dichroism implementation within a Slater-type-orbital based density functional framework and its application to hexa- and hepta-helicenes*, Theoretical Chemical Accounts 119, 245 (2008) (https://doi.org/10.1007/s00214-006-0234-x)

[18] M. J. Cohen, A. Willetts, R. D. Amos, and N. C. Handy, *Vibrational contributions to static polarizabilities and hyperpolarizabilities*, Journal of Chemical Physics 100, 4467 (1994) (https://doi.org/10.1063/1.474503)

CHAPTER

SEVEN

VIBRATIONALLY RESOLVED ELECTRONIC SPECTRA

7.1 AH-FC: Adiabatic Hessian Franck-Condon

Electronic spectra, such as absorption, emission, phosphorescence, and ionization, may contain a vibrational structure.

In the Adiabatic Hessian Franck-Condon (AH-FC) method one needs to do a frequency calculation both at the ground state as well as the excited state of interest. The model makes the following assumptions:

- 1. It employs the adiabatic (Born-Oppenheimer) approximation and treats the nuclei as moving in an effective potential defined by the electronic configuration.
- 2. It works at the Franck-Condon (FC) point and assumes that the transition occurs at the ground state equilibrium structure for absorption and at the excited state equilibrium structure for emission.
- 3. It applies the harmonic approximation to both the ground and excited state potential energy surfaces.

Franck-Condon factors can be calculated for the transition between the two electronic states, which can be done with the *FCF Module* (page 245), described below. These Franck-Condon factor can then be used to predict the relative intensities of absorption or emission lines in the electronic spectra. Note that the Herzberg-Teller effect is not taken into account.

In the vertical gradient Franck-Condon (VG-FC) method some extra assumptions are made compared to the AH-FC method. This approach is particularly effective for large molecules as it shows linear scaling with the number of normal modes.

- See the documentation of the *VG-FC method* (page 254).

7.1.1 FCF module: Franck-Condon Factors

fcf is an auxiliary program which can be used to calculate Franck-Condon factors from two vibrational mode calculations[1]. The program assumes that the starting vibrational wavefunction is in the ground state, as is the case for most spectroscopic experiments performed at room temperature.

fcf requires an ASCII input file where the user specifies the .rkf files from two vibrational mode calculations, carried out for two different electronic, spin or charge states of the same molecule. These calculations can be either numerical or analytical.

fcf produces a (binary) KF file TAPE61, which can be inspected using the KF utilities. Furthermore, *fcf* writes the frequencies, vibrational displacements and electron-phonon couplings for both states too the standard output, including any error messages.

In AMS2022 the algorithm for the calculation of the Franck-Condon factors has been changed in order to improve the precision, increase the speed, and lower the memory requirements.

[1] J.S. Seldenthuis, H.S.J. van der Zant, M.A. Ratner and J.M. Thijssen, *Vibrational Excitations in Weakly Coupled Single-Molecule Junctions: A Computational Analysis*, ACS Nano 2, 1445 (2008) (https://doi.org/10.1021/nn800170h)

Theory

Franck-Condon factors are the squares of the overlap integrals of vibrational wave functions. Given a transition between two electronic, spin or charge states, the Franck-Condon factors represent the probabilities for accompanying vibrational transitions. As such, they can be used to predict the relative intensities of absorption or emission lines in spectroscopy or excitation lines in transport measurements.

When a molecule makes a transition to another state, the equilibrium position of the nuclei changes, and this will give rise to vibrations. To determine which vibrational modes will be active, we first have to express the displacement of the nuclei in the normal modes:

$$\mathbf{k} = \mathbf{L'}^T \mathbf{m}^{1/2}(\mathbf{B}_0\mathbf{x}_0 - \mathbf{x'}_0)$$

Here, **k** is the displacement vector, **L** is the normal mode matrix, **m** is a matrix with the mass of the nuclei on the diagonal, **B** is the zero-order axis-switching matrix and $\mathbf{x}_0$ is the equilibrium position of the nuclei. For free molecules, depending on symmetry constraints, the geometries of both states may have been translated and/or rotated with respect to each other. To remove the six translational and rotational degrees of freedom, we can center the equilibrium positions around the center of mass and rotate one of the states to provide maximum overlap. The latter is included with the zero-order axis-switching matrix **B**, implemented according to[2].

When we have obtained the displacement vector, it is trivial to calculate the dimensionless electron-phonon couplings. They are given by:

$$\lambda = (⍰/2)^{1/2}\mathbf{k}$$

Here, $⍰ = 2\pi\omega/h$ is a vector containing the reduced frequencies.[3]. The Huang-Rhys factor **g** is related to λ as:

$$\mathbf{g} = \lambda^2$$

The reorganization energy per mode is

$$\mathbf{E} = (h/2\pi) * \omega\lambda^2$$

When the displacement vector **k**, the reduced frequencies ⍰ and ⍰′, and the Duschinsky rotation matrix $\mathbf{J} = \mathbf{L'}^T\mathbf{B}_0\mathbf{L}$ have been obtained, the Franck-Condon factors can be calculated using the two-dimensional array method of Ruhoff and Ratner[7].

There is one Franck-Condon factor for every permutation of the vibrational quanta over both states. Since they represent transition probabilities, all Franck-Condon factors of one state which respect to one vibrational state of the other state must sum to one. Since the total number of possible vibrational quanta, and hence the total number of permutations, is infinite, in practice we will calculate the Franck-Condon factors until those sums are sufficiently close to one. Since the number of permutations rapidly increases with increasing number of vibrational quanta, it is generally possible to already stop after the sum is greater than about two thirds. The remaining one third will be distributed over so many Franck-Condon factors that their individual contributions are negligible.

In the limiting case of one vibrational mode, with the same frequency in both states, the expression for the Franck-Condon factors of transitions from the ground vibrational state to an excited vibrational state are given by the familiar expression:

$$|l_{0,n}|^2 = e^{-\lambda^2}\lambda^{2n}/n!$$

[2] G.M. Sando and K.G. Spears, *Ab Initio Computation of the Duschinsky Mixing of Vibrations and Nonlinear Effects*, Journal of Physical Chemistry A 105, 5326 (2001) (https://doi.org/10.1021/jp004230b)

[3] P.T. Ruhoff and M.A. Ratner, *Algorithms for computing Franck-Condon overlap integrals*, International Journal of Quantum Chemistry 77, 383 (2000) (https://doi.org/10.1002/(SICI)1097-461X(2000)77:1%3C383::AID-QUA38%3E3.0.CO;2-0)

Algorithm

The algorithm for the calculation of the FC integrals is based on the work by Santoro et al.[4] which is here summarized. There are in principle infinite FC factors that should be computed in order to achieve 100% convergence in the spectrum. This number is reduced by dividing the vibrational into classes.

A class is defined based on the number of simultaneously excited vibrational modes, thus a class 3 state has exactly 3 modes which are simultaneously excited, while all the remaining modes have zero quanta. The *fcf* program first evaluates the class 1 e 2 FC up to a fairly large vibrational quantum number and uses these results to infer how much each mode should be excited for the calculation of the integrals involving states of higher classes. We refer to the original paper for the details of the algorithm.

The convergence of the results after each class can be estimated by summing all FC factors, which should converge to 1 in the limit of a complete set. The program is terminated when the maximum allowed class is reached, when there is little gain from one class to the next, or when a sufficient convergence criterion is met. It should be noted that if one is interested in the overall shape of the spectrum then in most cases it isn't necessary to reach a convergence that is close to 100%.

Input

The input for *fcf* is keyword-oriented and is read from the standard input. *fcf* recognizes several keywords, but only the states have to be specified to perform the calculation. All input therefore contains at least the following lines:

```
$AMSBIN/fcf << eor
   STATE1 state1
   STATE2 state2
eor
```

The spectrum is always calculated from the ground vibrational state belonging to the potential energy surface specified by *state1* to the vibronic states belonging to *state2*. Documentation for all keys of *fcf*:

```
$AMSBIN/fcf << eor
   State1 state1
   State2 state2
   Lambda float
   Modes first last
   Rotate [True | False]
   Translate [True | False]
   NumericalQuality ["Basic" | "Normal" | "Good" | "Excellent"]
   Prescreening
      Class1   integer
      Class2   integer
      MaxClass integer
      MaxFCI   integer
   End
   Spectrum FreqMin FreqMax NFreq
      LineShape ["Stick" | "Gaussian" | "Lorentzian" ]
      SpcMin float
      SpcMax float
      SpcLen integer
      HWHM   float
   End
   Printing
      Verbose
```

(continues on next page)

[4] F. Santoro, R. Improta, A. Lami, J. Bloino, V. Barone, *Effective method to compute Franck-Condon integrals for optical spectra of large molecules in solution*, J. Chem. Phys. 126, 084509 (2007) (https://doi.org/10.1063/1.2437197)

(continued from previous page)

```
      FCFThresh float
   End
eor
```

Convergence

Type Float

Description Minimum fraction of the FC factors sum to be calculated

Lambda

Type Float

Default value 0.0

GUI name Minimum coupling

Description Optional. The minimum value of the electron-phonon coupling for a mode to be taken into account in the calculation. Together with the MODES option, this provides a way to significantly reduce the total number of Franck-Condon factors. As with the MODES option, always check if the results do not change too much.

Modes

Type Integer List

Default value [0, 0]

Description Optional. The first and last mode to be taken into account in the calculation. By default, all modes are taken into account. This option can be used to effectively specify and energy range for the Franck-Condon factors. When using this options, always check if the results (electron-phonon couplings, ground state to ground overlap integral, average sum of Franck-Condon factors, etc.) do not change too much.

NumericalQuality

Type Multiple Choice

Default value Normal

Options [0-0, Basic, Normal, Good, Excellent]

Description Set the quality of several technical aspects of an FC calculation, including details for the prescreening, the amount of computed integrals, the maximum integral class evaluated, as well as the convergence criteria.

Printing

Type Block

Description Optional. Printing Options.

FCFThresh

Type Float

Default value 0.01

GUI name FC factor threshold

Description The minimum value for the printing of a FC factor.

Verbose

Type Bool

Default value No

GUI name Verbose printing

Description Increase output verbosity.

`Rotate`

Type Bool

Default value Yes

Description Recommended to be used. Rotate the geometries to maximize the overlap of the nuclear coordinates.

`Spectrum`

Type Block

Description Optional. Controls the details of the spectrum calculation

`HWHM`

Type Float

Default value 100.0

Description Half-Width at Half-Maximum for the spectral lineshape function

`LineShape`

Type Multiple Choice

Default value Stick

Options [Stick, Gaussian, Lorentzian]

Description Type of lineshape function

`SpcLen`

Type Integer

Default value 2001

Description Number of points in the spectrum

`SpcMax`

Type Float

Default value 9500.0

Description Maximum absolute energy difference between the states relative to the 0-0 transition

`SpcMin`

Type Float

Default value -500.0

Description Minimum absolute energy difference between the states relative to the 0-0 transition

`Type`

Type Multiple Choice

Default value Absorption

Options [Absorption, Emission]

Description Type of spectrum

State1

Type String

Description Filename of the result files of a numerical or analytical frequency calculation for the first (initial) state.

State2

Type String

Description Filename of the result files of a numerical or analytical frequency calculation for the second (final) state.

Translate

Type Bool

Default value Yes

Description Recommended to be used. Move the center of mass of both geometries to the origin.

Only a few keys from the .rkf file are used for the calculation of the Franck-Condon factors. Disk space usage can be significantly reduced by extracting just these keys from the .rkf file before further analysis. The following shell script will extract the keys from the KF file specified by the first argument and store them in a new KF file specified by the second argument using the *cpkf* utility:

```
#!/bin/sh
cpkf $1 $2 General Molecule Vibrations
```

Result: TAPE61

After a successful calculation, *fcf* produces a TAPE61 KF file. All results are stored in the Fcf section:

contents of TAPE61	**comments**
lambda	the minimum value of the electron-phonon coupling
translate, rotate	whether the TRANSLATE and ROTATE options were specified in the input
natoms	number of atoms in the molecule
mass	atomic mass vector (**m**)
xyz1, xyz2	equilibrium geometries of both states ($\mathbf{x}_0$ and $\mathbf{x}_0$ ')
b0	zero-order axis-switching matrix matrix ($\mathbf{B}_0$)
nmodes	number of vibrational modes with a non-zero frequency
gamma1, gamma2	reduced frequencies of both states (Γ and Γ')
lmat1, lmat2	mass-weighted normal modes of both states (**L** and **L**')
jmat	Duschinsky rotation matrix (**J**)
kvec1, kvec2	displacement vectors for both states (**k** and **k'**, kvec1 is used for the calculation of the Franck-Condon factors)
lambda1, lambda2	electron-phonon couplings for both states (λ and λ')
i0	ground state to ground state overlap integral ($I_{0,0}$)

In addition to producing a binary TAPE61 file, *fcf* also writes the frequencies, displacement vectors and electron-phonon couplings for both states to the standard output.

7.1.2 FCF example absorption and fluorescence

In this example it is assumed that the molecule has a singlet ground state S_0 , and the interesting excited state is the lowest singlet excited state S_1 . First one needs to a the ground state geometry optimization, followed by a frequency calculation. For the ground state frequency calculation we will use AMS_JOBNAME=S0. Next one needs to do an excited state geometry optimization. Here it is assumed that the lowest singlet excited state S_1 is of interest:

```
AMS_JOBNAME=S1_GEO $AMSBIN/ams <<eor
   ...
   Task GeometryOptimization
   Engine ADF
      ...
      Excitation
         Onlysing
         Lowest 1
      End
      ExcitedGO
         State A 1
         Singlet
      End
   EndEngine
eor
```

To get the frequencies for this excited state, numerical frequencies need to be calculated, at the optimized geometry of the first excited state:

```
AMS_JOBNAME=S1 $AMSBIN/ams <<eor
   ...
   LoadSystem
      File S1_GEO.results/adf.rkf
   End
   Task SinglePoint
   Properties
      NormalModes True
   End
   Engine ADF
      ...
      Excitation
         Onlysing
         Lowest 1
      End
      ExcitedGO
         State A 1
         Singlet
      End
   EndEngine
eor
```

Next for the absorption spectrum, we look at excitations from the lowest vibrational state of the electronic ground state to the vibrational levels of the first singlet excited state S_1 ($S_1 \leftarrow S_0$), using the *FCF program* (page 245), which calculates the Franck-Condon factors between the vibrational modes of the two electronic states, with input

```
$AMSBIN/fcf << eor
   STATE1 S0.results/adf.rkf
   STATE2 S1.results/adf.rkf
   TRANSLATE
   ROTATE
eor
```

See *the description of FCF program* (page 245) for more details.

For the fluorescence spectrum, we look at excitations from the lowest vibrational state of the first singlet excited state S_1 to the vibrational levels of the singlet ground state state S_0 ($S_1 \rightarrow S_0$). Input for the *FCF program* (page 245) is in this case:

```
$AMSBIN/fcf << eor
   STATE1 S1.results/adf.rkf
   STATE2 S0.results/adf.rkf
   TRANSLATE
   ROTATE
eor
```

Note that the FCF program calculates the spectrum relative to the 0-0 transition. Thus one should add to spectrum calculated with FCF the difference in energy of the lowest vibrational state of the ground state S_0 and the lowest vibrational state of the electronically singlet excited state S_1 .

7.1.3 FCF Example phosphorescence

In this example it is assumed that the molecule has a singlet ground state S_0 , and the interesting excited state is the lowest triplet excited state T_1 . Emission from a triplet state to a singlet state is spin forbidden, however, due to spin-orbit coupling such transitions may occur. In the following we assume that the geometry of the triplet excited state is not influenced much by spin-orbit coupling.

First one needs to a the ground state geometry optimization, followed by a frequency calculation, using AMS_JOBNAME=S0. Next one needs to do an excited state geometry optimization of the lowest triplet excited state, followed by a frequency calculation.

```
AMS_JOBNAME=T1 $AMSBIN/ams <<eor
   ...
   Task GeometryOptimization
   Properties
      NormalModes True
   End
   Engine ADF
      Unrestricted
      SpinPolarization 2.0
   EndEngine
eor
```

For the phosphorescence spectrum, we look at excitations from the lowest vibrational state of the first triplet excited state T_1 to the vibrational levels of the singlet ground state state S_0 ($T_1 \rightarrow S_0$). Input for the *FCF program* (page 245) is in this case:

```
$AMSBIN/fcf << eor
   STATE1 T1.results/adf.rkf
   STATE2 S0.results/adf.rkf
   TRANSLATE
   ROTATE
eor
```

Note that the FCF program calculates the spectrum relative to the 0-0 transition. Thus one should add to spectrum calculated with FCF the difference in energy of the lowest vibrational state of the ground state S_0 and the lowest vibrational state of the electronically triplet excited state T_1 .

Zero field splitting (ZFS) and the radiative rate constants (i.e. radiative phosphorescence lifetimes) could be calculated with spin-orbit coupled ZORA time-dependent density functional theory (ZORA-TDDFT). With the ADF engine spin-orbit coupling can be treated self-consistently (i.e. non perturbatively) during both the SCF and TDDFT parts of the computation.

An alternative to the use of the unrestricted formalism to calculate the lowest triplet excited state is to use the TDDFT formalism:

```
AMS_JOBNAME=T1_GEO $AMSBIN/ams <<eor
   ...
   Task GeometryOptimization
   Engine ADF
      Excitation
         Onlytrip
         Lowest 1
      End
      ExcitedGO
         State A 1
         Triplet
      End
   EndEngine
eor
```

To get the frequencies for this excited state, numerical frequencies need to be calculated, at the optimized geometry of the first excited state.

```
AMS_JOBNAME=T1 $AMSBIN/ams <<eor
   ...
   LoadSystem
      File T1_GEO.results/adf.rkf
   End
   Task SinglePoint
   Properties
      NormalModes True
   End
   Engine ADF
      ...
      Excitation
         Onlytrip
         Lowest 1
      End
      ExcitedGO
         State A 1
         Triplet
      End
   EndEngine
eor
```

7.1.4 Density of States computed with AH-FC method

The FCF module can also be used to evaluate the density of states *rho* that enters the expression of the rate constant for a number of transfer phenomena based on Fermi's Golden Rule:

$$\mathbf{k} = \frac{2\pi}{\hbar} J^2 \rho$$

To calculate the transfer rate from a donor molecule to an acceptor molecule it is sufficient to employ the FCF code as described above to evaluate the emission spectrum of the donor and the absorption spectrum of the acceptor. In fact, it can be shown[5] that the expression for the density of states can be written as:

$$\rho = \frac{1}{\hbar}\int_{-\infty}^{+\infty} F^{\mathrm{D}}(\omega)F^{\mathrm{A}}(\omega)d\omega$$

Where F denotes the Franck-Condon spectrum calculated by the FCF code, specifically the absorption for the acceptor and the emission for the donor.

The convolution may be easily calculated by using the PLAMS library.

7.2 VG-FC: Vertical Gradient Franck-Condon

Electronic spectra, such as absorption, emission, phosphorescence, and ionization, may contain a vibrational structure.

In the vertical gradient Franck-Condon (VG-FC) method some extra assumptions are made compared to the Adiabatic Hessian Franck-Condon (AH-FC) method. VG-FC is also called the Independent Mode Displaced Harmonic Oscillator (IMDHO) model. The AH-FC model (used in the *FCF Module* (page 245)) makes the following assumptions:

- 1. It employs the adiabatic (Born-Oppenheimer) approximation and treats the nuclei as moving in an effective potential defined by the electronic configuration.
- 2. It works at the Franck-Condon point and assumes that the transition occurs at the ground state equilibrium structure for absorption and at the excited state equilibrium structure for emission.
- 3. It applies the harmonic approximation to both the ground and excited state potential energy surfaces.

The VG-FC model makes following additional assumptions:

- 4. It assumes the excited state PES has the same shape as that of the ground state, but it is displaced from it, i.e. both states have the same normal modes and frequencies but different equilibrium geometries.
- 5. The excited state equilibrium structure is found from a Newton-Raphson step from the ground state geometry using the excited state gradient at this point.

Under these simplifying approximations we can reduce the ingredients necessary for a spectrum calculation to an excited state gradient and a set of ground state normal modes. Furthermore it uses a time-domain description of the absorption cross-section (this introduces no further approximations) so we do not need any explicit Franck-Condon factors as is done in the *FCF Module* (page 245). This approach is particularly effective for large molecules as it shows linear scaling with the number of normal modes. Further details on how to use this method, and the VG-FC model in general can be found below.

The approximations we make remove the need for an excited state geometry optimization and frequency analysis. This means the most expensive step in a typical calculation is actually the ground state frequency analysis. The ability of Mode Tracking to generate a set of approximate normal modes, without performing a full frequency analysis can be applied to the calculation of vibrationally resolved optical spectra. This is exactly what is done in *Vibronic-Structure Tracking* (page 256). On the other hand, the ability of Mode Refinement to refine entire spectral regions at once means this method can be transferred to calculating vibrationally resolved optical spectra from a select number of (vibronically active) approximate normal modes. This idea is applied in *Vibronic-Structure Refinement* (page 257). Under suitable assumptions, the computational cost of calculating an approximation of the vibronic-structure can be reduced significantly through the use of these two methods, allowing for application to large molecules inaccessible to more detailed methods. While they are clearly best suited for these large molecules, they can also serve as an efficient method to obtain quick, first approximations for more moderately sized molecule.

With the VG-FC model one can calculate the 0-0 energy difference between the ground state and excited state. In this VG-FC method the vibrationally resolved emission spectrum will be a mirror image of the vibrationally resolved absorption spectrum, in which the 0-0 transitions are the same.

[5] X. de Vries *High energy acceptor states strongly enhance exciton transfer between metal organic phosphorescent dyes*, Nature Communications 11, 1292 (2020) (https://doi.org/10.1038/s41467-020-15034-0)

Note: The VG-FC model uses certain approximations which may not always be valid. Something to look out for that may affect the reliability of VG-FC results are large changes in conformation upon excitation. In this case the normal modes of the excited state may be completely different from those of the ground state, at which point the model is not expected to produce reliable results. Should non-adiabatic effects become important, the BO approximation could potentially break down as well. In these cases the *FCF Module* (page 245) may provide a more suitable alternative to the VG-FC model.

See also:

Tutorials: Resonance Raman, Vibrationally resolved electronic spectra with ADF, Vibrationally resolved electronic spectra with DFTB

7.2.1 Theory

Here we will introduce the theory behind the model used to compute vibronic couplings. We use the so-called Vertical Gradient Franck-Condon (VG-FC) method, also called Independent Mode Displaced Harmonic Oscillator model (IMDHO). The VG-FC model as used here works as follows: The PES in the ground state is assumed parabolic (the harmonic approximation). Upon excitation, we assume that the only change to the PES that occurs is a shift in origin (i.e. no stretching or rotation of the parabolic well). This means, both the normal modes and their frequencies remain the same in both the ground and excited state. The result is that a spectrum can be calculated using only a single excited state gradient at the optimized ground state geometry. Hence we avoid the expensive excited state geometry optimization and frequency analysis used by methods such as the *FCF Module* (page 245).

Moving to a slightly more detailed discussion, we can start with an expression for the absorption cross-section in terms of a sum over contributions from different Franck-Condon factors, each homogeneously broadened with an assumed Lorentzian of linewidth Γ. For excitation from the vibrational ground state of electronic state m, to electronic state n we get the following expression (Hartree atomic units are used throughout):

$$\sigma_{n\leftarrow m}(\omega) = \frac{4\pi\omega}{3c}|\mu_{mn}|^2 \sum_{l_{n,1}} \dots \sum_{l_{n,N_{modes}}} \frac{\Gamma \prod_{i=1}^{N_{modes}} |\langle l_{n,i}|0_{m,i}\rangle|^2}{\left(E_{n,0} + \sum_i^{N_{modes}} \omega_i l_{n,i} - E_{m,0} - \omega\right)^2 + \Gamma^2}$$

Here the μ_{mn} is the transition dipole moment and the $\prod_{i=1}^{N_{modes}} |\langle l_{n,i}|0_{m,i}\rangle|^2$ denote the Franck-Condon factors for excitation from the vibrational ground state to the vibrationally excited state of the excited state PES, with quantum numbers $l_{n,i}$. This sum-over-states formulation is what is also used to compute the spectrum in the *FCF Module* (page 245). While efficient pre-screening and thresholding techniques can make this method applicable to moderately sized molecules, it is still quite expensive for large molecules. We can derive an expression which is equivalent to the one above, but which enjoys significant computational benefits. This is done by writing the cross-section as an integral over time:

$$\sigma_{n\leftarrow m}(\omega) = \frac{4\pi\omega}{3c}|\mu_{mn}|^2 Re \int_0^\infty \langle i|i_n(t)\rangle e^{i[\omega+E_{m,0}]t} \cdot e^{-\Gamma t} dt$$

Here, $\langle i|i_n(t)\rangle$ denotes the overlap of the initial state, propagated along the excited state PES with itself at time $t = 0$. This expression is still completely general, however, using the *assumptions of the VG-FC model* (page 244), this overlap admits a simple closed form expression:

$$\langle i|i_n(t)\rangle = \prod_{j=1}^{N_{modes}} \exp\left[-\frac{\Delta_{n,j}^2}{2}(1 - e^{-i\omega_j t})\right] e^{-iE_{n,0}t}$$

This expression can be derived by different methods and admits a few interpretations, the details of which we will not go into here. The interested reader is referred to reference[1]. Instead we will focus on its numerical implementation. The

[1] J.R. Reimers, K.R. Wilson and E.J. Heller, *Complex time dependent wave packet technique for thermal equilibrium systems: Electronic spectra* The Journal of Chemical Physics 79, 4749 (1983) (https://doi.org/10.1063/1.445618)

great computational advantage of this expression is that it scales only weakly with the number of degrees of freedom. Compare this with the sum-over-states formalism above, where the number of FCF's needed to have a converged sum proliferates for large molecules and the advantage becomes clear.

The $\Delta_{n,j}$ appearing in the expression are the dimensionless normal mode displacements at the equilibrium geometry in state n, compared to state m along normal mode j which has angular frequency ω_j. They represent the change in origin of the PES along a particular normal mode. These are the parameters which control the shape of the spectrum. Under the assumptions we listed above they can be calculated from the excited state energy gradient at the ground state equilibrium structure as:

$$\Delta_j = \frac{q_j^m \cdot \nabla_m E}{\omega_j^{3/2}}$$

Where we have suppressed the n subscript. The gradient is with respect to mass weighted coordinates and the q_j^m denote the mass-weighted normal modes.

Essentially, we use the (assumed) parabolic shape of the PES in the harmonic approximation along each of the normal modes to determine the displacement from the gradient projection along that mode. An important consequence of the simplified VG-FC model is that the Franck-Condon factors can be expressed in closed form:

$$|\langle l_i|0_i\rangle|^2 = \frac{\left(\frac{\Delta_i}{2}\right)^2}{l_i!}e^{-\frac{\Delta_i^2}{2}}$$

Modes with the largest displacement are then expected to also have the largest impact on the structure of the vibrational progression in the spectrum. This gives us an obvious candidate for a tracking method to be used with the Mode Tracking protocol. This approach is taken in the *Vibronic-Structure Tracking* (page 256) module.

Theory: Vibronic-Structure Tracking

Vibronic-structure tracking (VST) is a method for obtaining quick and approximate vibrationally resolved optical spectra for larger sized molecules. It is based on the mode-tracking algorithm and works by tracking those modes that are expected to have the largest impact on the vibronic-structure of the spectrum. Its AMS implementation follows that in reference[?].

The modes that are tracked by the mode tracking routine are used to generate a UV/vis spectrum. This is done using the Vertical Gradient Franck-Condon (VG-FC) method, also called the Independent Mode Displaced Harmonic Oscillator (IMDHO) model as described on the *Vibronic-Structure* (page 254) page. This model reduces the necessary TD-DFT calculations to a single excited state gradient performed at the ground state equilibrium geometry. At this point it is typically the ground state frequency analysis which becomes the bottleneck for large molecules. Through the use of Mode Tracking we can circumvent this step and calculate only those modes which will significantly impact the vibronic fine structure. This yields a very cheap and efficient method for obtaining vibrationally resolved optical spectra.

The use of Mode Tracking within the context of vibronic-structure calculations proceeds as follows: from an initial guess for a normal mode, we construct a new basis vector which we hope will improve the quality of our initial guess. We then iteratively expand the basis by refining those modes which have the largest impact on the vibronic fine structure. We keep iterating until we deem the spectrum to be converged. We'll address the technical details of this procedure in this section.

Let us first consider how we can gauge which modes will have a large impact on our spectrum. Over on the *Vibronic-Structure* (page 254) page, we showed that according to the VG-FC model, the Franck-Condon factors can be written as:

$$|\langle l_i|0_i\rangle|^2 = \frac{\left(\frac{\Delta_i}{2}\right)^2}{l_i!}e^{-\frac{\Delta_i^2}{2}}$$

This expression implies modes with large displacements Δ_j will have the largest Franck-Condon factors. Thus, we expect that modes with large oscillator displacements will contribute most strongly to the vibronic fine structure of the spectrum.

This suggests a tracking method in addition to those described in the *Mode Tracking* (page 219) documentation. Namely, to track the mode with the largest Δ_j. This is the only setting for the `TrackingMethod` supported by Vibronic-Structure Tracking and is automatically set when choosing Vibronic-Structure Tracking as the Vibrational Analysis type. As a reminder, the oscillator displacements can be obtained from the assumed parabolic shape of the excited state PES and the known excited state gradient:

$$\Delta_j = \frac{q_j^m \cdot \nabla_m E}{\omega_j^{3/2}}$$

This expression for our normal mode displacements suggests that a reasonable guess for a hypothetical normal mode with a large effect on the spectrum is given by the normalized excited state gradient, as this maximizes the projection.

The choice of preconditioner is of course an important one. While better preconditioners such as the Jacobi-Davidson method can lead to fast and tightly directed convergence of the modes, this may not be ideal in the case of Vibronic-Structure Tracking, as we are not necessarily focused on obtaining converged modes but rather obtaining a converged spectrum. By default the method does not use any preconditioner for generating normal modes from the residual vectors to allow the procedure to more freely explore the entire space of modes. This means that the new basis vector produced on each iteration is the (normalized) residual vector of that iterations selected mode. Note that this is different from using the Davidson method with an identity matrix as guess for the Hessian. The user is still able to use any of the pre-conditioning options provided by the stand-alone mode tracking method, however we suggest the user uses the default `I` (for identity) as the `UpdateMethod`. This also conveniently means no approximate Hessian is required.

It is important to choose a suitable convergence criterion. When using Vibronic-Structure Tracking, the aim is to get an approximation of the progression in the spectrum. The convergence of the modes then takes a backseat to the convergence of the spectrum. Although the two usually go hand in hand, requiring that all modes be converged in the usual mode-tracking sense is likely to be far too restrictive. Thus the convergence criterion used for VST is the following: at every iteration, the previous iteration's spectrum is subtracted from the new one. The absolute difference is then integrated on the requested frequency range. Convergence is achieved once the so-obtained number drops below a pre-set convergence threshold. The result is that it may not be the case that all modes are exact normal modes yet, however further refinement will have a limited effect on the resulting spectrum, for example due to these modes having very small Franck-Condon factors.

Convergence according to this criterion is affected by the other options that the user chooses, see the section on how the adiabatic excitation energy is calculated.

Theory: Vibronic-Structure Refinement

Vibronic-Structure Refinement takes the idea of Mode Refinement, and applies it to the calculation of vibrationally resolved optical spectra. Under the assumptions of the Vibronic-Structure application, the most time-consuming step becomes the calculation of the ground state normal modes. However, we may not be interested in all normal modes that contribute to the Vibronic fine structure of a spectrum. By using Mode Refinement we can limit ourselves to the spectral region of interest, or to modes which we expect to have the largest impact on the fine structure. The details of the Mode Refinement protocol can be found on the relevant *documentation page* (page 216).

Theory: Adiabatic excitation energy

The last aspect we will comment on here is the calculation of the adiabatic excitation energy. The number we get from an excited state calculation is the vertical excitation energy (ΔE_{vert}), this number is generally unobservable in spectra. The more interesting quantity is the adiabatic excitation energy (ΔE_{ad}). The former is the difference in energy between the two PES'es at the ground state geometry, the latter is the difference in energy between the ground and excited state vibrational ground states. Since we assumed both PES'es to have the same frequencies, the zero-point energy of the two states are the same and hence, the adiabatic energy difference is the same as the 0-0 energy difference (ΔE_{0-0}). This is simply the difference between the bottom of the two PES'es. It can be reconstructed from the excited state gradients projected onto our normal modes, as well as their frequencies. For a molecule with N modes we obtain:

$$\Delta E_{ad} = \Delta E_{vert} - \sum_{j}^{N_{modes}} \frac{1}{2}\omega_j \Delta_j^2$$

Where the sum represents the reorganization energy stored in the excited oscillator modes. Depending on the desired information, one can use two different representations of the spectrum. The first is to simply plot the spectrum against an energy range with the ground state energy as an offset. This would represent a true absorption spectrum that can be compared directly with experiment. However, the energy difference $\Delta E_{vert} - \Delta E_{ad}$ in the VG-FC model is reconstructed only from the ground state equilibrium structure and can thus be somewhat unreliable. If the user is primarily interested in the shape of the spectrum, using the 0-0 excitation energy as an offset may be a more suitable choice. The latter is the default setting in AMS, but the method supports both options.

Note that in case of a Vibronic-structure tracking (VST) calculation we only have access to a small set of approximate normal modes, we will have an approximation of ΔE_{ad} that changes from iteration to iteration as new normal modes are introduced and the old normal modes are refined. If a spectrum relative of the 0-0 energy is requested, the shift caused by the iterative convergence of ΔE_{ad} is not taken into account, although it will still have some effect on the spectrum as it also appears in the integral that defines the spectrum. If one is interested in a converged approximation of ΔE_{0-0} it may be more reliable to provide an absolute frequency range for the spectrum as the shift in the peak locations will then also affect convergence.

7.2.2 Input: Vibronic-Structure all modes

As mentioned, we need both a set of ground state normal modes as well as an excited state gradient. All the normal modes are calculated using the AMS engine that was selected, or, in case the user has a pre-calculated set of normal modes, these can be read from a .rkf file using the `ModeFile` key in the `NormalModes` sub-block. In this latter case, the engine is not used. One can then use the keys in the `ModeSelect` block to filter out specific modes, or, simply select all modes using the `Full` key in this block. For further details on how to use the Mode Select block for more specialized selection options, see the *Mode Select* (page 227) documentation. As for the excited state information, this is passed to the application via the `ExcitationSettings` block. Additionally there are (optional) settings related to the appearance of the spectrum under the `AbsorptionSpectrum` block. For an overview of the input options see the list of keys at the end of this page.

For completeness we provide an example of what the user input may look like:

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type VibronicStructure
   NormalModes
     # Select all modes present in the .rkf file
     ModeSelect
       Full True
     End
   End
   ExcitationSettings
     ExcitationInfo File
     ExcitationFile ./your_excitation.t21
     Singlet
       B1.u 2
     End
   End
   AbsorptionSpectrum
     LineWidth 100.0
     AbsorptionRange -500.0 4000.0
   End
End
```

7.2.3 Input: Vibronic-Structure Tracking

VST is notably the only Vibrational Analysis task that does not support the `NormalModes` block as no initial normal modes are necessary. The excited state gradient fills this role instead. Furthermore, the recommended default of using the identity matrix as a preconditioner means that no approximate Hessian is required either.

One thing to note regarding the Mode Tracking settings is that VST features a convergence criterion not present in standard Mode Tracking. The tolerance for the convergence of the spectrum is set using the `ToleranceForSpectrum` keyword in the `ModeTracking` block. The default is set to 0.01 and should be sufficient for most purposes, but *restarting* (page 259) with a lower value may improve the reliability of the convergence.

Note: The usual Mode Tracking tolerances are still present in addition to the spectral tolerance mentioned above. This is so we do not track modes that have already converged. Instead, once a mode is converged in the usual mode tracking sense, we switch to the next mode that satisfies our tracking criterion. The defaults should normally apply, but may be loosened a bit to allow for more free subspace exploration.

A typical Vibronic-Structure Tracking run may be setup as follows:

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type VibronicStructureTracking
   # Select our excited state energy+gradient from a previous calculation
   ExcitationSettings
     ExcitationInfo File
     ExcitationFile ./your_excitation.t21
   End
   # Tuning how our spectrum will look
   AbsorptionSpectrum
     LineWidth 250.0
     AbsorptionRange -500.0 6000.0
   End
   ModeTracking
     UpdateMethod I
   End
End
```

Input: Restarting VST

The Vibronic-Structure Tracking task is fully restartable from a previously completed VST run. The main reason why it may be useful to perform a restart is related to the way the spectrum is generated. Most modules/applications in AMS that calculate a spectrum usually produce a stick spectrum. This stick spectrum is then convoluted against either a gaussian or lorentzian of specified width or area. This allows one to tweak the homogeneous broadening post-calculation to improve agreement with experiments. VST operates differently, in that the Lorentzian linewidth is specified at the start of the calculation as an essential input parameter. If upon convergence it becomes clear that a different linewidth would have been better suited for the spectrum at hand, one can restart the calculation with this new linewidth. The program then computes a new spectrum using these new settings and repeats the last iteration of the previous run. The latter is done because the linewidth directly influences the convergence (larger linewidths tend to converge more easily as the features are not as sharply resolved). If the spectrum does not change after the first iteration the program terminates as usual and the new spectrum is now available to the user. However, if this additional iteration does not pass the convergence test, the program keeps iterating until the spectrum converges for this new linewidth.

In addition to changing the linewidth post-calculation, the user is also free to change the spectral range that is to be computed as well as its resolution through the `FrequencyGridPoints` keywords. Alternatively, the tolerance used may be lowered if tighter convergence is required. Importantly however, none of the previous run's input settings are retrieved upon restart, so any settings the user doesn't want to change have to be same in the new run script as in the old. The easiest way to restart is to simply re-use the previous run's runscript under a new name and then changing the relevant settings.

The restart functionality is controlled by the `RestartPath` keyword. One simply states the path to a previous calculation's .rkf file from which the relevant data is to be read. The .rkf file of any VST runs contains a section labeled `VSTRestart` which contains the data needed to restart from that run. Restarting is then a simple one-liner in the `VibrationalAnalysis` block:

```
VSTRestartFile ./previous_run.results/ams.rkf
```

7.2.4 Input: Vibronic-Structure Refinement

Vibronic-Structure Refinement (VSR) assumes that the modes relevant to the vibronic-structure are, at least in an approximate sense, known a priori. The VSR method takes these approximate modes and refines them via the Mode Refinement algorithm. The approximate normal modes should thereby span a subspace containing the exact normal modes and, the more similar they are to the exact mode, the better they allow to reproduce the spectrum of a full ground state frequency analysis. Naturally, the refinement becomes more accurate with increasing dimensionality of the spanned subspace, although this this increases the computational costs. In any case, the subspace needs to contain those modes that are most relevant for the vibronic progression for the entire approach to work, which leads to the question, how do we select such modes?

This is done using familiar `ModeSelect` block from the mode selective analysis tasks tasks. While all the usual options are available, for which further details can be found on the *Vibrational Analysis* (page 227) page, there are two selection methods that are geared specifically towards VSR. Within the VG-FC model, the parameters defining the effect a mode will have on the spectrum are the oscillator displacements Δ_j. We can determine these values from the projection of the approximate normal modes onto the gradient in combination with their respective frequencies. We are then interested in those modes with the largest displacement. To select these, two options are available:

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type VibronicStructureRefinement
   NormalModes
      ModeSelect
         LargestDisplacement integer
         DisplacementBound float
         ...
      End
      ...
   End
   ...
End
```

`LargestDisplacement integer` sets an integer value N, to select the N modes with the largest displacements as calculated within the VG-FC model. This method limits the total number of modes we refine and thus places an upper bound on the computational cost required by the method, but it does not ensure that all relevant modes have been selected. In particular there may still be modes with large displacements that have been omitted and as such peaks or progressions may be missing from the spectrum.

`DisplacementBound float` Alternatively this selects all approximate modes with a displacement greater than the supplied lower bound. An appropriate choice for this value ensures all modes which visibly affect the spectrum (at least at the lower level of theory used to produce the approximate modes) are included in the subspace basis used for Mode Refinement. The displacements Δ_j are dimensionless and the largest ones will typically be of order one. Based on this, a value of `0.01` for this parameter will generally select all relevant modes. This of course comes at the trade-off that for general molecules it is not known how many such modes there will be and the computational cost may be larger than expected. But, if one is not discouraged by this, this will of course yield the most accurate results. Values up to `0.05` may still provide reasonable results while minimizing computation times. Using larger linewidths (`AbsorptionSpectrum%LineWidth`) for the homogeneous broadening can help to correct for the non-resolved modes.

The calculation setup for Vibronic-Structure Refinement is essentially the same as that for Vibronic-Structure, the only difference being that the modes that we provide will first be refined, before a spectrum is computed. A detailed description is given on the *Vibronic-Structure* (page 254) page. A typical VSR calculation can be setup as follows:

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type VibronicStructureRefinement
   # Select our normal modes from a previous calculation
   NormalModes
     ModeFile ams.rkf
     ModeSelect
        # select all modes with VG-FC displacements over 0.01
        DisplacementBound 0.01
     End
   End
   # Select our excited state energy+gradient from a previous calculation
   ExcitationSettings
     ExcitationInfo File
     ExcitationFile ./your_excitation.t21
     # Select second singlet excitation with symmetry label A
     Singlet
       A 2
     End
   End
   # Tuning how our spectrum will look
   AbsorptionSpectrum
     LineWidth 250.0
     AbsorptionRange -500.0 6000.0
   End
End
```

7.2.5 Input: Excited State

Both the excited state gradient at the ground state equilibrium structure as well as the vertical excitation energy are necessary to obtain a spectrum. These can be provided by most TD-DFT programs, including ADF. Unfortunately, the AMS driver does not yet support computing these properties on the fly. As a result they are currently required as user input. One can use ADF or DFTB to compute them and then either read them from the produced output file, or copy and paste them to an inline input block.

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type ...
   ExcitationSettings
      ExcitationInputFormat [File | Inline]
      ExcitationFile string
      EnergyInline float
      GradientInline # Non-standard block. See details.
         ...
      End
      Singlet # Non-standard block. See details.
         ...
      End
```

(continues on next page)

(continued from previous page)

```
      Triplet # Non-standard block. See details.
         ...
      End
   End
End
```

ExcitationInputFormat [File | Inline] this keyword is used to specify whether the gradient and energy are to be read from a kf file or if one chooses to use the inline block for them. Currently, no TD-DFT engine is implemented in the AMS driver. Furthermore, ADF uses the old tape21 format for its output which is quite different from the more streamlined AMS format. The `inline` option allows one to bypass any possible confusion here. The `File` option requires the specification of the specific excitation to read, which we will discuss below.

GradientInline is the block where the gradient can be specified if the inline option is selected. The format can be either a N by 3 block (N rows, 3 columns) or a 3N long column vector if one happens to have a gradient in this format. The gradient values should be in the unit Hartree/Bohr.

EnergyInline float is used to specify the excitation energy. This will just be a single floating point number (in Hartree).

The resulting input would look like:

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type ...
   ...
   ExcitationSettings
     ExcitationInfo Inline
     # Excited state gradient for transhexatriene 14 atoms x 3 coordinates (to be␣
↪provided in Hartree/Bohr)
     GradientInline
        -0.03786125        0.01786798        0.00003833
         0.05322148       -0.00798712       -0.00004152
        -0.06658803        0.01373495        0.00004727
         0.06656379       -0.01374825        0.00002398
        -0.05318451        0.00799875       -0.00002097
         0.03783718       -0.01786722        0.00001362
         0.00382226        0.00327391        0.00001046
        -0.00046176       -0.00499971       -0.00003583
         0.00014312        0.00534412       -0.00001335
         0.00011081       -0.00558254       -0.00002107
        -0.00011074        0.00558350       -0.00000933
        -0.00014517       -0.00534330        0.00000839
        -0.00381513       -0.00327314       -0.00000248
         0.00046796        0.00499807        0.00000250
     End
     # The vertical excitation energy is simply a float (to be provided in Hartree)
     EnergyInline 0.17062882
   End
End
```

ExcitationFile string If `ExcitationInputFormat` is set to `File` one also has to set the `ExcitationFile` keyword to provide a path to the file from which the info should be read.

Singlet or Triplet In case the excited state information should be read directly from a file, one should specify which excitation AMS should read. This is done analogously to how this is done for excited state gradients in ADF. One chooses either the `Singlet` or `Triplet` blocks (for singlet-singlet or singlet-triplet excitations respectively). Once such a block is chosen, a line containing the symmetry label, followed by the number of the excitation of that symmetry. As for the symmetry labels, the notational convention used can be found in the ADF manual appendix on symmetry labels. If symmetry was disabled, either explicitly by the user or when using TD-DFTB which does not support symmetry, when calculating the excited state properties, the symmetry label `A` should be used. Vibronic-structure calculations are only supported for one excitation at a time.

The resulting input block looks something like this:

```
ExcitationSettings
   ExcitationInputFormat File
   ExcitationFile ./ExcitedState.results/myengine.rkf
   Singlet
     A 1
   End
 End
```

7.2.6 Input: Producing the spectrum

To go from normal modes to an actual spectrum, we have to solve the integral that we introduced in the first section, the details of which will be discussed here.

For long times, the integrand is dominated by the exponential damping term. We can define a suitable cut-off by demanding that this damping term be smaller than some threshold. As mentioned, the integral is evaluated using a Chebyshev quadrature. The number of Chebyshev nodes used for the integral can then be determined from this integration limit and the time step size. This time step size should be large enough to accurately represent the highest frequencies that are present in the highly oscillatory integrand. The Nyquist frequency can be used as a guide here: the highest frequency should be represented by at least two samples each period. Note however, that in principle there is no upper bound to the frequencies present in the integrand due to the fact that modes can be excited to arbitrarily high energy levels. Fortunately, the Franck-Condon factors will quickly act to dampen these high frequencies, restricting their significance. The user may either supply a time step size directly or leave this up to the program to determine. If the latter is chosen the highest relevant frequency is estimated by assuming that oscillator excitations are relevant up to about twice the Huang-Rhys parameter (which follow directly from the displacements). This default should in most cases be sufficient to produce a converged integral.

The keywords associated with the different input parameters are collected under the `AbsorptionSpectrum` block. It contains the following keys:

```
Task VibrationalAnalysis
VibrationalAnalysis
   Type ...
   ...
   AbsorptionSpectrum
      AbsorptionRange float_list
      FrequencyGridPoints integer
      LineWidth float
      SpectrumOffset [absolute | relative]
   End
End
```

`LineWidth float` sets the lorentzian line width and thus has a large impact on the appearance of the final spectrum. It may be used to improve the agreement of the computed spectrum with experiment. Another purpose that the linewidth may serve is that some low frequency modes may not be represented very accurately within the VG-FC model. However, these modes do not result in particularly distinct vibronic progressions but rather cause an unspecific broadening of existing peaks. Applying a homogeneous peak broadening by increasing the value of Γ may be an effective (albeit a little ad hoc) way of resolving such issues, should they occur. The default value is $200cm^{-1}$ but it is recommended to do some experimentation with this value.

`AbsorptionRange float_list` keyword specifies the frequency range (in cm^{-1}) that is to be computed by VST.

`SpectrumOffset [absolute | relative]` specifies whether the range provided by the `AbsorptionRange` keyword is relative to the 0-0 excitation energy (`Relative`), or relative to the vertical excitation energy (`Absolute`). Due to the limited accuracy of the VG-FC model at predicting ΔE_{0-0} the default is `Relative` with a `AbsorptionRange` of [-500,4000].

`FrequencyGridPoints integer` sets the number of points we use on our frequency grid. It is set to 400 by default which generally produces a smooth looking spectrum.

The current implementation of VG-FC vibronic-structure supports only spectra for one excitation at a time. The spectrum is normalized such that the highest peak is equal to 1 in arbitrary units. For this reason the prefactor of the integral is irrelevant and transition dipole moments do not affect the appearance of the spectrum.

CHAPTER

EIGHT

DIPOLE MOMENT, POLARIZABILITY, BOND ORDERS, ORBITAL ENERGIES

This page in the AMS manual describes the calculation of the dipole moment, the polarizability, and bond orders.

```
Properties
   DipoleMoment Yes/No
   Polarizability Yes/No
   BondOrders Yes/No
End
```

Note that because these properties are tied to a particular point on the potential energy surface, they are found on the *engine output files* (page 19). Note also that the properties are not always calculated in every PES point that the AMS driver visits during a calculation. By default they are only calculated in *special* PES points, where the definition of special depends on the *task* (page 45) AMS is performing: For a *geometry optimization* (page 47) properties would for example only be calculated at the final, converged geometry. This behavior can often be modified by keywords special to the particular running task.

8.1 Charges, Dipole Moment, Polarizability

```
Properties
   Charges Yes/No
   DipoleMoment Yes/No
   DipoleGradients Yes/No
   Polarizability Yes/No
End
```

`Properties`

`Charges`

Type Bool

Default value No

Description Requests the engine to calculate the atomic charges.

`DipoleMoment`

Type Bool

Default value No

Description Requests the engine to calculate the electric dipole moment of the molecule. This can only be requested for non-periodic systems.

DipoleGradients

Type Bool

Default value No

Description Requests the engine to calculate the nuclear gradients of the electric dipole moment of the molecule. This can only be requested for non-periodic systems.

Polarizability

Type Bool

Default value No

Description Requests the engine to calculate the polarizability tensor of the system.

8.2 Bond orders & Molecule detection

Many engines can determine bond orders between atoms. For engines based on force fields, these might just be the bond orders used internally by the force field, while for quantum mechanical engines the bond orders are usually determined by analyzing the results of the quantum mechanical calculation, e.g. the electronic density. We refer users to the manuals of the respective engine for details.

If bond orders are requested but the engine does not implement a method for determining bond orders, a bond guessing algorithm will be used instead (see also *BondOrders block* (page 266)). The bond guessing algorithm (which is also used by the graphical user interface to guess bonds) uses inter-atomic distances and atomic valences to guess the bond orders.

You can request bond orders to be calculated in the `Properties` input block:

```
Properties
   BondOrders Yes/No
End
```

Properties

BondOrders

Type Bool

Default value No

Description Requests the engine to calculate bond orders.

For MM engines these might just be the defined bond orders that go into the force-field, while for QM engines, this might trigger a bond order analysis based on the electronic structure. For engines that do not have a bond order analysis method, a bond guessing algorithm will be used. See also the input options in the BondOrders block.

More options can be specified in the `BondOrders` block:

```
BondOrders
   Method [Engine | Guess | EngineWithGuessFallback]
End
```

BondOrders

Method

Type Multiple Choice

Default value EngineWithGuessFallback

Options [Engine, Guess, EngineWithGuessFallback]

Description How to compute the bond orders when they are requested via the 'Properties%BondOrders' key.

'Engine': let the engine compute the bond orders. The specific method used to compute the bond orders depends on the engine selected, and it may be configurable in the engine's input. Note: the calculation may stop if the engine cannot compute bond orders.

'Guess': Use a bond guessing algorithm based on the system's geometry. This is the same algorithm that is used by the Graphical User Interface to guess bonds.

'EngineWithGuessFallback': let the engine compute the bond orders (same as in 'Engine' option) but if the engine did not produce any bond orders, use the bond guessing algorithm as a fallback opion.

Based on the bond orders, the AMS driver can analyze the atomic connectivity graph in order to determine which sets of atoms together constitute molecules. This allows for example to monitor the changes in molecular composition during a reactive molecular dynamics calculation. For *molecular dynamics* (page 91) calculations this option is enabled by default. For other *tasks* (page 45) the molecular analysis can explicitly be requested in the `Properties` block.

```
Properties
   Molecules Yes/No
End
```

`Properties`

`Molecules`

Type Bool

Default value No

Description Requests an analysis of the molecular components of a system, based on the bond orders calculated by the engine.

Details of the molecule detection are configured in a dedicated block:

```
Molecules
   AdsorptionSupportRegion string
   BondOrderCutoff float
End
```

`Molecules`

Type Block

Description Configures details of the molecular composition analysis enabled by the Properties%Molecules block.

`AdsorptionSupportRegion`

Type String

GUI name Adsorption support region

Description Select region that will represent a support for adsorption analysis. Adsorbed molecules will receive an '(ads)' suffix after name of the element bonded to the support. Such elements will be listed separate from atoms of the same element not bonded to the support, for example, HOH(ads) for a water molecule bonded to a surface via one of its H atoms.

`BondOrderCutoff`

Type Float

Default value 0.5

Description Bond order cutoff for analysis of the molecular composition. Bonds with bond order smaller than this value are neglected when determining the molecular composition.

8.3 Bond guessing algorithm

The algorithm to determine bond orders purely from atomic positions, which is used if `BondOrders%Method = Guess`, is roughly as follows:

- Each chemical element has a maximal number of bonds (`connectors` property taken from the PLAMS PeriodicTable class) and a covalent radius.
- Calculate interatomic distances
- Determine bond orders between all non-metal atoms
- Add bonds to any isolated H atoms (these bonds do not count towards the maximal number of bonds for an element).
- Find central atoms of common anions like carbonate, nitrate, sulfate, phosphate, and arsenate
- Add bonds between metal atoms and all other atoms, except the ones from the previous step
- Delete metal-metal bonds and metal-hydrogen bonds if the metal is bonded to enough electronegative atoms and not enough metal atoms. This means that the metal is likely a cation.

The calculated bonds are useful for visualization, but not necessarily for setting up ForceField simulations.

The bond orders to metal atoms are always 1.

Note: The problem of finding molecular bonds for a given set of atoms in space does not have a general solution, especially considering the fact the chemical bond in itself is not a precisely defined concept. For every method, no matter how sophisticated, there will always be corner cases for which the method produces disputable results. Moreover, depending on the context (area of application) the desired solution for a particular geometry may vary. The algorithm used here gives good results for geometries that are not very far from the optimal geometry, especially consisting of lighter atoms. All kinds of organic molecules, including aromatic ones, usually work very well. Problematic results can emerge for transition metal complexes, transition states, incomplete molecules etc.

Warning: This method works reliably only for geometries representing complete molecules. If some atoms are missing (for example, a protein without hydrogens) the resulting set of bonds would usually contain more bonds or bonds with higher order than expected.

A version of this algorithm is also implemented in the PLAMS Molecule.guess_bonds() method.

8.4 Orbital energies, HOMO-LUMO gap

Ab-initio or semiempirical engines, such as ADF or DFTB, internally compute molecular orbital energies and occupations (see *Summary of engine capabilities* (page 272)). This information is printed to the AMSResults section of the text output and is stored in the AMSResults section of the binary engine results.

Example of molecular orbitals information printed to the text output:

```
-----------------------
Molecular orbitals info
-----------------------
n orbitals:                8
n spin:                    1

HOMO (eV):             -13.5919
LUMO (eV):              -4.2036
HOMO-LUMO gap (eV):      9.3883

   Index   Energy (eV)    Occupation
       8       12.3038         0.000
       7        9.4801         0.000
       6       -1.3196         0.000
       5       -4.2036         0.000 < LUMO
       4      -13.5919         2.000 < HOMO
       3      -14.8182         2.000
       2      -16.6543         2.000
       1      -20.6183         2.000
```

`n spin`: 1 in case of spin-restricted or spin-orbit calculations, 2 in case of spin-unrestricted calculations.

`Occupations`: in case of spin-unrestricted calculations the occupation numbers will be in the range 0-2. In case of spin-restricted calculation or spin-orbit calculations, the the occupation numbers will be in the range 0-1.

Note: In case of **fractional occupation** (i.e. non-integer occupations numbers), the definition of HOMO and LUMO is somewhat ill defined.

If fractional occupations are detected, a message will be printed to the text output.

The logical variable `AMSResults%fractionalOccupation` in the engine .rkf results file indicates whether fractional occupation was detected.

Here, we use the following convention:

- The HOMO is the highest-energy orbital for which occupation[iOrbital] > occupied_threshold. The LUMO is HOMO+1.
- if occupation[LUMO] < unoccupied_threshold we have integer occupations.
- if occupation[LUMO] > unoccupied_threshold we have we have **fractional occupations**

where occupied_threshold = 0.9 * max_occupation, unoccupied_threshold = 0.1 * max_occupation (max occupation = 2 for spin-restricted calculations and 1 for spin-unrestricted or spin-orbit calculations)

In case of spin-unrestricted calculation, the “smallest HOMO-LUMO gap” is the smallest HOMO-LUMO gap irrespective of spin (i.e. min(LUMO) - max(HOMO)).

The molecular orbital information is generally automatically computed by engines supporting it.

You can explicitly request this in the input via the following keyword:

```
Properties
   OrbitalsInfo Yes/No
End
```

Properties

OrbitalsInfo

Type Bool

Default value No

Description Basic molecular orbitals information: orbital energies, occupations, HOMO, LUMO and HOMO-LUMO gap.

If you explicitly request `OrbitalsInfo` to be computed, but the engine cannot compute it, AMS will stop with an error.

Molecular orbital information can only calculated in case of non-periodic systems.

8.5 Uncertainties

Some engines may report uncertainties for some properties. Currently only the Hybrid engine supports uncertainties and only when running in committee mode.

Uncertainties are reported to text output:

```
Engine energy uncertainty (hartree)              0.01253685

Uncertainty in Gradients (hartree/bohr)
  Index   Atom            d/dx            d/dy            d/dz       Magnitude
      1      C    0.0005234578    0.0001727093    0.0002762926    0.0002311556
      2      C    0.0000008845    0.0007601116    0.0000014245    0.0007601017
      3      C    0.0005218907    0.0001737959    0.0002777874    0.0002325467
      4      O    0.0004150496    0.0002459280    0.0000738370    0.0004012048
      5      O    0.0004146230    0.0002469354    0.0000735124    0.0004003429
      6      H    0.0000668939    0.0001815939    0.0001866700    0.0001726131
      7      H    0.0001069923    0.0001412011    0.0001620722    0.0001367296
      8      H    0.0001069626    0.0001408593    0.0001624397    0.0001365849
      9      H    0.0000668212    0.0001810509    0.0001866413    0.0001723906
```

Additionally, they can be obtained from the engine rkf file in the `AMSResults%EnergyUncertainty`, `AMSResults%GradientsUncertainty` for the uncertainty in the energy in the energy and gradients respectively. For convenience, `AMSResults&GradientsMagnitudeUncertainty` is provided for convenience, which reports the uncertainty in the magnitude of the gradients based on the variance formula, or error propagation.

During `Task MolecularDynamics`, the uncertainties are additionally provided in the *History* section of *ams.rkf* in the variables `EngineEnergyU(#)`, `EngineGradientsU(#)` and `EngineGradientsNormU(#)` (Magnitude).

It is possible to define an *exit condition* (page 158) when uncertainties are too high.

See also:

In PLAMS, you can use dedicated getters to extract this information from AMSResults.

CHAPTER

NINE

ENGINES

The engines are the core of the Amsterdam Modeling Suite: While the AMS driver steers the calculation over the potential energy surface in e.g. a *geometry optimization* (page 47) or *molecular dynamics* (page 91) calculation, the engines calculate energies and gradients and in this way *define* the PES on which the driver works.

```
Engine header
```

Engine

Type Block

Description The input for the computational engine. The header of the block determines the type of the engine.

The engine used for an AMS calculation is selected and configured with the special `Engine` block in the AMS input:

```
Engine DFTB
   ... input for the DFTB engine ...
EndEngine
```

Here the type of engine, e.g. `DFTB` as in the example above, is specified on the line that opens the block. Note that the `Engine` block ends with `EndEngine`, and is in this way different from all the other blocks in the AMS input, which close just with `End`. The content of the engine block is what we call the "engine input". Generally the engine input consists of a series of blocks and keywords, and looks just like the AMS driver input. However, many engines have a lot of options and keywords, which are documented in a separate engine manual. In other words: This AMS driver manual documents all the keywords outside of the `Engine` block, while the individual engine manuals document the contents of the engine block.

9.1 Available engines

The following engines are available in the 2024.1 release of the Amsterdam Modeling Suite:

- **ADF** A DFT engine particularly strong in understanding and predicting structure, reactivity, and spectra of molecules.
- **BAND** An atomic-orbital based DFT engine aimed at periodic systems (crystals, slabs, chains) but supporting also molecular systems.
- **DFTB** An engine implementing Density Functional based Tight-Binding, a fast approximation to DFT.
- **ReaxFF** An engine for modeling chemical reactions with atomistic potentials based on the reactive force field approach.
- **MLPotential** Machine learning potentials (machine learning force fields).

- **ForceField** An engine implementing classical non-reactive force fields such as UFF (a non-reactive force field covering the entire periodic table).
- **GFNFF** The GFNFF force field
- **Hybrid** Hybrid engine, for embedding and QM/MM calculations that combine multiple engines.
- **MOPAC** An engine wrapping the MOPAC code, a general-purpose semiempirical molecular orbital package for the study of solid state and molecular structures and reactions.
- **ASE** A flexible scripting interface that allows advanced users to use external modeling programs as engines in AMS through the Atomic Simulation Environment (ASE).
- ***External* (page 274)** A flexible scripting interface that allows advanced users to use external modeling programs as engines in AMS.
- ***LennardJones* (page 278)** A simple toy engine implementing a Lennard-Jones potential.

9.2 Summary of engine capabilities

Some options/properties can only be computed in combination with some of the engines (i.e., not all engines support all features). These tables summarize the capabilities of the engines of the Amsterdam Modeling Suite:

Table 9.1: Engine support for AMS driver options

Feature	ADF	BAND	DFTB	ReaxFF	MLPot.	Force-Field	MOPAC	GFNFF	Engine ASE
All elements available	✓	✓	✓[2]			✓[3]	✓	✓	✓[5]
Non-periodic systems (page 31)	✓	✓	✓	✓	✓[4]	✓	✓	✓	✓[?]
1D periodic systems (page 31)		✓	✓	✓		✓	✓		✓[?]
2D periodic systems (page 31)		✓	✓	✓		✓	✓		✓[?]
3D periodic systems (page 31)		✓	✓	✓	✓[?]	✓	✓	✓	✓[?]
Charged molecular systems	✓	✓	✓	✓		✓	✓	✓	✓[?]
External electric field	✓	✓	✓				✓		
External point charges	✓	✓	✓						

[2] All elements are available for the GFN1-xTB model, but other DFTB parameter sets are not parametrized for all elements.
[3] All elements are available with UFF (universal force field), but other force fields are not parametrized for all elements.
[5] The ASE Engine only supports communicating these properties to and from the concomitant ASE Calculator. Actual support is determined by the ASE Calculator used.
[4] MLPotential backends may support non-periodic and/or 3D-periodic calculations.

Table 9.2: Engine support for AMS driver properties

Feature	ADF	BAND	DFTB	ReaxFF	MLPot.	Force-Field	MOPAC	GFNFF	Engine ASE
Atomic charges (page 265)	✓	✓	✓	✓		✓	✓	✓	
Bond orders (page 266)[1]	✓		✓	✓		✓	✓	✓	
Orbital energies (page 268)	✓	✓	✓				✓		
HOMO-LUMO gap (page 268)	✓	✓	✓				✓		
Dipole gradients (page 265)	✓	✓	✓				✓	✓	✓?
Dipole moment (page 265)	✓	✓	✓				✓	✓	✓?
Elastic tensor (page 204)		✓	✓	✓	✓	✓	✓	✓	
Gradients / Forces (page 199)	✓	✓	✓	✓	✓	✓	✓	✓	✓
Hessian (page 200)	✓	✓	✓	✓	✓	✓	✓	✓	✓
Infrared spectra (page 209)	✓	✓	✓				✓	✓	
Molecule detection	✓		✓	✓		✓	✓	✓	
Normal modes (page 209)	✓	✓	✓	✓	✓	✓	✓	✓	✓
PES point character (page 200)	✓	✓	✓	✓	✓	✓	✓	✓	✓
Phonons (page 233)		✓	✓	✓	✓	✓	✓	✓	✓
Polarizability (page 265)	✓								
Raman (page 237)	✓								
Stress tensor (page 203)		✓	✓	✓	✓	✓	✓	✓	✓
Thermodynamic properties (page 229)	✓	✓	✓	✓	✓	✓	✓	✓	✓
VCD (page 243)	✓	✓	✓				✓		
VROA (page 242)	✓								

Note: The features/options in the following tables are **engine-specific**, and are described in the corresponding engine's manual. The input for these options should be specified in the *Engine block* (page 9) section of the input file.

[1] If the engine does not support the calculation of bond orders, a bond guessing algorithm will be used instead. See *Bond Orders* (page 266).

Table 9.3: Engine-specific capabilities

Feature	ADF	BAND	DFTB	ReaxFF	MLPot.	Force-Field	MOPAC	GFNFF	Engine ASE
EFG	✓ (doc)	✓ (doc)							
Electronic transport	✓ (doc)	✓ (doc)	✓ (doc)						
Energy decomposition analysis	✓ (doc)	✓ (doc)							
ESR/EPR	✓ (doc)								
Hyperpolarizabilities	✓ (doc)								
NMR	✓ (doc)								
pKa							✓ (doc)		
Solvation models	✓ (doc)	✓ (doc)	✓ (doc)				✓ (doc)		
Spin-polarization	✓ (doc)	✓ (doc)	✓ (doc)				✓ (doc)		
UV-VIS optical spectra	✓ (doc)		✓ (doc)						

Table 9.4: Engine-specific capabilities for periodic systems

Feature	ADF	BAND	DFTB	ReaxFF	MLPot.	Force-Field	MOPAC	Engine ASE
Density of states (DOS)		✓ (doc)	✓ (doc)					
Dielectric function		✓ (doc)						
Effective mass		✓ (doc)	✓ (doc)					
Electronic band structures		✓ (doc)	✓ (doc)					
k-space sampling		✓ (doc)	✓ (doc)					
X-ray form factors		✓ (doc)						

9.3 External programs as engines

The AMS driver allows running external programs as an engine. In this way users can combine the functionality in the AMS driver (tasks and PES point properties) with the energies and gradients of any molecular modeling program they have access to. For example, the graphical user interface supports setting up VASP as an external engine to the AMS driver.

See also:

As an alternative to Engine External, Engine ASE also lets you couple external programs to AMS through the Python library ASE (Atomic Simulation Environment).

In general, the interfacing between the AMS driver and the external program has to be done by the user in form of a small script, which allows users to hook up any external program without access to the source code of AMS. The graphical user interface of the Amsterdam Modeling Suite can then be used to analyze the results of these calculations.

An external engine is specified with `Engine External`. The keyword `Execute` is used to specify the command that is run to execute the external program:

```
Engine External
    Execute /path/to/my_interface_script.sh
EndEngine
```

The command can in principle be anything, as it will just be executed as is by the system shell. However, it should not use relative paths (e.g. to files in the directory where the input file is). We recommend writing the interfacing script in Python and using the Python interpreter that ships with AMS:

```
Engine External
    Execute "$AMSBIN"/amspython /path/to/my_python_interface_script.py
EndEngine
```

AMS then starts running and for every geometry prepares a folder in which the external engine is supposed to run. This is the folder in which the interface script specified with the `Execute` key is executed (so any relative paths are relative to that folder). AMS puts two files into this folder:

```
system.xyz
request.json
```

The `system.xyz` just contains the geometry AMS wants the external engine to calculate. It is an *extended format XYZ file* (page 487) with the `VEC1`, `VEC2`, `VEC3` extension at the end for periodic systems, e.g. diamond would look like this:

```
2

C       -0.51292147    -0.51292147    -0.51292147
C        0.51292147     0.51292147     0.51292147
VEC1     0.00000000     2.05168587     2.05168587
VEC2     2.05168587    -0.00000000     2.05168587
VEC3     2.05168587     2.05168587     0.00000000
```

The `request.json` file is just a small JSON file that specifies what exactly AMS wants the external engine to calculate:

```
{
   "title": "GOStep28",
   "quiet": false,
   "gradients": true,
   "stressTensor": false,
   "hessian": true,
   "dipoleMoment": false,
   "properties": true,
   "prevResults": "GOStep27"
}
```

The job of the interfacing script is now to read these files, run the external program and convert its output into a format understood by AMS. Generally these are simple text files with the name of the property and the extension `.txt`. The bare minimum the interfacing script needs to produce is the file `energy.txt` containing a single number, i.e. the total energy in atomic units (Hartree). Other properties are optional, and it is easiest to go through the `request.json` entries one by one to see what AMS might request and what the interfacing script could produce in response.

title Just a title for this particular engine run. It can be passed on to the external program if desired, or can just be ignored.

quiet Whether AMS wants the external engine to write to standard output. This can be ignored in principle, but that might lead to really incomprehensible text output files of AMS if the external engine has to be called many times, e.g. for numerical derivatives.

gradients Whether or not to calculate nuclear gradients. The interface script should put the gradients in a file called `gradients.txt` with nAtoms lines of 3 real numbers each, in atomic units, i.e. Hartree/Bohr. Note that AMS wants the gradients, not forces (beware the - sign!).

stressTensor Whether to calculate the stressTensor for periodic systems. Should be written to `stresstensor.txt` in atomic units.

hessian Whether to calculate the Hessian, that is just the second derivative of the energy with respect to the nuclear coordinates, *without* applying any mass weighing to it. If the Hessian has been calculated, it should be put in `hessian.txt` as a 3 nAtoms x 3 nAtoms matrix in atomic units.

dipoleMoment If true, calculate the dipole moment and put it in `dipolemoment.txt` in atomic units, in one line with three numbers.

properties This is set to true if AMS considers this "geometry" important and wants the engine to calculate further properties that the user might be interested in. In practice this is set to "true" for e.g. the final converged step in a geometry optimization, so that the user can then let the engine calculate e.g. the band structure, which one would not want to do at all the steps *during* the optimization. AMS can't do anything with the properties that the engine might calculate, but the files will remain on disk for people to inspect them.

prevResults This is the title of a previous similar calculation that the engine has already performed. These results can be accessed in `../$prevResults/`, so for the example above `GOStep28` can access the results from the previous step in the geometry optimization in `../GOStep27/`. This is just the directory in which the interfacing script was run when the `title` field was set to `GOStep27`, so files that were written back then are still accessible. They can in principle be used to restart for example the SCF of the engine from step to step. Of course all of that has to be done by the interfacing script. The AMS driver does not know anything about how to restart the external program and can only point the interfacing script to the right location.

That is really all there is to the external engine: AMS prepares a folder with `system.xyz` and `request.json` and runs the user's interfacing script in there, which has to take care of preparing the input for the external engine, running it, and putting the results in the text files that AMS expects, e.g. `gradients.txt`.

Note for properties that are in one way or another derivatives of the energy, it is generally ok if the external engine does not calculate what was requested by the AMS driver in `request.json`. If AMS requests, for example, the gradients from the external engine, but then does not find the `gradients.txt` in the directory after the interfacing script has run, it will just assume that the engine was not capable of calculating the gradient analytically. AMS will then just do the gradient numerically by rerunning the external engine for displaced geometries, reading only the energy from `energy.txt`. In this sense it is only absolutely required for the external engine to produce the energy, the rest can be done numerically by AMS if required. It is of course best to let the engine do as much as possible, especially if it implements analytical derivatives. Note that currently AMS can not calculate the Hessian numerically for engines that do not provide gradients. This is just a technical limitation, as it is of course possible to do a second derivative numerically, but it is just not implemented in AMS yet. (And it would also be a very slow way to calculate a Hessian.)

In addition to the `Execute` keyword that specifies the interfacing script, it is also possible to use the `ExecuteAtEnd` keyword to specify another command to be run at the end of the calculation, for example after the last step of a geometry optimization or molecular dynamics simulation. This command is run in the results directory.

Moreover, the `Engine External` block can also contain some information about the capabilities of the external engines:

```
Engine External
   Execute {...}
```

(continues on next page)

(continued from previous page)

```
   ExecuteAtEnd {...}
   Supports
      DipoleMoment     {true|false}
      PeriodicityNone  {true|false}
      PeriodicityChain {true|false}
      PeriodicitySlab  {true|false}
      PeriodicityBulk  {true|false}
   End
EndEngine
```

The normal engines that come with AMS (e.g. DFTB and BAND) produce the engine output files with extension `.rkf` in the results directory, see *here* (page 19). These files are also produced when an external engine is used and the information on them (anything related to the shape of the PES at that point, e.g. normal modes, phonons, ...) can be visualized normally with the graphical interface. In addition to each engine output `.rkf` file, external engines will also produce a correspondingly named folder per engine file, which is just the working directory of the interfacing script for that particular invocation of the external program. These folders just contain the full output of the external program and anything that the interfacing script might have produced. In this way users still have access to all results from the external program, even if these results were not communicated back to the AMS driver.

This last point is probably best illustrated with a simple example. Consider the following job that uses an external engine to do a linear transit calculation of ethane, going from the staggered to the eclipsed configuration, calculating normal modes at all converged points along the path:

```
AMS_JOBNAME=ethane_torsion $AMSBIN/ams << EOF

Task PESScan

System
   Atoms
      C       0.00000000       0.00000000       0.76576000
      C       0.00000000       0.00000000      -0.76576000
      H      -0.88668938       0.51193036       1.16677000
      H       0.88668938       0.51193036       1.16677000
      H       0.00000000      -1.02386071       1.16677000
      H       0.00000000       1.02386071      -1.16677000
      H      -0.88668938      -0.51193036      -1.16677000
      H       0.88668938      -0.51193036      -1.16677000
   End
End

PESScan
   CalcPropertiesAtPESPoints True
   ScanCoordinate
      nPoints 5
      Dihedral  3 1 2 6   60.0  0.0
   End
End

Properties
   NormalModes True
End

Engine External
   ...
EndEngine

```

(continues on next page)

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```
EOF
```

If we run this job and look into the results folder, we will find the standard `ams.log` and `ams.rkf` as well as the usual engine result files `PESPoint(1).rkf` to `PESPoint(5).rkf`. Just as if we had used one of the native AMS engines, like DFTB. Each of these files can be opened in AMSspectra to visualize the normal modes for this particular point. For an external engine we additionally have one folder per engine file, so for this example we would have `PESPoint(1)/` to `PESPoint(5)/`. These are the folders in which the interfacing script ran for these particular points, so they contain all the native output files of the external program.

9.4 Toy engines

The AMS driver comes with a simple built-in toy engine that implements a Lennard-Jones potential. This can sometimes be useful for testing, as many properties of the Lennard-Jones gas/liquid/solid can be calculated analytically and compared to the results from AMS. Note that the potential is exactly the same for all elements, i.e. the N-N bond has exactly the same strength as the He-He bond.

The Lennard-Jones engine only has three keywords, which define the shape of the potential:

```
Engine LennardJones
   RMin   float
   Eps    float
   Cutoff float
EndEngine
```

`Cutoff`

Type Float

Default value 15.0

Unit Angstrom

Description The distance at which the interaction is truncated.

`Eps`

Type Float

Default value 1.0

Unit Hartree

Description The depth of the potential well.

`RMin`

Type Float

Default value 1.0

Unit Angstrom

Description The distance of the potential minimum.

9.5 Engine add-ons

Engine add-ons can be used to augment the results returned from an engine.

9.5.1 Dispersion corrections

For engines that do not natively support Grimme's D3 and D4 dispersion corrections, the `D3Dispersion` and `D4Dispersion` engine add-ons can be used to add such corrections.

```
EngineAddons
   D3Dispersion
      Damping [BJ | Zero]
      Enabled Yes/No
      Functional string
      a1 float
      a2 float
      s6 float
      s8 float
      sr6 float
   End
   D4Dispersion
      Enabled Yes/No
      Functional [...]
      Verbosity [Silent | Normal | Verbose | VeryVerbose]
      a1 float
      a2 float
      s6 float
      s8 float
      s9 float
   End
End
```

`EngineAddons`

`D3Dispersion`

Type Block

Description This block configures the add-on that adds the Grimme D3 dispersion correction to the engine's energy, gradients, and stress tensor.

`Damping`

Type Multiple Choice

Default value BJ

Options [BJ, Zero]

Description Type of damping: BJ (Becke-Johnson) or Zero. BJ is recommended for most applications.

`Enabled`

Type Bool

Default value No

GUI name D3 dispersion

Description Enables the D3 dispersion correction addon.

`Functional`

Type String

Default value PBE

Description Use the D3 parameterization by Grimme for a given xc-functional. Accepts the same values as the –func command line option of the official dftd3 program. Note: the naming convention is different from elsewhere in the AMS suite. For example, BLYP should be called b-lyp.

`a1`

Type Float

Description The a1 parameter. Only used if Damping is set to BJ. If set, it overwrites the a1 value for the chosen functional.

`a2`

Type Float

Description The a2 parameter. Only used if Damping is set to BJ. If set, it overwrites the a2 value for the chosen functional.

`s6`

Type Float

Description The s6 parameter, global scaling parameter. If set, it overwrites the s6 value for the chosen functional.

`s8`

Type Float

Description The s8 parameter. If set, it overwrites the s8 value for the chosen functional.

`sr6`

Type Float

Description The sr6 parameter. Only used if Damping is set to Zero. If set, it overwrites the sr6 value for the chosen functional.

`D4Dispersion`

Type Block

Description This block configures the addon that adds the Grimme D4(EEQ) dispersion correction to the engine's energy, gradients, stress tensor and Hessian.

`Enabled`

Type Bool

Default value No

GUI name D4 dispersion

Description Enables the D4 dispersion correction addon.

`Functional`

Type Multiple Choice

Default value PBE

Options [HF, BLYP, BPBE, BP86, BPW, LB94, MPWLYP, MPWPW91, OLYP, OPBE, PBE, RPBE, REVPBE, PW86PBE, RPW86PBE, PW91, PW91P86, XLYP, B97, TPSS, REVTPSS, SCAN, B1LYP, B3LYP, BHLYP, B1P86, B3P86, B1PW91, B3PW91, O3LYP, REVPBE0, REVPBE38, PBE0, PWP1, PW1PW, MPW1PW91, MPW1LYP, PW6B95, TPSSH, TPSS0, X3LYP, M06L, M06, OMEGAB97, OMEGAB97X, CAM-B3LYP, LC-BLYP, LH07TSVWN, LH07SSVWN, LH12CTSSIRPW92, LH12CTSSIFPW92, LH14TCALPBE, B2PLYP, B2GPPLYP, MPW2PLYP, PWPB95, DSDBLYP, DSDPBE, DSDPBEB95, DSDPBEP86, DSDSVWN, DODBLYP, DODPBE, DODPBEB95, DODPBEP86, DODSVWN, PBE02, PBE0DH, DFTB(3ob), DFTB(mio), DFTB(pbc), DFTB(matsci), DFTB(ob2), B1B95, MPWB1K, REVTPSSH, GLYP, REVPBE0DH, REVTPSS0, REVDSDPBEP86, REVDSDPBEPBE, REVDSDBLYP, REVDODPBEP86, B97M, OMEGAB97M, R2SCAN]

Description Use the D4 parameterization by Grimme for a given xc-functional.

`Verbosity`

Type Multiple Choice

Default value Silent

Options [Silent, Normal, Verbose, VeryVerbose]

Description Controls the verbosity of the dftd4 code. Equivalent to the –silent and –verbose command line switches of the official dftd4 program.

`a1`

Type Float

Description The a1 parameter, see D4 article. The physically reasonable range for a1 is [0.0,1.0]. If set, it overwrites the a1 value for the chosen functional.

`a2`

Type Float

Description The a2 parameter, see D4 article. The physically reasonable range for a2 is [0.0,7.0]. If set, it overwrites the a2 value for the chosen functional.

`s6`

Type Float

Description The s6 parameter, see D4 article. The physically reasonable range for s6 is [0.0,1.0]. If set, it overwrites the s6 value for the chosen functional.

`s8`

Type Float

Description The s8 parameter, see D4 article. The physically reasonable range for s8 is [0.0,3.0]. If set, it overwrites the s8 value for the chosen functional.

`s9`

Type Float

Description The s9 parameter, see D4 article. If set, it overwrites the s9 value for the chosen functional.

9.5.2 Pressure

Pressure can be included using the following keyword (this can only be used for **3D periodic systems**):

```
EngineAddons
   Pressure float
End
```

EngineAddons

Pressure

Type Float

Default value 0.0

Unit GPa

Description Add a hydrostatic pressure term to the engine's energy and stress tensor. Can only be used for 3D periodic boundary conditions.

The engine's energy will include the following extra term: $P \cdot V$, where V is the volume of the unit cell. The engine's stress tensor will include the following extra term: $P \cdot \mathbb{1}$, where $\mathbb{1}$ is the identity matrix. This can only be used for 3D periodic boundary conditions (i.e. bulk). The energy and stress tensor printed in output and written to the `.rkf` binary file will include these extra terms (i.e. the printed stress tensor is the sum of the internal stress and the external stress do to pressure).

When studying the effect that pressure has on the structure and properties of your system, one should generally start by *optimizing the structure* (page 47) **including the lattice vectors** under pressure. Properties such as *phonons* (page 233) or *elastic tensor* (page 204) can then be computed at the relaxed geometry. If you are investigating phase transitions under pressure (or if you simply expect some symmetry breaking) you should disable symmetry and/or perturb the initial geometry of your system.

See also:

Example: Periodic lattice optimization under pressure (page 381)

Warning: If you want to include pressure in *molecular dynamics* (page 91) calculations, you should not use this engine addon, but use the MD-specific pressure option.

9.5.3 Non-isotropic external stress

An **non-isotropic external stress tensor** can be included by using the following keywords:

```
EngineAddons
   ExternalStress
      StressTensorVoigt float_list
      UpdateReferenceCell Yes/No
   End
End
```

EngineAddons

ExternalStress

Type Block

Description This block configures the addon that adds external stress term to the engine's energy and stress tensor.

`StressTensorVoigt`

Type Float List

Unit Hartree/Bohr^3

GUI name External stress tensor

Description The elements of the external stress tensor in Voigt notation. One should specify 6 numbers for 3D periodic system (order: xx,yy,zz,yz,xz,xy), 3 numbers for 2D periodic systems (order: xx,yy,xy) or 1 number for 1D periodic systems.

`UpdateReferenceCell`

Type Bool

Default value No

Description Whether ot not the reference cell should be updated every time the system changes (see documentation).

The energy and stress tensor printed in output and written to the `.rkf` binary file already include the corresponding extra terms, i.e. the printed stress tensor is the sum of the internal stress and the input-specified external stress.

When studying the effect that an external stress has on the structure and properties of your system, one should generally start by *optimizing the structure* (page 47) **including the lattice vectors** under the external stress (depending on the magnitude of the applied external stress, you might have to adjust the *stress energy per atom convergence threshold* (page 48)). If your system is symmetric, you should **disable symmetry** when optimizing structures under external stress. Be aware that the geometry optimization might go completely astray (e.g. the material will break apart) if you apply a) too large shear stress or b) too large tension stress (too large negative stresses for the diagonal values).

Following this paper[6] from Parrinello and Rahman, the extra energy term due to a non-isotropic external stress[7] is defined with respect to a *reference unit cell*, which in our case is the unit cell at the beginning of the simulation. If, during the simulation, large deformations of the unit cell occur, the above mentioned energy expression is only approximately consistent with the stress tensor. This affects the calculation differently depending on whether the stress tensor is computed by the engine or by AMS via numerical differentiation: a) If the stress tensor is computed directly by the engine, for large unit-cell deformations the energy might increase during the optimization; b) If the stress tensor is computed by AMS via numerical differentiation, the actual final value of the stress tensor might not match perfectly the external stress specified in the input (for large cell deformations, this error can be in the order of 10%).

After the optimization under external stress is converged, it is therefore good practice to validate the results. To do this, you should compute the *stress tensor* (page 203) at the optimized geometry by performing a *single point calculation* (page 45) **without** applying the external stress. The values in the computed stress tensor should have opposite sign compare to the external stress applied during the optimization. If the values differ too much, then you can run a second geometry optimization under external stress starting from the optimized geometry.

See also:

Example: Boron nitride optimization under external stress (page 384)

[6] M. Parrinello, and A. Rahman, *Polymorphic transitions in single crystals: A new molecular dynamics method*, Journal of Applied Physics 52, 7182 (1981) (https://doi.org/10.1063/1.328693)

[7] The energy term due to a non-isotropic external stress is:

$$E_{\text{stress}} = p_h(V - V_0) + \frac{1}{2}V_0 Tr[(\sigma - p_h\mathbb{1})(h_0^{T-1}h^T h h_0^{-1} - \mathbb{1})]$$

where: σ is the external stress tensor, p_h is the hydrostatic pressure associated with σ (i.e. the average of the diagonal elements of σ), V is the volume of the unit cell (for 2D periodic systems this is the area of the cell, and for 1D periodic systems is the length of the cell), V_0 is the volume of the *reference unit cell*, h are the lattice vectors in matrix form, h_0 are the lattice vectors of the reference unit cell in matrix form and $\mathbb{1}$ is the identity matrix.

An alternative option is to set the key `ExternalStress%UpdateReferenceCell` to `True`; this will update the reference unit cell at every optimization step, effectively changing the definition of the energy expression at every geometry optimization step. The energy might not consistently go down during the optimization, but the resulting internal stress will match much better the applied external stress. This option should only be used during geometry optimizations (i.e. it should not be used when computing properties such as the elastic tensor).

See also:

Example: Graphene optimization under external stress (page 386)

9.5.4 Atom energies

This add-on adds an element-dependent energy for each atom in a system, effectively applying an energy shift. It does not affect any other property.

```
EngineAddons
   AtomEnergies # Non-standard block. See details.
      ...
   End
End
```

`EngineAddons`

Type Block

Description This block configures all the engine add-ons.

`AtomEnergies`

Type Non-standard block

Description Add an element-dependent energy per atom. On each line, give the chemical element followed by the energy (in atomic units).

The below example will add -0.5 Hartree for every H atom and -5.0 Hartree for every C atom in the system to the total energy. The add-on will ignore any atoms of other elements:

```
EngineAddons
   AtomEnergies
      H -0.5
      C -5.0
   End
End
```

9.5.5 Restraints

A restraint is potential energy function (a spring) attached to a certain coordinate, for example, an interatomic distance, the minimum of the potential energy being at the specified optimal value. A restraint can have one or two parameters: a ForceConstant and, for some types, a F(Inf) value. The ForceConstant parameter corresponds to second derivative of the restraint potential energy $\frac{d^2V(x)}{dx^2}$ for any x (harmonic restraints) or only at $x = 0$ (other restraints). Here, x is a deviation from the restraint's optimal value.

Geometry restraints can be added using the following input block:

```
Restraints
   Profile [Harmonic | Hyperbolic | Erf | GaussianWell]
   fInfinity float
```

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```
   Distance atomIdx1 atomIdx2 OptValue ForceConstant {Profile} {fInfinity}
   Angle
   Dihedral
   SumDist
   DifDist
End
```

The shape of the restraint potential function is defined by its profile type (`Harmonic`, `Hyperbolic`, `Erf`) and the appropriate parameter(s). The `Harmonic` profile is most suitable for geometry optimizations but may result in very large forces that can be problematic in molecular dynamics. For MD simulations the `Hyperbolic` or `Erf` may be more suitable because the restraint force is bounded by a user-defined value. A `Harmonic` restraint is defined as $V(x) = C\frac{x^2}{2}$. A `Hyperbolic` restraint is defined as $V(x) = a(\sqrt{1+(bx)^2} - 1)$. An `Erf` restraint is defined as $V(x) = a(bx \cdot erf(bx) + \frac{e^{-(bx)^2}-1}{\sqrt{\pi}})$, which corresponds to an indefinite integral of the error function $\frac{dV(x)}{dx} = ab \cdot erf(bx)$. The a and b parameters are calculated from the `FInfinity` and ForceConstant values. The `Erf` profile is very similar to `Hyperbolic` however its derivative converges to F(Inf) much faster.

There is a special restraint type, `GaussianWell`, that should only be used with MD BondBoost because it has a negligible force at large deviations. It is defined as $V(x) = a(1 - e^{-bx^2})$. Here, instead of the force constant and the asymptotic force value, the two parameters define the depth and the width of the well, respectively.

The following keys define global parameters for all restraints.

`Restraints`

`Profile`

Type Multiple Choice

Default value Harmonic

Options [Harmonic, Hyperbolic, Erf, GaussianWell]

GUI name Default restraint profile

Description Select the default type of restraint profile.

The harmonic profile is most suitable for geometry optimizations but may result is very large forces that can be problematic in molecular dynamic.

For MD simulations the Hyperbolic or Erf may be more suitable because the restraint force is bounded by a user-defined value.

A per-restraint profile type can be specified after the ForceConstant value on the corresponding restraint line.

`FInfinity`

Type Float

Default value 1.0

GUI name Default F(inf)

Description Specify the default asymptotic value for the restraint force for the Hyperbolic and Erf profiles, in Hartree/Bohr or Hartree/radian.

A per-restraint value can be specified after the profile type on the corresponding restraint line.

The following keys define individual restraints. The force constant, profile type and the F(Inf) value can be set for each restraint individually.

`Restraints`

`Distance`

Type String

Recurring True

Description Specify two atom indices followed by the distance in Angstrom and, optionally, by the ForceConstant (default is 1.0 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the distance between the two specified atoms at the given value. For periodic systems this restraint follows the minimum image convention.

`Angle`

Type String

Recurring True

Description Specify three atom indices i j k followed by an angle in degrees and, optionally, by the ForceConstant (default is 0.3 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the i-j-k angle at the given value. For periodic systems this restraint follows the minimum image convention.

`Dihedral`

Type String

Recurring True

Description Specify four atom indices i j k l followed by an angle in degrees and, optionally, by the ForceConstant (default is 0.1 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the i-j-k-l dihedral angle at the given value. For periodic systems this restraint follows the minimum image convention.

`DifDist`

Type String

Recurring True

Description Specify four atom indices i j k l followed by the distance in Angstrom and, optionally, by the ForceConstant (default is 1.0 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the difference R(ij)-R(kl) at the given value. For periodic systems this restraint follows the minimum image convention.

`SumDist`

Type String

Recurring True

Description Specify four atom indices i j k l followed by the distance in Angstrom and, optionally, by the ForceConstant (default is 1.0 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the sum R(ij)+R(kl) at the given value. For periodic systems this restraint follows the minimum image convention.

A default value for the force constant depends on the restraint type: 1.0 Hartree/Bohr for Distance, SumDist and DifDist, 0.3 Hartree/radian for Angle and 0.1 Hartree/radian for Dihedral.

Below is an example if the Restraints block.

```
Restraints
   Profile Hyperbolic      # Change the default profile type
   fInfinity 10.0          # Change the asymptotic value for the restraint force away␣
↪from optimum
```

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```
#  Type      Atoms    OptValue  FC   Profile   F(Inf)
   Distance 1 2        5.0     1.0  Erf       1.0
   Angle    1 2 3     90.0
   Dihedral 4 1 2 3  180.0     0.1
#  The next two together are equivalent to imposing two distance restraints: R(23) to
↪0.85 Angstrom and R(14) to 0.65 Angstrom
   SumDist  1 4 2 3    1.5     # Keep R(14)+R(23) as close to 1.5 Angstrom as possible
   DifDist  1 4 2 3    0.2     # Keep R(14)-R(23) as close to 0.2 Angstrom as possible
End
```

9.5.6 Wall potential

This add-on adds an inward repulsive potential around the origin of the form

$$E_{\text{wall}}(r) = k\log(1 + \exp(-b(R - r)))$$

where the prefactor k, the radius R, and the gradient b are parameters, and r is the distance to the origin. The potential is time-independent and spherical. Inside the radius R, values for potential and forces are near zero. Outside of R, the potential exerts a nearly constant inward pointing force of $k \cdot b$ on each mass point[8].

```
EngineAddons
   WallPotential
      Enabled Yes/No
      Gradient float
      Prefactor float
      Radius float
   End
End
```

EngineAddons

WallPotential

Type Block

Description This block configures the addon that adds a spherical wall potential to the engine's energy and gradients.

Enabled

Type Bool

Default value No

Description Enables the wall potential addon. When enabled, a spherical wall of radius [Radius] around the origin will be added. The force due to the potential will decay exponentially inside the wall, will be close to [Prefactor*Gradient] outside and exactly half of that at the wall.

Gradient

Type Float

Default value 10.0

Unit 1/Angstrom

[8] S. Grimme, *Exploration of Chemical Compound, Conformer, and Reaction Space with Meta-Dynamics Simulations Based on Tight-Binding Quantum Chemical Calculations*, Journal of Chemical Theory and Computation 15, 2847-2862 (2019) (https://doi.org/10.1021/acs.jctc.9b00143)

Description The radial gradient outside the sphere.

Prefactor

Type Float

Default value 0.01

Unit Hartree

Description The multiplier for the overall strength of the potential.

Radius

Type Float

Default value 30.0

Unit Angstrom

Value Range value > 0

Description The radius of the sphere, wherein the potential is close to zero.

9.5.7 Short-range repulsive potential

This add-on adds a repulsive Weeks-Chandler-Andersen potential to all atom pairs, which is equivalent to the shifted and truncated Lennard-Jones potential. It is useful when running high-temperature dynamics with a force-field that does not have a strong enough repulsion term of its own.

$$E_{\mathrm{WCA}}(r) = \begin{cases} 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right), & \text{if } r < \sqrt[6]{2}\sigma \\ 0, & \text{if } r \geq \sqrt[6]{2}\sigma \end{cases}$$

The addon parameters are listed below.

```
EngineAddons
   Repulsion
      Enabled Yes/No
      Epsilon float
      HydrogenSigmaScale float
      Sigma float
      SkinLength float
   End
End
```

EngineAddons

Repulsion

Type Block

Description This block configures an addon that adds a repulsive Weeks-Chandler-Andersen potential to all atom pairs.

Enabled

Type Bool

Default value No

GUI name Repulsion

Description Enables the repulsive Weeks-Chandler-Andersen potential addon.

When enabled, all atom pairs will experience repulsion E = 4*epsilon*((sigma/r)^12 - (sigma/r)^6 + 1/4) at the distances shorter than about 1.12*sigma.

`Epsilon`

Type Float

Default value 0.01

Unit Hartree

Description The epsilon parameter in the potential equation. It is equal to the amount of energy added at r=sigma.

`HydrogenSigmaScale`

Type Float

Default value 0.75

Unit Angstrom

Description The sigma parameter for a pair of atoms where one of them is hydrogen is scaled with the given factor. For H-H interactions the sigma is scaled with this value squared.

`Sigma`

Type Float

Default value 0.55

Unit Angstrom

Description The sigma parameter in the potential equation. The potential is exactly zero at the distances larger than about 1.12*sigma

`SkinLength`

Type Float

Default value 2.0

Unit Angstrom

Description Technical parameter specifying skin length for the neighbor list generation. A larger value increases the neighbor list cutoff (and cost) but reduces the frequency it needs to be re-created.

CHAPTER

TEN

UTILITIES

10.1 AMSbatch

It is often necessary to repeat an identical job for many different systems. The 2023 release of the Amsterdam Modeling Suite adds the AMSbatch utility program to do this.

Tip: AMSbatch only covers the very simple case of repeating the exact same jobs for multiple systems. More complicated workflows with processing of results can easily be implemented by using our *scripting tools* (page 25) (e.g. PLAMS).

10.1.1 Overview

The input of AMSbatch is basically identical to the input of an AMS job. The only difference is with the *System blocks* (page 31). For AMSbatch every System block needs to have a unique name (supplied in the header of the block), which will be used as the identifier of the system. Consider the following example input, which independently does a geometry optimization followed by a normal modes calculation for two systems (CO and water):

```
#!/bin/sh

AMS_JOBNAME=go_freq $AMSBIN/amsbatch << EOF

   Task GeometryOptimization
   Properties NormalModes=True

   Engine DFTB
      [...]
   EndEngine

   System Water
       Atoms
           O 0 0 0
           H 0 1 0
           H 1 0 0
       End
   End

   System CO
       Atoms
           C 0 0 0
           O 0 0 1
       End
```

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```
   End

EOF
```

Just like the AMS driver, running AMSbatch will create a *results directory* (page 18) on disk. Inside of the results directory, you will find subdirectories for the individual jobs (identified by their System name), containing the usual AMS output files. Running the script above would produce the following output:

```
go_freq.results/
├── amsbatch.log
├── amsbatch.rkf
├── CO
│   ├── ams.log
│   ├── ams.rkf
│   ├── CO.dill
│   ├── CO.err
│   ├── CO.in
│   ├── CO.out
│   ├── CO.run
│   ├── dftb.rkf
│   └── output.xyz
└── Water
    ├── ams.log
    ├── ams.rkf
    ├── dftb.rkf
    ├── output.xyz
    ├── Water.dill
    ├── Water.err
    ├── Water.in
    ├── Water.out
    └── Water.run
```

10.1.2 Loading systems from file

Instead of supplying all systems individually in the input, AMSbatch also supports to a few ways to load multiple systems from files at once.

The `SystemsFromSMILES` keyword allows to run jobs directly on collections of SMILES strings, using RDKit to generate the initial 3D structure of the system:

```
SystemsFromSMILES
   Methane, C
   Ethane,  CC
   Propane, CCC
   Butane,  CCCC
   Pentane, CCCCC
   Hexane,  CCCCCC
End
```

`SystemsFromSMILES`

Type Non-standard block

Description Generates systems from SMILES strings using the plams.from_smiles() functions. Each line should contain first the system identifier separated by a comma from its SMILES string, e.g.: ‘propanol, CCCO’

The `SystemsFromConformers` keyword can be used to load a set of conformers as found by our *Conformers tool* (page 295). This is especially useful as the last step of a conformer workflow, e.g. to do a single point for the calculation of spectra on each conformer within an energy window:

```
SystemsFromConformers
   File string
   MaxEnergy float
End
```

SystemsFromConformers

Type Block

Description Constructs a series of systems (with identifiers 'conformer1', 'conformer2', etc.) from a RKF or XYZ file from a Conformers run.

File

Type String

Description A path to an RKF or concatenated XYZ file.

MaxEnergy

Type Float

Unit Hartree

Description Energy cut-off relative to lowest energy conformer.

See also:

Tutorial on Conformer generation and Boltzmann-weighted spectra

Finally, the `SystemsFromTrajectory` keyword allows reading frames from a trajectory in RKF or XYZ format:

```
SystemsFromTrajectory
   File string
   Frames integer_list
End
```

SystemsFromTrajectory

Type Block

Description Constructs a series of systems (with identifiers 'frame1', 'frame2', etc.) from a trajectory file.

File

Type String

Description A path to an RKF or concatenated XYZ file.

Frames

Type Integer List

Description List of frames to load from the file. If not specified, all frames will be loaded.

10.1.3 Restart

AMSbatch based on the PLAMS scripting framework. As such it can rely on the PLAMS rerun prevention to implement restarting of interrupted depositions. The easiest way to restart an AMSbatch job is to include the `--restart` (or short: `-r`) command line flag:

```
#!/bin/sh

AMS_JOBNAME=myjob $AMSBIN/amsbatch --restart << EOF
...
EOF
```

This first (interrupted) run will have created the `myjob.results` directory. Running the above script again will move that directory to `myjob.results.bak` and reuse all successful jobs from the first run. (People already familiar with PLAMS will recognize that this works just like the `-r` flag on the PLAMS launch script.)

10.2 AtomTyping

AtomTyping is a simple tool for assigning atom types fo molecular systems. Currently only the GAFF force field is implemented. It uses AMBERs Antechamber under the hood.

10.2.1 Command Line Tool

This is a simple example showing how to generate force field parameters for ethanol:

```
#!/bin/sh

$AMSBIN/atomtyping << EOF

   Type GAFF

   System
      Atoms
         C -4.537101 -0.602542 -0.008859
         C -3.601843 -1.804345  0.037274
         O -2.267293 -1.387375 -0.058902
         H -4.301877  0.096761  0.821305
         H -5.588912 -0.942676  0.095614
         H -4.425039 -0.071643 -0.977931
         H -3.829607 -2.474689 -0.818032
         H -3.766077 -2.377916  0.977441
         H -2.012143 -1.043722  0.837186
      End
   End
EOF
```

The most important input options are:

- **Type**: The force field type for which atom types and charges should be generated. Currently only GAFF is implemented, and this is also default.
- **System**: in the *System block* (page 31) we specify the initial structure of the molecule for which you want to generate force field information.

The utility creates a new AMS input file for a ForceField engine job using the new forcefield parameters. The new input is written to the logfile, and it is also stored in the .rkf file. The user can change the file as needed, or import it into amsinput and change settings from there.

Tip: GAFF atomtyping by Antechamber involves an AM1 geometry optimization of all molecules, in order to determine the atomic charges. For very big systems this can be very tome consuming. There is an option to only compute AM1 single point atomic charges, with the option *AntechamberTask SinglePoint*. Do keep in mind that this will make the resulting force field parameters less reliable.

10.2.2 Python scripting

It is also possible to run atomtyping via Python scripting.

```
from scm.plams import Settings, Molecule
from scm.plams import init, finish
from scm.atomtyping import AtomTypingJob, AtomTypingResults

init()

# Run the atomtyping job
mol = Molecule('mol.in')
settings = Settings()
job = AtomTypingJob(molecule=mol,settings=settings)
results = job.run()

# Create the forcefield job (change the settings if needed)
newjob = results.get_plamsjob()
newjob.settings.input.ams.Task = GeometryOptimization

finish()
```

10.3 Conformers

Conformers is a flexible tool for conformer generation. It implements the RDKit[1], CREST[2] and Simulated Annealing conformer generation methods and can be combined with any *AMS engine* (page 270).

Tip: You can use **Conformers** from the Graphical User Interface or from python with PLAMS.

See also:

Tutorial on Conformer generation and Boltzmann-weighted spectra

[1] G. Landrum, *Rdkit documentation* Release 2013 (https://buildmedia.readthedocs.org/media/pdf/rdkit/latest/rdkit.pdf)

[2] P. Pracht, F. Bohle, S. Grimme, *Automated exploration of the low-energy chemical space with fast quantum chemical methods* Physical Chemistry Chemical Physics: PCCP, 19 Feb 2020, 22(14):7169-7192 (https://doi.org/10.1039/c9cp06869d)

10.3.1 Overview

This is a simple example showing how to generate conformers of ethanol:

```
#!/bin/sh

$AMSBIN/conformers << EOF

   Task Generate

   System
      Atoms
         C -4.537101 -0.602542 -0.008859
         C -3.601843 -1.804345  0.037274
         O -2.267293 -1.387375 -0.058902
         H -4.301877  0.096761  0.821305
         H -5.588912 -0.942676  0.095614
         H -4.425039 -0.071643 -0.977931
         H -3.829607 -2.474689 -0.818032
         H -3.766077 -2.377916  0.977441
         H -2.012143 -1.043722  0.837186
      End
   End

   Engine ForceField
   EndEngine
EOF
```

The most important input options are:

- **Task**: the task for the Conformers tool. Here we simply **Generate** a set of conformers starting from an initial structure. See the *Tasks* (page 297) section for more information.
- **System**: in the *System block* (page 31) we specify the initial structure of the molecule for which you want to generate conformers, in this case an ethanol molecule.
- **Engine**: during the conformers generation, atomistic calculations will be executed under the hood to compute energy and forces. With the *engine* (page 298) block you can specify which atomistic engine to use and the options for the engine.

Tip: By default, the computationally fast (but not very accurate) ForceField engine is used to compute energy and forces. If you need more accurate geometries and energies for your conformers, you can specify a more accurate (but slow) engine in the generation step. Alternatively, you can use the `Optimize`, `Filter` and `Score` *tasks* (page 297) to efficiently get accurate geometries and energies while keeping the computational cost to a minimum. See *Workflow* (page 303) for an example.

When running the script above, a folder called `conformers.results` will be created and the generated conformers will be saved in there (in `.xyz` and `.rkf` formats). See the general *Input, execution and output* (page 9) section for more information.

10.3.2 Main Input Options

Tasks

You can specify the task for the Conformers tool via the `Task` input option:

```
Task [Generate | Optimize | Filter | Score | Expand]
```

The main (and default) **Task** is **Generate**: given an initial structure, the Conformers tool will generate a set of conformers.

The other tasks, described below, can be used to refine or combine previously generated conformer sets. The *Workflow* (page 303) example shows how the various tasks can be combined in a simple workflow to efficiently obtain accurate conformers.

`Task`

Type Multiple Choice

Default value Generate

Options [Generate, Optimize, Filter, Score, Expand]

Description The task to be performed by the Conformers tool.

‘Generate’: given a molecule, generate a set of conformers. Note: this task will automatically optimize, filter and score the conformers.

‘Optimize’: given a previously generated set of conformers, optimize, filter and score the structures using the specified engine.

‘Filter’: given one or more previously generated set of conformers, merge them into a single conformer set and filter out duplicate conformers. Note: this will not optimize or re-score the conformers.

‘Score’ given one or more previously generated set of conformers, re-score them by computing the energy using the specified engine. Note: this will only do a single point calculation, and will not optimize the structures.

In case of ‘Optimize’, ‘Filter’ and ‘Score’ you can specify the input conformer set(s) using the ‘InputConformersSet’ keyword.

Input molecule(s)

For the `Generate` task you can use the `System` or `LoadSystem` blocks to specify the input molecule. See the *System block* (page 31) documentation for a detailed description.

For the `Optimize`, `Filter` and `Score` tasks, you should instead provide the results of a previously run Conformers calculation as input via the `InputConformersSet` keyword. See also the *Constraints, Restraints, Walls* (page 300) section.

```
InputConformersSet string
```

`InputConformersSet`

Type String

Recurring True

Description The path to a file containing a set of conformers.

The file should be either an 'conformers.rkf' file (i.e. the results file of conformers) or a concatenated .xyz file.

You can specify multiple input conformers sets by including the InputConformersSet keyword multiple times.

When loading conformers using the `InputConformersSet` key, you can optionally specify the `InputMaxEnergy` option:

```
InputMaxEnergy float
```

`InputMaxEnergy`

Type Float

Unit kcal/mol

Description Threshold for filtering out high-energy conformers when loading conformers sets using the InputConformerSet keyword. Conformers with an larger relative energy will not be loaded.

A similar option is the `InputMaxConfs` key, which will use only the k lowest energy conformers for an integer input k:

```
InputMaxConfs integer
```

`InputMaxConfs`

Type Integer

Description The maximum number of conformers to carry forward when loading conformer sets. If this input is not specified, this limit will not be imposed.

Engine

With the **Engine block** you can specify which atomistic engine to use and the options for the engine. See the *AMS engine* (page 270) documentation for more info.

If no engine block is specified, the ForceField engine (with the UFF force field) will be used as default.

Generators

Three different methods of conformer generation are implemented: RDKit[?], CREST[?] and ANNEALING. The **default** generation method is **RDKit**.

You can select which method to use in the `Generator` block:

```
Generator
   Method [RDKit | CREST | ANNEALING]
End
```

`Generator`

Type Block

Description Options for the conformer generator.

`Method`

Type Multiple Choice

Default value RDKit

Options [RDKit, CREST, ANNEALING]

GUI name Generator method

Description Method used to generate the conformers.

The RDKit generator is based on random distance matrix method. This is the recommended (and default) method.

The CREST Generator uses a multi-step workflow with meta-dynamics simulations to explore the conformers space of a molecule. This can be a powerful conformer search method, but it is generally computationally expensive compared to the RDKit generator.

THe ANNEALING generator performs a simulated annealing simulation to explore conformer space.

Input options for the various methods can be specified in their respective input blocks. See the section *Other input options* (page 304) for the complete set of input options.

Conformers Equivalence

An important aspect of conformers generation is the reduction of a set of geometries into a set of unique conformers. As the Conformer tool generates new potential conformers, it needs to be able to determine whether a structure is a new conformer (in which case it is added to the list of unique conformers) or whether is simply a slightly different geometry of an already observed conformer (in which case, the structure is discarded).

The conformer tool therefore needs a procedure that, given two geometries, is able to discriminate between the following situations:

- the two geometries correspond to the same conformer
- the two geometries correspond to distinct conformers

In the `Equivalence` block various options related to this equivalence procedure can be specified.

```
Equivalence
   Method [AMS | TFD | RMSD | CREST]
End
```

`Equivalence`

Type Block

Description Options for the procedure determining whether two structures are equivalent or distinct conformers.

`Method`

Type Multiple Choice

Default value CREST

Options [AMS, TFD, RMSD, CREST]

GUI name Equivalence method

Description Method used to determine (and filter out) equivalent conformers.

The CREST equivalence method relies on rotational constants comparisons. For this reason, conformers with the same rotational constants (such as mirror images) will be considered equivalent conformers.

The AMS equivalence method uses a distance matrix and dihedrals to compare conformers. This equivalence method can be computationally expensive for large molecules.

The TFD equivalence method uses the Torsion Fingerprint Difference as implemented in RDKit.

The RMSD equivalence method uses the RDKit GetBestRMS implementation.

Input options for the various methods can be specified in their respective input blocks. See the section *Other input options* (page 304) for the complete set of input options.

Filtering

The Conformers tool can automatically filter out conformers based on some criteria, e.g. it will discard high energy conformers.

The filtering options can be specified in the `Filter` block:

```
Filter
   MaxEnergy float
   RemoveNonMinima Yes/No
End
```

`Filter`

Type Block

Description Options for the conformer filtering.

`MaxEnergy`

Type Float

Unit kcal/mol

Description Threshold for filtering out high-energy conformers. If the relative energy of a conformer with respect to the lowest conformer is larger than this value, the conformer will be discarded.

`RemoveNonMinima`

Type Bool

Default value No

Description For the final set of conformers, explicitly check that the geometry corresponds to a local minimum, and remove it if it does not. Note: this will run a PES point characterization, which can be computationally expensive!

Constraints, Restraints, Walls

The Conformers tool can be used in combination with Constraints (*constraints* (page 52)), Restraints (*restraints* (page 284)), and EngineAddons (*engine addons* (page 278)).

The constraints fix the specified degrees of freedom to certain values, while the restraints restricts the specified degrees of freedom to be near the specified values using an added potential energy function. The engine add-ons cover a wide range of functionality, but the most important one for conformers is the `WallPotential`, which adds a spherical repulsive potential around the origin, trapping the atoms inside.

It is discouraged to use the RDKit `Generate` method (the default) in combination with constraints and restraints. The RDKit `Generate` method consists of two steps:

1. Call to RDKit ETKGD method for initial conformer generation

2. Geometry optimization of all conformer candidates with an AMS engine

Step 1 does not accept constraints, restraints, or engine add-ons, and therefore too many undesirable conformers will be passed to the constrained optimizer.

It is possible to use constraints in the RDKit ETKDG procedure as well, but they are limited to fixed atoms, and have to be set manually in the `Generator` block.

`Generator`

`RDKitETKDG`

Type Block

Description Settings for the call to RDKits ETKDG conformer generator tool.

`BestRMSDThreshold`

Type Float

Default value -1.0

Description After ETKDG conformer generation by RDKit, RDKit can be used to remove duplicates via the BestRMS algorithm. This filter does exactly the same as the RMSD equivalence detector in the Equivalence block.

`ConstrainedAtoms`

Type Integer List

Description The indices of the atoms to constrain during ETKDG conformer generation.

`Forcefield`

Type Multiple Choice

Default value None

Options [None, UFF, MMFF]

Description The name of the RDKit forcefield to use for geometry optimization at the end of ETKDG conformer generation (by default no geometry optimization is performed). Using the RDKit internal optimization may make the subsequent geometry optimizations with AMS faster.

`Parallel`

Type Bool

Default value No

Description Experimental: Parallelize the RDKit generation step by calling the RDKit conformer generation method in parallel from multiple processes.

`RMSDThreshold`

Type Float

Default value -1.0

Description Root Mean Square deviation threshold for removing similar/equivalent conformations during the RDKit ETKDG procedure. By default there is no pruning (value: -1).

`UseExpTorsionAnglePrefs`

Type String

Default value default

Description Impose experimental torsion angle preferences in RDKit ETKDG conformer generation. By default the RDKit version determines wether or not to switch this on.

The other `Generate` methods of the Conformers tool make use of both molecular dynamics simulations (Crest and Annealing) and geometry optimizations. Not all constraints are can be used in molecular dynamics simulations, so where possible constraints are automatically converted to the corresponding restraints.

Conformer Generation with Multiple Molecules

The wall potential described above can be used in combination with the `Crest` and `Annealing` methods to generate conformers for systems with multiple molecules. A simple example below demonstrates this for an acetic acid molecule in the presence of water. The radius of the spherical constraint is manually set to 4.5 Angstrom.

```
#!/bin/sh

"$AMSBIN/conformers" << eor
    Engine ForceField
    EndEngine
    Generator
        Method CREST
    End
    System
        Atoms
            C -5.168356138856709 -0.9040308913456915 -0.14509537743978
            C -3.674177007131515 -0.8549162177628133 -0.1466485108795087
            O -3.036130963738181 0.3677379219191289 -0.1592569297095029
            O -3.033827233992448 -1.897394223042741 -0.1762700959655665
            H -5.578445514437495 0.05058176564435996 0.2458678935590599
            H -5.524620190394747 -1.732922198697688 0.5010944819578638
            H -5.536566707641177 -1.061832129921519 -1.180309622581397
            H -2.058681010424327 0.197909193054116 -0.1773409518219506
            O -4.51655946130152 -4.444022963974381 0.9796661086035751
            H -4.406160106170592 -3.748388119201934 1.675984760241468
            H -5.428884582974359 -4.296939008632186 0.6238436183248668
        End
        BondOrders
          1 2 1.0
          1 5 1.0
          1 6 1.0
          1 7 1.0
          2 3 1.0
          2 4 2.0
          3 8 1.0
          9 10 1.0
          9 11 1.0
        End
    End
    EngineAddons
        WallPotential
            Enabled Yes
            Radius 4.5
        End
    End
eor
```

10.3.3 Examples

Workflow

During the conformers generation (i.e. the "generate" *task* (page 297)), a large number of atomistic calculations will be executed under the hood. This can get computationally very expensive if an accurate *engine* (page 298) (such as ADF) is used. This is why the default engine is the computationally fast (but not very accurate) ForceField engine.

By combining the `Generate`, `Optimize` and `Score` tasks you can build a simple workflow to get accurate geometries and energies while keeping the computational cost to a minimum.

A typical workflow might look like this:

1. Generate a set of conformers using `Task Generate` with the fast but approximate ForceField engine
2. Re-optimize the geometries generated in the previous step using `Task Optimize` with a more accurate engine (e.g. DFTB)
3. Re-score the conformers using the using `Task Score` with an accurate engine (e.g. ADF)

```
#!/bin/sh

# Simple workflow:
# - generate an initial set of 1-bromo-3-chloropropane conformers with UFF␣
↪(ForceField engine)
# - re-optimize the conformers with GFN1-xTB (DFTB engine)
# - re-score the GFN1-xTB-optimized conformers using DFT energies (ADF engine)

AMS_JOBNAME=generate_uff $AMSBIN/conformers << EOF

    Task Generate

    System
        Atoms
            Br     -4.16969843       2.48953245      -0.00000000
            C      -2.69926018       3.75062981      -0.00000000
            C      -1.36372383       3.00977020      -0.00000000
            C      -0.19648214       3.99512105       0.00000000
            Cl      1.35297276       3.11657146       0.00000000
            H      -2.78129583       4.39009878       0.90457474
            H      -2.78129583       4.39009878      -0.90457474
            H      -1.30112035       2.36381643      -0.90271681
            H      -1.30112035       2.36381643       0.90271681
            H      -0.24025734       4.63864134       0.90438917
            H      -0.24025734       4.63864134      -0.90438917
        End
    End

    Engine ForceField
        Type UFF
    EndEngine
EOF


AMS_JOBNAME=optimize_gfn1xtb $AMSBIN/conformers << EOF

    Task Optimize

    InputConformersSet generate_uff.results/conformers.rkf
```

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```
    Engine DFTB
        Model GFN1-xTB
    EndEngine
EOF


AMS_JOBNAME=score_dft $AMSBIN/conformers << EOF

    Task Score

    InputConformersSet optimize_gfn1xtb.results/conformers.rkf

    # Here we use the default ADF settings. For real calculations, you
    # should use a larger basis set (e.g. TZP) and a better XC functional

    Engine ADF
    EndEngine
EOF


echo "Final conformers:"
cat score_dft.results/conformers.xyz
```

10.3.4 References

10.3.5 Other input options

Here we document more advanced input options for the Conformer tool. **See the section** *Main Input Options* (page 297) **for the most important input option.**

`Output`

Type Block

Description Options regarding the output and result files.

`KeepWorkDir`

Type Bool

Default value No

Description Do not remove the working directories after the conformer generation is finished.

`rkf`

Type Bool

Default value Yes

Description Save the final conformers in .rkf format. The file 'conformers.rkf' will be located in the results directory. You can visualize this file using the AMSMovie GUI module.

`sdf`

Type Bool

Default value Yes

Description Save the final conformers in .sdf format. The file 'conformers.sdf' will be located in the results directory.

`xyz`

Type Bool

Default value Yes

Description Save the final conformers in .xyz format. The file 'conformers.xyz' will be located in the results directory.

`RNGSeed`

Type Integer

Description Initial seed for the (pseudo)random number generator. If this is unset, the generator will be seeded randomly from external sources of entropy and the generated conformers will be non-deterministic.

`Generator`

Type Block

Description Options for the conformer generator.

`ANNEALING`

Type Block

Description Options for the annealing generator. This generator creates conformers by performing a simulated annealing simulation.

`MolecularDynamics`

Type Block

Description Configures molecular dynamics (with the velocity-Verlet algorithm) with and without thermostats. This block allows to specify the details of the molecular dynamics calculation. Default values will be ignored.

`Checkpoint`

Type Block

Description Sets the frequency for storing the entire MD state necessary for restarting the calculation.

`Frequency`

Type Integer

Default value 1000

GUI name Checkpoint frequency

Description Write the MD state and engine-specific data to the respective .rkf files once every N steps.

`WriteProperties`

Type Bool

Default value No

Description Write the properties from the properties section to the ChecoPoint file once every N steps.

`InitialVelocities`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`File`

Type String

Description AMS RKF file containing the initial velocities.

`RandomVelocitiesMethod`

Type Multiple Choice

Default value Exact

Options [Exact, Boltzmann, Gromacs]

GUI name Velocity randomization method

Description Specifies how are random velocities generated. Three methods are available.

Exact: Velocities are scaled to exactly match set random velocities temperature.

Boltzmann: Velocities are not scaled and sample Maxwell-Boltzmann distribution. However, the distribution is not corrected for constraints.

Gromacs: Velocities are scaled to match set random velocities temperature, but removal of net momentum is performed only after the scaling. Resulting kinetic energy is lower based on how much net momentum the system had.

`Temperature`

Type Float

Unit Kelvin

GUI name Initial temperature

Description Sets the temperature for the Maxwell-Boltzmann distribution when the type of the initial velocities is set to random, in which case specifying this key is mandatory.

AMSinput will use the first temperature of the first thermostat as default.

`Type`

Type Multiple Choice

Default value Random

Options [Zero, Random, FromFile, Input]

GUI name Initial velocities

Description Specifies the initial velocities to assign to the atoms. Three methods to assign velocities are available.

Zero: All atom are at rest at the beginning of the calculation.

Random: Initial atom velocities follow a Maxwell-Boltzmann distribution for the temperature given by the [MolecularDynamics%InitialVelocities%Temperature] keyword.

FromFile: Load the velocities from a previous ams result file.

Input: Atom's velocities are set to the values specified in the [MolecularDynamics%InitialVelocities%Values] block, which can be accessed via the Expert AMS panel in AMSinput.

Values

Type Non-standard block

Description This block specifies the velocity of each atom, in Angstrom/fs, when [MolecularDynamics%InitialVelocities%Type] is set to Input. Each row must contain three floating point values (corresponding to the x,y,z component of the velocity vector) and a number of rows equal to the number of atoms must be present, given in the same order as the [System%Atoms] block.

NSteps

Type Integer

Default value 1000

GUI name Number of steps

Description The number of steps to be taken in the MD simulation.

Preserve

Type Block

Description Periodically remove numerical drift accumulated during the simulation to preserve different whole-system parameters.

AngularMomentum

Type Bool

Default value Yes

GUI name : Angular momentum

Description Remove overall angular momentum of the system. This option is ignored for 2D and 3D-periodic systems, and disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

CenterOfMass

Type Bool

Default value No

GUI name : Center of mass

Description Translate the system to keep its center of mass at the coordinate origin. This option is not very useful for 3D-periodic systems.

Momentum

Type Bool

Default value Yes

GUI name Preserve: Total momentum

Description Remove overall (linear) momentum of the system. This is disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

Print

Type Block

Description This block controls the printing of additional information to stdout.

`System`

Type Bool

Default value No

Description Print the chemical system before and after the simulation.

`Velocities`

Type Bool

Default value No

Description Print the atomic velocities before and after the simulation.

`Restart`

Type String

GUI name Restart from

Description The path to the ams.rkf file from which to restart the simulation.

`Shake`

Type Block

Description Parameters of the Shake/Rattle algorithm.

`All`

Type String

Recurring True

GUI name Constrain all

Description Constraint description in one the following formats: All [bondOrder] bonds at1 at2 [to distance] All triangles at1 at2 at3

The first option constrains all bonds between atoms at1 at2 to a certain length, while the second - bonds at1-at2 and at2-at3 and the angle between them.

The [bondOrder] can be a number or a string such as single, double, triple or aromatic. If it's omitted then all bonds between specified atoms will be constrained. Atom names are case-sensitive and they must be as they are in the Atoms block, or an asterisk '*' denoting any atom. The distance, if present, must be in Angstrom. If it is omitted then the bond length from the initial geometry is used.

Important: only the bonds present in the system at certain points of the simulation (at the start or right after adding/removing atoms) can be constrained, which means that the bonds may need to be specified in the System block.

Warning: the triangles constraint should be used with care because each constrained bond or angle means removing one degree of freedom from the dynamics. When there are too many constraints (for example, "All triangles H C H" in methane) some of them may be linearly dependent, which will lead to an error in the temperature computation.

Valid examples: All single bonds C C to 1.4 All bonds O H to 0.98 All bonds O H All bonds H * All triangles H * H

`ConvergeR2`

Type Float

Default value 1e-08

Description Convergence criterion on the max squared difference, in atomic units.

`ConvergeRV`

Type Float

Default value 1e-08

Description Convergence criterion on the orthogonality of the constraint and the relative atomic velocity, in atomic units.

`Iterations`

Type Integer

Default value 100

Description Number of iterations.

`ShakeInitialCoordinates`

Type Bool

Default value Yes

Description Apply constraints before computing the first energy and gradients.

`Thermostat`

Type Block

Recurring True

Description This block allows to specify the use of a thermostat during the simulation. Depending on the selected thermostat type, different additional options may be needed to characterize the specific thermostat' behavior.

`BerendsenApply`

Type Multiple Choice

Default value Global

Options [Local, Global]

GUI name Apply Berendsen

Description Select how to apply the scaling correction for the Berendsen thermostat:

- per-atom-velocity (Local) - on the molecular system as a whole (Global).

`ChainLength`

Type Integer

Default value 10

GUI name NHC chain length

Description Number of individual thermostats forming the NHC thermostat

`Duration`

Type Integer List

GUI name Duration(s)

Description Specifies how many steps should a transition from a particular temperature to the next one in sequence take.

`Region`

Type String

Default value *

Description The identifier of the region to thermostat. The default '*' applies the thermostat to the entire system. The value can by a plain region name, or a region expression, e.g. '*-myregion' to thermostat all atoms that are not in myregion, or 'regionA+regionB' to thermostat the union of the 'regionA' and 'regionB'. Note that if multiple thermostats are used, their regions may not overlap.

`Tau`

Type Float

Unit Femtoseconds

GUI name Damping constant

Description The time constant of the thermostat.

`Temperature`

Type Float List

Unit Kelvin

GUI name Temperature(s)

Description The target temperature of the thermostat.

You can specify multiple temperatures (separated by spaces). In that case the Duration field specifies how many steps to use for the transition from one T to the next T (using a linear ramp). For NHC thermostat, the temperature may not be zero.

`Type`

Type Multiple Choice

Default value None

Options [None, Berendsen, NHC]

GUI name Thermostat

Description Selects the type of the thermostat.

`TimeStep`

Type Float

Default value 0.25

Unit Femtoseconds

Description The time difference per step.

`Trajectory`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`ExitConditionFreq`

Type Integer

GUI name Exit condition frequency

Description Check the exit conditions every N steps. By default this is done every SamplingFreq steps.

`PrintFreq`

Type Integer

GUI name Printing frequency

Description Print current thermodynamic properties to the output every N steps. By default this is done every SamplingFreq steps.

`SamplingFreq`

Type Integer

Default value 100

GUI name Sample frequency

Description Write the the molecular geometry (and possibly other properties) to the .rkf file once every N steps.

`TProfileGridPoints`

Type Integer

Default value 0

Description Number of points in the temperature profile. If TProfileGridPoints > 0, a temperature profile along each of the three lattice axes will be written to the .rkf file. The temperature at a given profile point is calculated as the total temperature of all atoms inside the corresponding slice of the simulation box, time-averaged over all MD steps since the previous snapshot. By default, no profile is generated.

`WriteBonds`

Type Bool

Default value Yes

Description Write detected bonds to the .rkf file.

`WriteCharges`

Type Bool

Default value Yes

Description Write current atomic point charges (if available) to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze charges.

`WriteCoordinates`

Type Bool

Default value Yes

Description Write atomic coordinates to the .rkf file.

`WriteEngineGradients`

Type Bool

Default value No

Description Write atomic gradients (negative of the atomic forces, as calculated by the engine) to the History section of ams.rkf.

`WriteMolecules`

Type Bool

Default value Yes

Description Write the results of molecule analysis to the .rkf file.

`WriteVelocities`

Type Bool

Default value Yes

Description Write velocities to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze the velocities.

`Temperatures`

Type Float List

Default value [298.0, 798.0]

Unit Kelvin

Description The minimum and maximum temperature of the annealing simulation. The simulation will start at the highest temperature, and cool down to the lowest.

`UseShake`

Type Bool

Default value No

Description Constrain all -H bonds with shake. If turned on, the MD timestep is automatically increased.

`CREST`

Type Block

Description Options for the CREST generator. The CREST generator performs a set of metadynamics simulations (using the METADYNAMICS generator), then a set of MD simulations (using the MD expander), and finally it does a combinatorial expansion of the generated conformers using the GC expander. This sequence is repeated in an iterative fashion until the lowest energy conformer no longer changes.

`ConvergenceQualityCrude`

Type Multiple Choice

Default value None

Options [Normal, Good, VeryGood, Excellent, None]

Description The tightness of the convergence of the crude geometry pre-optimizations. If set to none it will be selected two levels below ConvergenceQuality.

`ConvergenceQualityTight`

Type Multiple Choice

Default value None

Options [Normal, Good, VeryGood, Excellent, None]

Description The tightness of the convergence of the final geometry optimizations. If set to none it will be selected the same as ConvergenceQuality.

`GCStep`

Type Bool

Default value Yes

Description Wether or not to include the combinatorial expansion of the conformers using the GC Generator. For big systems this step can be very time consuming. By default it is set to True.

`NCycles`

Type Integer

Default value 10

Description The maximum number of CREST cycles (by default the number is 10). If the lowest conformer energy converges before then, Crest exits.

`UseShake`

Type Bool

Default value Yes

Description Wether or not SHAKE should be turned on in the MD and Metadynamics simulations. If this is turned on, the MD timestep is automatically increased (from 2 to 5 fs).

`METADYNAMICS`

Type Block

Description Produces conformers by running a set of CREST-RMSD metadynamics simulations with different biases, extracting snapshots, and optimizing those.

`ConvergenceQualityCrude`

Type Multiple Choice

Default value none

Options [normal, good, verygood, excellent, none]

Description The tightness of the convergence of the crude geometry pre-optimizations. If set to none it will be selected two levels below ConvergenceQuality.

`MolecularDynamics`

Type Block

Description Configures molecular dynamics (with the velocity-Verlet algorithm) with and without thermostats. This block allows to specify the details of the molecular dynamics calculation. Default values will be ignored.

`Checkpoint`

Type Block

Description Sets the frequency for storing the entire MD state necessary for restarting the calculation.

`Frequency`

Type Integer

Default value 1000

GUI name Checkpoint frequency

Description Write the MD state and engine-specific data to the respective .rkf files once every N steps.

`WriteProperties`

Type Bool

Default value No

Description Write the properties from the properties section to the ChecoPoint file once every N steps.

`InitialVelocities`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`File`

Type String

Description AMS RKF file containing the initial velocities.

`RandomVelocitiesMethod`

Type Multiple Choice

Default value Exact

Options [Exact, Boltzmann, Gromacs]

GUI name Velocity randomization method

Description Specifies how are random velocities generated. Three methods are available.

Exact: Velocities are scaled to exactly match set random velocities temperature.

Boltzmann: Velocities are not scaled and sample Maxwell-Boltzmann distribution. However, the distribution is not corrected for constraints.

Gromacs: Velocities are scaled to match set random velocities temperature, but removal of net momentum is performed only after the scaling. Resulting kinetic energy is lower based on how much net momentum the system had.

`Temperature`

Type Float

Unit Kelvin

GUI name Initial temperature

Description Sets the temperature for the Maxwell-Boltzmann distribution when the type of the initial velocities is set to random, in which case specifying this key is mandatory.

AMSinput will use the first temperature of the first thermostat as default.

`Type`

Type Multiple Choice

Default value Random

Options [Zero, Random, FromFile, Input]

GUI name Initial velocities

Description Specifies the initial velocities to assign to the atoms. Three methods to assign velocities are available.

Zero: All atom are at rest at the beginning of the calculation.

Random: Initial atom velocities follow a Maxwell-Boltzmann distribution for the temperature given by the [MolecularDynamics%InitialVelocities%Temperature] keyword.

FromFile: Load the velocities from a previous ams result file.

Input: Atom's velocities are set to the values specified in the [MolecularDynamics%InitialVelocities%Values] block, which can be accessed via the Expert AMS panel in AMSinput.

`Values`

Type Non-standard block

Description This block specifies the velocity of each atom, in Angstrom/fs, when [MolecularDynamics%InitialVelocities%Type] is set to Input. Each row must contain three floating point values (corresponding to the x,y,z component of the velocity vector) and a number of rows equal to the number of atoms must be present, given in the same order as the [System%Atoms] block.

`NSteps`

Type Integer

Default value 1000

GUI name Number of steps

Description The number of steps to be taken in the MD simulation.

`Preserve`

Type Block

Description Periodically remove numerical drift accumulated during the simulation to preserve different whole-system parameters.

`AngularMomentum`

Type Bool

Default value Yes

GUI name : Angular momentum

Description Remove overall angular momentum of the system. This option is ignored for 2D and 3D-periodic systems, and disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

`CenterOfMass`

Type Bool

Default value No

GUI name : Center of mass

Description Translate the system to keep its center of mass at the coordinate origin. This option is not very useful for 3D-periodic systems.

`Momentum`

Type Bool

Default value Yes

GUI name Preserve: Total momentum

Description Remove overall (linear) momentum of the system. This is disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

`Print`

Type Block

Description This block controls the printing of additional information to stdout.

`System`

Type Bool

Default value No

Description Print the chemical system before and after the simulation.

`Velocities`

Type Bool

Default value No

Description Print the atomic velocities before and after the simulation.

`Restart`

Type String

GUI name Restart from

Description The path to the ams.rkf file from which to restart the simulation.

`Shake`

Type Block

Description Parameters of the Shake/Rattle algorithm.

`All`

Type String

Recurring True

GUI name Constrain all

Description Constraint description in one the following formats: All [bondOrder] bonds at1 at2 [to distance] All triangles at1 at2 at3

The first option constrains all bonds between atoms at1 at2 to a certain length, while the second - bonds at1-at2 and at2-at3 and the angle between them.

The [bondOrder] can be a number or a string such as single, double, triple or aromatic. If it's omitted then all bonds between specified atoms will be constrained. Atom names are case-sensitive and they must be as they are in the Atoms block, or an asterisk '*' denoting any atom. The distance, if present, must be in Angstrom. If it is omitted then the bond length from the initial geometry is used.

Important: only the bonds present in the system at certain points of the simulation (at the start or right after adding/removing atoms) can be constrained, which means that the bonds may need to be specified in the System block.

Warning: the triangles constraint should be used with care because each constrained bond or angle means removing one degree of freedom from the dynamics. When there are too many constraints (for example, "All triangles H C H" in methane) some of them may be linearly dependent, which will lead to an error in the temperature computation.

Valid examples: All single bonds C C to 1.4 All bonds O H to 0.98 All bonds O H All bonds H * All triangles H * H

`ConvergeR2`

Type Float

Default value 1e-08

Description Convergence criterion on the max squared difference, in atomic units.

`ConvergeRV`

Type Float

Default value 1e-08

Description Convergence criterion on the orthogonality of the constraint and the relative atomic velocity, in atomic units.

`Iterations`

Type Integer

Default value 100

Description Number of iterations.

`ShakeInitialCoordinates`

Type Bool

Default value Yes

Description Apply constraints before computing the first energy and gradients.

`Thermostat`

Type Block

Recurring True

Description This block allows to specify the use of a thermostat during the simulation. Depending on the selected thermostat type, different additional options may be needed to characterize the specific thermostat' behavior.

`BerendsenApply`

Type Multiple Choice

Default value Global

Options [Local, Global]

GUI name Apply Berendsen

Description Select how to apply the scaling correction for the Berendsen thermostat:

- per-atom-velocity (Local) - on the molecular system as a whole (Global).

`ChainLength`

Type Integer

Default value 10

GUI name NHC chain length

Description Number of individual thermostats forming the NHC thermostat

`Duration`

Type Integer List

GUI name Duration(s)

Description Specifies how many steps should a transition from a particular temperature to the next one in sequence take.

`Region`

Type String

Default value *

Description The identifier of the region to thermostat. The default '*' applies the thermostat to the entire system. The value can by a plain region name, or a region expression, e.g. '*-myregion' to thermostat all atoms that are not in myregion, or 'regionA+regionB' to thermostat the union of the 'regionA' and 'regionB'. Note that if multiple thermostats are used, their regions may not overlap.

`Tau`

Type Float

Unit Femtoseconds

GUI name Damping constant

Description The time constant of the thermostat.

`Temperature`

Type Float List

Unit Kelvin

GUI name Temperature(s)

Description The target temperature of the thermostat.

You can specify multiple temperatures (separated by spaces). In that case the Duration field specifies how many steps to use for the transition from one T to the next T (using a linear ramp). For NHC thermostat, the temperature may not be zero.

`Type`

Type Multiple Choice

Default value None

Options [None, Berendsen, NHC]

GUI name Thermostat

Description Selects the type of the thermostat.

`TimeStep`

Type Float

Default value 0.25

Unit Femtoseconds

Description The time difference per step.

`Trajectory`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`ExitConditionFreq`

Type Integer

GUI name Exit condition frequency

Description Check the exit conditions every N steps. By default this is done every SamplingFreq steps.

`PrintFreq`

Type Integer

GUI name Printing frequency

Description Print current thermodynamic properties to the output every N steps. By default this is done every SamplingFreq steps.

`SamplingFreq`

Type Integer

Default value 100

GUI name Sample frequency

Description Write the the molecular geometry (and possibly other properties) to the .rkf file once every N steps.

`TProfileGridPoints`

Type Integer

Default value 0

Description Number of points in the temperature profile. If TProfileGridPoints > 0, a temperature profile along each of the three lattice axes will be written to the .rkf file. The temperature at a given profile point is calculated as the total temperature of all atoms inside the corresponding slice of the simulation box, time-averaged over all MD steps since the previous snapshot. By default, no profile is generated.

`WriteBonds`

Type Bool

Default value Yes

Description Write detected bonds to the .rkf file.

`WriteCharges`

Type Bool

Default value Yes

Description Write current atomic point charges (if available) to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze charges.

`WriteCoordinates`

Type Bool

Default value Yes

Description Write atomic coordinates to the .rkf file.

`WriteEngineGradients`

Type Bool

Default value No

Description Write atomic gradients (negative of the atomic forces, as calculated by the engine) to the History section of ams.rkf.

`WriteMolecules`

Type Bool

Default value Yes

Description Write the results of molecule analysis to the .rkf file.

`WriteVelocities`

Type Bool

Default value Yes

Description Write velocities to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze the velocities.

`NCycles`

Type Integer

Default value 5

Description The maximum number of cycles of metadynamics simulations. The generator stops when either this number is reached, or the conformer set is stable.

`NWidthsHeights`

Type Integer List

Default value [4, 3]

Description The number of different Gaussian widths and heights respectively used in the metadynamics simulations. By default 4 different widths are used and 3 different heights, resulting in 12 different metadynamics simulations.

`SimulationSuccessFraction`

Type Float

Default value 0.4

Description The fraction of planned metadynamics steps that has to have succeeded in order for the metadynamics iteration to be considered a success.

`UseShake`

Type Bool

Default value No

Description Constrain all -H bonds with shake. If turned on, the MD timestep is automatically increased.

MaxEnergy

Type Float

Unit kcal/mol

Description Threshold for filtering out high-energy conformers. If the relative energy of a conformer with respect to the lowest conformer is larger than this value, the conformer will be discarded.

Method

Type Multiple Choice

Default value RDKit

Options [RDKit, CREST, ANNEALING]

GUI name Generator method

Description Method used to generate the conformers.

The RDKit generator is based on random distance matrix method. This is the recommended (and default) method.

The CREST Generator uses a multi-step workflow with meta-dynamics simulations to explore the conformers space of a molecule. This can be a powerful conformer search method, but it is generally computationally expensive compared to the RDKit generator.

THe ANNEALING generator performs a simulated annealing simulation to explore conformer space.

Preoptimization

Type Block

Description If this block is enabled geometries will be preoptimized. After preoptimization the high energy conformers will be discarded, and then from the remaining set the unoptimized geometries will be optimized at higher level. This is to prevent the preoptimizer from collapsing different conformers into a single false minimum. As a result, preoptimization is only useful if MaxEnergy is chosen low.

Enable

Type Bool

Default value No

Description Perform preoptimization at a low level of accuracy.

Engine

Type Block

Description The engine specifics to be used for preoptimization.

PreoptFactor

Type Integer

Default value 2

Description This factor is multiplied with MaxEnergy, to determine which high energy conformers can be discarded after preoptimization.

RDKit

Type Block

Description Options for the RDKit generator. This generator produces initial guesses for conformers using the RDKit ETKDG method, followed by AMS geometry optimizations.

InitialNConformers

Type Integer

GUI name Initial no. of conformers

Description Number of geometries initially created by RDKit, before AMS geometry optimization and filtering. If not set, the number will be automatically set, based on the number of rotational bonds.

MaxConfs

Type Integer

Default value 5000

Description If InitialNConformers is not set, then the number of conformers will be automatically set, with a maximum of MaxConfs.

MinConfs

Type Integer

Default value 10

Description If InitialNConformers is not set, then the number of conformers will be automatically set, with a minimum of MinConfs.

NconfsEstimationFactor

Type Integer

Default value 100

Description If InitialNConformers is not set, then the number of conformers will be automatically set based on the number of rotational bonds. The resulting number is then multiplied by this factor (default: 100), to ensure that enough conformers will be created.

RDKitETKDG

Type Block

Description Settings for the call to RDKits ETKDG conformer generator tool.

BestRMSDThreshold

Type Float

Default value -1.0

Description After ETKDG conformer generation by RDKit, RDKit can be used to remove duplicates via the BestRMS algorithm. This filter does exactly the same as the RMSD equivalence detector in the Equivalence block.

ConstrainedAtoms

Type Integer List

Description The indices of the atoms to constrain during ETKDG conformer generation.

`Forcefield`

Type Multiple Choice

Default value None

Options [None, UFF, MMFF]

Description The name of the RDKit forcefield to use for geometry optimization at the end of ETKDG conformer generation (by default no geometry optimization is performed). Using the RDKit internal optimization may make the subsequent geometry optimizations with AMS faster.

`Parallel`

Type Bool

Default value No

Description Experimental: Parallelize the RDKit generation step by calling the RDKit conformer generation method in parallel from multiple processes.

`RMSDThreshold`

Type Float

Default value -1.0

Description Root Mean Square deviation threshold for removing similar/equivalent conformations during the RDKit ETKDG procedure. By default there is no pruning (value: -1).

`UseExpTorsionAnglePrefs`

Type String

Default value default

Description Impose experimental torsion angle preferences in RDKit ETKDG conformer generation. By default the RDKit version determines wether or not to switch this on.

`RNGSeed`

Type Integer

Description Initial guesses for conformers can be randomly generated by RDKit, using the ETKDG algorithm. For reproducability, a random number seed can be provided here.

`TORSION`

Type Block

Description Options for the TorsionGenerator, which generates geometries by enumerative rotation around rotatable bonds. This is the slowest of all generator, and quickly becomes infeasible for large systems. Currently does not work for systems with interconnected rings.

`Dtheta`

Type Float

Default value 60.0

Description The angle over which the bonds are rotated, in order to create a new conformer.

`Expander`

Type Block

Description Options for the conformer expander. The Expander expands an existing conformer set, by adding new conformers to it. The new conformers are generated from the original conformers in the set. Unlike the generators, the outcome of an expander is therefore very dependent on the input conformations.

The GC generator uses a genetic algorithm to create a combinatorial expansion by combining local substructures. The MD expander start MD simulations from the conformers in the set, and extracts snapshots to create new conformers. Both these expanders are part of the CREST generator.

`GC`

Type Block

Description Options for the genetic algorithm for combinatorial expansion of conformer geometries. This generator only works if a non-zero set of conformers is already provided.

`MaxGCenergy`

Type Float

Default value 6.0

Description The maximum energy (relative to the lowest in the set) of the conformers we are going to use for expansion. The default is 6.0 kcal/mol, but if MaxEnergy was set, then that value is used.

`Parallel`

Type Bool

Default value Yes

Description Determines if the combinatorial expansion of conformers should be performed in parallel or not (default: True).

`RMSDThreshold`

Type Float

Default value 0.25

Description Newly generated geometries are only considered unique if their RMSD from all other newly generated geometries is larger than this threshold.

`MD`

Type Block

Description Produces conformers by running a set of MD simulations at different elevated temperatures, etracting snapshots, and optimizing those.

`MolecularDynamics`

Type Block

Description Configures molecular dynamics (with the velocity-Verlet algorithm) with and without thermostats. This block allows to specify the details of the molecular dynamics calculation. Default values will be ignored.

`Checkpoint`

Type Block

Description Sets the frequency for storing the entire MD state necessary for restarting the calculation.

`Frequency`

Type Integer

Default value 1000

GUI name Checkpoint frequency

Description Write the MD state and engine-specific data to the respective .rkf files once every N steps.

`WriteProperties`

Type Bool

Default value No

Description Write the properties from the properties section to the ChecoPoint file once every N steps.

`InitialVelocities`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`File`

Type String

Description AMS RKF file containing the initial velocities.

`RandomVelocitiesMethod`

Type Multiple Choice

Default value Exact

Options [Exact, Boltzmann, Gromacs]

GUI name Velocity randomization method

Description Specifies how are random velocities generated. Three methods are available.

Exact: Velocities are scaled to exactly match set random velocities temperature.

Boltzmann: Velocities are not scaled and sample Maxwell-Boltzmann distribution. However, the distribution is not corrected for constraints.

Gromacs: Velocities are scaled to match set random velocities temperature, but removal of net momentum is performed only after the scaling. Resulting kinetic energy is lower based on how much net momentum the system had.

`Temperature`

Type Float

Unit Kelvin

GUI name Initial temperature

Description Sets the temperature for the Maxwell-Boltzmann distribution when the type of the initial velocities is set to random, in which case specifying this key is mandatory.

AMSinput will use the first temperature of the first thermostat as default.

`Type`

Type Multiple Choice

Default value Random

Options [Zero, Random, FromFile, Input]

GUI name Initial velocities

Description Specifies the initial velocities to assign to the atoms. Three methods to assign velocities are available.

Zero: All atom are at rest at the beginning of the calculation.

Random: Initial atom velocities follow a Maxwell-Boltzmann distribution for the temperature given by the [MolecularDynamics%InitialVelocities%Temperature] keyword.

FromFile: Load the velocities from a previous ams result file.

Input: Atom's velocities are set to the values specified in the [MolecularDynamics%InitialVelocities%Values] block, which can be accessed via the Expert AMS panel in AMSinput.

`Values`

Type Non-standard block

Description This block specifies the velocity of each atom, in Angstrom/fs, when [MolecularDynamics%InitialVelocities%Type] is set to Input. Each row must contain three floating point values (corresponding to the x,y,z component of the velocity vector) and a number of rows equal to the number of atoms must be present, given in the same order as the [System%Atoms] block.

`NSteps`

Type Integer

Default value 1000

GUI name Number of steps

Description The number of steps to be taken in the MD simulation.

`Preserve`

Type Block

Description Periodically remove numerical drift accumulated during the simulation to preserve different whole-system parameters.

`AngularMomentum`

Type Bool

Default value Yes

GUI name : Angular momentum

Description Remove overall angular momentum of the system. This option is ignored for 2D and 3D-periodic systems, and disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

`CenterOfMass`

Type Bool

Default value No

GUI name : Center of mass

Description Translate the system to keep its center of mass at the coordinate origin. This option is not very useful for 3D-periodic systems.

`Momentum`

Type Bool

Default value Yes

GUI name Preserve: Total momentum

Description Remove overall (linear) momentum of the system. This is disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

`Print`

Type Block

Description This block controls the printing of additional information to stdout.

`System`

Type Bool

Default value No

Description Print the chemical system before and after the simulation.

`Velocities`

Type Bool

Default value No

Description Print the atomic velocities before and after the simulation.

`Restart`

Type String

GUI name Restart from

Description The path to the ams.rkf file from which to restart the simulation.

`Shake`

Type Block

Description Parameters of the Shake/Rattle algorithm.

`All`

Type String

Recurring True

GUI name Constrain all

Description Constraint description in one the following formats: All [bondOrder] bonds at1 at2 [to distance] All triangles at1 at2 at3

The first option constrains all bonds between atoms at1 at2 to a certain length, while the second - bonds at1-at2 and at2-at3 and the angle between them.

The [bondOrder] can be a number or a string such as single, double, triple or aromatic. If it's omitted then all bonds between specified atoms will be constrained. Atom names are case-sensitive and they must be as they are in the Atoms block, or an asterisk '*' denoting any atom. The distance, if present, must be in Angstrom. If it is omitted then the bond length from the initial geometry is used.

Important: only the bonds present in the system at certain points of the simulation (at the start or right after adding/removing atoms) can be constrained, which means that the bonds may need to be specified in the System block.

Warning: the triangles constraint should be used with care because each constrained bond or angle means removing one degree of freedom from the dynamics. When there are too many constraints (for example, "All triangles H C H" in methane) some of them may be linearly dependent, which will lead to an error in the temperature computation.

Valid examples: All single bonds C C to 1.4 All bonds O H to 0.98 All bonds O H All bonds H * All triangles H * H

`ConvergeR2`

Type Float

Default value 1e-08

Description Convergence criterion on the max squared difference, in atomic units.

`ConvergeRV`

Type Float

Default value 1e-08

Description Convergence criterion on the orthogonality of the constraint and the relative atomic velocity, in atomic units.

`Iterations`

Type Integer

Default value 100

Description Number of iterations.

`ShakeInitialCoordinates`

Type Bool

Default value Yes

Description Apply constraints before computing the first energy and gradients.

`Thermostat`

Type Block

Recurring True

Description This block allows to specify the use of a thermostat during the simulation. Depending on the selected thermostat type, different additional options may be needed to characterize the specific thermostat' behavior.

`BerendsenApply`

Type Multiple Choice

Default value Global

Options [Local, Global]

GUI name Apply Berendsen

Description Select how to apply the scaling correction for the Berendsen thermostat:

- per-atom-velocity (Local) - on the molecular system as a whole (Global).

`ChainLength`

Type Integer

Default value 10

GUI name NHC chain length

Description Number of individual thermostats forming the NHC thermostat

`Duration`

Type Integer List

GUI name Duration(s)

Description Specifies how many steps should a transition from a particular temperature to the next one in sequence take.

`Region`

Type String

Default value *

Description The identifier of the region to thermostat. The default '*' applies the thermostat to the entire system. The value can by a plain region name, or a region expression, e.g. '*-myregion' to thermostat all atoms that are not in myregion, or 'regionA+regionB' to thermostat the union of the 'regionA' and 'regionB'. Note that if multiple thermostats are used, their regions may not overlap.

`Tau`

Type Float

Unit Femtoseconds

GUI name Damping constant

Description The time constant of the thermostat.

`Temperature`

Type Float List

Unit Kelvin

GUI name Temperature(s)

Description The target temperature of the thermostat.

You can specify multiple temperatures (separated by spaces). In that case the Duration field specifies how many steps to use for the transition from one T to the next T (using a linear ramp). For NHC thermostat, the temperature may not be zero.

`Type`

Type Multiple Choice

Default value None

Options [None, Berendsen, NHC]

GUI name Thermostat

Description Selects the type of the thermostat.

`TimeStep`

Type Float

Default value 0.25

Unit Femtoseconds

Description The time difference per step.

`Trajectory`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`ExitConditionFreq`

Type Integer

GUI name Exit condition frequency

Description Check the exit conditions every N steps. By default this is done every SamplingFreq steps.

`PrintFreq`

Type Integer

GUI name Printing frequency

Description Print current thermodynamic properties to the output every N steps. By default this is done every SamplingFreq steps.

`SamplingFreq`

Type Integer

Default value 100

GUI name Sample frequency

Description Write the the molecular geometry (and possibly other properties) to the .rkf file once every N steps.

`TProfileGridPoints`

Type Integer

Default value 0

Description Number of points in the temperature profile. If TProfileGridPoints > 0, a temperature profile along each of the three lattice axes will be written to the .rkf file. The temperature at a given profile point is calculated as the total temperature of all atoms inside the corresponding slice of the simulation box, time-averaged over all MD steps since the previous snapshot. By default, no profile is generated.

`WriteBonds`

Type Bool

Default value Yes

Description Write detected bonds to the .rkf file.

`WriteCharges`

Type Bool

Default value Yes

Description Write current atomic point charges (if available) to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze charges.

`WriteCoordinates`

Type Bool

Default value Yes

Description Write atomic coordinates to the .rkf file.

`WriteEngineGradients`

Type Bool

Default value No

Description Write atomic gradients (negative of the atomic forces, as calculated by the engine) to the History section of ams.rkf.

`WriteMolecules`

Type Bool

Default value Yes

Description Write the results of molecule analysis to the .rkf file.

`WriteVelocities`

Type Bool

Default value Yes

Description Write velocities to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze the velocities.

`Ngeoms`

Type Integer

Default value 4

Description At each temperature, MD simulations are started from Ngeoms different starting geometries. The starting geometries are extracted from the provided conformer set. If the conformer set is empty, then no more than a single geometry per temperature can be provided, limiting the total number of MD simulations.

`Temperatures`

Type Float List

Default value [400.0, 500.0]

Unit Kelvin

Description The list of different temperatures at which MD simulations are run.

`UseShake`

Type Bool

Default value No

Description Constrain all -H bonds with shake. If turned on, the MD timestep is automatically increased.

`MaxEnergy`

Type Float

Unit kcal/mol

Description Threshold for filtering out high-energy conformers. If the relative energy of a conformer with respect to the lowest conformer is larger than this value, the conformer will be discarded.

`Method`

Type Multiple Choice

Default value GC

Options [MD, GC]

GUI name Generator method

Description Method used to generate the conformers.

`Preoptimization`

Type Block

Description If this block is enabled geometries will be preoptimized. After preoptimization the high energy conformers will be discarded, and then from the remaining set the unoptimized geometries will be optimized at higher level. This is to prevent the preoptimizer from collapsing different conformers into a single false minimum. As a result, preoptimization is only useful if MaxEnergy is chosen low.

`Enable`

Type Bool

Default value No

Description Perform preoptimization at a low level of accuracy.

`Engine`

Type Block

Description The engine specifics to be used for preoptimization.

`PreoptFactor`

Type Integer

Default value 2

Description This factor is multiplied with MaxEnergy, to determine which high energy conformers can be discarded after preoptimization.

`RDKitETKDG`

Type Block

Description Settings for the call to RDKits ETKDG conformer generator tool.

`BestRMSDThreshold`

Type Float

Default value -1.0

Description After ETKDG conformer generation by RDKit, RDKit can be used to remove duplicates via the BestRMS algorithm. This filter does exactly the same as the RMSD equivalence detector in the Equivalence block.

`Forcefield`

Type Multiple Choice

Default value None

Options [None, UFF, MMFF]

Description The name of the RDKit forcefield to use for geometry optimization at the end of ETKDG conformer generation (by default no geometry optimization is performed). Using the RDKit internal optimization may make the subsequent geometry optimizations with AMS faster.

`Parallel`

Type Bool

Default value No

Description Experimental: Parallelize the RDKit generation step by calling the RDKit conformer generation method in parallel from multiple processes.

`RMSDThreshold`

Type Float

Default value -1.0

Description Root Mean Square deviation threshold for removing similar/equivalent conformations during the RDKit ETKDG procedure. By default there is no pruning (value: -1).

`UseExpTorsionAnglePrefs`

Type String

Default value default

Description Impose experimental torsion angle preferences in RDKit ETKDG conformer generation. By default the RDKit version determines wether or not to switch this on.

`RNGSeed`

Type Integer

Description Initial guesses for conformers can be randomly generated by RDKit, using the ETKDG algorithm. For reproducability, a random number seed can be provided here.

`Equivalence`

Type Block

Description Options for the procedure determining whether two structures are equivalent or distinct conformers.

`AMS`

Type Block

Description Options for the AMS method of checking equivalence. This method uses the atomic distance matrices and the torsion angles between heavy atoms to determine if conformer candidates are duplicates.

`DihedralThreshold`

Type Float

Default value 30.0

Description Maximum difference a dihedral can have for a conformer to be considered a duplicate.

`DistanceThreshold`

Type Float

Default value 0.1

Description Maximum difference a distance between two atoms can have for a conformer to be considered a duplicate.

`EnergyThreshold`

Type Float

Default value 0.2

Unit kcal/mol

Description The energy difference beyond which two conformers are always considered distinct.

`IrrelevantAtoms`

Type Integer List

Description To detect equivalence, only a subset of atoms is used. The atoms that are excluded from equivalence comparison should be specified here. By default only non-hydrogen atoms will be used for the comparison. Numbering starts at 0.

`AcceptAll`

Type Bool

Default value No

Description If set to True, add any candidate to the set without checks of connectivity changes, stereo- or cis/trans isomerization, or duplication.

`AcceptIsomers`

Type Bool

Default value No

Description If set to True, perform all checks of a new conformer candidate, except for the stereo- or cis/trans isomerization check.

`CREST`

Type Block

Description Options for the CREST method of checking equivalence. This method uses the rotational constants of conformer candidates to determine if they are duplicates.

`EnergyThreshold`

Type Float

Default value 0.05

Unit kcal/mol

Description The energy difference beyond which two conformers are always considered distinct.

RMSDThreshold

Type Float

Default value 0.125

Description Threshold for the RMSD between two conformers that determines if they are duplicates or rotamers (according to the CREST rotamer definition.)

ScaledRotationalConstantSettings

Type Block

Description By default, the equivalence of two geometries is determined mainly by comparing the rotational constants, and weighing the difference based on the average anisotropy of the two systems. This procedure has several settings that can be user defined.

RotationalConstantThreshold

Type Float

Default value 0.003

Description Threshold for the difference in rotational constants that determines if two geometries are duplicates. The threshold is weighed by the anisotropy of the systems. Note: in the grimme code they use 0.01 as bconst_threshold, but this leads to a lot of misclassifications (i.e. different conformers are classified as equivalent rotamers) So, here we use a smaller default value.

CheckForDuplicates

Type Bool

Default value Yes

Description If set to True, check any new conformer candidate for duplication, and only accept unique conformers. If set to False, accept duplicates into the set.

Method

Type Multiple Choice

Default value CREST

Options [AMS, TFD, RMSD, CREST]

GUI name Equivalence method

Description Method used to determine (and filter out) equivalent conformers.

The CREST equivalence method relies on rotational constants comparisons. For this reason, conformers with the same rotational constants (such as mirror images) will be considered equivalent conformers.

The AMS equivalence method uses a distance matrix and dihedrals to compare conformers. This equivalence method can be computationally expensive for large molecules.

The TFD equivalence method uses the Torsion Fingerprint Difference as implemented in RDKit.

The RMSD equivalence method uses the RDKit GetBestRMS implementation.

RMSD

Type Block

Description Options for the RMSD method of checking equivalence. This method uses the RDKit implementation of GetBestRMS, which enumerates over atomic permutations for pairs of geometries to detect duplicates based on the RMSD value.

`EnergyThreshold`

Type Float

Default value 0.05

Unit kcal/mol

Description The energy difference beyond which two conformers are always considered distinct.

`RMSDThreshold`

Type Float

Default value 0.125

Description Threshold on the RMSD difference to determine if two geometries represent the same conformer. This value is in Angstrom.

`Reorder`

Type Bool

Default value Yes

Description Reorder conformers based on energy, whenever a new conformer is added.

`TFD`

Type Block

Description Options for the TFD method of checking equivalence. This method uses the Torsion Finger Print method to determine if two conformer candidates are duplicates.

`EnergyThreshold`

Type Float

Default value 0.05

Unit kcal/mol

Description The energy difference beyond which two conformers are always considered distinct.

`TFDThreshold`

Type Float

Default value 0.05

Description Threshold on the torsion fingerprint difference to determine if two geometries represent the same conformer. This value is unit-less.

`GeometryOptimization`

Type Block

Description Some options / details regarding the optimization procedure.

`ConvergenceQuality`

Type Multiple Choice

Default value VeryGood

Options [Normal, Good, VeryGood, Excellent]

GUI name Convergence

Description The tightness of the convergence of the geometry optimizations. Lower quality levels may lead to badly converged geometries being classified as distinct conformers.

`GeometryOptimization`

Type Block

Description Configures details of the geometry optimization and transition state searches.

`CalcPropertiesOnlyIfConverged`

Type Bool

Default value Yes

Description Compute the properties requested in the 'Properties' block, e.g. Frequencies or Phonons, only if the optimization (or transition state search) converged. If False, the properties will be computed even if the optimization did not converge.

`Convergence`

Type Block

Description Convergence is monitored for up to 4 quantities: the energy change, the Cartesian gradients, the Cartesian step size, and for lattice optimizations the stress energy per atom. Convergence criteria can be specified separately for each of these items.

`Energy`

Type Float

Default value 1e-05

Unit Hartree

Value Range value > 0

GUI name Energy convergence

Description The criterion for changes in the energy. The energy is considered converged when the change in energy is smaller than this threshold times the number of atoms.

`Gradients`

Type Float

Default value 0.001

Unit Hartree/Angstrom

Value Range value > 0

GUI name Gradient convergence

Description Threshold for nuclear gradients.

`Quality`

Type Multiple Choice

Default value Custom

Options [VeryBasic, Basic, Normal, Good, VeryGood, Custom]

GUI name Convergence

Description A quick way to change convergence thresholds: 'Good' will reduce all thresholds by an order of magnitude from their default value. 'VeryGood' will tighten them by two orders of magnitude. 'Basic' and 'VeryBasic' will increase the thresholds by one or two orders of magnitude respectively.

`Step`

Type Float

Default value 0.01

Unit Angstrom

Value Range value > 0

GUI name Step convergence

Description The maximum Cartesian step allowed for a converged geometry.

`StressEnergyPerAtom`

Type Float

Default value 0.0005

Unit Hartree

Value Range value > 0

Description Threshold used when optimizing the lattice vectors. The stress is considered 'converged' when the maximum value of stress_tensor * cell_volume / number_of_atoms is smaller than this threshold (for 2D and 1D systems, the cell_volume is replaced by the cell_area and cell_length respectively).

`CoordinateType`

Type Multiple Choice

Default value Auto

Options [Auto, Delocalized, Cartesian]

GUI name Optimization space

Description Select the type of coordinates in which to perform the optimization. 'Auto' automatically selects the most appropriate CoordinateType for a given Method.

If 'Auto' is selected, Delocalized coordinates will be used for the Quasi-Newton method, while Cartesian coordinates will be used for all other methods.

`Dimer`

Type Block

Description Options for the Dimer method for transition state search.

`AngleThreshold`

Type Float

Default value 1.0

Unit Degree

Description The rotation is considered converged when the the rotation angle falls below the specified threshold.

`DimerDelta`

Type Float

Default value 0.01

Unit Angstrom

Description Eucledian distance between the midpoint and the endpoint.

`ExtrapolateForces`

Type Bool

Default value Yes

Description Set to false to call engine to calculate forces at the extrapolated rotation angle instead of extrapolating them.

`LBFGSMaxVectors`

Type Integer

Default value 10

Description Max number of vectors for the L-BFGS algorithm to save.

`MaxRotationIterations`

Type Integer

Default value 10

Description Maximum number of rotation iterations for a single translation step.

`Region`

Type String

Default value *

Description Include only atoms of the specified region(s) in the rotations, which allows searching for a transition state involving selected atoms only.

`RotationTrustRadius`

Type Float

Default value 0.1

Unit Angstrom

Description L-BFGS trust radius during rotation iterations.

`TranslationTrustRadius`

Type Float

Default value 0.1

Unit Angstrom

Description L-BFGS trust radius during translation iterations.

`EngineAutomations`

Type Block

Description The optimizer can change some settings of the engine, based for instance on the error. The idea is to allow the engine to be a bit quicker at the start, and more accurate towards the end. Automations are always engine specific.

`Enabled`

Type Bool

Default value Yes

Description Whether or not autotions are enabled at all.

`Gradient`

Type Block

Recurring True

Description A gradient-based automation.

`FinalValue`

Type Float

Description This value will be used whenever the gradient is less than GradientLow

`HighGradient`

Type Float

Default value 1.0

Unit Hartree/Angstrom

Description Defines a large gradient. When the actual gradient is between GradientHigh and GradientLow a linear interpolation scheme is used for kT (on a log scale).

`InitialValue`

Type Float

Description This value will be used at the first geometry, and whenever the gradient is higher than GradientHigh

`LowGradient`

Type Float

Default value 1.0

Unit Hartree/Angstrom

Description Defines a small gradient, see GradientHigh

`UseLogInterpolation`

Type Bool

Default value Yes

Description Whether to use interpolation on a log (y) scale or not

`Variable`

Type String

Default value

Description variable to be tweaked for the engine.

`Iteration`

Type Block

Recurring True

Description Geometry step based automation.

`FinalValue`

Type Float

Description

`FirstIteration`

Type Integer

Default value 1

Description When the actual gradient is between the first and last iteration, a linear interpolation is used.

`InitialValue`

Type Float

Description This value will be used when the iteration number is smaller or equal to FirstIteration

`LastIteration`

Type Integer

Default value 10

Description Where the automation should reach the FinalValue

`UseLogInterpolation`

Type Bool

Default value Yes

Description Whether to use interpolation on a log (y) scale or not

`Variable`

Type String

Default value

Description variable to be tweaked for the engine.

`FIRE`

Type Block

Description This block configures the details of the FIRE optimizer. The keywords name correspond the the symbols used in the article describing the method, see PRL 97, 170201 (2006).

`AllowOverallRotation`

Type Bool

Default value Yes

Description Whether or not the system is allowed to freely rotate during the optimization. This is relevant when optimizing structures in the presence of external fields.

`AllowOverallTranslation`

Type Bool

Default value No

Description Whether or not the system is allowed to translate during the optimization. This is relevant when optimizing structures in the presence of external fields.

`MapAtomsToUnitCell`

Type Bool

Default value No

Description Map the atoms to the central cell at each geometry step.

`NMin`

Type Integer

Default value 5

Description Number of steps after stopping before increasing the time step again.

`alphaStart`

Type Float

Default value 0.1

Description Steering coefficient.

`dtMax`

Type Float

Default value 1.0

Unit Femtoseconds

Description Maximum time step used for the integration. For ReaxFF and APPLE&P, this value is reduced by 50%.

`dtStart`

Type Float

Default value 0.25

Unit Femtoseconds

Description Initial time step for the integration.

`fAlpha`

Type Float

Default value 0.99

Description Reduction factor for the steering coefficient.

`fDec`

Type Float

Default value 0.5

Description Reduction factor for reducing the time step in case of uphill movement.

`fInc`

Type Float

Default value 1.1

Description Growth factor for the integration time step.

`strainMass`

Type Float

Default value 0.5

Description Fictitious relative mass of the lattice degrees of freedom. This controls the stiffness of the lattice degrees of freedom relative to the atomic degrees of freedom, with smaller values resulting in a more aggressive optimization of the lattice.

`HessianFree`

Type Block

Description Configures details of the Hessian-free (conjugate gradients or L-BFGS) geometry optimizer.

`Step`

Type Block

Description

`MaxCartesianStep`

Type Float

Default value 0.1

Unit Angstrom

Description Limit on a single Cartesian component of the step.

`MinRadius`

Type Float

Default value 0.0

Unit Angstrom

Description Minimum value for the trust radius.

`TrialStep`

Type Float

Default value 0.0005

Unit Angstrom

Description Length of the finite-difference step when determining curvature. Should be smaller than the step convergence criterion.

`TrustRadius`

Type Float

Default value 0.2

Unit Angstrom

Description Initial value of the trust radius.

`InitialHessian`

Type Block

Description Options for initial model Hessian when optimizing systems with the Quasi-Newton method.

`File`

Type String

GUI name Initial Hessian from

Description KF file containing the initial Hessian (or the results dir. containing it). This can be used to load a Hessian calculated in a previously with the [Properties%Hessian] keyword.

`Type`

Type Multiple Choice

Default value Auto

Options [Auto, UnitMatrix, Swart, FromFile, Calculate, CalculateWithFastEngine]

GUI name Initial Hessian

Description Select the type of initial Hessian. Auto: let the program pick an initial model Hessian. UnitMatrix: simplest initial model Hessian, just a unit matrix in the optimization coordinates. Swart: model Hessian from M. Swart. FromFile: load the Hessian from the results of a previous calculation (see InitialHessian%File). Calculate: compute the initial Hessian (this may be computationally expensive and it is mostly recommended for TransitionStateSearch calculations). CalculateWithFastEngine: compute the initial Hessian with a faster engine.

`KeepIntermediateResults`

Type Bool

Default value No

Description Whether the full engine result files of all intermediate steps are stored on disk. By default only the last step is kept, and only if the geometry optimization converged. This can easily lead to huge amounts of data being stored on disk, but it can sometimes be convenient to closely monitor a tricky optimization, e.g. excited state optimizations going through conical intersections, etc. …

`MaxIterations`

Type Integer

Value Range value >= 0

GUI name Maximum number of iterations

Description The maximum number of geometry iterations allowed to converge to the desired structure.

`MaxRestarts`

Type Integer

Default value 0

Description If a geometry optimization of a system with no symmetry operators (or with explicitly disabled symmetry: `UseSymmetry False`) and enabled PES point characterization converges to a transition state (or higher order saddle point), it can be restarted automatically after a small displacement along the imaginary vibrational mode. In case the restarted optimization again does not find a minimum, this can happen multiple times in succession. This keyword sets the maximum number of restarts. The default value is 0, so the automatic restarting is disabled by default.

`Method`

Type Multiple Choice

Default value Auto

Options [Auto, Quasi-Newton, FIRE, L-BFGS, ConjugateGradients, Dimer]

GUI name Optimization method

Description Select the optimization algorithm employed for the geometry relaxation. Currently supported are:

the Hessian-based Quasi-Newton-type BFGS algorithm,

the fast inertial relaxation method (FIRE),

the limited-memory BFGS method,

and the conjugate gradients method. The default is to choose an appropriate method automatically based on the engine's speed, the system size and the supported optimization options.

`OptimizeLattice`

Type Bool

Default value No

Description Whether to also optimize the lattice for periodic structures. This is currently supported with the Quasi-Newton, FIRE, and L-BFGS optimizers.

`PretendConverged`

Type Bool

Default value No

Description Normally a non-converged geometry optimization is considered an error. If this keyword is set to True, the optimizer will only produce a warning and still claim that the optimization is converged. (This is mostly useful for scripting applications, where one might want to consider non-converged optimizations still successful jobs.)

`Quasi-Newton`

Type Block

Description Configures details of the Quasi-Newton geometry optimizer.

`MaxGDIISVectors`

Type Integer

Default value 0

Description Sets the maximum number of GDIIS vectors. Setting this to a number >0 enables the GDIIS method.

`Step`

Type Block

Description

`TrustRadius`

Type Float

Description Initial value of the trust radius.

`VaryTrustRadius`

Type Bool

Description Whether to allow the trust radius to change during optimization. By default True during energy minimization and False during transition state search.

`UpdateTSVectorEveryStep`

Type Bool

Default value Yes

GUI name Update TSRC vector every step

Description Whether to update the TS reaction coordinate at each step with the current eigenvector.

`RestartDisplacement`

Type Float

Default value 0.05

Unit Angstrom

Description If a geometry optimization of a system with no symmetry operators (or with explicitly disabled symmetry: `UseSymmetry False`) and enabled PES point characterization converges to a transition state (or higher order saddle point), it can be restarted automatically after a small displacement along the imaginary vibrational mode. This keywords sets the size of the displacement for the furthest moving atom.

`Keep`

Type Multiple Choice

Default value None

Options [None, all]

Description Keep all the output files of the geometry optimizations. If set to 'all', must be used in combination with Output%KeepWorkDir.

`MaxConvergenceTime`

Type Multiple Choice

Default value Default

Options [Default, High]

Description The number of iterations for the geometry optimization, based on the number of atoms in the system. The default value is the general AMS value for geometry optimization. Often, for conformer generation, it needs to be set higher.

`MaxOptimizations`

Type Integer

Default value 1000

Description Set a maximum to the number of geometries accepted for optimization at once, per AMSWorker (so should be multiplied by the number of cores used). If not set, the disc size requirements can become too large.

`OptimizationMethod`

Type Multiple Choice

Default value Quasi-Newton

Options [Auto, Quasi-Newton, FIRE, L-BFGS, ConjugateGradients, Dimer]

Description Select the optimization algorithm employed for the geometry relaxation. Currently supported are:

the Hessian-based Quasi-Newton-type BFGS algorithm,

the fast inertial relaxation method (FIRE),

the limited-memory BFGS method,

and the conjugate gradients method. The default is Quasi-Newton, which gives the most reliable results for conformers. The Auto method leaves it to the AMS GeometryOptimization task to select a method.

`UseAMSWorker`

Type Bool

Default value Yes

Description Whether the set of optimizations should be run via the AMSWorkerPool or via regular AMSJobs.

`WriteGeometries`

Type Block

Description Determines if and where optimized geometries will be written to file during optimization. When the AMSWorker is used, then the write interval depends on MaxOptimizations. If enabled, must be used in combination with Output%KeepWorkDir.

`Dirname`

Type String

Default value conf_tmpdir

Description The name of the folder that should contain the optimized geometries.

`Enabled`

Type Bool

Default value No

Description Enables or disables the periodic writing of optimized geometries to file

10.4 Trajectory Analysis

`analysis` is a standalone program that performs analysis of molecular dynamics trajectories created with AMS. It can produce histograms and radial distribution functions. It is used under the hood in AMSmovie (**MD Properties** menu bar).

10.4.1 New in Trajectory Analysis-2023

- Intra- and inter-molecular radial distribution functions
- Properties used to compute autocorrelation or mean square displacement can be stored to file
- Manual selection of coordinate unwrapping for autocorrelation or mean square displacement functions

10.4.2 Quickstart Guide

This example computes the oxygen-oxygen radial distribution function of a MD simulation using the analysis utility program:

```
#!bin/sh

"$AMSBIN/analysis" << eor

Task RadialDistribution

TrajectoryInfo
    Trajectory
        KFFilename ams.results/ams.rkf
        Range 1 1000 2
    End
End

RadialDistribution
    NBins 1000
    AtomsFrom
        Element O
    End
    AtomsTo
        Element O
    End
End
eor
```

The analysis program reads one or more trajectory files (filename.rkf) from an AMS molecular dynamics (MD) or a Grand Canonical Monte Carlo (GCMC) simulation. The file information is supplied in the `TrajectoryInfo` input block. In this block, a separate `Trajectory` subblock needs to be supplied for each trajectory file. The `Trajectory` subblock contains a mandatory keyword `KFFilename`, and an optional keyword `Range`. The latter contains the initial frame to be read, the final frame to be read, and optionally the stepsize. By default all frames on the trajectory file are read.

```
TrajectoryInfo
   NBlocksToCompare integer
   Trajectory
      KFFilename string
      Range integer_list
```

(continues on next page)

(continued from previous page)

```
      StepSize integer
   End
End
```

TrajectoryInfo

Type Block

Description All the info regarding the reading of the trajectory files.

NBlocksToCompare

Type Integer

Default value 1

Description Get an error estimate by comparing histograms for NBLocks time blocks of the trajectory.

Trajectory

Type Block

Recurring True

Description All info regarding the reading of a single trajectory file.

KFFilename

Type String

Default value ams.rkf

Description The name of the AMS trajectory file.

Range

Type Integer List

Description One or two values: start frame, and optionally end frame. By default the first and last frame are read.

StepSize

Type Integer

Default value 1

Description The step size at which frames are read from the RKF (default 1, every frame is read).

All tools in the analysis program provide an option to obtain information on the equilibration of the simulation. If the optional keyword `NBlocksToCompare` in the `TrajectoryInfo` block is set to a value N higher than 1, the trajectory is divided into N blocks, and the analysis results for each block are compared. The variation in the analysis result is provided as a standard deviation.

10.4.3 Radial Distribution Function (RDF)

The Analysis tool computes radial distribution functions $g(r)$ if the `Task` keyword is set to RadialDistribution.

```
Task [RadialDistribution | Histogram | AutoCorrelation | MeanSquareDisplacement |␣
↪AverageBinPlot]
```

`Task`

Type Multiple Choice

Options [RadialDistribution, Histogram, AutoCorrelation, MeanSquareDisplacement, AverageBinPlot]

Description The analysis task.

Further details on the radial distribution functions are then set in the `RadialDistribution` block. If more than one `RadialDistribution` block is present in the input, more than one radial distribution function will be computed. The result is printed to output as text, as well as stored in a binary file (plot.kf).

Description

A radial distribution function $g(r)$, or pair correlation function, is a density of distances between particles, relative to the average distance density. The *x*-axis variable represents a distance r, while the *y*-axis represents the relative density of that distance. For a complete homogeneous system of particles the $g(r)$ values for the distances between all particles equals 1 everywhere.

Two sets of atoms $\mathbb{S}_{\text{from}}$ and $\mathbb{S}_{\text{to}}$, of length n_{from} and n_{to} respectively, are specified with the keywords `AtomsFrom` and `AtomsTo` in the `RadialDistribution` block. As a result the program computes $n_{\text{from}} * n_{\text{to}}$ distances r^s_{ij} between atom i in $\mathbb{S}_{\text{from}}$ and atom j in $\mathbb{S}_{\text{to}}$ for each trajectory frame s out of a total of n_{frames} frames.

A normalized histogram is then computed from these distances, resulting in a function $N(r)$.

$N(r) = \frac{1}{n_{\text{frames}}} \sum_{s=1}^{n_{\text{frames}}} \sum_{i=1}^{n_{\text{from}}} \sum_{j=1}^{n_{\text{to}}} \delta(r^s_{ij} - r)$.

This histogram is converted to a density, by dividing all values $N(r)$ with the volume $V(r) = 4\pi r^2 dr$ of a sphere-slice at radius r with thickness dr.

The density is further converted to a relative density by dividing with the total density of the system $\rho_{\text{tot}} = \frac{n_{\text{from}} * n_{\text{to}}}{V_{\text{tot}}}$, yielding the final radial distribution function $g(r)$.

$g(r) = \frac{N(r)}{V(r) * \rho_{\text{tot}}}$

Atom Selecion

The variables n_{from} and n_{to} detemining the atom pairs that contribute to the radial distribution can be selected in the `AtomsFrom` and `AtomsTo` blocks. Both can be selected using element names (`Element`), region names (`Region`) or atom indices (`Atom`).

```
RadialDistribution
   AtomsFrom
      Atom integer
      Element string
      Region string
   End
End
```

`RadialDistribution`

Type Block

Recurring True

Description All input related to radial distribution functions.

`AtomsFrom`

Type Block

Description Atom numbers or elements for the first set of atoms in the radial distribution.

`Atom`

Type Integer

Default value 0

Recurring True

Description Atom number.

`Element`

Type String

Recurring True

Description Element Symbol Atom.

`Region`

Type String

Recurring True

Description Region name.

`RadialDistribution`

Type Block

Recurring True

Description All input related to radial distribution functions.

`AtomsTo`

Type Block

Description Atom numbers or elements for the second set of atoms in the radial distribution.

`Atom`

Type Integer

Default value 0

Recurring True

Description Atom number.

`Element`

Type String

Recurring True

Description Element Symbol Atom.

`Region`

Type String

Recurring True

Description Region name.

Options

Non-periodic systems The above equation assumes that the volume V_{tot} of the system is a well-defined quantity. This assumption is correct for systems with 3D periodicity, where the V_{tot} is defined as the volume of the periodic cell. In such a system the value of r can be no larger than r_{max}, the radius of the largest sphere that can be placed inside the periodic cell.

If a system is non-periodic in one or more direction, then the program still computes a $g(r)$, only if the radius r_{max} is supplied by the user with the `Range` keyword in the `RadialDistribution` block. The radius is the second value supplied.

```
RadialDistribution
   Range float_list
End
```

`RadialDistribution`

Type Block

Recurring True

Description All input related to radial distribution functions.

`Range`

Type Float List

Description Either one, two, or three real values. If one it is the stepsize. If two, it is the minimum value and the maximum value. If three, it is the minimum value, the maximum value, and the stepsize. The stepsize overrides NBins.

In this case the volume V_{tot} is assumed to be the volume of a sphere with radius r_{max}.

NPT simulations The above equation further assumes that the volume V_{tot} is constant throughout the simulation. The $g(r)$ of the trajectory from an NPT simulation can still be computed, and in this case V_{tot} is the average value of the volume of the periodic cell.

Simulations with varying numbers of atoms The above equation also assumes that n_{from} and n_{to} remain constant throughout the simulation. However, in a Molecular Gun simulation particles can be added to the system, and in a GCMC simulation particles can be both added and removed from the system. Nonetheless, the program still computes a $g(r)$ in these situations.

If the `AtomsFrom` and `AtomsTo` blocks contain element names (supplied with the recurring `Element` keyword), then every time atoms are added to or removed from the system, the sets of atoms $\mathbb{S}_{\mathrm{from}}$ and $\mathbb{S}_{\mathrm{to}}$ are re-evaluated.

If the `AtomsFrom` and `AtomsTo` blocks contain atom numbers (supplied with the recurring `Atom` keyword), these numbers are updated in the sets $\mathbb{S}_{from}$ and $\mathbb{S}_{to}$ every time atoms are added to or removed from the system. If one of the atoms from the set disappears, the number of distances contributing to the $g(r)$ decreases.

Note: Currently, the values of n_{from} and n_{to} in the normalization factor are taken from the last frame of the simulation.

Warning: If multiple trajectories are supplied, and the number of atoms changes between the end of one trajectory and the beginning of another, this may result in an error in the atom numbers used by the program internally.

Inter- or intra-molecular atom-pairs By default, all $n_{\text{from}} * n_{\text{to}}$ distances are included. Sometimes it can be convenient to view exclusively the distances between atoms within a molecule, or those between different molecules. This can be controlled with the keyword `DistanceTypeSelection` in the `RadialDistribution` block.

```
RadialDistribution
   DistanceTypeSelection [All | InterMolecular | IntraMolecular]
End
```

RadialDistribution

Type Block

Recurring True

Description All input related to radial distribution functions.

DistanceTypeSelection

Type Multiple Choice

Default value All

Options [All, InterMolecular, IntraMolecular]

Description Select only a certain type of interatomic distances.

10.4.4 Histogram

The Analysis program computes histograms if the `Task` keyword is set to Histogram.

```
Task [RadialDistribution | Histogram | AutoCorrelation | MeanSquareDisplacement |␣
↪AverageBinPlot]
```

Task

Type Multiple Choice

Options [RadialDistribution, Histogram, AutoCorrelation, MeanSquareDisplacement, AverageBinPlot]

Description The analysis task.

Further details on the histogram need to be specified in the `Histogram` block. If more than one `Histogram` block is present in the input, more than one histogram will be computed. The result is printed to output as text, as well as stored in a binary file (plot.kf). By default the histogram contains the number of occurrences of a certain value, but the normalized occurrence is provided if the keyword `Normalized` in the `Histogram` block is specified.

```
Histogram
   Normalized Yes/No
End
```

Histogram

Normalized

Type Bool

Default value No

Description Give the normalized histogram.

Histograms can be computed for every quantity stored on the molecular dynamics trajectory file (ams.rkf) in the section History or MDHistory. Examples are scalar quantities like `PotentialEnergy`, `KineticEnergy`, `TotalEnergy`, `Temperature`. In the histogram block, this quantity is selected with the keyword `Variable` in the `Axis` subblock. If more than one `Axis` subblock is present, the dimensionality of the histogram is increased: Three `Axis` subblocks result in a 3D histogram.

It is also possible to select quantities that have scalar or vector values for each atom, such as `Coords` or `Velocities`. If this is combined with multiple axes, then the number of values along all axes must be the same. It is, for example, not possible to plot the atom velocities along one axis, and the temperature per frame along the other. A subset of atoms for which the atom-wise quantity should be selected can be provided in the subblock `Atoms`. The block can contain element names (recurring keyword `Element`), region names (recurring keyword `Region`), or individual atom numbers (recurring keyword `Atom`).

```
Atoms
   Atom integer
   Element string
   Region string
End
```

Atoms

Type Block

Description Relevant if variable has a value per atom (e.g. Coords, Velocities). This block specifies indices or elements for the set of atoms for which the variable is to be read. By default all atoms are used.

Atom

Type Integer

Recurring True

Description Atom index.

Element

Type String

Recurring True

Description Element Symbol Atom.

Region

Type String

Recurring True

Description Region name

A subset of vector elements can be provided with the subblock `VecElements`. By default all vector elements found on the RKF file will be used.

```
VecElements
   Index integer
End
```

VecElements

Type Block

Description A set of indices referring to a subset of a vector. If the variable to be plotted has non-scalar values per step, then this block allows the selection of a subset of vector elements (e.g. 1 and 2 for the x and y values). Can be used in combination with the Atoms block.

Index

Type Integer

Recurring True

Description Element of the property vector.

For each histogram axis, the number of bins can be selected with the `NBins` keyword in the `Axis block`, in which case the range of values along each axis is automatically determined. The default `NBins` value is 100.

Alternatively, a range and a stepsize can be selected with the keyword `Range` in the `Axis` subblock. The keyword `Range` can contain one, two, or three values: 1: Only a stepsize. 2: A smallest value and a largest value. 3: A smallest value, a largest value, and the stepsize.

```
Histogram
   Axes
      Axis
         Atoms
            Atom integer
            Element string
            Region string
         End
         NBins integer
         Range float_list
         Variable string
         VecElements
            Index integer
         End
      End
   End
End
```

Histogram

Type Block

Recurring True

Description All input related to histograms.

Axes

Type Block

Description Specifications for the histogram axes.

Axis

Type Block

Recurring True

Description Specifications for a single histogram axis.

Atoms

Type Block

Description Relevant if variable has a value per atom (e.g. Coords, Velocities). This block specifies indices or elements for the set of atoms for which the variable is to be read. By default all atoms are used.

`Atom`

Type Integer

Recurring True

Description Atom index.

`Element`

Type String

Recurring True

Description Element Symbol Atom.

`Region`

Type String

Recurring True

Description Region name

`NBins`

Type Integer

Default value 100

Description The number of bins along the histogram axis.

`Range`

Type Float List

Description Either one, two, or three real values. If one it is the stepsize. If two, it is the minimum value and the maximum value. If three, it is the minimum value, the maximum value, and the stepsize. The stepsize overrides NBins.

`Variable`

Type String

Description The quantity along the histogram axis.

`VecElements`

Type Block

Description A set of indices referring to a subset of a vector. If the variable to be plotted has non-scalar values per step, then this block allows the selection of a subset of vector elements (e.g. 1 and 2 for the x and y values). Can be used in combination with the Atoms block.

`Index`

Type Integer

Recurring True

Description Element of the property vector.

10.4.5 Autocorrelation Functions

The Analysis program computes autocorrelation functions (ACF) if the `Task` keyword is set to AutoCorrelation.

```
Task [RadialDistribution | Histogram | AutoCorrelation | MeanSquareDisplacement |␣
↪AverageBinPlot]
```

Task

Type Multiple Choice

Options [RadialDistribution, Histogram, AutoCorrelation, MeanSquareDisplacement, AverageBinPlot]

Description The analysis task.

Further details need to be specified in the `AutoCorrelation` block. If more than one `AutoCorrelation` block is present in the input, more than one ACF will be computed. The result is printed to output as text, as well as stored in a binary file (plot.kf).

```
AutoCorrelation
   Atoms
      Atom integer
      Element string
      Region string
   End
   DataReading [Auto | AtOnce | BlockWise]
   InputValues
      Values float_list
   End
   MaxFrame integer
   NPointsHighestFreq integer
   PerElement Yes/No
   Property [Velocities | DipoleMomentFromCharges | DiffusionCoefficient |␣
↪DipoleDerivativeFromCharges |
             PressureTensor | Viscosity | DipoleMomentFromBinLog |␣
↪ViscosityFromBinLog]
   TimeStep float
   UnwrapCoordinates [Auto | Yes | No]
   UseAllValues Yes/No
   UseTimeDerivative
      Enabled Yes/No
   End
   VecElements
      Index integer
   End
   WritePropertyToKF Yes/No
End
```

AutoCorrelation

Atoms

Type Block

Description Relevant if Property is set to Velocities, DipoleMomentFromCharges, DipoleDerivativeFromCharges, or DiffusionCoefficient. Atom numbers or elements for the set of atoms for which the property is read/computed. By default all atoms are used.

Atom

Type Integer

Recurring True

Description Atom number.

`Element`

Type String

Recurring True

Description Element Symbol Atom.

`Region`

Type String

Recurring True

Description Region name.

`DataReading`

Type Multiple Choice

Default value Auto

Options [Auto, AtOnce, BlockWise]

Description The KF data can be read in and handled once, or blockwise. The former is memory intensive, but mostly faster. If Auto is selected, the data is read at once if it is less than 1 GB, and blockwise if it is more.

`InputValues`

Type Block

Description Relevant if Property is set to InputValues. All input values (a vector on each line) need to be provided in this block, using the keyword Values (possibly multiple times).

`Values`

Type Float List

Recurring True

Description The values at each step (on a single line)

`MaxFrame`

Type Integer

Description The maximum number of frames for which the autocorrelation function will be computed. The default is half of the number of provided frames.

`NPointsHighestFreq`

Type Integer

Default value 4

Description The number of points (timesteps) used for the highest frequency displayed in spectrum. This determines up to which frequency the spectrum is displayed. If the spacing between time-steps used for the ACF is 1 fs, then by default the maximum frequency displayed is 0.25 fs-1 (or 8339 cm-1). This corresponds to a (default) value of NPointsHighestFreq of 4. A higher number selected here, will result in a lower maximum frequency returned by the program. The lowest possible value (spectrum up to highest possible frequency) is 2.

`PerElement`

Type Bool

Default value No

Description Compute ACF for all elements in the system. Any other settings in the block will be used.

`Property`

Type Multiple Choice

Default value DipoleDerivativeFromCharges

Options [Velocities, DipoleMomentFromCharges, DiffusionCoefficient, DipoleDerivativeFromCharges, PressureTensor, Viscosity, DipoleMomentFromBinLog, ViscosityFromBinLog]

Description Compute the ACF either from velocities (from rkf), the dipole moment (from coordinates and atomic charges in rkf), the dipole moment derivative (from velocities and atomic charges in rkf), from the pressure tensor (from rkf), or from values specified in input. Selecting DiffusionCoefficient is equivalent to selecting Velocities. The default, DipoleDerivativeFromCharges, results in the computation of an IR spectrum.DipoleMomentFromBinLog and ViscosityFromBinLog allow the relevant properties (dipole moment and pressure tensor respectively) to be read from the BinLog section of the trajectory file. In the BinLog section requested properties are stored every step (even if SamplingFreq was set to a higher number than 1) but only if this was specifically requested at the start of the MD simulation.

`TimeStep`

Type Float

Description Relevant if Property is set to InputValues. The time separating the entries (in fs). If Property is set to any of the other quantities, it can be read from an RKF file, and the timestep is read from the RKF file as well. The read value then overrides this keyword.

`UnwrapCoordinates`

Type Multiple Choice

Default value Auto

Options [Auto, Yes, No]

Description If the coordinates are involved in the requested property, those coordinates are wrapped into the box at each time step. If set to true, this keyword unwraps those coordinates so that the trajectory is continuous. If not provided the code uses automatic defaults.

`UseAllValues`

Type Bool

Default value No

Description By default the same number of values are used for each t-step in the ACF. This has the advantage that all values in the ACF are equally reliable, but it does mean that for the smaller timesteps much of the data is not used. To switch this off and use all data, UseAllValues can be set to true

`UseTimeDerivative`

Type Block

Description Possibly use the time derivative of the selected property (e.g. velocity or dipole moments).

Enabled

Type Bool

Default value No

Description Enable the use of the time derivative of the property.

VecElements

Type Block

Description A set of indices referring to a subset of the property vector. Works in combination with the atoms block. For example, in combination with the property Velocities, the Atoms block allows the selection of a subset of atoms, while the VecElelements block allows the selection of a subset of vector elements (e.g. 1 and 2 for the elements x and y). Currently not implemented with InputValues.

Index

Type Integer

Recurring True

Description Element of the property vector.

WritePropertyToKF

Type Bool

Default value No

Description Write the selected property to the KF files for every requested frame

Description

An autocorrelation function $C(t)$ describes the average correlation (overlap) of a (vector) property **A** with itself as a function of time.

$C(t) = \langle \mathbf{A}(0) \cdot \mathbf{A}(t) \rangle$

The average runs over all time-intervals $(t_0, t_0 + t), (t_1, t_1 + t), ..., (t_N, t_N + t)$, with $t_N = t_n - t_m$. Here n is the total number of frames read from the trajectory (as determined in the block `TrajectoryInfo`), and m is the number of discrete t values for which $C(t)$ is computed. The value m can be set with the keyword `MaxFrame`, and defaults to half the total number of frames read. As stated above, the default average runs over the same number of time intervals for each value of t. If `UseAllValues` is selected, the average runs over all available time intervals for each value of t, which is large for small t, and smallest (N) for t_m.

The normalized autocorrelation function $c(t)$ describes the decorrelation of the property with time, and always starts at 1.0 at $t = 0$.

$c(t) = \frac{\langle \mathbf{A}(0) \cdot \mathbf{A}(t) \rangle}{\langle \mathbf{A}(0) \cdot \mathbf{A}(0) \rangle}$

In most cases short timescale fluctuations are important, so frequent storage of the desired property is required (when preparing the molecular dynamics simulation, set the `SamplingFreq` keyword in the `Trajectory` block of the `MolecularDynanimcs` settings low, preferably to 1).

Setting `SamplingFreq` to 1 results in the storage of a lot of superfluous information, which takes both time and disc space. For a few selected properties this can be circumvented with the `MolecularDynamics%BinLog` block. Properties requested in this block will be stored every step, even if `SamplingFreq` is set to a higher value. The trajectory analysis tool can take advantage of this for the computation of some autocorrelation functions, through the `Property` keyword.

A power spectrum is automatically computed by Fourier transform of the autocorrelation function, and provides information on the frequencies of the signal. When the selected property is the dipole moment time derivative, the power spectrum matches the IR spectrum.

Properties

Autocorrelation functions can be computed for different simulation properties:

1) Dipole moments from coordinates and atomic charges
2) Dipole moment derivatives from velocities and atomic charges
3) Velocities
4) The pressure tensor
5) Diffusion coefficient (equivalent to selecting *Velocities*).
6) Viscosity (equivalent to selecting *PressureTensor*, if only the off-diagonal elements are selected using `VecElements`)
7) DipoleMomentFromBinLog (approximately equivalent to `DipoleMomentFromCharges` if available)
8) ViscosityFromBinlog (equivalent to `Viscosity` if available)
9) User provided values

```
AutoCorrelation
   Property [Velocities | DipoleMomentFromCharges | DiffusionCoefficient |␣
↪DipoleDerivativeFromCharges |
             PressureTensor | Viscosity | DipoleMomentFromBinLog |␣
↪ViscosityFromBinLog]
End
```

AutoCorrelation

Type Block

Recurring True

Description All input related to auto correlation functions.

Property

Type Multiple Choice

Default value DipoleDerivativeFromCharges

Options [Velocities, DipoleMomentFromCharges, DiffusionCoefficient, DipoleDerivativeFromCharges, PressureTensor, Viscosity, DipoleMomentFromBinLog, ViscosityFromBinLog]

Description Compute the ACF either from velocities (from rkf), the dipole moment (from coordinates and atomic charges in rkf), the dipole moment derivative (from velocities and atomic charges in rkf), from the pressure tensor (from rkf), or from values specified in input. Selecting DiffusionCoefficient is equivalent to selecting Velocities. The default, DipoleDerivativeFromCharges, results in the computation of an IR spectrum.DipoleMomentFromBinLog and ViscosityFromBinLog allow the relevant properties (dipole moment and pressure tensor respectively) to be read from the BinLog section of the trajectory file. In the BinLog section requested properties are stored every step (even if SamplingFreq was set to a higher number than 1) but only if this was specifically requested at the start of the MD simulation.

Some of the properties for which an autocorrelation function can be computed are simply read as is from the trajectory RKF file, but others are quite complex. For example, the dipole moment is a property obtained by reading the coordinates and the atomic charges, multiplying each atomic position vector with the corresponding charge, and then summing over all atoms. With the keyword `WritePropertyToKF` in the `AutoCorrelation` block, the user can choose to store not only the autocorrelation function, but also the property used to produce it.

When selectong options 7) or 8) the program attempts to read the dipole moment or the pressure tensor respectively from the BinLog section of the ams.rkf file. This will fail if the data is not stored there. The data will only be stored there if the user selected `MoleclarDynamics%BinLog%DipoleMoment` and `MoleculatDynamics%BinLog%PressureTensor` when setting up the MD simulation.

```
AutoCorrelation
   WritePropertyToKF Yes/No
End
```

AutoCorrelation

Type Block

Recurring True

Description All input related to auto correlation functions.

WritePropertyToKF

Type Bool

Default value No

Description Write the selected property to the KF files for every requested frame

If a property involves atomic coordinates, then this generally means atomic coordinates wrapped into the periodic box at every time step. As a result, coordinates can make seemingly big jumps from one side of the box to another between two consecutive frames. The code is able to unwrap the coordinates, so that all atoms follow a continuous trajectory. For the DipoleMoment property, the wrapped coordinates will be used by default, but an experienced user can determine whether the wrapped or unwrapped coordinates are used with the keyword `UnwrapCoordinates` in the `AutoCorrelation` block.

```
AutoCorrelation
   UnwrapCoordinates [Auto | Yes | No]
End
```

AutoCorrelation

Type Block

Recurring True

Description All input related to auto correlation functions.

UnwrapCoordinates

Type Multiple Choice

Default value Auto

Options [Auto, Yes, No]

Description If the coordinates are involved in the requested property, those coordinates are wrapped into the box at each time step. If set to true, this keyword unwraps those coordinates so that the trajectory is continuous. If not provided the code uses automatic defaults.

Options

With the keyword `MaxFrame` the number of values m in the autocorrelation function ($t = [0, t_1, t_2, ..., t_m]$) can be set. The default value is half of the total number of frames n read from the trajectory.

A subset of atoms for which the property **A** should be selected/computed can be provided in the block `Atoms`. The block can contain element names (recurring keyword `Element`), region names (recurring keyword `Region`),or individual atom numbers (recurring keyword `Atom`).

```
AutoCorrelation
   Atoms
      Atom integer
      Element string
      Region string
   End
End
```

AutoCorrelation

Type Block

Recurring True

Description All input related to auto correlation functions.

Atoms

Type Block

Description Relevant if Property is set to Velocities, DipoleMomentFromCharges, DipoleDerivativeFromCharges, or DiffusionCoefficient. Atom numbers or elements for the set of atoms for which the property is read/computed. By default all atoms are used.

Atom

Type Integer

Recurring True

Description Atom number.

Element

Type String

Recurring True

Description Element Symbol Atom.

Region

Type String

Recurring True

Description Region name.

A subset of vector elements can be provided with the subblock `VecElements`. By default all vector elements found on the RKF file will be used.

```
AutoCorrelation
   VecElements
      Index integer
   End
End
```

AutoCorrelation

Type Block

Recurring True

Description All input related to auto correlation functions.

VecElements

Type Block

Description A set of indices referring to a subset of the property vector. Works in combination with the atoms block. For example, in combination with the property Velocities, the Atoms block allows the selection of a subset of atoms, while the VecElelements block allows the selection of a subset of vector elements (e.g. 1 and 2 for the elements x and y). Currently not implemented with InputValues.

Index

Type Integer

Recurring True

Description Element of the property vector.

10.4.6 Mean Square Displacement

The Analysis program computes mean square displacements (MSD) if the `Task` keyword is set to MeansSquareDisplacement.

```
Task [RadialDistribution | Histogram | AutoCorrelation | MeanSquareDisplacement |␣
↪AverageBinPlot]
```

Task

Type Multiple Choice

Options [RadialDistribution, Histogram, AutoCorrelation, MeanSquareDisplacement, AverageBinPlot]

Description The analysis task.

Further details need to be specified in the `MeanSquareDisplacement` block. If more than one `MeanSquareDisplacement` block is present in the input, more than one MSD will be computed. The result is printed to output as text, as well as stored in a binary file (plot.kf).

```
MeanSquareDisplacement
   Atoms
      Atom integer
      Element string
      Region string
   End
   DataReading [Auto | AtOnce | BlockWise]
   InputValues
      Values float_list
   End
   MaxFrame integer
   PerElement Yes/No
   Property [Coords | DiffusionCoefficient | Conductivity]
   StartTimeSlope float
```

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```
   TimeStep float
   UnwrapCoordinates [Auto | Yes | No]
   UseAllValues Yes/No
   VecElements
      Index integer
   End
   WritePropertyToKF Yes/No
End
```

MeanSquareDisplacement

Atoms

Type Block

Description Relevant if Property is set to any quantity that is available per atom (Coords, DiffusionCoefficient). Atom numbers or elements for the set of atoms for which the property is read/computed are provided here. By default all atoms are used.

Atom

Type Integer

Recurring True

Description Atom number.

Element

Type String

Recurring True

Description Element Symbol Atom.

Region

Type String

Recurring True

Description Region name.

DataReading

Type Multiple Choice

Default value Auto

Options [Auto, AtOnce, BlockWise]

Description The KF data can be read in and handled once, or blockwise. The former is memory intensive, but mostly faster. If Auto is selected, the data is read at once if it is less than 1 GB, and blockwise if it is more.

InputValues

Type Block

Description Relevant if Property is set to InputValues. All input values (a vector on each line) need to be provided in this block, using the keyword Values (possibly multiple times).

Values

Type Float List

Recurring True

Description The values at each step (on a single line)

`MaxFrame`

Type Integer

Description The maximum number of frames for which the mean square displacement function will be computed. The default is half of the number of provided frames.

`PerElement`

Type Bool

Default value No

Description Compute MSD for all elements in the system. Any other settings in thie block will be used.

`Property`

Type Multiple Choice

Default value Coords

Options [Coords, DiffusionCoefficient, Conductivity]

Description Compute the MSD from the property selected here (from rkf). Selecting Diffusion-Coefficient is equivalent to selecting the property Coords.

`StartTimeSlope`

Type Float

Default value 0.0

Description The MSD has a nonlinear regime at short timescales, and a linear regime at long timescales. To determine the slope, the starting point for the linear regime has to be determined. This keyword sets the starting time in fs. If set to zero, the starttime will be automatically determined.

`TimeStep`

Type Float

Description Relevant if Property is set to InputValues. The time separating the entries (in fs). If Property is set to any of the other quantities, it can be read from an RKF file, and the timestep is read from the RKF file as well. The read value then overrides this keyword.

`UnwrapCoordinates`

Type Multiple Choice

Default value Auto

Options [Auto, Yes, No]

Description If the coordinates are involved in the requested property, those coordinates are wrapped into the box at each time step. If seti to true, this keyword unwraps those coordinates so that the trajectory is continuous. If not provided the code uses automatic defaults.

`UseAllValues`

Type Bool

Default value No

Description By default the same number of values are used for each t-step in the MSD. This has the advantage that all values in the MSD are equally reliable, but it does mean that for the smaller timesteps much of the data is not used. To switch this off and use all data, UseAllValues can be set to true

`VecElements`

Type Block

Description A set of indices referring to a subset of the property vector. Works in combination with the atoms block. For example, in combination with the property Coords, the Atoms block allows the selection of a subset of atoms, while the VecElelements block allows the selection of a subset of vector elements (e.g. 1 and 2 for the elements x and y). Currently not implemented with InputValues.

`Index`

Type Integer

Recurring True

Description Element of the property vector.

`WritePropertyToKF`

Type Bool

Default value No

Description Write the selected property to the KF files for every requested frame

Description

The mean square displacement $MSD(t)$ describes the average change of a (vector) property **A** over time. This property is usually a set of atom coordinate vectors, but the implementation is entirely general.

$MSD(t) = \langle [\mathbf{A}(0) - \mathbf{A}(t)]^2 \rangle$

The average runs over all time-intervals $(t_0, t_0 + t)$, $(t_1, t_1 + t)$, ..., $(t_N, t_N + t)$, with $t_N = t_n - t_m$. Here n is the total number of frames read from the trajectory, and m is the number of discrete t values for which $MSD(t)$ is computed. The value m can be set with the keyword `MaxFrame`, and defaults to half the total number of frames read from the trajectory. As stated above, the default average runs over the same number of time intervals for each value of t. If `UseAllValues` is selected, the average runs over all available time intervals for each value of t, which is large for small t, and smallest (N) for t_m.

The most common use of the mean square displacement is for the computation of the diffusion coefficient, in which case the selected property is the set of atom coordinates (`Coords`). The diffusion coefficient is proportionate to the slope of this mean square displacement function, and therefore this slope is automatically computed. The function $MSD(t)$ becomes linear only after an initial time interval, and the user can set this initial time with the keyword `StartTimeSlope`. If not provided, this start time is automatically determined. To allow the user to determine if the linear regime has been sufficiently sampled, the slope of $MSD(t)$ as a function of t is computed as well. If the slope has not converged to a stable value, the user should select a larger value of t_m or continue the molecular dynamics simulation for a longer time.

Properties

Autocorrelation functions can be computed for different simulation properties: 1) Coordinates 2) User provided values. Option 3) Diffusion coefficient is equivalent to option 1).

```
MeanSquareDisplacement
   Property [Coords | DiffusionCoefficient | Conductivity]
End
```

MeanSquareDisplacement

Type Block

Recurring True

Description All input related to auto correlation functions.

Property

Type Multiple Choice

Default value Coords

Options [Coords, DiffusionCoefficient, Conductivity]

Description Compute the MSD from the property selected here (from rkf). Selecting DiffusionCoefficient is equivalent to selecting the property Coords.

When read from file, the atomic coordinates will be wrapped inside the periodic box at every time step. As a result, coordinates can make seemingly big jumps from one side of the box to another between two consecutive frames. By default, the coordinates are unwrapped before the computation of the mean square displacement, so that all atoms follow a continuous trajectory. For the experienced users, the option exist to manually determine whether the wrapped or unwrapped coordinates are used with the keyword `UnwrapCoordinates` in the `MeanSquareDisplacement` block.

```
MeanSquareDisplacement
   UnwrapCoordinates [Auto | Yes | No]
End
```

MeanSquareDisplacement

Type Block

Recurring True

Description All input related to auto correlation functions.

UnwrapCoordinates

Type Multiple Choice

Default value Auto

Options [Auto, Yes, No]

Description If the coordinates are involved in the requested property, those coordinates are wrapped into the box at each time step. If seti to true, this keyword unwraps those coordinates so that the trajectory is continuous. If not provided the code uses automatic defaults.

Since the coordinates used to compute the mean square displacement often differ from the coordinates as read from the trajectory (they will be unwrapped, so that the trajectory becomes continuous). With the keyword `WritePropertyToKF` in the `MeanSquareDisplacement` block, the user can choose to store not only the mean square displacement results, but also the property used to produce it.

```
MeanSquareDisplacement
   WritePropertyToKF Yes/No
End
```

`MeanSquareDisplacement`

Type Block

Recurring True

Description All input related to auto correlation functions.

`WritePropertyToKF`

Type Bool

Default value No

Description Write the selected property to the KF files for every requested frame

Options

A subset of atoms for which the property **A** should be selected/computed can be provided in the block `Atoms`. The block can contain element names (recurring keyword `Element`), region names (recurring keyword `Region`),or individual atom numbers (recurring keyword `Atom`).

```
MeanSquareDisplacement
   Atoms
      Atom integer
      Element string
      Region string
   End
End
```

`MeanSquareDisplacement`

Type Block

Recurring True

Description All input related to auto correlation functions.

`Atoms`

Type Block

Description Relevant if Property is set to any quantity that is available per atom (Coords, DiffusionCoefficient). Atom numbers or elements for the set of atoms for which the property is read/computed are provided here. By default all atoms are used.

`Atom`

Type Integer

Recurring True

Description Atom number.

`Element`

Type String

Recurring True

Description Element Symbol Atom.

Region

Type String

Recurring True

Description Region name.

A subset of vector elements can be provided with the subblock `VecElements`. By default all vector elements found on the RKF file will be used.

```
MeanSquareDisplacement
   VecElements
      Index integer
   End
End
```

MeanSquareDisplacement

Type Block

Recurring True

Description All input related to auto correlation functions.

VecElements

Type Block

Description A set of indices referring to a subset of the property vector. Works in combination with the atoms block. For example, in combination with the property Coords, the Atoms block allows the selection of a subset of atoms, while the VecElelements block allows the selection of a subset of vector elements (e.g. 1 and 2 for the elements x and y). Currently not implemented with InputValues.

Index

Type Integer

Recurring True

Description Element of the property vector.

10.4.7 AverageBinPlot

The Analysis program can plot two arbitrary properties, present on the RKF file, against each other averaged over each bin if the `Task` keyword is set to AverageBinPlot.

```
Task [RadialDistribution | Histogram | AutoCorrelation | MeanSquareDisplacement |␣
↪AverageBinPlot]
```

Task

Type Multiple Choice

Options [RadialDistribution, Histogram, AutoCorrelation, MeanSquareDisplacement, AverageBinPlot]

Description The analysis task.

Further details need to be specified in the `AverageBinPlot` block. If more than one `AverageBinPlot` block is present in the input, more than one AverageBinPlot will be computed. The result is printed to output as text, as well as stored in a binary file (analysis.kf).

```
AverageBinPlot
   Atoms
      Atom integer
      Element string
      Region string
   End
   Nbins integer
   Property
      Axis float_list
      Name [FrictionCoefficient | Viscosity | Velocities | EngineGradients]
   End
   XProperty
      Name [Time | Coords]
      VecElements
         Index integer
      End
   End
End
```

AverageBinPlot

Atoms

Type Block

Description Relevant if Properties are atom dependent. Atom numbers or elements for the set of atoms for which the property is read/computed. By default all atoms are used.

Atom

Type Integer

Recurring True

Description Atom number.

Element

Type String

Recurring True

Description Element Symbol Atom.

Region

Type String

Recurring True

Description Region name.

Nbins

Type Integer

Default value 10

Description Number of bins that are plotted

Property

Type Block

Description Property to be plotted along the Y-axis

`Axis`

Type Float List

Description If defined the dot_product along this axis will be taken. Otherwise, the length of the property vector will be used.

`Name`

Type Multiple Choice

Options [FrictionCoefficient, Viscosity, Velocities, EngineGradients]

Description Name of the property

`XProperty`

Type Block

Description Property to be plotted along the Y-axis

`Name`

Type Multiple Choice

Default value Time

Options [Time, Coords]

Description Timestep used for the plotting

`VecElements`

Type Block

Description A set of indices referring to a subset of the property vector. Works in combination with the atoms block. For example, in combination with the property Velocities, the Atoms block allows the selection of a subset of atoms, while the VecElelements block allows the selection of a subset of vector elements (e.g. 1 and 2 for the elements x and y). Currently not implemented with InputValues.

`Index`

Type Integer

Default value 3

Description Element of the x_property, in case it is a vector (For Coords: 1 for X, 2 for Y, 3 for Z).

10.4.8 Viscosity

The viscosity can be computed from an equilibrated Molecular Dynamics run as the integral over the autocorrelation function of the pressure tensor off-diagonal elements.

$\eta = \frac{V}{k_B T} \int_{t=0}^{t=t_{max}} \langle P_{ij}(0) \cdot P_{ij}(t) \rangle_{i \neq j} dt$

The viscosity is computed if the task `AutoCorrelation` is selected, and if in the `AutoCorrelation` block *Viscosity* is selected as the `Property`.

```
$AMSBIN/analysis <<eor
   Task AutoCorrelation
   AutoCorrelation
      Property Viscosity
   End
eor
```

AutoCorrelation

Type Block

Recurring True

Description All input related to auto correlation functions.

Property

Type Multiple Choice

Default value DipoleDerivativeFromCharges

Options [Velocities, DipoleMomentFromCharges, DiffusionCoefficient, DipoleDerivativeFromCharges, PressureTensor, Viscosity, DipoleMomentFromBinLog, ViscosityFromBinLog]

Description Compute the ACF either from velocities (from rkf), the dipole moment (from coordinates and atomic charges in rkf), the dipole moment derivative (from velocities and atomic charges in rkf), from the pressure tensor (from rkf), or from values specified in input. Selecting DiffusionCoefficient is equivalent to selecting Velocities. The default, DipoleDerivativeFromCharges, results in the computation of an IR spectrum.DipoleMomentFromBinLog and ViscosityFromBinLog allow the relevant properties (dipole moment and pressure tensor respectively) to be read from the BinLog section of the trajectory file. In the BinLog section requested properties are stored every step (even if SamplingFreq was set to a higher number than 1) but only if this was specifically requested at the start of the MD simulation.

Again, a subset of atoms can be selected with the sublock `Atoms`.

The value of the viscosity is written to the output, as well as to the KF file.

If the pressure tensor was written to the BinLog section during the MD simulation, then the viscosity can be computed with the keyword `AutoCorrelation%Property` set to *ViscosityFromBinLog*. This is equivalent to setting `AutoCorrelation%Property` to *Viscosity*, but since values are written to the BinLog section at every step, there will be more data available.

10.4.9 Diffusion Coefficient

The diffusion coefficient can be computed from a molecular dynamics trajectory in two ways.

1. As the integral over the velocity autocorrelation function.
2. As the slope of the mean square displacement of the atomic coordinates.

The latter is more commonly used, as the former requires trajectory information to be stored at very short time intervals. Note that the obtained values for the diffusion coefficients correspond to the temperature of the molecular dynamics simulation.

From Velocity Autocorrelation

The diffusion coefficient can be defined as an integral over the velocity autocorrelation function.

$D = \frac{1}{d} \int_{t=0}^{t=t_{max}} \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle dt$

The factor $\frac{1}{d}$ corrects for the dimension of the system, which we assume to equal the length of the provided vector **v**. The dimension d equals 3, unless specified otherwise in the subblock `VecElements`. In a system that is periodic in less than 3 dimensions, it may make sense to provide only the vector elements along the periodic dimensions. By default, however, all vector elements provided are used.

The diffusion coefficient is computed if the task `AutoCorrelation` is selected, and if in the `AutoCorrelation` block *DiffusionCoefficient* is selected as the `Property`. The result is completely equivalent to selecting the task `AutoCorrelation` with *Velocities* as the `Property` keyword.

```
$AMSBIN/analysis <<eor
   Task AutoCorrelation
   AutoCorrelation
      Property DiffusionCoefficient
   End
eor
```

AutoCorrelation

Type Block

Recurring True

Description All input related to auto correlation functions.

Property

Type Multiple Choice

Default value DipoleDerivativeFromCharges

Options [Velocities, DipoleMomentFromCharges, DiffusionCoefficient, DipoleDerivativeFromCharges, PressureTensor, Viscosity, DipoleMomentFromBinLog, ViscosityFromBinLog]

Description Compute the ACF either from velocities (from rkf), the dipole moment (from coordinates and atomic charges in rkf), the dipole moment derivative (from velocities and atomic charges in rkf), from the pressure tensor (from rkf), or from values specified in input. Selecting DiffusionCoefficient is equivalent to selecting Velocities. The default, DipoleDerivativeFromCharges, results in the computation of an IR spectrum.DipoleMomentFromBinLog and ViscosityFromBinLog allow the relevant properties (dipole moment and pressure tensor respectively) to be read from the BinLog section of the trajectory file. In the BinLog section requested properties are stored every step (even if SamplingFreq was set to a higher number than 1) but only if this was specifically requested at the start of the MD simulation.

From Mean Square Displacement

The mean square displacement becomes linear with time, after an initial time interval. We can therefore define the linear part of the function as follows.

$MSD(t) = \langle (\mathbf{r}(0) - \mathbf{r}(t))^2 \rangle = at + b,$

with a as the slope of the function. The diffusion coefficient is proportional to the slope a.

$D = \frac{1}{2d} a$

Here, d is the dimensionality of the system, or the length of the provided vector **r**. The dimension d equals 3, unless specified otherwise in the subblock `VecElements`. In a system that is periodic in less than 3 dimensions, it may make sense to provide only the vector elements along the periodic dimensions. By default, however, all vector elements provided are used.

The diffusion coefficient is computed if the task `MeanSquareDisplacement` is selected, and if in the `MeanSquareDisplacement` block *DiffusionCoefficient* is selected as the `Property`. The result is completely equivalent to selecting the task `MeanSquareDisplacement` with *Coords* as the `Property` keyword.

```
$AMSBIN/analysis <<eor
   Task MeanSquareDisplacement
   MeanSquareDisplacement
      Property DiffusionCoefficient
   End
eor
```

`MeanSquareDisplacement`

Type Block

Recurring True

Description All input related to auto correlation functions.

`Property`

Type Multiple Choice

Default value Coords

Options [Coords, DiffusionCoefficient, Conductivity]

Description Compute the MSD from the property selected here (from rkf). Selecting DiffusionCoefficient is equivalent to selecting the property Coords.

In both cases, a subset of atoms can be selected with the sublock `Atoms`, and a subset of vector elements (in this case elements 1=X, 2=Y, 3=Z for the Cartesian coordinates) can be selected with the subblock `VecElements`.

The value of the diffusion coefficient is written to the output, as well as to the KF file.

10.4.10 Ionic Conductivity

Ionic conductivity can be computed from atomic charge weighted diffusion coefficients. In this case, we compute the diffusion coefficients from the mean square displacement. It can be computed by selecting the `Property` *Conductivity* in the `MeanSquareDisplacement` block.

The set of atoms for which the conductivity is to be computed can be selected as described in the Mean Square Displacement section.

Note that it the ionic conductivity should be computed only for simulations with constant volume and constant atomic charges. By default, only the ForceField engine keeps the atomic charges constant. Any other engine (e.g. REAXFF) varies the atomic charges throughout the simulation. As a result, the computed ionic conductivity values may have some meaning, but the definition of ionic conductivity below is no longer valid.

```
$AMSBIN/analysis <<eor
   Task MeanSquareDisplacement
   MeanSquareDisplacement
      Property Conductivity
   End
eor
```

`MeanSquareDisplacement`

Type Block

Recurring True

Description All input related to auto correlation functions.

`Property`

Type Multiple Choice

Default value Coords

Options [Coords, DiffusionCoefficient, Conductivity]

Description Compute the MSD from the property selected here (from rkf). Selecting DiffusionCoefficient is equivalent to selecting the property Coords.

Behind the scenes, the mean square displacement is then computed using the coordinates multiplied by the atomic charges, as read from the RKF file.

$MSD(t) = \frac{1}{N}\sum_i^N \langle (q_i(0)\mathbf{r_i}(0) - q_i(t)\mathbf{r_i}(t))^2 \rangle$

Here N is the number of atoms for which the conductivity is computed, and i runs over those atoms. The average runs over all time-intervals of length t throughout the simulation. If the atomic charges remain constant throughout the simulation, then they can be moved outside the average.

$MSD(t) = \frac{1}{N}\sum_i^N q_i^2 \langle (\mathbf{r_i}(0) - \mathbf{r_i}(t))^2 \rangle$

The charge weighted diffusion coefficient is defined as the time derivative of the MSD, which is assumed constant.

$D_q = \lim_{t\to\infty} \frac{1}{2dN} \frac{d\sum_i^N q_i^2 \langle (\mathbf{r_i}(0) - \mathbf{r_i}(t))^2 \rangle}{dt}$

Here d is the dimensionality of the systems (usually $d = 3$).

The ionic conductivity can now be defined as

$\sigma = \frac{N}{V k_B T} D_q$

Here, V is the volume of the system, k_B is the Boltzmann constant, and T is the average temperature.

10.5 VCD Analysis: VCDtools

The auxiliary program *VCDtools* provides insight regarding the origin of the VCD intensity of a given normal mode. This is done by analyzing and visualizing the various contributions to the total Electric (E) and Magnetic (M) Dipole Transition Moments (DTM). *e.g.*, the contributions from atoms, electrons, nuclei and molecular fragments. The *VCDtools* program is accessible through the AMS-GUI and allows one to:

1) Scale the size of the atoms with the magnitude of their atomic EDTM or MDTM contributions.
2) Visualize the various contributions to the EDTMs and MDTMs by arrows.
3) Perform a General Coupled Oscillator (GCO) analysis to evaluate the interactions between the different parts of a molecule.
4) Decompose the total EDTM and MDTM into nuclear and electronic contributions to gain insight into effects induced in the VCD spectra by charge transfer.
5) Perform a VCD robustness analysis.

See also:

Tutorial: Analysis of the VCD spectrum of Oxirane with VCDtools

VCDtools requires only the standard result file adf.rkf from an VCD calculation using the *ADF* engine. Once this file is opened with *AMSspectra* the *VCDtools* program will be accessible through the standard user interface of *AMSspectra*.

VCDtools produces one ASCII file, VCDtools.out where all output from the program is printed. This file will be located in the *.results* folder in the directory of the opened adf.rkf result file. Additionally, VCDtools will run on the background every time a new normal mode is selected. It then computes the atomic EDTM and MDTM which can be displayed inside *AMSspectra* in various ways.

The following references should be cited when publishing results obtained with VCDtools Refs.[1][2][3].

10.5.1 General Theory

The VCD intensity associated with the fundamental vibrational transition for a given normal mode j is given by the rotational strength (RS):

$$R_{01}(j) = -i\vec{E}_{01}^{tot}(j) \cdot \vec{M}_{10}^{tot}(j)$$

where $E_{01}^{tot}(j)$ and $M_{10}^{tot}(j)$ are the total EDTM and MDTM of normal mode j , i is the unit imaginary number.

Whiten the harmonic approximation the total EDTM and MDTM can be written as sums of atomic contributions:

$$\vec{E}_{01}^{tot}(j) = \sum_{\lambda=1}^{N} \vec{E}_{01}^{\lambda}(j)$$

$$\vec{M}_{10}^{tot}(j) = \sum_{\lambda=1}^{N} \vec{M}_{10}^{\lambda}(j)$$

where N is the total number of atoms in the molecule and λ runs over all atoms.

10.5.2 General Coupled Oscillator Analysis

The GCO analysis computes the contribution to total rotational strength from the interaction of two molecular fragments. This information provides important insight regarding the source of the VCD intensity and the robustness of the computed VCD sign. In the following, a brief summary of the GCO theory originally published in Ref.[?] is given.

Following the original coupled oscillator VCD mechanism, the atoms of a molecule are grouped into three fragments: **A**, **B**, and **R**. The fragments **A** and **B** represent the important Coupling Oscillator (CO) fragments, while fragment **R** is the ancillary fragment containing the rest of the atoms. As a result, the total RS can be decomposed in three components:

$$R_{01}(j) = R_{01}^{\mathbf{GCO}}(j) + R_{01}^{\mathbf{IF}}(j) + R_{01}^{\mathbf{R}}(j)$$

The first contribution $R_{01}^{\mathbf{GCO}}(j)$, is the GCO contribution to the RS and is given by the interaction between the EDTM and MDTM of fragments **A** and **B**:

$$R_{01}^{\mathbf{GCO}}(j) = -i \cdot \left[\vec{E}_{01}^{\mathbf{A}}(j) \cdot \vec{M}_{10}^{\mathbf{B}}(j) + \vec{E}_{01}^{\mathbf{B}}(j) \cdot \vec{M}_{10}^{\mathbf{A}}(j)\right]$$

The $R_{01}^{\mathbf{IF}}(j)$ term represents the contribution from the individual fragments (IF) **A** and **B** without any interaction with other fragments:

$$R_{01}^{\mathbf{IF}}(j) = -i \cdot \left[\vec{E}_{01}^{\mathbf{A}}(j) \cdot \vec{M}_{10}^{\mathbf{A}}(j) + \vec{E}_{01}^{\mathbf{B}}(j) \cdot \vec{M}_{10}^{\mathbf{B}}(j)\right]$$

[1] V.P. Nicu, *Revisiting an old concept: the coupled oscillator model for VCD. Part 1: the generalised coupled oscillator mechanism and its intrinsic connection to the strength of VCD signals*, Physical Chemistry Chemical Physics 18, 21202 (2016) (https://doi.org/10.1039/C6CP01282E)

[2] V.P. Nicu, J. Neugebauer and E.J. Baerends, *Effects of Complex Formation on Vibrational Circular Dichroism Spectra*, Journal of Physical Chemistry A 112, 6978 (2008) (https://doi.org/10.1021/jp710201q)

[3] M.A.J. Koenis, O. Visser, L. Visscher, W.J. Buma, V.P. Nicu, *GUI Implementation of VCDtools, A Program to Analyze Computed Vibrational Circular Dichroism Spectra*, J. Chem. Inf. Model 60, 259 (2020) (https://pubs.acs.org/doi/abs/10.1021/acs.jcim.9b00956)

and the $R_{01}^{\mathbf{R}}(j)$ contribution contains all contributions from fragment **R**:

$$\begin{aligned} R_{01}^{\mathbf{R}}(j) = &- i \cdot \left[\vec{E}_{01}^{\mathbf{A}}(j) \cdot \vec{M}_{10}^{\mathbf{R}}(j) + \vec{E}_{01}^{\mathbf{R}}(j) \cdot \vec{M}_{10}^{\mathbf{A}}(j)\right] \\ &- i \cdot \left[\vec{E}_{01}^{\mathbf{B}}(j) \cdot \vec{M}_{10}^{\mathbf{R}}(j) + \vec{E}_{01}^{\mathbf{R}}(j) \cdot \vec{M}_{10}^{\mathbf{B}}(j) + \vec{E}_{01}^{\mathbf{R}}(j) \cdot \vec{M}_{10}^{\mathbf{R}}(j)\right] \end{aligned}$$

In the above equations $\vec{E}_{01}^{\mathbf{X}}(j)$ and $\vec{M}_{01}^{\mathbf{X}}(j)$, with $\mathbf{X} = (\mathbf{A}, \mathbf{B}, \mathbf{R})$, are the EDTM and MDTM associated with the three fragments.

Using the origin dependency of the MDTM, the GCO contribution can be rewritten in a form similar to the original CO term:

$$R_{01}^{\mathbf{GCO}}(j) = \frac{\pi \nu_j}{c} \cdot \vec{Y}^{\mathbf{GCO}}(j) \cdot \left[\vec{E}_{01}^{\mathbf{A}}(j) \times \vec{E}_{01}^{\mathbf{B}}(j)\right]$$

where $\vec{Y}^{\mathbf{GCO}}(j)$ is the general coupled oscillator vector.

As shown in ref.? most normal modes of a molecule (i.e. not just the carbonyl stretching modes) can be interpreted in terms of the GCO mechanism. That is, for most normal modes one can define the GCO fragments **A** and **B** fragments in such a way that the $R_{01}^{\mathbf{GCO}}(j)$ term represent the dominant contributions to the rotational strengths. This second expression for $R_{01}^{\mathbf{GCO}}(j)$ does not depend on the MDTM (which is origin dependent). As such, it allows one to interpret the VCD intensity of a mode in terms of interacting EDTMs that are associated with the various moieties of a molecule and their relative orientation.

The identification of the GCO fragments (which are normal mode dependent) is not always trivial, especially, in molecules without symmetry. Consequently, *VCDtools* offers several options for dividing the molecule into fragments. In *AMSspectra* these fragments are referred as *'Regions'* in analogy to the regions in the *AMSinput* program. Under the **Regions**-menu there are many options to set, alter and save the fragments. Additionally, *VCDtools* is able to make a guess for fragments **A** and **B** as will be discussed in more detail below.

10.5.3 Available options

Beside the standard calculation and visualization of the atomic contributions to the normal mode (NM) motion, EDTM and MDTM, *VCDtools* offers three more advanced tools that can be utilized when analyzing VCD spectra inside *AMSspectra:*

- GCO Analysis
- Guess GCO Fragments
- NM Localization on Regions

The first option, *"GCO Analysis"*, uses the above equations to decompose the RS in its different contributions. Printing both the values and important angles between the vectors. Before this option can be run two regions inside the molecule should be defined as fragments **A** and **B**. It is important that these regions do not contain the same atoms. Also since the decomposition is different for each NM, a specific NM should be selected.

The second option, *"Guess Fragments"*, guesses which atoms belong the fragments **A** and **B** for a selected normal mode. In doing so the $R_{01}^{\mathbf{GCO}}(j)$ is maximized while keeping $R_{01}^{\mathbf{R}}(j)$ low. Additionally, it ensures that the fragments are localized on a part of the molecule.

The third option, *"NM Localization on Regions"*, computes the percentage of the mass-weighed normal mode motion that is located on the atoms in the selected regions. One or multiple regions can be computed at the same time and the localizations are determined for all modes within a selected frequency window.

CHAPTER

ELEVEN

EXAMPLES

11.1 Geometry optimization

11.1.1 Example: Simple geometry optimization

Download GO_formaldehyde_noSCC.run

```
#!/bin/sh

$AMSBIN/ams << EOF

   Task GeometryOptimization

   System
       Atoms [Bohr]
          C   0.0   0.0    -1.0
          O   0.0   0.0     1.247
          H   0.0  -1.738  -2.097
          H   0.0   1.738  -2.097
       End
   End

   Engine DFTB
       ResourcesDir Dresden
       Model DFTB0
       DispersionCorrection Auto
   EndEngine

EOF
```

11.1.2 Example: Two-stage geometry optimization with initial Hessian

Download 2StepGO.run

```
#!/bin/sh

# Preoptimization with DFTB and calculation of the Hessian
# ========================================================
#
# We will reuse the geometry optimized at the DFTB level as a starting point for
# the DFT geometry optimization. We will also calculate the real Hessian with
```

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```
# DFTB and use that as the initial Hessian for the Quasi-Newton based
# optimization at the DFT level. DFTB is so fast compared to DFT, that all of
# this is basically instantaneous. Our goal here is really just to reduce the
# number of steps in the DFT geometry optimization. If we save just a single
# step there, the initial DFTB calculation will already have paid for itself ...

AMS_JOBNAME=dftb_preopt $AMSBIN/ams << EOF

   # Specify the system geometry: Aspirin
   System
       Atoms
           C          0.000000  0.000000  0.000000
           C          1.402231  0.000000  0.000000
           C          2.091015  1.220378  0.000000
           C          1.373539  2.425321  0.004387
           C         -0.034554  2.451759  0.016301
           C         -0.711248  1.213529  0.005497
           O         -0.709522  3.637718  0.019949
           C         -2.141910  1.166077 -0.004384
           O         -2.727881  2.161939 -0.690916
           C         -0.730162  4.530447  1.037168
           C         -0.066705  4.031914  2.307663
           H         -0.531323 -0.967191 -0.007490
           H          1.959047 -0.952181 -0.004252
           H          3.194073  1.231720 -0.005862
           H          1.933090  3.376356 -0.002746
           O         -2.795018  0.309504  0.548870
           H         -2.174822  2.832497 -1.125018
           O         -1.263773  5.613383  0.944221
           H         -0.337334  4.693941  3.161150
           H          1.041646  4.053111  2.214199
           H         -0.405932  3.005321  2.572927
       End
   End

   # Do a geometry optimization.
   Task GeometryOptimization

   # Also compute the Hessian at the optimized geometry.
   Properties
      Hessian True
   End

   # Settings for the DFTB engine:
   Engine DFTB
      Model DFTB3
      ResourcesDir DFTB.org/3ob-3-1
   EndEngine

EOF


# Geometry optimization with DFT
# ==============================

AMS_JOBNAME=dft_opt $AMSBIN/ams << EOF
```

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```
   # Start from the geometry that is already optimized at the DFTB level.
   LoadSystem
      File dftb_preopt.results/dftb.rkf
   End
   # (equivalent to loading the system from dftb_preopt.results/ams.rkf)

   Task GeometryOptimization

   GeometryOptimization
      InitialHessian
         # Load the DFTB Hessian as the initial Hessian for the
         # Quasi-Newton based optimizer.
         Type FromFile
         File dftb_preopt.results
      End
   End

   # Settings for the BAND engine:
   Engine BAND
      Basis Type=TZP
      XC GGA=PBE
   EndEngine

EOF
```

11.1.3 Example: Periodic lattice optimization under pressure

Download Diamond_under_pressure.run

```
#! /bin/sh

# Calculate the phonon dispersion curves for diamond under pressure.

# Loop over pressure values (in GPa):
for P in -40 0 40 160 ; do
AMS_JOBNAME=pressure_$P $AMSBIN/ams << EOF

   Task GeometryOptimization

   System
       Atoms
           C -0.44625 -0.44625 -0.44625
           C  0.44625  0.44625  0.44625
       End
       Lattice
           0.0    1.785  1.785
           1.785  0.0    1.785
           1.785  1.785  0.0
       End
   End

   GeometryOptimization
       OptimizeLattice Yes
       Convergence Gradients=1e-5 StressEnergyPerAtom=1E-5
       Method Quasi-Newton
```

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```
   End

   EngineAddons
       Pressure $P
   End

   Properties
       # Request the calculation of phonons at the optimized geometry.
       Phonons Yes
   End

   NumericalPhonons
       SuperCell
           2 0 0
           0 2 0
           0 0 2
       End
   End

   Engine DFTB
       Model SCC-DFTB
       ResourcesDir DFTB.org/mio-1-1
       KSpace
           Type Symmetric
           Symmetric KInteg=5
       End
       Technical AnalyticalStressTensor=False
   EndEngine

EOF
done
```

11.1.4 Example: Phase Transition Due To External Nonuniform Stress

Download Diamond_from_pressure.run

```
#!/bin/sh

# Starting from hexagonal graphite we optimize the crystal
# under the influence of a non-uniform stress tensor.
# The system will undergo a phase transition to a diamond structure
AMS_JOBNAME=Graphite2Diamond $AMSBIN/ams << eor

Task GeometryOptimization
EngineAddons
    ExternalStress
        StressTensorVoigt 0 0 0.01 0 -0.0003 0
    End
End
System
    Atoms
        C  0.0000   0.0000   1.6507
        C  0.0000   0.0000  -1.6507
        C  0.0000  -1.4225   1.6507
        C  0.0000   1.4225  -1.6507
```

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```
    End
    Lattice
        1.2319  -2.1338   0.0000
        1.2319   2.1338   0.0000
        0.0000   0.0000   6.6029
    End
End
GeometryOptimization
    MaxIterations 300
    OptimizeLattice Yes
    Convergence
        Energy 1.0e-6
        Gradients 1.0e-5
        Step 1.0e-4
    End
End
UseSymmetry No
Engine DFTB
    Model SCC-DFTB
    ResourcesDir DFTB.org/3ob-3-1
    DispersionCorrection D3-BJ
    KSpace
        Quality Basic
    End
EndEngine

eor

# The diamond structure is still compressed under the influence of the external␣
↪stress.
# We now disable this term and relax the unit cell with the same DFTB model
AMS_JOBNAME=DiamondRelaxation $AMSBIN/ams << eor

Task GeometryOptimization
LoadSystem
    File Graphite2Diamond.results/ams.rkf
End
GeometryOptimization
    MaxIterations 300
    OptimizeLattice Yes
    Convergence
        Energy 1.0e-6
        Gradients 1.0e-5
        Step 1.0e-4
    End
End
UseSymmetry No
LoadEngine Graphite2Diamond.results/dftb.rkf

eor
```

11.1.5 Example: Boron nitride optimization under external stress

Download ExternalStress_BN.run

```
#!/bin/sh

# Some (fairly arbitrary) external stress in atomic units:
external_stress='0.001 0.0003 -0.0007 0.0005 0.0004 0.001'

# The external stress applied here will result in pretty large deformations.
# Since the external stress energy term becomes more and more approximate the
# larger the deformation from the initial cell is, after the first optimization,
# one should run a second geometry optimization starting from the converged
# results of the first one.

# It is always good practice to validate the optimization under external stress
# by computing the stress tensor of the final optimized geometry: the stress
# tensor at the optimized geometry should match the external stress applied during
# the optimization, but with reversed signs.

AMS_JOBNAME=first_go $AMSBIN/ams << eor

Task GeometryOptimization

System
    Atoms
        B 0.0 0.0 0.0
        N 0.905 0.905 0.905
    End
    Lattice
        0.0 1.81 1.81
        1.81 0.0 1.81
        1.81 1.81 0.0
    End
    SuperCell 2 2 2
End

GeometryOptimization
    OptimizeLattice Yes
    # The convergence threshold should be samller than the applied external stress:
    Convergence Gradients=1.0E-4
End

# We want the external stress to break the symmetry:
UseSymmetry No

EngineAddons
    ExternalStress
        StressTensorVoigt $external_stress
    End
End

Engine ForceField
EndEngine
eor

# The second geometry optimization starting from the results of the first one:
```

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```
AMS_JOBNAME=second_go $AMSBIN/ams << eor

Task GeometryOptimization

LoadSystem
    File first_go.results/ams.rkf
End

GeometryOptimization
    OptimizeLattice Yes
    Convergence Gradients=1.0E-5
End

UseSymmetry No

EngineAddons
    ExternalStress
        StressTensorVoigt $external_stress
    End
End

LoadEngine first_go.results/forcefield.rkf
eor

# In the final calculation we simply compute the stress tensor of the final
# geometry, which should be the opposite of the external stress tensor applied
# during the optimization.

AMS_JOBNAME=sp $AMSBIN/ams << eor

Task SinglePoint

LoadSystem
    File second_go.results/ams.rkf
End

UseSymmetry No

Properties StressTensor=Yes

LoadEngine first_go.results/forcefield.rkf
eor

echo "Applied external stress tensor (order: xx,yy,zz,yz,xz,xy):"
echo $external_stress
echo "Resulting final stress tensor:"
$AMSBIN/amsreport sp.results/forcefield.rkf -r "AMSResults%StressTensor#12.6f##3"
```

11.1.6 Example: Graphene optimization under external stress

Download ExternalStress_graphene.run

```
#!/bin/sh

# Here we perform an optimization under external stress using the
# UpdateReferenceCell option. When using this option the energy during
# the geometry optimization will not necessairly go down, but the final
# stress will match the ExternalStress with much hihger accuracy.

AMS_JOBNAME=go $AMSBIN/ams << eor

Task GeometryOptimization

System

    Atoms
        C 0.0            0.0          0.0
        C 1.23647204352 0.7138774661 0.0
    End
    Lattice
        1.23647204352 -2.1416324015 0.0
        1.23647204352  2.1416324015 0.0
    End
End

UseSymmetry no

EngineAddons
    ExternalStress
        StressTensorVoigt 0.01 0.02 0.003
        UpdateReferenceCell Yes
    End
End

GeometryOptimization
    OptimizeLattice Yes
    Convergence Gradients=1.0E-4
End

Engine DFTB
    Model SCC-DFTB
    ResourcesDir DFTB.org/pbc-0-3
    KSpace Quality=Normal
EndEngine
eor

# Here we compute the stress tensor at the optimized geometry to validate
# the optimization under stress

AMS_JOBNAME=sp $AMSBIN/ams << eor

Task SinglePoint

LoadSystem
    File go.results/ams.rkf
End
```

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```

UseSymmetry no

Properties
    StressTensor Yes
End

LoadEngine go.results/dftb.rkf
eor

echo "Resulting final stress tensor:"
$AMSBIN/amsreport sp.results/dftb.rkf -r "AMSResults%StressTensor#12.6f##2"
```

11.1.7 Example: Constrained optimizations

Download constraints.run

```
#!/bin/sh

# This example demonstrates the setup of all different types of constraints.
# Note that all constraints types can be combined with each other, as long as
# the resulting set of constraints actually makes sense. (It must of course be
# possible to satisfy all of them at the same time. AMS is not able to check
# that and you might get really surprising results if that is not the case ...)


# 1. Angle constraints
# ====================

AMS_JOBNAME=angle "$AMSBIN/ams" << EOF

   Task GeometryOptimization

   GeometryOptimization
      Convergence Step=1.0e-3
   End

   System
       Atoms
          O   0.001356   0.000999   0.000000
          H   0.994442  -0.037855   0.000000
          H  -0.298554   0.948531   0.000000
       End
   End

   Constraints
     # Fix the H--O--H angle to 125 degrees.
     Angle  3 1 2 125.0
   End

   Engine DFTB
       Model SCC-DFTB
       ResourcesDir Dresden
       DispersionCorrection Auto
   EndEngine
```

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```
EOF


# 2. Distance constraints
# =======================

AMS_JOBNAME=dist "$AMSBIN/ams" << EOF

   Task GeometryOptimization

   GeometryOptimization
      Convergence Step=1.0e-3
   End

   System
       Atoms
          O    0.001356    0.000999    0.000000
          H    0.994442   -0.037855    0.000000
          H   -0.298554    0.948531    0.000000
       End
       BondOrders
          1 2 1.0
          1 3 1.0
       End
   End
   Constraints
      # Fix the OH bond distances to 1.03 Angstrom, for which bonds need to be␣
↪defined in the System block
      All bonds O H to 1.03
      # Alternatively you can list the distances one by one as follows
      # Distance  1 2 1.03
      # Distance  1 3 1.03
   End

   Engine DFTB
       Model SCC-DFTB
       ResourcesDir Dresden
       DispersionCorrection Auto
   EndEngine

EOF


# 3. Dihedral angle constraint
# ============================

AMS_JOBNAME=dihed "$AMSBIN/ams" << EOF

   Task GeometryOptimization

   GeometryOptimization
      Convergence Step=1.0e-3
   End

   System
       Atoms
```

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```
          C   -0.004115   -0.000021    0.000023
          C    1.535711    0.000022    0.000008
          H   -0.399693    1.027812   -0.000082
          H   -0.399745   -0.513934    0.890139
          H   -0.399612   -0.513952   -0.890156
          H    1.931188    0.514066    0.890140
          H    1.931432    0.513819   -0.890121
          H    1.931281   -1.027824    0.000244
       End
   End

   Constraints
      # Fix the dihedral angle H(6)--C(2)--C(1)--H(3) to 20 degrees.
      Dihedral  6 2 1 3 20.00
   End

   Engine DFTB
       Model SCC-DFTB
       ResourcesDir Dresden
       DispersionCorrection Auto
   EndEngine

EOF


# 4a. Fixed atom constraint (Atoms keyword)
# =========================================

AMS_JOBNAME=atom "$AMSBIN/ams" << EOF

   Task GeometryOptimization

   GeometryOptimization
      Convergence Energy=1.0e-6 Gradients=1.0e-4 Step=1.0e-3
      CoordinateType Cartesian
   End

   System
      Atoms
         C   -0.2460249052   -1.70363153     0.0005128649944
         O    1.152833576    -1.81594932    -0.0004409224206
         C    1.489235475     0.61782051    10.0004771689226
         O    0.5700116914    0.627761615   10.0005491194077
      End
   End

   Constraints
      # Fix atom 1 and 2 at their initial positions.
      Atom 1
      Atom 2
   End

   Engine DFTB
      Model SCC-DFTB
      ResourcesDir DFTB.org/mio-1-1
   EndEngine
```

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```
EOF


# 4b. Fixed atom constraint (AtomList keyword)
# ============================================

AMS_JOBNAME=atomlist "$AMSBIN/ams" << EOF

   Task GeometryOptimization

   GeometryOptimization
      Convergence Energy=1.0e-6 Gradients=1.0e-4 Step=1.0e-3
      CoordinateType Cartesian
   End

   System
      Atoms
         C   -0.2460249052   -1.70363153      0.0005128649944
         O    1.152833576    -1.81594932     -0.0004409224206
         C    1.489235475     0.61782051     10.0004771689226
         O    0.5700116914    0.627761615    10.0005491194077
      End
   End

   Constraints
      # Fix atom 1 and 2 at their initial positions.
      AtomList 1:2
   End

   Engine DFTB
      Model SCC-DFTB
      ResourcesDir DFTB.org/mio-1-1
   EndEngine

EOF


# 4c. Fixed atom constraint (FixedRegion keyword)
# ===============================================

AMS_JOBNAME=region "$AMSBIN/ams" << EOF

   Task GeometryOptimization

   GeometryOptimization
      Convergence Energy=1.0e-6 Gradients=1.0e-4 Step=1.0e-3
      CoordinateType Cartesian
   End

   System
      Atoms
         C   -0.2460249052   -1.70363153      0.0005128649944    region=fixed
         O    1.152833576    -1.81594932     -0.0004409224206    region=fixed
         C    1.489235475     0.61782051     10.0004771689226
         O    0.5700116914    0.627761615    10.0005491194077
      End
   End
```

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```
   Constraints
      # Fix all atoms in region "fixed"
      FixedRegion fixed
   End

   Engine DFTB
      Model SCC-DFTB
      ResourcesDir DFTB.org/mio-1-1
   EndEngine

EOF


# 4d. Fixed atom constraint (overlapping combination)
# ===================================================

AMS_JOBNAME=combination "$AMSBIN/ams" << EOF

   Task GeometryOptimization

   GeometryOptimization
      Convergence Energy=1.0e-6 Gradients=1.0e-4 Step=1.0e-3
      CoordinateType Cartesian
   End

   System
      Atoms
         C   -0.2460249052   -1.70363153     0.0005128649944    region=fixed
         O    1.152833576    -1.81594932    -0.0004409224206    region=fixed
         C    1.489235475     0.61782051    10.0004771689226
         O    0.5700116914    0.627761615   10.0005491194077
      End
   End

   Constraints
      Atom 1
      AtomList 1 2
      FixedRegion fixed
   End

   Engine DFTB
      Model SCC-DFTB
      ResourcesDir DFTB.org/mio-1-1
   EndEngine

EOF


# 5. Fixed coordinate constraint
# ==============================

AMS_JOBNAME=coord "$AMSBIN/ams" << EOF

   Task GeometryOptimization

   GeometryOptimization
```

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```
      Convergence Energy=1.0e-6 Gradients=1.0e-4 Step=1.0e-3
      CoordinateType Cartesian
   End

   System
      Atoms
         C   -0.2460249052   -1.70363153     0.0005128649944
         O    1.152833576    -1.81594932    -0.0004409224206
         C    1.489235475     0.61782051    10.0004771689226
         O    0.5700116914    0.627761615   10.0005491194077
      End
   End

   Constraints
      # Fix the x-coordinate of all atoms.
      Coordinate 1 x
      Coordinate 2 x
      Coordinate 3 x
      Coordinate 4 x
   End

   Engine DFTB
      Model SCC-DFTB
      ResourcesDir DFTB.org/mio-1-1
   EndEngine

EOF


# 6. Fixed atom constraint (in periodic system)
# =============================================

AMS_JOBNAME=pbcatom "$AMSBIN/ams" << EOF

   Task GeometryOptimization

   GeometryOptimization
      Convergence Step=1.0e-3
   End

   System
       Atoms
           C  -1.23  -0.710140830   0.0
           C  -1.23  -0.710140830   3.8
           C   0.0    0.0           0.4
           C   0.0   -1.42028166    3.355
       End

       Lattice
           1.23  -2.130422493309719  0.0
           1.23   2.130422493309719  0.0
       End
   End

   Constraints
      # Fix atom 1 and 3 at their initial positions.
      Atom 1
```

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```
      Atom 3
   End

   Engine DFTB
      Model SCC-DFTB
      ResourcesDir DFTB.org/mio-1-1
      KSpace Quality=GammaOnly
   EndEngine

EOF


# 7. Block constraints (with listing the atoms in a block)
# ==========================================================

AMS_JOBNAME=block_list "$AMSBIN/ams" << EOF

   Task GeometryOptimization

   System
       Atoms
           C    0.5584839616765542   0.5023705181144142  -0.4625483159356394
           C    1.07173137896726     0.2125484528111251  -1.892767990599312
           C    1.699248504588085   -1.006061067555322   -2.191856791501442
           C    2.242484629452111   -1.236470028363516   -3.455616615521399
           C    2.18874580207099    -0.2444337131062739  -4.435483595049287
           C    1.604409798904145    0.9866950282217637  -4.135465239465763
           C    1.061086793296828    1.217355116664161   -2.871773146851866
           H    1.763625603740592   -1.780903563899969   -1.431707209662057
           H    2.716038261390732   -2.190869049673275   -3.672115451399807
           H    2.611833078693977   -0.4241619800888815  -5.420308290235123
           H    1.578029796368043    1.774138556616255   -4.884624561698751
           H    0.6247213391616491   2.187200330357715   -2.64521108544713
           C    1.303528070245188   -0.1416812092038768   0.7303699949711653
           C    0.8164830922475474  -1.314631142230651    1.326337082260565
           C    1.531799364672407   -1.947399963062604    2.342825210379356
           C    2.757684862125068   -1.432061688813837    2.765634667957531
           C    3.271640455523863   -0.2897364031184506   2.150731553729188
           C    2.556535912403799    0.3432056352653093   1.134221563049466
           H   -0.128925843064934   -1.7366201913903      0.9939642396630857
           H    1.133600273086767   -2.849990046242235    2.799740694330775
           H    3.31486005979636    -1.925049398411132    3.557912279830031
           H    4.236604921323707    0.1064455961800578   2.457138367063388
           H    2.976510069814392    1.222131876866508    0.6510413538003352
           C   -0.930165749820548    0.9153412637395284  -0.5420710991631585
           C   -1.791729737216814    0.6892660986048864   0.5418285200469819
           C   -3.111373625199894    1.139542032267652    0.5090625363459357
           C   -3.586568528476239    1.843983986018719   -0.5977864609101087
           C   -2.726152821786783    2.111108432452229   -1.663369105880468
           C   -1.406454626777386    1.660929752085611   -1.63085383469072
           H   -1.428888457076976    0.1571120160719108   1.417905619994904
           H   -3.76723983501283     0.9462006794587581   1.35432032282366
           H   -4.614972346570283    2.194578435055282   -0.6233521468909432
           H   -3.080200905921361    2.678981846821393   -2.520207901691867
           H   -0.7413545301831963   1.891248563160919   -2.459672151335554
           C    1.235557647765805    1.735720249011045    0.1803884343948648
           C    1.377191890012647    1.826646222422494    1.573181692925026
```

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```
            C   1.905898822116255    2.975086608901246    2.16214311213053
            C   2.280792642899383    4.061906342938987    1.371311861877147
            C   2.105006642447361    3.998471351380415   -0.0115253875199488
            C   1.576317094651283    2.850163227898022   -0.6007264381779673
            H   1.072424817958776    0.9937816064904853   2.202306496283991
            H   2.017471491684088    3.023369029562452    3.242524256706377
            H   2.693031233132915    4.956641734238467    1.830324484771476
            H   2.372569859099136    4.8485771293401     -0.6342066225733602
            H   1.427765851939196    2.820397327218896   -1.677480576376967
        End
    End

    GeometryOptimization
        Convergence
            Energy 1.0e-6
            Gradients 1.0e-4
            Step 1.0e-4
        End
    End

    Constraints
       # Create blocks from the 4 phenyl groups by specifying the atom indices
       # explicitly. (The indices follow the order in the System%Atoms block,
       # where we happen to have the atoms belonging to the different phenyl
       # groups consecutive.)
       BlockAtoms  2  3  4  5  6  7  8  9 10 11 12
       BlockAtoms 13 14 15 16 17 18 19 20 21 22 23
       BlockAtoms 24 25 26 27 28 29 30 31 32 33 34
       BlockAtoms 35 36 37 38 39 40 41 42 43 44 45
    End

    Engine DFTB
        Model DFTB3
        ResourcesDir DFTB.org/3ob-3-1
        DispersionCorrection D3-BJ
    EndEngine

EOF


# 8. Block constraints (with named blocks)
# ==========================================

AMS_JOBNAME=block_names "$AMSBIN/ams" << EOF

    Task GeometryOptimization

    System
        Atoms
            C   0.5584839616765542   0.5023705181144142  -0.4625483159356394
            C   1.07173137896726     0.2125484528111251  -1.892767990599312       ␣
 ↪region=phenyl1
            C   1.699248504588085   -1.006061067555322   -2.191856791501442       ␣
 ↪region=phenyl1
            C   2.242484629452111   -1.236470028363516   -3.455616615521399       ␣
 ↪region=phenyl1
            C   2.18874580207099    -0.2444337131062739  -4.435483595049287       ␣
 ↪region=phenyl1
```

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```
          C   1.604409798904145    0.98669502822217637  -4.135465239465763      ␣
↪region=phenyl1
          C   1.061086793296828    1.217355116664161   -2.871773146851866      ␣
↪region=phenyl1
          H   1.763625603740592   -1.780903563899969   -1.431707209662057      ␣
↪region=phenyl1
          H   2.716038261390732   -2.190869049673275   -3.672115451399807      ␣
↪region=phenyl1
          H   2.611833078693977   -0.4241619800888815  -5.420308290235123      ␣
↪region=phenyl1
          H   1.578029796368043    1.774138556616255   -4.884624561698751      ␣
↪region=phenyl1
          H   0.6247213391616491   2.187200330357715   -2.64521108544713       ␣
↪region=phenyl1
          C   1.303528070245188   -0.1416812092038768   0.7303699949711653     ␣
↪region=phenyl2
          C   0.8164830922475474  -1.314631142230651    1.326337082260565      ␣
↪region=phenyl2
          C   1.531799364672407   -1.947399963062604    2.342825210379356      ␣
↪region=phenyl2
          C   2.757684862125068   -1.432061688813837    2.765634667957531      ␣
↪region=phenyl2
          C   3.271640455523863   -0.2897364031184506   2.150731553729188      ␣
↪region=phenyl2
          C   2.556535912403799    0.3432056352653093   1.134221563049466      ␣
↪region=phenyl2
          H  -0.128925843064934   -1.7366201913903      0.9939642396630857     ␣
↪region=phenyl2
          H   1.133600273086767   -2.849990046242235    2.799740694330775      ␣
↪region=phenyl2
          H   3.31486005979636    -1.925049398411132    3.557912279830031      ␣
↪region=phenyl2
          H   4.236604921323707    0.1064455961800578   2.457138367063388      ␣
↪region=phenyl2
          H   2.976510069814392    1.222131876866508    0.6510413538003352     ␣
↪region=phenyl2
          C  -0.930165749820548    0.9153412637395284  -0.5420710991631585     ␣
↪region=phenyl3
          C  -1.791729737216814    0.6892660986048864   0.5418285200469819     ␣
↪region=phenyl3
          C  -3.111373625199894    1.139542032267652    0.5090625363459357     ␣
↪region=phenyl3
          C  -3.586568528476239    1.843983986018719   -0.5977864609101087     ␣
↪region=phenyl3
          C  -2.726152821786783    2.111108432452229   -1.663369105880468      ␣
↪region=phenyl3
          C  -1.406454626777386    1.660929752085611   -1.63085383469072       ␣
↪region=phenyl3
          H  -1.428888457076976    0.1571120160719108   1.417905619994904      ␣
↪region=phenyl3
          H  -3.76723983501283     0.9462006794587581   1.35432032282366       ␣
↪region=phenyl3
          H  -4.614972346570283    2.194578435055282   -0.6233521468909432     ␣
↪region=phenyl3
          H  -3.080200905921361    2.678981846821393   -2.520207901691867      ␣
↪region=phenyl3
          H  -0.7413545301831963   1.891248563160919   -2.459672151335554      ␣
↪region=phenyl3
```

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```
           C    1.235557647765805    1.735720249011045    0.1803884343948648      ␣
↪region=phenyl4
           C    1.377191890012647    1.826646222422494    1.573181692925026       ␣
↪region=phenyl4
           C    1.905898822116255    2.975086608901246    2.16214311213053        ␣
↪region=phenyl4
           C    2.280792642899383    4.061906342938987    1.371311861877147       ␣
↪region=phenyl4
           C    2.105006642447361    3.998471351380415   -0.0115253875199488      ␣
↪region=phenyl4
           C    1.576317094651283    2.850163227898022   -0.6007264381779673      ␣
↪region=phenyl4
           H    1.072424817958776    0.9937816064904853   2.202306496283991       ␣
↪region=phenyl4
           H    2.017471491684088    3.023369029562452    3.242524256706377       ␣
↪region=phenyl4
           H    2.693031233132915    4.956641734238467    1.830324484771476       ␣
↪region=phenyl4
           H    2.372569859099136    4.8485771293401     -0.6342066225733602      ␣
↪region=phenyl4
           H    1.427765851939196    2.820397327218896   -1.677480576376967       ␣
↪region=phenyl4
       End
   End

   GeometryOptimization
       Convergence
           Energy 1.0e-6
           Gradients 1.0e-4
           Step 1.0e-4
       End
   End

   Constraints
      # Use the region from System%Atoms to set up the block constraints.
      Block phenyl1
      Block phenyl2
      Block phenyl3
      Block phenyl4
   End

   Engine DFTB
       Model DFTB3
       ResourcesDir DFTB.org/3ob-3-1
       DispersionCorrection D3-BJ
   EndEngine

EOF


# 9. Frozen strain components
# ============================

AMS_JOBNAME=freezestrain "$AMSBIN/ams" << EOF

Task GeometryOptimization
```

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```
GeometryOptimization
    OptimizeLattice Yes
    Convergence Step=1.0e-3
End

Constraints
   # Keeps first two lattice vectors orthogonal to the third.  Also fixes the
   # length of the third vector, keeping the graphene layer compressed.
   FreezeStrain xz yz zz
End

System
    Atoms
        C 1.332002504889882e-05 -0.0005830055256093706 -8.209389319526933e-06
        C -1.22799350000696 -0.7102112812520209 2.281155685325205e-06
        C -0.0006872840163290542 -0.0003386565731411325 -1.981477647175959
        C 1.2274512359848 0.7092866246929653 -1.981478017299119
        C 2.455989750017203 -0.000767672446473915 -5.638209535859324e-06
        C 1.227983749989149 -0.7105220051279582 3.556077144406634e-06
        C 2.455553905980411 -0.0003697961984884611 -1.981476578954899
        C 3.68349483597652 0.7093774139714127 -1.981475303736415
        C 4.912014119974971 -0.0004697689000645081 8.202057640607653e-06
        C 3.68401303002027 -0.7103327188132248 -6.644074866545941e-06
        C 4.911561265976663 -0.0002732185613776612 -1.98147535090646
        C -3.685503114025999 0.7094747213946447 -1.98147447813657
        C -2.457004890026731 -0.0008782302621621878 8.760751751649826e-06
        C -3.684994169978904 -0.7103491590560944 -6.913500704937906e-06
        C -2.45740142402999 -0.0002120088132086839 -1.981473170030486
        C -1.229200584026242 0.709517932531879 -1.98147439816519
        C 1.227980230018157 2.127401471357515 -5.950364005944094e-06
        C 9.469984377119545e-06 1.417970232416515 5.120417805695729e-06
        C 1.227229005981529 2.127790824745807 -1.981476944534885
        C 2.45544009594217 2.837313001498961 -1.981464045820237
        C 3.683977240012926 2.127396400995821 -4.237131224100653e-06
        C 2.456019429974761 1.41770041892015 8.271514976735398e-06
        C 3.683520895940616 2.127826615636785 -1.981463536474189
        C 4.911484545967099 2.837408990674362 -1.981472216079415
        C 6.140019459971655 2.127636216669431 9.289406940173374e-06
        C 4.912011129977858 1.417969521782559 7.256699431696856e-06
        C 6.139527915931508 2.12792209328836 -1.981460550680031
        C -2.457504644023984 2.837506078460876 -1.981475136785154
        C -1.229001220032881 2.127025640069692 1.077705178964691e-05
        C -2.457025360024441 1.417788944250494 8.010947395781608e-06
        C -1.229428944072945 2.128012192586653 -1.981459091806229
        C -0.001217694074323372 2.837543459113209 -1.981458639351295
        C 2.455982410005773 4.255441598373883 -1.892083560740779e-06
        C 1.228003499971814 3.545886142064043 9.237737681677788e-06
        C 2.455221785970465 4.255792992279458 -1.981473318340598
        C -1.228386974045185 -3.547700260767117 -1.981468190394571
        C 4.911976899993052 4.255411828501257 2.27723146438149e-06
        C 3.684014579960917 3.545723396055813 1.280915829951697e-05
        C 4.911520375955087 4.255828023455356 -1.981468278811
        C 1.227655395958869 -3.547614761418386 -1.98146951906497
        C -2.457018900008975 4.255512695928259 2.943041159330732e-06
        C 6.140026009993287 3.545891232143294 2.20060806891485e-06
        C 7.367526315913146 4.255927240986645 -1.981454533470139
        C -6.141340994042006 -3.547511474074143 -1.981469232026619
```

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```
        C -0.001002500050462096 4.255387679251578 1.654017565004685e-05
        C -1.228981830007242 3.545851372434187 2.37503105142233e-06
        C -0.00142595404759982 4.256013860539822 -1.981467396982039
        C -3.685044664049419 -3.547477052980626 -1.981466802486946
        C -1.227808819999351 -2.12938224692705 -2.127801149456805e-07
        C -2.455832350038186 -2.838708610558109 1.251523005803983e-05
        C -1.228620264037983 -2.129205540950233 -1.981470550283798
        C -0.0004192140835714842 -1.419477849521901 -1.981455609514733
        C 1.228193719957573 -2.129406616582517 1.390527520593389e-05
        C 0.0001477699611014405 -2.839255138681037 1.274825905530347e-05
        C 1.227684425953123 -2.129163359695275 -1.981467635427455
        C 2.455626385910209 -1.419413169537493 -1.981453570671329
        C -6.140842350045955 -2.129322170430451 1.506226938282425e-05
        C 2.456153479955113 -2.839200210115958 1.47101339575357e-05
        C 3.683689305925244 -2.129064842197087 -1.981458500475127
        C -4.913374384079035 -1.419316522220884 -1.981457095053834
        C -3.684843340052955 -2.129350560151249 1.735547419229382e-05
        C -4.912808430047692 -2.839071261955975 1.563048016823986e-05
        C -3.685268534086676 -2.128978772839927 -1.98145459141338
        C -2.45712732409351 -1.419353221465499 -1.981452351546793
        C -2.996192032925579e-05 -0.000699242152149526 3.962939886687566
        C -1.228003971875175 -0.7103778453492622 3.962925088122617
        C -0.000700355908038296 -0.0003332148789394825 1.981452859744668
        C 1.227439704045832 0.7092909964964251 1.981467977918086
        C 2.455972288079895 -0.000591484995550912 3.962939812711258
        C 1.228003298120663 -0.7104549535647978 3.962926452096982
        C 2.455542044092204 -0.0003647244468015716 1.981452779807835
        C 3.683482354040657 0.7093820057289575 1.981469673526022
        C 4.912000348117807 -0.0004686671456845799 3.96292738718769
        C 3.683997778083127 -0.7103249572456309 3.962938753391991
        C 4.911548884078128 -0.0002680168299863262 1.981457393146928
        C -3.685515265933381 0.7094801331342701 1.981461165904004
        C -2.457014661901717 -0.0008761383582568633 3.962933787286889
        C -3.685007531928472 -0.7103425373777408 3.962942555784025
        C -2.457412705931413 -0.0002065770405354501 1.981460520958165
        C -1.229211335932976 0.7095228343414065 1.98146103281522
        C 1.227967348110556 2.127386193561453 3.962929764672974
        C -4.281883530521391e-06 1.417919455416095 3.96292782690195
        C 1.227218624090811 2.127796526544795 1.981453236878594
        C 2.455427384033809 2.83731889320433 1.981471917810995
        C 3.683966438104317 2.127406352683383 3.962931809362267
        C 2.456006178071116 1.417740879775001 3.962942690498066
        C 3.683508864080636 2.127831077384122 1.981456571921596
        C 4.911472874041424 2.837414422441095 1.981469423240322
        C 6.140006188100173 2.127640908364754 3.96293316778528
        C 4.912000948062944 1.417975193600739 3.962945368689221
        C 6.139515384034993 2.127928054994523 1.981471530520008
        C -2.457516635928298 2.837511270211092 1.981459501137365
        C -1.229012451945974 2.127104470095207 3.962948291371187
        C -2.457033631907664 1.417792836176979 3.962935736248542
        C -1.229441855971066 2.128017364296635 1.981473516125039
        C -0.001231065982844282 2.83754798082405 1.981477377543141
        C 2.455970918062962 4.255446730162459 3.962945363741043
        C 1.227990978068837 3.545888883850297 3.962943437699987
        C 2.455207564067417 4.255798083939164 1.981460905296909
        C -1.228397585936881 -3.54769452897796 1.981462310609218
        C 4.911964488060532 4.255420650159205 3.962946159605713
```

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```
        C 3.684002968100828 3.545727757822979 3.962932953064215
        C 4.911507194030889 4.25583213519047 1.981472875202606
        C 1.22764468406568 -3.547609799614339 1.981461473160161
        C -2.457027591902453 4.255510887977889 3.962934029953071
        C 6.140011718057854 3.545898453762834 3.962947035832434
        C 7.367513404018803 4.25593209270268 1.981476837527609
        C -6.141352815949912 -3.547506482310592 1.981466583645511
        C -0.001013701916043441 4.255385511194097 3.962938483249906
        C -1.228995721948309 3.545866003895579 3.962949056786192
        C -0.001438315946372004 4.256019262267359 1.98146542401001
        C -3.68505504595736 -3.547472521146422 1.981469025022036
        C -1.227817711946263 -2.129397354545356 3.962948386486201
        C -2.45584760189824 -2.838693919188594 3.962932647309199
        C -1.22863031596877 -2.129200899095368 1.981472763926178
        C -0.0004312259786934947 -1.419471387806733 1.981476015973903
        C 1.228183428085925 -2.129384525179524 3.962937836939656
        C 0.0001342880538246494 -2.839225227582055 3.962948356816577
        C 1.227671624025677 -2.129158527960262 1.981474583888431
        C 2.455614294015247 -1.419407657803005 1.981478001551132
        C -6.140855951953014 -2.129314868796188 3.962950599781267
        C 2.456139408049645 -2.839212628030558 3.962949726809414
        C 3.683677514018658 -2.12905939044384 1.98147688315868
        C -4.913386125957436 -1.419311390469788 1.981469050050141
        C -3.68485488196171 -2.129348928295441 3.96295344930467
        C -4.91282016191732 -2.839063750265042 3.962938899273355
        C -3.685281025994509 -2.12897353111013 1.981481200585353
        C -2.457141595966529 -1.419347949824808 1.981472029890663
    End
    Lattice
        9.825000579999999 0.0 0.0
        4.91182904 8.51302256 0.0
        0.0 0.0 8.0
    End
End

Engine DFTB
    Model DFTB
    ResourcesDir DFTB.org/mio-1-1
    KSpace
        Quality GammaOnly
    End
EndEngine

EOF


# 10. Equalized strain components
# ===============================

AMS_JOBNAME=equalstrain "$AMSBIN/ams" << EOF

Task GeometryOptimization

GeometryOptimization
    OptimizeLattice Yes
    Convergence Step=1.0e-3
End
```

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```
Constraints
   # Keep the cell cubic, but allow the size of the cube to vary.
   FreezeStrain xy xz yz
   EqualStrain  xx yy zz
End

System
    Atoms
        C -0.132285 3.230196 3.399625
        H 0.67231 2.571995 3.747816
        H -0.546925 3.782407 4.25108
        H -0.921872 2.627955 2.935193
        H 0.267346 3.938428 2.664409
        C 2.647972 3.79511 0.161215
        H 2.745753 2.707187 0.254494
        H 2.108302 4.189352 1.030219
        H 2.093026 4.03506 -0.753279
        H 3.644808 4.248843 0.113424
        C -3.290954 -3.607704 -3.419879
        H -4.099867 -4.000479 -4.046956
        H -2.386445 -3.482146 -4.026458
        H -3.088346 -4.309774 -2.602634
        H -3.589157 -2.638419 -3.003466
        C -3.900392 1.971446 -2.092972
        H -2.821972 1.97396 -1.895882
        H -4.303924 2.977719 -1.930439
        H -4.394183 1.265761 -1.414725
        H -4.081488 1.668344 -3.130841
        C -3.143958 -3.520015 3.393796
        H -3.128547 -4.088022 2.456262
        H -3.994325 -3.845525 4.004334
        H -3.24151 -2.450891 3.171766
        H -2.211449 -3.695621 3.94282
        C -0.31406 -0.626145 3.522914
        H -0.044022 0.228271 4.154493
        H -1.353702 -0.912447 3.720437
        H 0.346904 -1.471041 3.749005
        H -0.205421 -0.349364 2.467723
        C 3.411151 -3.454122 0.161835
        H 2.877462 -2.569463 0.528433
        H 4.211866 -3.141886 -0.518755
        H 2.711585 -4.107617 -0.372385
        H 3.843691 -3.997522 1.010048
        H -3.283653 -0.451758 -4.172013
        H -1.922139 0.6502520000000001 -3.802207
        H -2.586463 -0.412172 -2.523601
        C -2.360175 -0.332772 -3.593334
        H -1.648446 -1.117408 -3.875514
        C 3.046249 -3.33059 3.76859
        H 2.414628 -3.18136 2.88506
        H 2.465863 -3.831302 4.55235
        H 3.39517 -2.358701 4.136729
        H 3.909333 -3.950995 3.500222
        C -3.086408 3.73574 0.4638
        H -2.559805 3.990117 -0.463465
        H -2.394025 3.813016 1.310247
```

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```
        H -3.469203 2.710618 0.397221
        H -3.922599 4.429208 0.611196
        C 3.736451 0.338903 -0.234383
        H 4.139844 -0.659226 -0.441391
        H 4.286082 0.789262 0.6004350000000001
        H 2.675343 0.256879 0.028602
        H 3.844535 0.968696 -1.125179
        C -0.953217 3.761489 -3.029722
        H -0.738671 2.687271 -2.986546
        H -2.017033 3.913231 -3.24677
        H -0.349572 4.223228 -3.819817
        H -0.707592 4.222226 -2.065757
        C 3.438238 3.368005 3.536049
        H 3.718968 3.030104 2.531632
        H 4.305113 3.831685 4.021198
        H 3.102844 2.509703 4.129906
        H 2.62603 4.10053 3.461459
        C -0.093351 2.447961 0.147782
        H 0.412783 2.191741 -0.790311
        H -1.100739 2.015519 0.149423
        H -0.163522 3.53817 0.239205
        H 0.478074 2.046413 0.99281
        C -0.06737899999999999 -1.067744 -0.644773
        H 0.831493 -1.69444 -0.611303
        H -0.920384 -1.630791 -0.248288
        H -0.271712 -0.77696 -1.681851
        H 0.091087 -0.168785 -0.037648
        C -3.13266 0.095347 1.684164
        H -2.468956 -0.758832 1.506078
        H -3.797646 -0.127993 2.526632
        H -3.731911 0.285949 0.786162
        H -2.532126 0.982263 1.917783
        C -3.650862 -2.700373 -0.074687
        H -4.155919 -2.467829 0.87013
        H -2.740814 -3.276506 0.129574
        H -3.385824 -1.767849 -0.58654
        H -4.32089 -3.289309 -0.711913
        C 3.803884 3.754796 -3.348637
        H 3.946713 2.667857 -3.350306
        H 2.769436 3.987861 -3.626912
        H 4.48894 4.214494 -4.07059
        H 4.010448 4.148971 -2.34674
        C 2.868209 0.11231 2.894284
        H 2.317604 0.914041 2.388417
        H 2.406222 -0.09055000000000001 3.867554
        H 3.909847 0.420825 3.041412
        H 2.839161 -0.7950739999999999 2.279753
        C -0.320765 -3.560008 1.887422
        H -0.965068 -2.68183 2.011986
        H 0.02585 -3.901247 2.869895
        H 0.543227 -3.294315 1.26713
        H -0.88707 -4.36264 1.400678
        C 2.415398 -1.437717 -2.776235
        H 1.964383 -1.676188 -3.746573
        H 2.445411 -2.340763 -2.155392
        H 1.816728 -0.668767 -2.274091
        H 3.43507 -1.065149 -2.928883
```

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```
        C -3.625996 2.934989 3.78523
        H -4.070333 2.734452 2.803299
        H -3.043299 2.064066 4.107404
        H -4.421782 3.131813 4.513121
        H -2.968572 3.809626 3.717096
        C 1.422335 1.538945 -3.931672
        H 0.608488 0.8054 -3.894205
        H 2.3282 1.060135 -4.321529
        H 1.616409 1.921293 -2.92272
        H 1.136242 2.368954 -4.588236
        C 0.028875 -3.521123 -2.677443
        H 0.240436 -2.624091 -3.271089
        H -0.857142 -3.347281 -2.055678
        H 0.888225 -3.744967 -2.034598
        H -0.156019 -4.368152 -3.348409
    End
    Lattice
        10.0 0.0 0.0
        0.0 10.0 0.0
        0.0 0.0 10.0
    End
End

Engine DFTB
    Model DFTB
    ResourcesDir DFTB.org/mio-1-1
    KSpace
        Quality GammaOnly
    End
EndEngine

EOF
```

11.2 Transition state search

11.2.1 Example: TS search starting from initial Hessian

Download COChainFreqTS.run

```
#! /bin/sh

# This example demonstrates in the first step how to calculate the Hessian.
# The second run uses the pre-calculated Hessian and performs a transition
# state search along the frequency mode with the smallest frequency.


# First run: Calculate Hessian
# ============================

AMS_JOBNAME=hessian $AMSBIN/ams << EOF

   Task SinglePoint
```

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```
   Properties
      Hessian True
   End

   System
      Atoms
         C  0.0  0.0  0.0
         O  1.5  0.5  0.0
      End
      Lattice
         3.2  0.0  0.0
      End
   End

   Engine Band
      Basis Type=DZP
      KSpace Quality=Good
   EndEngine

EOF


# Second run: TS search with initial Hessian
# ===========================================

AMS_JOBNAME=TS $AMSBIN/ams << EOF

   Task TransitionStateSearch

   System
      Atoms
         C  0.0  0.0  0.0
         O  1.5  0.5  0.0
      End
      Lattice
         3.2  0.0  0.0
      End
   End

   GeometryOptimization
      Convergence Gradients=1.0e-4
      InitialHessian
         # Load the pre-calculated Hessian as the initial Hessian for the
         # transition state search using the Quasi-Newton based optimizer.
         Type FromFile
         File hessian.results/band.rkf
      End
   End

   Properties
      # Also calculate normal modes in the end, so we can see if we actually
      # found a transition state.
      NormalModes True
   End

   Engine Band
      Basis Type=DZP
```

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```
      KSpace Quality=Good
   EndEngine

EOF
```

11.2.2 Example: PES scan and TS search for H2 on graphene

Download PESScan_and_TS_H2_on_Graphene.run

```
#! /bin/sh

# First we do a 2D PES scan varying the z-coordinate of the two hydrogen atoms
# In this example we will keep the graphene slab fixed. From a physical/chemical
# standpoint this is not a good approximation. The graphene slab is
# intentionally not perfectly symmetric.

AMS_JOBNAME=PESScan $AMSBIN/ams << EOF

   Task PESScan

   System
      Atoms
         H   0.0      1.53633037    1.1
         H   0.0     -0.11341359    1.1
         C   0.001    1.42028166    0.0
         C   1.230    2.13042249    0.0
         C   1.230   -0.71014083    0.0
         C   2.460    0.00000000    0.0
         C   2.460    1.42028167    0.0
         C   0.000    0.00000000    0.0
      End
      Lattice
         3.69   -2.13042249   0.0
         0.00    4.26084499   0.0
      End
   End

   PESScan
      ScanCoordinate
         nPoints 10
         Coordinate 1 Z 1.1 2.0
      End
      ScanCoordinate
         nPoints 10
         Coordinate 2 Z 1.1 2.0
      End
   End

   GeometryOptimization
      Convergence Step=1.0e-3
   End

   Constraints
      # Fix the entire graphene slab.
      Atom 3
```

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```
      Atom 4
      Atom 5
      Atom 6
      Atom 7
      Atom 8
   End

   Engine DFTB
      Model DFTB
      ResourcesDir DFTB.org/3ob-3-1
      DispersionCorrection D3-BJ
      KSpace
        Type Symmetric
        Symmetric KInteg=3
      End
   EndEngine

EOF


# A human looks at the PES scan and picks a reasonable starting point for the
# TS search. (Normally you would do that in AMSMovie by looking at the PES and
# then exporting the geometry into an xyz file.)

#           _           ____
#        ___))         [  | \
#        ) //o          | | ]
#     _ (_    >         | | ]
#    (O)  \__<          | | ]
#    [/] /   \)        [__|/_
#    [\]|  ( \         __/___\_____
#    [/]|   \ \__  ___|            |
#    [\]|    \___E/%%/|____________|_
#    [/]|=====__   (_________________)

cat << EOF > initial_geometry_for_TS.xyz
8

H    0.4145668856457391      1.72927656037925      1.100000023839768     region=H2
H   -0.05533871972549955    -0.06805093626643093   1.500000013242627     region=H2
C    0.001                   1.42028166            0.0
C    1.230                   2.13042249            0.0
C    1.230                  -0.71014083            0.0
C    2.460                   0.00000000            0.0
C    2.460                   1.42028167            0.0
C    0.000                   0.00000000            0.0
VEC1 3.69 -2.13042249 0.0
VEC2 0.0   4.26084499 0.0
EOF


# Compute the partial initial Hessian to be used in the transition state
# search. (The Hessian will be computed only for the hydrogen atoms.)

AMS_JOBNAME=Hessian $AMSBIN/ams << EOF

   Task SinglePoint
```

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```
   System
      # Load the geometry we just saved.
      GeometryFile initial_geometry_for_TS.xyz
   End

   Properties
      # Calculate the Hessian (implied when calculating normal modes) ...
      NormalModes True
      # ... but only the part related to the hydrogen atoms.
      SelectedRegionForHessian H2
   End

   Engine DFTB
      Model DFTB
      ResourcesDir DFTB.org/3ob-3-1
      DispersionCorrection D3-BJ
      KSpace
        Type Symmetric
        Symmetric KInteg=3
      End
   EndEngine

EOF

echo "Extract the frequencies from the kf file using amsreport:"
$AMSBIN/amsreport Hessian.results/dftb.rkf -r "Vibrations%Frequencies[cm-1]##1"


# Do a transition state search using the initial Hessian just computed (the
# Graphene slab is constrained). Also compute the final Hessian for the
# hydrogen atoms to validate the TS.

AMS_JOBNAME=TS $AMSBIN/ams << EOF

   Task TransitionStateSearch

   System
      # Load the geometry we just saved.
      GeometryFile initial_geometry_for_TS.xyz
   End

   GeometryOptimization
      Quasi-Newton
         Step TrustRadius=0.05
      End
      Convergence Gradients=1.0e-4
      InitialHessian
          # Load previously calculated Hessian as initial Hessian for a
          # transition state search with the Quasi-Newton optimizer.
          Type FromFile
          File Hessian.results/dftb.rkf
      End
   End

   TransitionStateSearch
       # Follow the mode with the smallest frequency.
```

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```
       ModeToFollow 1
       # (This is also the default, we wouldn't need to specify this.)
   End

   Constraints
      # Fix the entire graphene slab.
      Atom 3
      Atom 4
      Atom 5
      Atom 6
      Atom 7
      Atom 8
   End

   Properties
      NormalModes Yes
      SelectedRegionForHessian H2
   End

   Engine DFTB
       Model DFTB
       ResourcesDir DFTB.org/3ob-3-1
       DispersionCorrection D3-BJ
      KSpace
        Type Symmetric
        Symmetric KInteg=3
      End
   EndEngine

EOF

echo "Extract energy from the rkf file using amsreport:"
$AMSBIN/amsreport TS.results/dftb.rkf -r "AMSResults%Energy"
```

11.3 Nudged Elastic Band (NEB)

11.3.1 Nudged Elastic Band (NEB) Examples

Here are a few examples showing how the NEB method can be used to obtain the the path and transition state of a reaction.

See also:

Nudged Elastic Band (NEB) Documentation (page 76)

HCN isomerization reaction with NEB

Download NEB_HCN.run

H2 dissociation on graphene

Download NEB_H2_on_graphene.run

Running multiple NEB calculations using PLAMS

Download NEB.plms

This example should be executed using PLAMS.

See also:

PLAMS documentation and tutorial

11.4 Intrinsic reaction coordinate (IRC)

11.4.1 Example: IRC for HCN

Download IRC_HCN.run

```
#!/bin/sh

# == IRC scan of the reaction path ==


# The IRC calculation is split in two steps to illustrate the Restart feature.

# In the first calculation only a few points are computed along the so-called
# 'forward' path. The definition of which is 'forward' and which is
# 'backward' depends on the sign of the largest component of the normal mode
# corresponding to the reaction coordinate.

# The RKF file from this partial IRC scan serves as restart file
# for the next calculations that will continue the IRC scan.

# The 'MaxPoints' key in the IRC block is used to limit the number of IRC
# points to compute.


AMS_JOBNAME=irc1 $AMSBIN/ams << eor

Task IRC
System
    Atoms
        C       0.000000000000       0.000000000000       0.000000000000
        N       0.000000000000       0.000000000000      -1.182644220000
        H      -1.103250760411       0.000000000000      -0.322462130000
    End
End
```

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```
IRC
    MaxPoints 5
    Direction Forward
    CoordinateType Cartesian
    InitialHessian
        Type Calculate
    End
End

Engine DFTB
    Model DFTB3
    ResourcesDir DFTB.org/3ob-3-1
EndEngine

eor

# In the second IRC run, the IRC scan is finished. We start with the RKF file
# from the previous run and omit the MaxPoints from the settings, which means
# that the default 100 will be used. Note that the 100 also includes any points
# computed in the previous calculation. The program starts on
# the forward path, continuing where the first calculation had stopped,
# and completes it. Since we set the Direction to Both
# then AMS proceeds to the backward path. After both paths are finished a summary
# of the path characteristics is printed at the end of the output file.


AMS_JOBNAME=irc2 $AMSBIN/ams << eor

Task IRC
System
    Atoms
        C       0.000000000000       0.000000000000       0.000000000000
        N       0.000000000000       0.000000000000      -1.182644220000
        H      -1.103250760411       0.000000000000      -0.322462130000
    End
End

IRC
    Restart
        File irc1.results/ams.rkf
    End
    ! Change options from the ones found in the restart file
    ! (MaxIRCPoints and MaxPoints will be reset to defaults automatically)
    Direction Both
End

Engine DFTB
    Model DFTB3
    ResourcesDir DFTB.org/3ob-3-1
EndEngine

eor
```

11.4.2 Example: TS and IRC for Claisen reaction

Download TS_and_IRC_Claisen.run

```
#! /bin/sh

# Transition State Search (TS search) followed by Intrinsic Reaction
# Coordinates (IRC) for two similar Claisen rearrangement reactions.


# =============================================================
# Claisen rearrangement from C=CCC1C=CC=CC1=O to C=CCOc1ccccc1
# =============================================================

AMS_JOBNAME=TS_molecule $AMSBIN/ams << eor

Task TransitionStateSearch

System
   Atoms
      C  -1.6622561642524  -1.4933421191817   0.6484353677288
      C  -2.6070283916282  -1.7718977641902  -0.3933564306530
      C  -2.7546368861548  -3.0534770331072  -0.8757259422474
      C  -1.9443405437492  -4.1131780924428  -0.3870796280948
      C  -1.0139402388630  -3.8827189276564   0.5979937257975
      C  -0.7543606665660  -2.5518266272325   1.0788971265869
      H  -3.2590342954832  -0.9734836183880  -0.7410179986476
      H  -3.5074724102535  -3.2690301027846  -1.6324229738243
      H  -2.1044351565280  -5.1220091436618  -0.7615296311573
      H  -0.4323033724363  -4.7107876462166   1.0021729248699
      H  -0.3533176373037  -2.4841001370767   2.0927436180830
      O  -1.5058234397159  -0.2844936546832   1.1029538316409
      C   0.1375150486634   0.3928947854321   0.4626789880484
      C   1.0578648498087  -0.6180364119671   0.7737587143345
      C   0.8861173890663  -1.8991002496105   0.2125497351161
      H   0.5725481135101  -1.9591100578644  -0.8292382400922
      H  -0.2171264706145   0.4859594211539  -0.5641152540806
      H   0.1902646842718   1.3359879065177   1.0025369222419
      H   1.5779002347488  -0.5540482019233   1.7307360489935
      H   1.6031168776346  -2.6724262749099   0.4842127285858
   End
End

Properties NormalModes=Yes

GeometryOptimization
    InitialHessian Type=Calculate
End

Engine DFTB
    Model SCC-DFTB
    ResourcesDir DFTB.org/3ob-3-1
EndEngine
eor


AMS_JOBNAME=IRC_molecule $AMSBIN/ams << eor
```

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```
Task IRC

IRC
   MaxIterations 1000
   InitialHessian
      Type FromFile
      File TS_molecule.results
   End
end
GeometryOptimization
   Convergence
     Gradients 2e-4
   End
End

LoadSystem
    File TS_molecule.results/ams.rkf
End

Engine DFTB
    Model SCC-DFTB
    ResourcesDir DFTB.org/3ob-3-1
EndEngine
eor


# ===========================================================================
# Claisen rearrangement for a (periodic) polymer containing the same aromatic
# ring of the previous calculation (from C=CCC1C=CC=CC1=O to C=CCOc1ccccc1)
# ===========================================================================

AMS_JOBNAME=TS_polymer $AMSBIN/ams << eor

Task TransitionStateSearch

System
   Atoms
      C   9.4367476128766   1.6156795441351   0.8542644025030
      C   8.6813349262903   0.7302865575002   0.0170374963868
      C   9.3238583586638  -0.1438417574104  -0.8314773024306
      C   10.741095802442  -0.1538813927018  -0.9297572682512
      C   11.499909556383   0.6929842950328  -0.1576524435776
      C   10.884234857485   1.6861365363275   0.6817028097694
      C   7.1928255650616   0.6847044785103   0.0090333093191
      H   8.7472521390038  -0.8479982636647  -1.4293934603813
      H   11.224348014063  -0.8771406786637  -1.5831686891584
      C   12.930798908912   0.8113031163622  -0.1971191730819
      H   11.474366091679   2.0120169601893   1.5412690799783
      O   8.8401614254340   2.4539245100299   1.6503819438045
      C   9.0152184164720   4.1939147755043   0.9354292967913
      C   10.386800460742   4.3070474573655   0.6675488559614
      C   10.983233806221   3.4166811386158  -0.2473786535066
      H   10.425317882010   3.1661173633779  -1.1491528320010
      H   8.3301833043316   4.0024301166114   0.1091130317749
      H   8.5863952766270   4.7863410214548   1.7409077918798
      H   11.023307058306   4.7274400682699   1.4475913648158
      H   12.053474297431   3.5124067242738  -0.4244212846926
```

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```
      C  13.897191373368  -0.0308805104165  -0.7206407708622
      C  15.267346128343   0.2274543686942  -0.4348415320624
      C  16.387786908031  -0.4341710477973  -0.8962646879782
      C  6.2048264493065  -0.0924013581064  -0.6266734325417
      C  4.8694123304551   0.1638639419185  -0.3442585289372
      C  3.7074226634814  -0.4584344973285  -0.8689206409329
      C  2.4653410147781   0.0102007864139  -0.4848760767909
      H  16.298210512111  -1.2787892169088  -1.5797017846452
      H  3.7984002771976  -1.2806821291979  -1.5787594353897
      H  6.8240750625775   1.4435007199212   0.7047818340481
      H  13.314194383001   1.6434188966421   0.3984353613768
      H  13.626424975736  -0.8770823766787  -1.3528414377622
      H  15.451469431625   1.0743039058568   0.2322503424471
      H  2.4641684561885   0.8477050600186   0.2182734314177
      H  6.4819803798672  -0.8741436365939  -1.3339335062636
      H  4.6807561767470   0.9698264886906   0.3703766590249
   End
   Lattice
      15.210 0.0 0.0
   End
End

Properties
    NormalModes Yes
End

GeometryOptimization
    Method Quasi-Newton
    InitialHessian Type=Calculate
End

Engine DFTB
    Model SCC-DFTB
    ResourcesDir DFTB.org/3ob-3-1
EndEngine
eor


AMS_JOBNAME=IRC_polymer $AMSBIN/ams << eor

Task IRC

IRC
   MaxIterations 1000
   InitialHessian
      Type FromFile
      File TS_polymer.results
   End
   Direction Forward
end

LoadSystem
    File TS_polymer.results/ams.rkf
End

Engine DFTB
    Model SCC-DFTB
```

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```
    ResourcesDir DFTB.org/3ob-3-1
EndEngine
eor
```

11.5 PES scan

11.5.1 Example: Linear transit

Download LinearTransit.run

```
#!/bin/sh



echo "=================="
echo "HCN isomerization"
echo "=================="
echo

AMS_JOBNAME=HCN_isomerization $AMSBIN/ams << EOF

   Task PESScan
   # (Linear transit is just a PES scan with 1 scan coordinate.)

   System
      Atoms
         C       0.00000000       0.00000000       1.04219000
         H       0.00000000       0.00000000      -0.03324000
         N       0.00000000       0.00000000       2.20064000
      End
   End

   PESScan
      ScanCoordinate
         nPoints 25
         Angle  2 1 3  180.0 0.0
      End
   End

   Engine DFTB
      Model DFTB0
      ResourcesDir DFTB.org/mio-1-1
   EndEngine

EOF



echo
echo "===================="
echo "Water angle transit"
echo "===================="
echo
```

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```
AMS_JOBNAME=water_angle $AMSBIN/ams << EOF

   Task PESScan

   System
      Atoms
         O       0.00000000       0.00000000       0.59372000
         H       0.00000000       0.76544000      -0.00836000
         H       0.00000000      -0.76544000      -0.00836000
      End
   End

   PESScan
      ScanCoordinate
         nPoints 25
         Angle  2 1 3  80.0 180.0
      End
   End

   GeometryOptimization
      ! Delocalized coordinates currently have a problem with linear systems.
      ! So we will use cartesian coordinates here.
      CoordinateType Cartesian
   End

   Engine DFTB
      Model DFTB0
      ResourcesDir DFTB.org/mio-1-1
   EndEngine

EOF



echo
echo "===================="
echo "Hydrocarbon reaction"
echo "===================="
echo

AMS_JOBNAME=hydcarb $AMSBIN/ams << EOF

   Task PESScan

   System
      Atoms
         C       0.14667300      -0.21503500       0.40053800
         C       1.45297400      -0.07836900       0.12424400
         C       2.23119700       1.15868100       0.12912100
         C       1.78331500       2.39701500       0.38779700
         H      -0.48348000       0.63110600       0.67664100
         H      -0.33261900      -1.19332100       0.35411600
         H       2.01546300      -0.97840100      -0.14506700
         H       3.29046200       1.03872500      -0.12139700
         H       2.45728900       3.25301000       0.35150400
         H       0.74193400       2.60120700       0.64028800
```

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```
         C      -0.75086900       1.37782400      -2.43303700
         C      -0.05392100       2.51281000      -2.41769100
         H      -1.78964800       1.33942600      -2.09651100
         H      -0.30849400       0.43896500      -2.76734700
         H      -0.49177100       3.45043100      -2.06789100
         H       0.98633900       2.54913500      -2.74329400
      End
   End

   PESScan
      ScanCoordinate
         nPoints 25
         Distance  1 11   3.36  1.538
         Distance  4 12   3.36  1.538
      End
   End

   Engine DFTB
      Model DFTB0
      ResourcesDir DFTB.org/mio-1-1
   EndEngine

EOF



echo
echo "======================================"
echo "Retinal trans -> 11-cis isomerization"
echo "======================================"
echo

AMS_JOBNAME=retinal_transcis $AMSBIN/ams << EOF

   Task PESScan

   System
      Atoms
         H      -2.10968473      -1.58238733       0.78224517
         C      -2.10306857      -0.54058322       0.46363503
         C      -0.89436995       0.04807217       0.25528247
         H      -0.85555481       1.05432693      -0.15803658
         C       0.38987539      -0.58661182       0.49038464
         C       1.53213446       0.09657801       0.14394773
         H       1.40518949       1.08783970      -0.29205231
         H       3.05232192      -1.34477492       0.72115301
         C       2.88311454      -0.36358433       0.28105432
         C       3.96024700       0.37378345      -0.12385974
         H       3.77965758       1.35231793      -0.56821856
         C       5.34627719      -0.04025647      -0.02249097
         C       6.32191717       0.80135945      -0.49190463
         H       6.00090638       1.74979100      -0.92101391
         C      -4.46825064      -0.90426552      -0.39585925
         C      -5.87277429      -0.25303564      -0.45007491
         C      -3.41139545       0.06493448       0.19516310
         C      -3.67932839       1.38221399       0.41656971
         C      -5.81598497       1.19032366      -0.92660753
```

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```
         C      -5.00049358       2.01922634       0.05561242
         C      -4.58391145      -2.18782901       0.46346394
         C      -4.01729542      -1.30039402      -1.82272212
         C      -2.72429960       2.32303313       1.10290124
         C       0.40919453      -1.96244629       1.09501374
         C       5.64155973      -1.38034133       0.59419110
         C       7.76996060       0.56699126      -0.48750226
         O       8.57693167       1.36615612      -0.92976322
         H      -6.51997817      -0.84904979      -1.10100203
         H      -6.32039371      -0.28079023       0.54871092
         H      -5.36159995       1.23817633      -1.92112092
         H      -6.82595442       1.60207678      -1.01946858
         H      -5.58216571       2.18390764       0.97424181
         H      -4.81292271       3.01993001      -0.35246294
         H      -4.74166770      -1.94289144       1.51126095
         H      -5.43008715      -2.78247632       0.12572479
         H      -3.69644845      -2.81116549       0.38705593
         H      -3.02900804      -1.75403268      -1.79820003
         H      -4.71056940      -2.01489741      -2.26202914
         H      -3.97070839      -0.42860260      -2.47090348
         H      -2.16469005       2.92261100       0.38111736
         H      -3.27791517       3.02297911       1.72885233
         H      -2.00470188       1.79865198       1.72726573
         H      -0.13689001      -1.97717074       2.03825359
         H      -0.07664772      -2.68134154       0.43362393
         H       1.41837401      -2.31391556       1.28591185
         H       5.15278730      -2.17622743       0.03222328
         H       6.70436647      -1.59729505       0.62729622
         H       5.25700064      -1.42489613       1.61313095
         H       8.12614442      -0.41441814      -0.04549414
      End
   End

   PESScan
      ScanCoordinate
         nPoints 25
         Dihedral  6 9 10 12  180  0
         Dihedral  8 9 10 11  180  0
      End
   End

   Engine DFTB
      Model DFTB0
      ResourcesDir DFTB.org/mio-1-1
   EndEngine

EOF
```

11.5.2 Example: 2D PES scan

Download PESScan.run

```
#!/bin/sh


echo "=============="
echo "Ethane torsion"
echo "=============="
echo

AMS_JOBNAME=ethane_torsion $AMSBIN/ams << EOF

   Task PESScan

   System
      Atoms
         C   0.0          0.0          0.76576
         C   0.0          0.0         -0.76576
         H  -0.88668938   0.51193036   1.16677
         H   0.88668938   0.51193036   1.16677
         H   0.0         -1.02386071   1.16677
         H   0.0          1.02386071  -1.16677
         H  -0.88668938  -0.51193036  -1.16677
         H   0.88668938  -0.51193036  -1.16677
      End
   End

   PESScan
      # First scan coordinate: C--C bond distance
      ScanCoordinate
         nPoints 5
         Distance  1 2  1.3 1.7
      End
      # Second scan coordinate: One of the H--C--C--H dihedral angles (others will␣
↪follow naturally)
      ScanCoordinate
         nPoints 21
         Dihedral  3 1 2 6  60.0 0.0
      End
   End

   GeometryOptimization
      Convergence Step=1.0e-3
   End

   Engine DFTB
      Model DFTB3
      ResourcesDir DFTB.org/3ob-3-1
      DispersionCorrection D3-BJ
   EndEngine

EOF


echo "=============="
echo "Ethene torsion"
```

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```
echo "=============="
echo

AMS_JOBNAME=ethene_torsion $AMSBIN/ams << EOF

   Task PESScan

   System
      Atoms
         C    0.0    0.0        0.66687
         C    0.0    0.0       -0.66687
         H    0.0    0.92974   -1.23912
         H    0.0    0.92974    1.23912
         H    0.0   -0.92974    1.23912
         H    0.0   -0.92974   -1.23912
      End
   End

   PESScan
      # First scan coordinate: C--C bond distance
      ScanCoordinate
         nPoints 5
         Distance  1 2  1.1 1.8
      End
      # Second scan coordinate: Two of the H--C--C--H dihedrals
      ScanCoordinate
         nPoints 21
         Dihedral  4 1 2 3  0.0 60.0
         Dihedral  5 1 2 6  0.0 60.0
      End
   End

   GeometryOptimization
      Convergence Step=1.0e-3
   End

   Engine DFTB
      Model DFTB3
      ResourcesDir DFTB.org/3ob-3-1
      DispersionCorrection D3-BJ
   EndEngine

EOF



# Below are more technical examples, demonstrating the PES scan gap filling.
# The QUASINANO2015 parameter set shows some discontinuities in the PES,
# which leads to problems with convergence. The first job leaves the
# non-converged steps as is while the second job instructs AMS to
# attept a second optimization for non-converged point starting from
# a different initial geometry.

echo "=============================="
echo "Ethane gap filling test (1/2)"
echo "=============================="
echo
```

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```
AMS_JOBNAME=ethane_nofillgaps $AMSBIN/ams << EOF

   Task PESScan

   System
      Atoms
         C  -2.333834610464788   -2.268837915270455  -0.2417723425321957
         C  -0.8081611038872945  -2.334371994724881  -0.04271045326758349
         H  -0.2505615773096904  -1.473443563856088  -0.38077110593546
         H  -0.3249814761083244  -3.235478579439597  -0.3904810245975267
         H  -0.583247370537557   -2.349691649662279   1.013499336841977
         H  -2.817014238243758   -1.367731330555738   0.1059982287977475
         H  -2.891434137042391   -3.129766346139247   0.09628831013568076
         H  -2.558748343814525   -2.253518260333056  -1.297982132641757
      End
   End

   GeometryOptimization
      CoordinateType Cartesian
      Convergence Step=1.0e-3
   End

   PESScan
      FillUnconvergedGaps False
      CalcPropertiesAtPESPoints True
      ScanCoordinate
         nPoints 10
         Distance 1 2  1.4 1.7
      End
      ScanCoordinate
         nPoints 10
         Distance 7 1  1.0 1.2
         Dihedral 7 1 2 3  60.0 180.0
      End
   End

   Engine DFTB
      Model SCC-DFTB
      ResourcesDir QUASINANO2015
   EndEngine

EOF


echo "=============================="
echo "Ethane gap filling test (2/2)"
echo "=============================="
echo

AMS_JOBNAME=ethane_fillgaps $AMSBIN/ams << EOF

   Task PESScan

   System
      Atoms
         C  -2.333834610464788   -2.268837915270455  -0.2417723425321957
```

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```
         C  -0.8081611038872945  -2.334371994724881  -0.04271045326758349
         H  -0.2505615773096904  -1.473443563856088  -0.38077110593546
         H  -0.3249814761083244  -3.235478579439597  -0.3904810245975267
         H  -0.583247370537557   -2.349691649662279   1.013499336841977
         H  -2.817014238243758   -1.367731330555738   0.1059982287977475
         H  -2.891434137042391   -3.129766346139247   0.09628831013568076
         H  -2.558748343814525   -2.253518260333056  -1.297982132641757
      End
   End

   GeometryOptimization
      CoordinateType Cartesian
      Convergence Step=1.0e-3
   End

   PESScan
      FillUnconvergedGaps True
      CalcPropertiesAtPESPoints True
      ScanCoordinate
         nPoints 10
         Distance 1 2  1.4 1.7
      End
      ScanCoordinate
         nPoints 10
         Distance 7 1  1.0 1.2
         Dihedral 7 1 2 3  60.0 180.0
      End
   End

   Engine DFTB
      Model SCC-DFTB
      ResourcesDir QUASINANO2015
   EndEngine

EOF
```

11.5.3 Example: PES scan for lattice degrees of freedom

Download PESScan_lattice.run

```
#!/bin/sh


AMS_JOBNAME=aramide_twist_stretch "$AMSBIN/ams" << eor

Task PESScan

PESScan
    ScanCoordinate
        nPoints 11
        Dihedral 28 2 19 25 0 125
        Dihedral 28 2 19 17 180.0 305
    End
    ScanCoordinate
        nPoints 5
```

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```
        FromLattice
           13.05 0.0 0.0
        End
        ToLattice
           13.25 0.0 0.0
        End
    End
End

System
    Atoms
        C 0.9216531199085832 -0.5454515169645626 -0.2340697410375409
        N 7.445957794299515 -0.01681964756070911 0.06597315465223283
        H 3.355037052904425 -1.688703702390754 -0.8816252752735284
        H 9.500951967451224 -1.431847829691195 -0.7477789274312976
        H 5.95132493510865 1.984563817105728 1.200973659205526
        H 12.85473854569853 1.727718149230879 1.067133628354558
        H 3.505268840981867 2.045685273157995 1.235853514670207
        H 10.46827545285599 2.196297117037482 1.332327137819838
        H 5.801094666247189 -1.749824820538445 -0.9165045876907203
        H 11.88742341712797 -1.900439221973683 -1.012979952512364
        O 1.177299854143639 -1.578051954645684 -0.8209290818960512
        H 7.76304211724438 -0.8491313767219947 -0.4061010828807728
        H 1.543350207091979 1.145009665092428 0.7254639267720714
        O 8.129085729296452 1.87393928672803 1.140288046892258
        C 5.295013835525856 -0.9149565254466551 -0.4430653247614506
        C 11.56877839022646 -1.000603430504764 -0.4978381858642764
        C 3.910823555244332 -0.8828087052616261 -0.4247213344032906
        C 10.22040985505902 -0.7280213735372861 -0.3433304227374022
        C 6.047229053946179 0.1077887625542279 0.1368149617061501
        C 12.54387637027615 -0.133469498676877 5.429319732480154e-05
        C 3.259131208138235 0.1880726458368187 0.1825325811252197
        C 9.811866044761443 0.4293238039083616 0.3192924938584955
        C 5.395538021020841 1.178670009771766 0.7440678521670584
        C 12.13529814513992 1.023878258864663 0.662679127884124
        C 4.011348680350846 1.210817677954059 0.762411994086449
        C 10.78693136481616 1.296462367210578 0.8171881914852902
        N 1.860406855610308 0.3126927007099983 0.2533844179661697
        C 8.384662974014494 0.8413381653458467 0.553433102061532
    End
    Lattice
        13.04933362476033 0.0 0.0
    End
End

Engine DFTB
EndEngine

eor


AMS_JOBNAME=graphene_shear "$AMSBIN/ams" << eor

Task PESScan

PESScan
   ScanCoordinate
```

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```
      nPoints 21
      FromLattice
         4.92000000       0.00000000       0.00000000
         0.00000000       8.52169000       0.00000000
      End
      ToLattice
         4.92000000       0.00000000       0.00000000
         4.92000000       8.52169000       0.00000000
      End
   End
End

GeometryOptimization
   Convergence
      Energy 1.0e-6
      Gradients 1.0e-4
      Step 1.0e-3
   End
End

System
   Atoms
      C      -1.23000000      -0.71014083       0.00000000
      C      -1.23000000       3.55070417       0.00000000
      C       1.23000000      -0.71014083       0.00000000
      C       1.23000000       3.55070417       0.00000000
      C      -2.46000000      -4.26084500       0.00000000
      C      -2.46000000       0.00000000       0.00000000
      C       0.00000000      -4.26084500       0.00000000
      C       0.00000000       0.00000000       0.00000000
      C      -2.46000000      -2.84056333       0.00000000
      C      -2.46000000       1.42028167       0.00000000
      C       0.00000000      -2.84056333       0.00000000
      C       0.00000000       1.42028167       0.00000000
      C      -1.23000000      -2.13042250       0.00000000
      C      -1.23000000       2.13042250       0.00000000
      C       1.23000000      -2.13042250       0.00000000
      C       1.23000000       2.13042250       0.00000000
   End
   Lattice
      4.92000000       0.00000000       0.00000000
      0.00000000       8.52169000       0.00000000
   End
End

Engine ForceField
EndEngine

eor


AMS_JOBNAME=kevlar_compression "$AMSBIN/ams" << eor

Task PESScan

PESScan
   ScanCoordinate
```

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```
      nPoints 20
      FromLattice
         VEC1       4.46344907       0.00000000       0.00000000
         VEC2       0.00000000      15.00000000       0.00000000
         VEC3      -4.15619754       0.00000000       7.88460768
      End
      ToLattice
         VEC1       4.46344907       0.00000000       0.00000000
         VEC2       0.00000000      10.00000000       0.00000000
         VEC3      -4.15619754       0.00000000       7.88460768
      End
   End
End

GeometryOptimization
   Convergence
      Energy 1.0e-6
      Gradients 1.0e-4
      Step 1.0e-3
   End
End

System
   Atoms
      H      -2.34574255      10.46947046       6.67609071
      H      -0.21566118       9.39070300       5.31032622
      H       1.86323468       3.63186532       1.36675944
      H       0.91346507       8.66345932       2.72468894
      H      -1.16691150       4.36193098       6.67034725
      O       0.68270622       0.35139274       3.28609533
      O      -1.39626502      12.67182069       7.22653591
      O      -0.38377339       7.08567440       4.63239262
      O       1.69448120       5.93755213       0.69230693
      N      -1.77963457       0.94576156       4.16255748
      N       0.29699209      12.07879149       0.22096612
      N       2.09175597       6.51059740       3.71380310
      N       0.01425402       6.51383083       7.65821075
      C       1.78077337      13.06266669       3.74496897
      C      -0.29869254      -0.03890117       7.68614442
      C       2.15256370      11.62041659       3.86515960
      C       0.07290835       1.40360669       7.80683608
      C      -1.25820404      11.13456872       4.63597235
      C       0.81898860       1.88918756       0.69223960
      C      -1.03413359       9.76886805       4.71156187
      C       1.04382335       3.25459780       0.76864405
      C      -1.84321511       8.85293722       4.03709183
      C       0.23429106       4.17122113       0.09564705
      C       1.56385944       9.33860183       3.26763920
      C      -0.51592344       3.68621895       7.21191051
      C       1.34444793      10.70471794       3.18555782
      C      -0.73592207       2.32019944       7.12929096
      C      -1.95926167       2.34708714       4.02068710
      C       0.11835470      10.67722153       0.08003469
      C       1.48642930       3.00363604       4.70160260
      C       3.56353841      10.02077981       0.76017378
      C       1.37833294       4.38413148       4.62212487
      C       3.45526706       8.64027066       0.68061721
```

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```
      C       2.27121884       5.11078244       3.84153940
      C       0.19337160       7.91355330       7.78646448
      C      -1.17724825       4.45615536       3.15531864
      C      -3.25414982       8.56800675       7.10151848
      C      -1.05881000       3.07587289       3.25293559
      C      -3.13673047       9.94838835       7.19779875
      C      -1.47236454       7.40647135       4.16074741
      C       0.60580388       5.61750577       0.22026971
      H      -0.81007305       0.64728338       4.20563108
      H       1.26623048      12.37812387       0.26423466
      H       1.12367626       6.80447595       3.64285507
      H      -0.95355823       6.21973701       7.58479288
      H      -0.61732754      11.80995952       5.18500113
      H       1.46048855       1.21353041       1.24041623
      H       0.52432261      11.08730485       2.59181576
      H      -1.55764558       1.93835499       6.53737820
      H       0.78524131       2.43214154       5.29441455
      H       2.86125712      10.59243593       1.35153830
      H       0.59209290       4.90748377       5.15056713
      H       2.66790223       8.11715076       1.20764332
      H      -0.48947479       5.02445608       2.54346024
      H      -2.56564408       7.99935355       6.49077972
      H      -0.26677134       2.55599700       2.73158401
   End
   Lattice
      VEC1       4.46344907       0.00000000       0.00000000
      VEC2       0.00000000      13.02426461       0.00000000
      VEC3      -4.15619754       0.00000000       7.88460768
   End
End

Engine ForceField
EndEngine

eor


AMS_JOBNAME=diamond_volumescan "$AMSBIN/ams" << eor

Task PESScan

PESScan
    ScanCoordinate
        nPoints 5
        CellVolumeScalingRange 0.8 1.2
    End
End
System
    Atoms
        C 3.12375 3.12375 3.12375
        C 0.44625 0.44625 0.44625
        C 3.12375 1.33875 1.33875
        C 0.44625 2.23125 2.23125
        C 1.33875 3.12375 1.33875
        C 2.23125 0.44625 2.23125
        C 1.33875 1.33875 3.12375
        C 2.23125 2.23125 0.44625
```

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```
    End
    Lattice
        3.57 0.0 0.0
        0.0 3.57 0.0
        0.0 0.0 3.57
    End
    BondOrders
         1 2 1.0 1 1 1
         1 4 1.0 1 0 0
         1 6 1.0 0 1 0
         1 8 1.0 0 0 1
         2 3 1.0 -1 0 0
         2 5 1.0 0 -1 0
         2 7 1.0 0 0 -1
         3 4 1.0 1 0 0
         3 6 1.0
         3 8 1.0
         4 5 1.0
         4 7 1.0
         5 6 1.0 0 1 0
         5 8 1.0
         6 7 1.0
         7 8 1.0 0 0 1
    End
End

Engine DFTB
EndEngine
eor
```

11.6 PES Exploration

11.6.1 Example: Basin Hopping for Ar 13 cluster

Download BasinHopping_Ar13.run

```
#!/bin/sh

# This example shows how the Basin Hopping procedure can be used to find the
# global minimum (and several local minima) of an Argon-13 cluster.
# The LennardJones engine is used for computing energy and gradients.


"$AMSBIN/ams" << EOF

Task PESExploration

System
    Atoms
        Ar       3.19796865788947       1.15934987330252      -1.33239534934505
        Ar       0.77363272043336       0.86005279907579       4.44840472306942
        Ar       6.16557782618638       1.42715657126078       1.00292335487038
        Ar       1.31188973509015      -2.14075518617674      -0.96878076867831
```

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```
        Ar      -2.41087887202771      -1.38658115989663      -0.47288216008194
        Ar      -0.21272211859964      -2.33529094743978       2.53956949757235
        Ar       0.68146295080450       4.04228262113743      -1.08313269600570
        Ar      -0.30271346683735       0.77172238432013      -2.86122291101125
        Ar      -2.82554186881390       0.46651994777473       2.87593685953916
        Ar       3.25381032839757      -0.76862912920592       2.01893019694943
        Ar      -2.88251373018356       2.43351471156095      -0.54320785580135
        Ar       0.18478571590318       0.93399697546301       0.81886912458718
        Ar       2.90785012175754       3.08435653882379       2.01057298433565
    End
End

PESExploration
    Job BasinHopping
    RandomSeed 10
    Temperature 50.0
    NumExpeditions 5
    NumExplorers 5
    FiniteDifference 1e-7

    BasinHopping
        Displacement 5.0
        Steps 50
        DisplacementDistribution gaussian
        WriteUnique T
    End

    Optimizer
        ConvergedForce 1e-8
        MaxIterations 1000
    End

    StructureComparison
        DistanceDifference 0.5
        NeighborCutoff 7.6
    End
End

#Engine ForceField
#EndEngine
Engine LennardJones
    Rmin 3.81749342630018000  # sigma=3.401*angs, rmin=2**(1.0/6.0)*3.401*angs
    Eps 0.000369915709507261  # eps=116.81*K
    Cutoff 15.00              # 15*angs
EndEngine

EOF
```

11.6.2 Example: PES Exploration, Process Search for alanine with PLAMS

Download ProcessSearch_alanine.plms

```
from tools.plams_test_utils import validate_energy_landscape

config.log.stdout = 0

alanine = from_smiles("CC(C(=O)O)N")

# Let's run a process search job on Alanine:

engine_sett = Settings()
engine_sett.input.ForceField = Settings()

sett = Settings()
sett.input.ams.Task = "PESExploration"
sett.input.ams.PESExploration.Job = "ProcessSearch"
sett.input.ams.PESExploration.NumExpeditions = 32
sett.input.ams.PESExploration.NumExplorers = 16

job = AMSJob(name="alanine_process_search", molecule=alanine, settings=sett + engine_
↪sett)
results = job.run()
energy_landscape = results.get_energy_landscape()
print(energy_landscape)

# Let's run single point calculations on the found states to verify the
# correctness of the results:

validate_energy_landscape(energy_landscape, engine_sett)
```

11.6.3 Example: PES Exploration, Binding Sites for O on Pt 111

Download BindingSites_O+Pt111.run

```
#!/bin/sh

export OMP_NUM_THREADS=1 # Reduce ReaxFF engine noise

AMS_JOBNAME=process_search "$AMSBIN/ams" << EOF

Task PESExploration

System
    Atoms
         O      5.54003937      1.60484089      8.92740946       region=adsorbate
        Pt      8.31521714      4.80239136      7.78926430       region=surface
        Pt      5.54298786      0.00160612      7.79128800       region=surface
        Pt      6.92910250      2.40199874      7.79027615       region=surface
        Pt     11.08707571      4.80244586      7.78854885       region=surface
        Pt      8.31484643      0.00166062      7.79057254       region=surface
        Pt      9.70096096      2.40178486      7.79068672       region=surface
        Pt      5.54335868      4.80260524      7.78885374       region=surface
        Pt      2.77112940      0.00182001      7.79087743       region=surface
        Pt      4.15724404      2.40221263      7.78986559       region=surface
```

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```
        Pt     9.70154331     5.60130339     5.52585419       region=surface
        Pt     6.92931403     0.80051815     5.52787789       region=surface
        Pt     8.31542867     3.20091077     5.52686604       region=surface
        Pt     4.15782639     5.60173116     5.52503306       region=surface
        Pt     1.38559711     0.80094593     5.52705675       region=surface
        Pt     2.77171175     3.20133854     5.52604491       region=surface
        Pt     6.92968485     5.60151727     5.52544363       region=surface
        Pt     4.15745557     0.80073204     5.52746732       region=surface
        Pt     5.54357021     3.20112466     5.52645547       region=surface
        Pt     6.92989639     4.00003668     3.26303536       region=surface
        Pt     8.31601103     6.40042930     3.26202352       region=surface
        Pt     5.54378174     1.59964406     3.26404721       region=surface
        Pt     9.70175484     3.99982280     3.26344593       region=surface
        Pt    11.08786948     6.40021541     3.26243408       region=surface
        Pt     8.31564020     1.59943018     3.26445778       region=surface
        Pt     4.15803792     4.00025057     3.26262480       region=surface
        Pt     5.54415256     6.40064318     3.26161295       region=surface
        Pt     2.77192328     1.59985795     3.26363664       region=surface
        Pt     1.38639089     2.39871548     1.00094199       region=surface
        Pt     5.54436409     4.79916260     0.99921469       region=surface
        Pt     6.93024583     7.19969029     1.00043291       region=surface
        Pt     4.15824945     2.39876998     1.00022653       region=surface
        Pt     8.31622256     4.79894871     0.99962525       region=surface
        Pt     9.70210429     7.19947641     1.00084348       region=surface
        Pt     6.93010792     2.39855609     1.00063710       region=surface
        Pt     2.77250564     4.79937648     0.99880412       region=surface
        Pt     4.15838737     7.19990418     1.00002234       region=surface
    End
    Lattice
        8.31557575     0.00000000     0.00000000
        4.15778787     7.20149984     0.00000000
    End
End

Constraints
    FixedRegion surface
End

PESExploration
    Job ProcessSearch

    RandomSeed 100
    NumExpeditions 50
    NumExplorers 5
    DynamicSeedStates T

    Temperature 100.0

    Optimizer
        ConvergedForce 0.0001
    End

    SaddleSearch
        MaxEnergy 2.0
    End

    StructureComparison
```

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```
        DistanceDifference 0.1
        NeighborCutoff 10.0
        EnergyDifference 0.01
    End
End

Engine ReaxFF
    ForceField CHONSFPtClNi.ff
    Charges Solver=Direct # Reduce ReaxFF engine noise
EndEngine

EOF


AMS_JOBNAME=binding_sites "$AMSBIN/ams" << EOF

Task PESExploration

System
    Atoms
         O      5.54003937      1.60484089      8.92740946       region=adsorbate
        Pt      8.31521714      4.80239136      7.78926430       region=surface
        Pt      5.54298786      0.00160612      7.79128800       region=surface
        Pt      6.92910250      2.40199874      7.79027615       region=surface
        Pt     11.08707571      4.80244586      7.78854885       region=surface
        Pt      8.31484643      0.00166062      7.79057254       region=surface
        Pt      9.70096096      2.40178486      7.79068672       region=surface
        Pt      5.54335868      4.80260524      7.78885374       region=surface
        Pt      2.77112940      0.00182001      7.79087743       region=surface
        Pt      4.15724404      2.40221263      7.78986559       region=surface
        Pt      9.70154331      5.60130339      5.52585419       region=surface
        Pt      6.92931403      0.80051815      5.52787789       region=surface
        Pt      8.31542867      3.20091077      5.52686604       region=surface
        Pt      4.15782639      5.60173116      5.52503306       region=surface
        Pt      1.38559711      0.80094593      5.52705675       region=surface
        Pt      2.77171175      3.20133854      5.52604491       region=surface
        Pt      6.92968485      5.60151727      5.52544363       region=surface
        Pt      4.15745557      0.80073204      5.52746732       region=surface
        Pt      5.54357021      3.20112466      5.52645547       region=surface
        Pt      6.92989639      4.00003668      3.26303536       region=surface
        Pt      8.31601103      6.40042930      3.26202352       region=surface
        Pt      5.54378174      1.59964406      3.26404721       region=surface
        Pt      9.70175484      3.99982280      3.26344593       region=surface
        Pt     11.08786948      6.40021541      3.26243408       region=surface
        Pt      8.31564020      1.59943018      3.26445778       region=surface
        Pt      4.15803792      4.00025057      3.26262480       region=surface
        Pt      5.54415256      6.40064318      3.26161295       region=surface
        Pt      2.77192328      1.59985795      3.26363664       region=surface
        Pt      1.38639089      2.39871548      1.00094199       region=surface
        Pt      5.54436409      4.79916260      0.99921469       region=surface
        Pt      6.93024583      7.19969029      1.00043291       region=surface
        Pt      4.15824945      2.39876998      1.00022653       region=surface
        Pt      8.31622256      4.79894871      0.99962525       region=surface
        Pt      9.70210429      7.19947641      1.00084348       region=surface
        Pt      6.93010792      2.39855609      1.00063710       region=surface
        Pt      2.77250564      4.79937648      0.99880412       region=surface
        Pt      4.15838737      7.19990418      1.00002234       region=surface
```

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```
    End
    Lattice
        8.31557575     0.00000000
        4.15778787     7.20149984
    End
End

Constraints
    FixedRegion surface
End

PESExploration
    Job BindingSites
    LoadEnergyLandscape
       Path process_search.results/ams.rkf
    End

    StatesAlignment
        ReferenceRegion surface
    End

    StructureComparison
        DistanceDifference 0.1
        NeighborCutoff 3.5
        EnergyDifference 0.1
    End
End

Engine ReaxFF
    ForceField CHONSFPtClNi.ff
    Charges Solver=Direct # Reduce ReaxFF engine noise
EndEngine

EOF
```

11.6.4 Example: Importing conformers into PES explorations

Download import_into_pesexp.run

```
#!/bin/sh


# Step 1: Run the conformer tool to quickly get a set of minima on the PES
# ------------------------------------------------------------------------

$AMSBIN/conformers << EOF

Generator
   RDKit
      InitialNConformers 100
   End
End

System
    Atoms
```

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```
        N -1.912873733399416 2.022897940092991 -0.1378294583620503
        C -0.871664156578182 3.02960778940094 0.06584379364356192
        C 0.5013812000791015 2.352115382193892 0.0410146984615521
        O 0.812167345172201 1.847076794564962 -1.240836870209463
        H -1.850257440384896 1.675835972092315 -1.088966428216949
        H -2.82010628990089 2.459772455658122 -0.02412199180453132
        H -1.024866752021569 3.492408399687411 1.045420209976512
        H -0.9134720948542179 3.809309747393572 -0.7093004343600406
        H 0.5270488401868264 1.547182041972351 0.7934160458635944
        H 1.275876827761384 3.088526288396493 0.2854207086154862
        H 0.2041922851100986 1.132993293447435 -1.463777763138591
    End
    BondOrders
         1 2 1.0
         1 5 1.0
         1 6 1.0
         2 3 1.0
         2 7 1.0
         2 8 1.0
         3 4 1.0
         3 9 1.0
         3 10 1.0
         4 11 1.0
    End
End

Engine DFTB
   Model DFTB0
   ResourcesDir DFTB.org/mio-1-1
EndEngine

RNGSeed 20200512 # Just to make the test output deterministic ...

EOF


# Step 2: Import energy landscape by running a LandscapeRefinement on it
# ----------------------------------------------------------------------
#
# The energy landscape that is produced by the conformers tool does not contain
# the engine output files of the individual states, which contain e.g. the
# normal modes. It can be used as input to the PESExploration ->
# LandscapeRefinement job, but not for the other PESExploration jobs (e.g.
# ProcessSearch). You should therefore always run the conformers output through
# a quick LandscapeRefinement before proceeding to other PES exploration jobs.
#
# At this point you can also trim down the number of minima loaded from the set
# of conformers. In the example below, we only load the 10 lowest energy
# conformers.


AMS_JOBNAME=refinement $AMSBIN/ams << EOF

Task PESExploration

PESExploration
   Job LandscapeRefinement
```

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```
   LoadEnergyLandscape
     Path conformers.results/conformers.rkf
     KeepOnly 1:10
   End
End

Engine DFTB
   Model DFTB0
   ResourcesDir DFTB.org/mio-1-1
EndEngine

RNGSeed 20200512 # Just to make the test output deterministic ...

EOF


# Step 3: Run a process search around the lowest energy conformer
# ---------------------------------------------------------------
#
# We load all states we got from the LandscapeRefinement and run a single
# expedition around the lowest energy conformer. This will give us a set of
# transition states connecting it to other conformers, but possibly also other
# isomers.


AMS_JOBNAME=process_search $AMSBIN/ams << EOF

Task PESExploration

PESExploration
   Job ProcessSearch
   LoadEnergyLandscape
     Path refinement.results
     SeedStates 1
   End
   DynamicSeedStates False
   NumExpeditions 1
   NumExplorers 64
End

LoadSystem
   File refinement.results/ams.rkf
End

Engine DFTB
   Model DFTB0
   ResourcesDir DFTB.org/mio-1-1
EndEngine

RNGSeed 20200512 # Just to make the test output deterministic ...

EOF

# Note that DFTB0 wrongly predicts an energetically favorable proton transfer
# from the OH group to the NH2 group. This would not have happened if we had
# used SCC-DFTB, but it is a nice example to show off the input for these jobs
# and that the PES exploration can discover also isomers, while the conformer
```

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```
# tool should only produce conformers.
```

11.7 Molecular dynamics

11.7.1 Example: Simple MD for H2

Download MD_hydrogen_longrun.run

```
#!/bin/sh

$AMSBIN/ams << eor

Task MolecularDynamics

MolecularDynamics
    nSteps 1000
    TimeStep 0.1
    InitialVelocities Type=zero
    Preserve Momentum=False AngularMomentum=False
    Thermostat Type=none
    Trajectory SamplingFreq=100
End

System
    Atoms [Bohr]
        H  -2.0  0.0  0.0
        H   2.0  0.0  0.0
    End
End

Engine DFTB
   Model SCC-DFTB
   ResourcesDir Dresden
   Occupation Strategy=Fermi Temperature=5
   Repulsion
       forcePolynomial true
   End
   DispersionCorrection Auto
EndEngine

eor
```

11.7.2 Example: MD for a box of water

Download H2O_nreac.run

11.7.3 Example: Lattice deformations in MD

Download MD_Deformation.run

```
#!/bin/sh

# This example consists of three MD runs exercising the Deformation feature in MD:
#   1. Simple deformations of a 2D slab
#   2. Complex sequence of deformations of a 3D box including multiple simultaneous␣
↪deformations
#   3. Combination of a uniaxial strain with barostatting the remaining directions

# This run first oscillates the lengths of the lattice vectors of the original non-
↪orthogonal
# lattice of an argon slab to 20 and 12 Angstrom respectively and back to the␣
↪original values,
# with a period of 125 fs. Afterwards, it linearly morphs the lattice to a 5 by 5␣
↪Angstrom square.
AMS_JOBNAME=Ar-2D "$AMSBIN/ams" <<EOR
# Set the random number seed to ensure reproducible results for testing. Omit this in␣
↪normal runs.
RNGSeed -2056449389 -1942239902 -422783941 -563204803 439708673 85320298 1328648683 -
↪688288369

Task MolecularDynamics

MolecularDynamics
    nSteps 1000
    TimeStep 0.25
    CalcPressure True
    InitialVelocities Type=Zero
    Trajectory SamplingFreq=10
    Deformation
        StopStep 500
        Type Cosine
        TargetLength 20 12
        Period 125
    End
    Deformation
        StartStep 500
        Type Linear
        TargetLattice
            5 0 0
            0 5 0
        End
    End
    BinLog
        Step
        Time
        PressureTensor
        Pressure
        Volume
        Density
    End
End

System
    Atoms
```

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```
        Ar 0.5 0.6 0.7
        Ar 3.0 3.2 3.4
    End
    Lattice
        10.0 2.0 0.0
        1.0 10.0 0.0
    End
End

Engine LennardJones
    Rmin 3.753962043231411
    Eps 3.98e-4
    Cutoff 12.0
EndEngine
EOR

# Print the evolution of the lattice parameters in the "fort.59" format
# of old standalone reaxff for testing purposes.
echo "BEGIN fort59 nobarostat"
"$AMSBIN/amspython" "$AMSHOME/scripting/standalone/reaxff-ams/fort59.py" Ar-2D.results
echo "END fort59"


# This run applies a sequence of deformations to a box of Lennard-Jones argon atoms.
AMS_JOBNAME=Ar-box "$AMSBIN/ams" <<EOR
# Set the random number seed to ensure reproducible results for testing. Omit this in␣
↪normal runs.
RNGSeed 1450250278 2029462689 827312839 1518230169 1408825437 1769469410 -406759494 -
↪1006638501

Task MolecularDynamics

MolecularDynamics
    nSteps 10000
    InitialVelocities Type=Random Temperature=300
    Thermostat Type=NHC Temperature=300 Tau=100
    Timestep 1
    Trajectory SamplingFreq=100
    CalcPressure True
    # Compress the a and b vectors to 20 Angstrom and stretch the c vector to 40␣
↪Angstrom over 2000 steps.
    Deformation
        StartStep 0
        StopStep 2000
        Type Linear
        TargetLength 20 20 40
    End
    # Oscillate the c vector (z axis) from 40 to 30 Angstroms and back again with a␣
↪period of 1000 fs.
    Deformation
        StartStep 2000
        StopStep 3500
        Type Cosine
        TargetLattice
            20.0  0.0  0.0
            0.0  20.0  0.0
            0.0   0.0 30.0
```

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```
        End
        Period 1000
    End
    # Shear the box by tilting the c vector 10 A away from the z axis in the xz plane.
    Deformation
        StartStep 3500
        StopStep 4000
        Type Linear
        TargetLattice
            20.0  0.0  0.0
            0.0  20.0  0.0
            10.0  0.0 30.0
        End
    End
    # The following two blocks apply simultaneous cosine and sine oscillations to the
    # x and y components of the c vector. The amplitude of both oscillations is the␣
↪same,
    # indirectly defined by the maximum velocity (velocity at the inflection point).
    # The c vector thus traces out a cone around the z axis over 2000 fs.
    Deformation
        StartStep 4000
        StopStep 8000
        Type Cosine
        LatticeVelocity
            0.0  0.0  0.0
            0.0  0.0  0.0
           -3e-2 0.0  0.0
        End
        Period 2000
    End
    Deformation
        StartStep 4000
        StopStep 8000
        Type Sine
        LatticeVelocity
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0 3e-2  0.0
        End
        Period 2000
    End
    # This un-shears the box again, returning the c vector to the z axis.
    Deformation
        StartStep 8000
        StopStep 8500
        Type Linear
        TargetLattice
            20.0  0.0  0.0
            0.0  20.0  0.0
            0.0  0.0  30.0
        End
    End
    # Finally, apply an exponential ("true") strain by compressing the c vector by 1/
↪1000th every step.
    Deformation
        StartStep 8500
        Type Exponential
```

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```
        LengthRate 0.0 0.0 -1e-3
    End
End

System
    Atoms
        Ar  22.97333  5.533091  19.78068
        Ar  5.255777  10.75370  3.164254
        Ar  8.594419  0.957110  14.00514
        Ar  8.407438  7.306515  2.762099
        Ar  5.335001  18.10475  11.25000
        Ar  13.84870  24.00523  1.485310
        Ar  18.65495  8.812906  24.08580
        Ar  23.50126  5.372569  24.77962
        Ar  20.32336  23.84153  3.669808
        Ar  7.692337  5.389691  10.57909
        Ar  2.407753  7.779618  0.755645
        Ar  1.520220  15.74803  13.75000
        Ar  2.921397  15.34413  20.41981
        Ar  1.660913  18.10666  3.895263
        Ar  19.54458  18.76246  20.66279
        Ar  3.853819  4.537228  14.15265
        Ar  17.57174  15.47554  17.14501
        Ar  8.601399  2.836638  1.872337
        Ar  2.786004  3.601185  22.17957
        Ar  0.047572  18.11282  24.78959
        Ar  0.172965  0.035326  0.223982
        Ar  6.604983  7.254174  21.83257
        Ar  16.63254  15.02432  7.992034
        Ar  7.941898  9.130224  17.89523
        Ar  18.26063  20.70600  5.643385
        Ar  22.63932  15.20789  23.33429
        Ar  1.138343  21.37810  13.97294
        Ar  0.461841  18.99572  6.401096
        Ar  22.67542  22.89935  9.344785
        Ar  7.215648  18.28717  3.411308
    End
    Lattice
        25.0   0.0   0.0
        0.0   25.0   0.0
        0.0    0.0 25.0
  end
end

Engine LennardJones
  Eps 3.67e-4
  RMin 3.4
  Cutoff 12.0
EndEngine
EOR

# Print the evolution of the lattice parameters in the "fort.59" format
# of old standalone reaxff for testing purposes.
echo "BEGIN fort59 nobarostat"
"$AMSBIN/amspython" "$AMSHOME/scripting/standalone/reaxff-ams/fort59.py" Ar-box.
↪results | cut -c 1-86
echo "END fort59"
```

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```
# This run simulates an experiment to measure the mechanical properties of an argon␣
↪box
# by stretching the lattice in the z direction by 100 ppm per timestep (1 fs) while␣
↪simultaneously
# keeping the x and y axes relaxed using a barostat.
AMS_JOBNAME=Ar-box-barostat "$AMSBIN/ams" <<EOR
# Set the random number seed to ensure reproducible results for testing. Omit this in␣
↪normal runs.
RNGSeed 877404503 1621112889 -559440914 -1857103174 -1082101960 -1842609385 -
↪845245172 -279655974

Task MolecularDynamics

MolecularDynamics
    nSteps 8000
    InitialVelocities Type=Random Temperature=300
    Thermostat Type=NHC Temperature=300 Tau=100
    Barostat Type=MTK Pressure=1e7 Tau=1000 Scale=XY Equal=XY
    Timestep 1
    Trajectory SamplingFreq=100
    Deformation
        Type Exponential
        StrainRate
            0.0 0.0 0.0
            0.0 0.0 0.0
            0.0 0.0 1e-4
        End
    End
End

System
    Atoms
        Ar  22.97333  5.533091  19.78068
        Ar  5.255777  10.75370  3.164254
        Ar  8.594419  0.957110  14.00514
        Ar  8.407438  7.306515  2.762099
        Ar  5.335001  18.10475  11.25000
        Ar  13.84870  24.00523  1.485310
        Ar  18.65495  8.812906  24.08580
        Ar  23.50126  5.372569  24.77962
        Ar  20.32336  23.84153  3.669808
        Ar  7.692337  5.389691  10.57909
        Ar  2.407753  7.779618  0.755645
        Ar  1.520220  15.74803  13.75000
        Ar  2.921397  15.34413  20.41981
        Ar  1.660913  18.10666  3.895263
        Ar  19.54458  18.76246  20.66279
        Ar  3.853819  4.537228  14.15265
        Ar  17.57174  15.47554  17.14501
        Ar  8.601399  2.836638  1.872337
        Ar  2.786004  3.601185  22.17957
        Ar  0.047572  18.11282  24.78959
        Ar  0.172965  0.035326  0.223982
        Ar  6.604983  7.254174  21.83257
        Ar  16.63254  15.02432  7.992034
```

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```
        Ar  7.941898  9.130224  17.89523
        Ar  18.26063  20.70600  5.643385
        Ar  22.63932  15.20789  23.33429
        Ar  1.138343  21.37810  13.97294
        Ar  0.461841  18.99572  6.401096
        Ar  22.67542  22.89935  9.344785
        Ar  7.215648  18.28717  3.411308
    End
    Lattice
        25.0  0.0  0.0
        0.0  25.0  0.0
        0.0   0.0 25.0
  end
end

Engine LennardJones
  Eps 3.67e-4
  RMin 3.4
  Cutoff 12.0
EndEngine
EOR

# Print the evolution of the lattice parameters in the "fort.59" format
# of old standalone reaxff for testing purposes.
echo "BEGIN fort59 barostat"
"$AMSBIN/amspython" "$AMSHOME/scripting/standalone/reaxff-ams/fort59.py" Ar-box-
↪barostat.results | cut -c 1-86
echo "END fort59"
```

11.7.4 Example: PLUMED spherical constraint on Ion-Water cluster

Download IonWaterClusterPlumed.run

```
#!/bin/sh

##########################################################################
# A molecular dynamics simulation of a sodium ion in a small water cluster.
# The oxygen atoms of the water molecules are constrained to be within 0.45 nm of the␣
↪central ion.
#
# The constraint is a harmonic function U(r)=kappa*(r-0.45)**2.
# The constrained value r is the maximum distance out of the set of Na-O distances.
# It is a continuous function that approximates the maximum out of a set of values.
# The parameter beta determines the gradient of the function.
# Choosing a small beta value results in a better match between the actual
# and approximate maximum values, but also in a less continuous function.
##########################################################################

$AMSBIN/ams << eor

Task MolecularDynamics

MolecularDynamics
    NSteps 1000
    TimeStep 0.5
```

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```
    InitialVelocities
        Temperature 300
    End
    Thermostat
        Type Berendsen
        Temperature 300
        Tau 100
    End
    Trajectory
        SamplingFreq 1
    End
    Plumed
        Input
GROUP ATOMS=2,5,8,11,14,17,20,23,26 LABEL=oxygens
DISTANCES GROUPA=1 GROUPB=oxygens MAX={BETA=0.05} LABEL=wallcv
UPPER_WALLS ARG=wallcv.max AT=0.45 KAPPA=5000.0
PRINT ARG=wallcv.max STRIDE=1 FILE=COLVAR
        End
    End
End

system
  Atoms
             Na       0.0000000000       0.0000000000       0.0000000000
              O       1.7119252402      -2.0080034855       1.0155335456
              H       2.5731328659      -2.4678020432       1.2672765294
              H       1.4480244399      -2.5303870208       0.1729165635
              O       0.6300542373       0.5761441595       2.8226448718
              H       1.2391579321      -0.0089304214       2.3349735783
              H       0.9338206205       1.4729694268       2.4878846070
              O       0.1647045543       2.0208702482      -2.3249601218
              H      -0.7307215954       2.0625495942      -2.7797813945
              H       0.2097075116       1.0635963204      -2.1125352562
              O      -1.7025066874      -1.0780652110      -3.0700032660
              H      -2.3616744611      -0.4381207399      -3.4654803274
              H      -1.8354437418      -1.8757732529      -3.6203721171
              O       3.0658874271       0.7135749531      -2.1674092521
              H       3.9052706085       1.2362759268      -2.1017219618
              H       2.5231505825       1.3717470880      -2.6845066156
              O      -2.8805081861       2.6302885978      -0.3532568156
              H      -3.8762635503       2.6712519969      -0.4669367452
              H      -2.6280204633       2.2152595735      -1.2369080650
              O      -3.5076002124      -1.7860735453      -0.4319799526
              H      -3.8213733752      -1.9705946207      -1.3583130388
              H      -2.8954116001      -1.0294541930      -0.5563055520
              O       2.9868579456       2.5941122968       0.9208652453
              H       2.2983746780       3.1353478114       0.4089961955
              H       3.1905202107       1.8321429488       0.2760998864
              O      -2.9007338617       1.4515370844       2.5612078673
              H      -2.1648641984       1.4189029227       1.8879229015
              H      -3.6017400767       1.9414536506       2.1086226997
  End
  BondOrders
     20 21 1.0
     20 22 1.0
     26 27 1.0
     26 28 1.0
```

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```
      23 24 1.0
      23 25 1.0
      2 3 1.0
      2 4 1.0
      11 12 1.0
      11 13 1.0
      17 18 1.0
      17 19 1.0
      14 15 1.0
      14 16 1.0
      5 6 1.0
      5 7 1.0
      8 9 1.0
      8 10 1.0
  End
  Charge 1.0
End

Engine ForceField
  Type UFF
EndEngine

RNGSeed 1

eor

##########################################################################
# The constrained values are stored in the file named COLVAR.
# Below we use Python to read the COLVAR file, and print the average, maximum, and␣
↪minimum value.
##########################################################################

$AMSBIN/amspython << eor
infile = open('COLVAR')
lines = infile.readlines()
infile.close()

values = [float(line.split()[1]) for line in lines[1:]]
print()
print('Average value constraint: ',sum(values)/len(values))
print('Minimum value constraint: ',min(values))
print('Maximum value constraint: ',max(values))
eor
```

11.7.5 Example: MM/MM with constrained ion-water cluster in periodic water box

Download IonWaterHybridSolvationPlumed.run

```
#!/bin/sh

##########################################################################
# A molecular dynamics simulation of MgCl2 dissolved in a small periodic water box.
# The setup mimics a multi-scale (QM/MM) simulation,
# but with both sides described by the UFF force field.
#
```

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```
# In an actual QM/MM simulation it is crucial that
# the QM and MM water molecules do not diffuse into one another.
# We accomplish this by constraining the water molecules according to the FIRES␣
↪procedure
# (doi: 10.1021/ct300091w).
# The constraint f({r_O}) is a function of the set of distances of
# all oxygen atoms to the central ion.
# {r_O}={r_QM}+{r_MM}
# f({r_O}) = min({r_MM}) - max({r_QM}).
# This function is constrained to be greater than zero using a half-harmonic␣
↪potential.
# U(f)=kappa*(f)**2 for f<0
# U(f)=0            for f>=0
#
# The min() and max() functions are continuous functions that
# approximate respectively the minimum and the maximum out of a set of values.
# The parameter beta determines the continuity of the function.
# Choosing a beta value further from 1
# (larger and smaller for the min() and max() functions respectively)
# results in a better match between the actual
# and approximate minimum/maximum values, but also in a less continuous function.
##########################################################################

$AMSBIN/ams << eor

MolecularDynamics
  InitialVelocities
    Temperature 300.0
  End
  NSteps 200
  Plumed
    Input
GROUP ATOMS=27,36,63,93,102,138,198,213,276 LABEL=qm
GROUP ATOMS=3,6,9,12,15,18,21,24,30,33,39,42,45,48,51,54,57,60,66,69,72,75,78,81,84,
↪87,90,96,99,105,108,111,114,117,120,123,126,129,132,135,141,144,147,150,153,156,159,
↪162,165,168,171,174,177,180,183,186,189,192,195,201,204,207,210,216,219,222,225,228,
↪231,234,237,240,243,246,249,252,255,258,261,264,267,270,273,279,282,285,288,291,294,
↪297,300,303,306 LABEL=mm
DISTANCES GROUPA=1 GROUPB=qm MAX={BETA=0.005} LABEL=maxcv
DISTANCES GROUPA=1 GROUPB=mm MIN={BETA=100.0} LABEL=mincv
COMBINE ARG=mincv.min,maxcv.max COEFFICIENTS=1,-1 PERIODIC=NO LABEL=cv
LOWER_WALLS ARG=cv AT=0. KAPPA=5000.0
PRINT ARG=maxcv.max,mincv.min,cv STRIDE=1 FILE=COLVAR
    End
  End
  Thermostat
    Tau 100.0
    Temperature 300.0
    Type Berendsen
  End
  TimeStep 0.5
  Trajectory
    SamplingFreq 1
  End
End

Task MolecularDynamics
```

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```
system
  Atoms
              Mg       5.7200350720      -2.9328800664       0.7897499036 region=qm
               H       1.8099054637      -4.4220924299       4.8703260963 region=mm
               O       7.1694504052      -8.8515558080      -4.2753237457 region=mm
               H      -7.1267761804      -8.3665468365      -4.8452690067 region=mm
               H       6.7102946636      -8.0997193116      -3.7685132509 region=mm
               O       2.7088914434       1.0610825031       4.6923243683 region=mm
               H       3.3054833375       0.4921267903       5.2402434951 region=mm
               H       1.8233363292       0.6530077196       4.7305392172 region=mm
               O      -1.4764148218      -6.8788850509      -2.6003412213 region=mm
               H      -2.0005170531      -7.6500792651      -2.8620779463 region=mm
               H      -2.1885584491      -6.3289735405      -2.1092174532 region=mm
               O       3.8478147995      -7.4795251060      -6.6736084141 region=mm
               H       4.3989126832      -6.7783144126      -7.0250045541 region=mm
               H       2.9555533860      -7.0654023511      -6.8252343194 region=mm
               O      -4.7471764043      -8.6077953930      -2.2377385210 region=mm
               H      -5.5092008380      -8.5969300931      -2.8802846966 region=mm
               H      -5.2576468285      -8.9527935768      -1.4219979311 region=mm
               O      -4.7772922849      -4.8474333611      -2.1581380915 region=mm
               H      -4.8239240982      -4.7790577136      -3.1075173037 region=mm
               H      -5.0338948567      -5.7924530112      -2.0117434690 region=mm
               O       2.4515102733       0.8469564304      -3.2719985082 region=mm
               H       2.3774951038      -0.1397894447      -3.4984484181 region=mm
               H       1.8468114255       0.8917317291      -2.4779777927 region=mm
               O      -3.3840665349      -4.0437270402       4.9817876227 region=mm
               H      -4.0089551919      -4.0145592434       5.6903827994 region=mm
               H      -2.8889478457      -3.1965528132       5.0436088929 region=mm
               O       3.3018776783      -3.8565105302       0.1699379171 region=qm
               H       2.8411614398      -2.9527284257       0.2152811292 region=qm
               H       3.3278682045      -4.1059629877      -0.8090519740 region=qm
               O      -0.3029454571       0.3223547569       3.0869293987 region=mm
               H       0.2531700096       0.3756415457       2.2625874250 region=mm
               H      -0.6800920306      -0.5897179149       2.9611527639 region=mm
               O      -5.3484100952       1.5806960236       0.2989946199 region=mm
               H      -4.7381235203       2.3283676440       0.2109523156 region=mm
               H      -6.1446741550       2.0700615293       0.6143220874 region=mm
               O      -5.9927569909      -4.5445068094       0.7252872361 region=qm
               H      -6.1165384480      -5.5153290275       0.4900339104 region=qm
               H      -6.2159199095      -4.0455250579      -0.1412140829 region=qm
               O      -0.9099199619      -1.8881647338       5.2995851295 region=mm
               H      -0.2497687678      -2.4792433544       4.9371760594 region=mm
               H      -0.3480512141      -1.3260802954       5.9009948331 region=mm
               O       3.6215242959       2.1814508127       1.6874751538 region=mm
               H       4.5165073769       2.5415115300       1.9221949954 region=mm
               H       3.4064165275       1.6332209215       2.4834093017 region=mm
               O       5.1833051040      -1.2908175195       6.4042504661 region=mm
               H       5.0111822889      -1.5205203085       7.3487966849 region=mm
               H       5.1785123947      -0.3057599544       6.5543696690 region=mm
               O       0.4603933279      -1.2441515414      -0.2033532097 region=mm
               H       0.7445254512      -0.6039397934      -0.9167026803 region=mm
               H      -0.5688268735      -1.2243571151      -0.2572139023 region=mm
               O      -5.4968287382      -8.9609194175       1.2499552393 region=mm
               H      -5.1571901876      -8.8988514057       2.1941505053 region=mm
               H      -6.4529456019       5.8448385545       1.3244900622 region=mm
               O      -5.0649038431      -1.5925489571       5.4791046507 region=mm
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        H      -4.6322521004      -1.5417498356       4.5302003438 region=mm
        O       0.3677337844      -8.5810760971       5.8032571443 region=mm
        H      -0.1086349973       5.8640829165       5.1172774803 region=mm
        H       0.3027415357      -7.6611857343       5.5038587712 region=mm
        O       1.5717316961      -8.1886314470      -4.1347530444 region=mm
        H       0.6160556952      -7.9037370683      -4.2849423181 region=mm
        H       1.5976518950      -8.8465245437      -3.3851806828 region=mm
        O       6.0759336250      -1.6447775457      -1.9957055354 region=qm
        H       5.0826000738      -1.6154040577      -2.1716448087 region=qm
        H       6.2225213454      -0.9240536977      -1.3190154430 region=qm
        O       7.0411997183      -6.3306028762       2.6673264477 region=mm
        H       7.2603015022      -6.4603061816       3.6331777655 region=mm
        H       6.8554828937      -5.4038722790       2.3804719901 region=mm
        O       5.4891620764       1.7626392649       5.4506129348 region=mm
        H       5.1390437356       2.4184645147       6.1374986521 region=mm
        H       5.0532883869       2.1669956638       4.6417895438 region=mm
        O      -4.2394186994       0.8168239717       3.3776299556 region=mm
        H      -5.1876861457       0.9406435176       3.6467381795 region=mm
        H      -4.3280295844       0.9981858500       2.4035538318 region=mm
        O       1.6209849652      -6.0322658389      -1.7020131060 region=mm
        H       1.9033980535      -6.6148231926      -0.9312205097 region=mm
        H       0.6074913843      -6.2050854204      -1.6495119106 region=mm
        O       2.3347829393      -2.1734816277       6.0621168212 region=mm
        H       2.3757060915      -2.0614469403       7.0710797559 region=mm
        H       3.1815618956      -2.6859727964       5.8159286113 region=mm
        O       2.6526456824      -4.5252677481      -6.7120333812 region=mm
        H       2.8020328735      -4.0500353548      -5.8761570391 region=mm
        H       3.5420462524      -4.3070798418      -7.1561049884 region=mm
        O      -5.1041720806      -2.2728098033      -4.3516727544 region=mm
        H      -4.3561610138      -2.4109430620      -4.9834336502 region=mm
        H      -5.2187295786      -1.2775902805      -4.3031347846 region=mm
        O      -6.7183990792      -5.6026203305       5.5769211366 region=mm
        H      -6.2276316883      -4.8397127501       6.0169261502 region=mm
        H      -6.8644442921      -6.2360671517       6.3313904040 region=mm
        O      -0.2997249631      -2.3248611096      -6.0652301268 region=mm
        H       0.4480748249      -1.7420695578      -5.7844640285 region=mm
        H      -0.2345271923      -3.0579113415      -5.3963109343 region=mm
        O       4.4557229323      -4.0321409485       3.4229510135 region=qm
        H       4.8228557987      -3.1175556198       3.2353382785 region=qm
        H       3.6117875931      -4.0360335014       2.8114358246 region=qm
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        H      -0.7298836601       0.7814998411       7.3663632337 region=mm
        H       0.8452573517       1.1002106587       7.2018710420 region=mm
        O       0.5132549970      -3.4758845845       2.4755554365 region=mm
        H       0.7192096520      -4.4568118056       2.3329907178 region=mm
        H      -0.4531120524      -3.3351695953       2.3773299504 region=mm
        O       3.7669484301      -0.0561634528      -0.5323383617 region=qm
        H       3.3380366522      -0.6568105740       0.1454732327 region=qm
        H       3.3744123064       0.8333772867      -0.3424611610 region=qm
        O      -3.0203045076       4.5213182503      -0.5452112002 region=mm
        H      -3.2392487263       4.4060241441      -1.4939704819 region=mm
        H      -3.1245969727       5.4811933760      -0.4039600780 region=mm
        O      -6.7794338138       0.4373660034      -3.4123297388 region=mm
        H      -7.3506733030       1.2324326950      -3.2821835254 region=mm
        H      -7.0467839805      -0.1662989127      -2.6296147182 region=mm
        O      -7.2132673344      -6.9058350093      -0.9498762639 region=mm
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            H      -7.2921175047      -7.5034525041      -0.1967566459 region=mm
            O      -3.4217194872      -7.0004057995       0.2176912260 region=mm
            H      -4.4126912325      -6.9974370339       0.2326646720 region=mm
            H      -3.2536051030      -6.8635041363       1.1841799205 region=mm
            O       5.5910174783       2.1763450404      -2.4932345279 region=mm
            H       4.6852021649       2.5693050423      -2.2779105192 region=mm
            H       5.3066397633       1.4214774177      -3.1080658731 region=mm
            O      -2.4065506310      -7.2932513323       5.7623954624 region=mm
            H      -2.7119429920      -7.7054547466       6.5983438564 region=mm
            H      -2.6278433895      -6.2775197492       5.8969552032 region=mm
            O       3.6640031160       1.8922352246      -6.2296569654 region=mm
            H       2.8532764044       2.2115544890      -5.7709024750 region=mm
            H       4.3856544177       2.5355822019      -5.8712770223 region=mm
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            H      -2.1735583778       5.4660643939       2.7300346193 region=mm
            H      -2.9009994050      -8.4965918575       3.5413436006 region=mm
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            H       5.9002289371       4.7710058802       6.1556779744 region=mm
            O       2.7885658031      -0.8611341888      -5.9360278211 region=mm
            H       2.1091805613      -0.1354528711      -6.0003389022 region=mm
            H       3.5887596075      -0.3300691963      -5.6526108069 region=mm
            O      -7.3714532064      -2.7223839233      -7.2784923252 region=mm
            H      -7.1791818261      -2.2678828420       6.8553882382 region=mm
            H      -6.4996545488      -2.5177748518      -6.7900553649 region=mm
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            H      -0.5066511890      -7.1774442433       1.4825039769 region=mm
            O       1.8600464739       4.3473997665      -7.1437429628 region=mm
            H       1.3996822124       5.0181731916       7.3159348797 region=mm
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            H      -1.9090302118       3.2846493549       5.9694982028 region=mm
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            H       0.0071023946      -7.5564900267      -6.8187063304 region=mm
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            H      -3.1402066242       1.0834994773       5.5167535098 region=mm
            H      -2.0336367686       0.0007013596       5.3230337832 region=mm
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        H       -6.3730841010        0.7190796050       -6.4056830813 region=mm
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        H       -0.9850206033       -5.8319014903        4.0612631213 region=mm
        H       -2.2290327112       -5.7688269115        3.2007651071 region=mm
        O       -4.9043214995        5.6519654141       -5.4508370598 region=mm
        H       -4.2942510297       -8.7887223286       -4.9708446990 region=mm
        H       -4.4193283168        4.7703067795       -5.4563625441 region=mm
        O       -2.5247612340        0.5732653081        0.0472599717 region=mm
        H       -3.3924069268        0.1521030415       -0.1584794862 region=mm
        H       -2.3892053288        0.2230100537        0.9885150093 region=mm
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        H        0.3906039249        2.9422839706        5.4734024052 region=mm
        H        0.3838958897        2.3769700045        4.0139213002 region=mm
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        H       -3.3997184963        0.2439643116       -3.6677294861 region=mm
        H       -2.3084400234        0.1141270972       -4.6000318007 region=mm
        O       -3.6653412109        2.2731181202       -6.1284820314 region=mm
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        H        5.8186543832       -3.6850578037       -5.9995996723 region=mm
        H        5.6184071998       -2.7108787147       -4.7924321672 region=mm
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        H        5.0190229119       -7.1138138521        4.1998727672 region=mm
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        H       -1.4362228840       -3.8887325443        6.7864428723 region=mm
        H       -0.3747219308       -4.9651044260        7.3167935631 region=mm
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            H      -2.1008600242       3.9220171023      -4.3346962477 region=mm
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            H      -2.3793757109      -4.6115566902       0.1880014661 region=mm
            H      -0.8619995170      -4.5482091047       0.1181706395 region=mm
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            H       3.3499869346       4.8246344996       0.0656770670 region=mm
            H       3.9194874435       5.1825851342      -1.3432740979 region=mm
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            H      -4.0359502299      -5.0251773009      -6.7947097709 region=mm
            H      -4.3397042788      -6.5601909701      -6.6311674198 region=mm
            O       2.3837305449      -7.0019574341       2.8932940349 region=mm
            H       1.5843595021      -6.5819302317       3.2063062063 region=mm
            H       2.5110710808      -6.4985063424       2.0690005115 region=mm
            O       4.3480000521       4.6575725755      -4.8007895809 region=mm
            H       3.6918814150       5.3893598759      -4.6122940939 region=mm
            H       5.1810645873       5.1658353534      -5.0129492914 region=mm
            O       0.9105420244       2.0399129451      -0.2709605351 region=mm
            H       0.4502824090       2.6330572019       0.3791216068 region=mm
            H       1.7544905017       2.6157672486      -0.3305092813 region=mm
            O       6.3707479202       1.9225951795       0.5271756371 region=mm
            H       6.1104155087       1.4272322940      -0.2591354170 region=mm
            H       6.3108235294       1.1855175540       1.1809221336 region=mm
            O       4.9793112969       5.7720777956       2.5371259504 region=mm
            H       5.4410948138      -8.6373822889       1.8401865423 region=mm
            H       4.0732573198      -8.8547465508       2.6355542548 region=mm
            O      -1.5069942574       2.1175389224      -2.6413269953 region=mm
            H      -2.2772337306       2.2001260822      -2.0840108235 region=mm
            H      -0.8183840708       1.8070130896      -1.9384258703 region=mm
            O      -3.1778696685      -2.2850690637      -7.0670100441 region=mm
            H      -2.4447728292      -1.6521612371      -6.8766103444 region=mm
            H      -3.6202120836      -1.7154370846       7.2497112917 region=mm
            O       2.6192086546      -1.2244922235       2.4518195104 region=qm
            H       1.8351686207      -1.4137948393       1.8609661449 region=qm
            H       2.5964459046      -1.8062454655       3.2887419185 region=qm
            O      -7.3321456538       2.9732498807      -5.9518392574 region=mm
            H      -6.6099217284       3.5423516492      -5.5423303270 region=mm
            H       6.8861073462       3.5653655129      -6.0522063293 region=mm
            O       3.5659080357       4.5187085880       5.0152611102 region=mm
```

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```
             H       3.5206873771       4.2674900037       4.0721000327 region=mm
             H       2.7215092257       4.1357642662       5.4053293417 region=mm
             O       0.0671456473      -1.3384369103      -3.1666600421 region=mm
             H      -0.8744551748      -1.6446509153      -3.3302330139 region=mm
             H       0.5025521594      -2.2006073634      -2.8295670561 region=mm
             O      -4.7331769248      -1.9735610859      -1.1710931100 region=mm
             H      -4.1695543501      -2.8050647365      -1.1464150457 region=mm
             H      -5.3822945516      -2.0965866117      -1.9311157594 region=mm
             O       2.7575468577      -3.0372722381      -2.9953973324 region=mm
             H       3.3068657454      -3.8611606289      -3.0419899298 region=mm
             H       2.3763274374      -2.9947684277      -3.9059578245 region=mm
             O       0.5580418210      -4.9464761608      -4.2804053084 region=mm
             H       0.0324857624      -4.8267051729      -3.4837664784 region=mm
             H       1.0961942044      -5.7302405505      -4.1506399120 region=mm
             O      -7.2757328853       4.1642190639       3.0300970932 region=mm
             H       6.9121825713       4.5448659465       3.3081894379 region=mm
             H      -7.4863485302       3.2969249860       2.5402164796 region=mm
             O      -4.1054878322      -1.9430177652       2.0669797525 region=mm
             H      -3.6008873069      -2.6082159778       2.6226459577 region=mm
             H      -4.6226134371      -2.6261274449       1.5495079114 region=mm
             O       5.3816120650      -5.1804053954      -2.7240970290 region=mm
             H       5.9660533434      -4.3648474016      -2.5314171173 region=mm
             H       5.7143244302      -5.4848887180      -3.6381896932 region=mm
             O       1.3959632716      -5.2927847809       5.0843716744 region=mm
             H       1.7762736990      -5.4289533682       5.9772747488 region=mm
            Cl      -5.4680212411       3.4130263189      -2.7136231556 region=mm
            Cl      -5.9988494351       5.4081934954       5.7964537819 region=mm
End
BondOrders
   2 306 1.0
   3 4 1.0
   3 5 1.0
   6 7 1.0
   6 8 1.0
   9 10 1.0
   9 11 1.0
   12 13 1.0
   12 14 1.0
   15 16 1.0
   15 17 1.0
   18 19 1.0
   18 20 1.0
   21 22 1.0
   21 23 1.0
   24 25 1.0
   24 26 1.0
   27 28 1.0
   27 29 1.0
   30 31 1.0
   30 32 1.0
   33 34 1.0
   33 35 1.0
   36 37 1.0
   36 38 1.0
   39 40 1.0
   39 41 1.0
   42 43 1.0
```

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```
      42 44 1.0
      45 46 1.0
      45 47 1.0
      48 49 1.0
      48 50 1.0
      51 52 1.0
      51 53 1.0
      54 55 1.0
      54 56 1.0
      57 58 1.0
      57 59 1.0
      60 61 1.0
      60 62 1.0
      63 64 1.0
      63 65 1.0
      66 67 1.0
      66 68 1.0
      69 70 1.0
      69 71 1.0
      72 73 1.0
      72 74 1.0
      75 76 1.0
      75 77 1.0
      78 79 1.0
      78 80 1.0
      81 82 1.0
      81 83 1.0
      84 85 1.0
      84 86 1.0
      87 88 1.0
      87 89 1.0
      90 91 1.0
      90 92 1.0
      93 94 1.0
      93 95 1.0
      96 97 1.0
      96 98 1.0
      99 100 1.0
      99 101 1.0
      102 103 1.0
      102 104 1.0
      105 106 1.0
      105 107 1.0
      108 109 1.0
      108 110 1.0
      111 112 1.0
      111 113 1.0
      114 115 1.0
      114 116 1.0
      117 118 1.0
      117 119 1.0
      120 121 1.0
      120 122 1.0
      123 124 1.0
      123 125 1.0
      126 127 1.0
      126 128 1.0
```

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```
    129 130 1.0
    129 131 1.0
    132 133 1.0
    132 134 1.0
    135 136 1.0
    135 137 1.0
    138 139 1.0
    138 140 1.0
    141 142 1.0
    141 143 1.0
    144 145 1.0
    144 146 1.0
    147 148 1.0
    147 149 1.0
    150 151 1.0
    150 152 1.0
    153 154 1.0
    153 155 1.0
    156 157 1.0
    156 158 1.0
    159 160 1.0
    159 161 1.0
    162 163 1.0
    162 164 1.0
    165 166 1.0
    165 167 1.0
    168 169 1.0
    168 170 1.0
    171 172 1.0
    171 173 1.0
    174 175 1.0
    174 176 1.0
    177 178 1.0
    177 179 1.0
    180 181 1.0
    180 182 1.0
    183 184 1.0
    183 185 1.0
    186 187 1.0
    186 188 1.0
    189 190 1.0
    189 191 1.0
    192 193 1.0
    192 194 1.0
    195 196 1.0
    195 197 1.0
    198 199 1.0
    198 200 1.0
    201 202 1.0
    201 203 1.0
    204 205 1.0
    204 206 1.0
    207 208 1.0
    207 209 1.0
    210 211 1.0
    210 212 1.0
    213 214 1.0
```

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```
      213 215 1.0
      216 217 1.0
      216 218 1.0
      219 220 1.0
      219 221 1.0
      222 223 1.0
      222 224 1.0
      225 226 1.0
      225 227 1.0
      228 229 1.0
      228 230 1.0
      231 232 1.0
      231 233 1.0
      234 235 1.0
      234 236 1.0
      237 238 1.0
      237 239 1.0
      240 241 1.0
      240 242 1.0
      243 244 1.0
      243 245 1.0
      246 247 1.0
      246 248 1.0
      249 250 1.0
      249 251 1.0
      252 253 1.0
      252 254 1.0
      255 256 1.0
      255 257 1.0
      258 259 1.0
      258 260 1.0
      261 262 1.0
      261 263 1.0
      264 265 1.0
      264 266 1.0
      267 268 1.0
      267 269 1.0
      270 271 1.0
      270 272 1.0
      273 274 1.0
      273 275 1.0
      276 277 1.0
      276 278 1.0
      279 280 1.0
      279 281 1.0
      282 283 1.0
      282 284 1.0
      285 286 1.0
      285 287 1.0
      288 289 1.0
      288 290 1.0
      291 292 1.0
      291 293 1.0
      294 295 1.0
      294 296 1.0
      297 298 1.0
      297 299 1.0
```

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```
      300 301 1.0
      300 302 1.0
      303 304 1.0
      303 305 1.0
      306 307 1.0
  End
  Lattice
        15.0000000000     0.0000000000     0.0000000000
         0.0000000000    15.0000000000     0.0000000000
         0.0000000000     0.0000000000    15.0000000000
  End
End

Engine Hybrid
  Engine ForceField ForceField1
    Type UFF
  EndEngine

  Engine ForceField ForceField2
    Type UFF
  EndEngine

  QMMM
    Embedding Mechanical
    mmEngineID ForceField2
    qmEngineID ForceField1
    qmRegion qm
  End

   GuessAttributesOnce No
EndEngine

RNGSeed 1
eor

##########################################################################
# The constrained values are stored in the file named COLVAR.
# Below we use Python to read the COLVAR file, and print the averages for max({r_QM})␣
↪and min({r_MM}).
##########################################################################

$AMSBIN/amspython << eor
infile = open('COLVAR')
lines = infile.readlines()
infile.close()

maxdist = [float(line.split()[1]) for line in lines[1:]]
mindist = [float(line.split()[2]) for line in lines[1:]]
print()
print('Average of max QM O-Eu distance: ',sum(maxdist)/len(maxdist))
print('Average of min MM O-Eu distance: ',sum(mindist)/len(mindist))
eor
```

11.7.6 Example: Measuring the friction coefficient using NEMD

Download MD_friction.run

```
#!/bin/sh

# This example measures the friction coefficient between two diamond slabs.
#
# The top slab (B) is being pressed onto slab A by a -Z force while being pulled in␣
↪the +X direction
# with a velocity of 200 m/s. The normal force used in this test is very high (5 nN␣
↪per atom in B,
# corresponding to a pressure around 20 GPa) to make the friction coefficient␣
↪measurably nonzero.

"$AMSBIN/ams" << eor
# Set the RNG seed to make results reproducible for regression testing, delete this␣
↪line for real simulations
RNGSeed 1354700531 -1828372117 1981811283 531897225 -1777170443 -138867001 572543905 -
↪1932870903

Task MolecularDynamics
MolecularDynamics
    NSteps 10000
    TimeStep 2
    Trajectory
        SamplingFreq 10
        WriteEngineGradients Yes
        WriteVelocities No
        WriteCharges No
        WriteBonds No
        WriteMolecules No
    End
    InitialVelocities
        Temperature 300
    End
    Thermostat
        Type NHC
        Temperature 300
        Tau 100
        Region free
    End
    ApplyVelocity
        Velocity 0.002 0 0
        Components XY
        Region B
    End
    ApplyForce
        Force 0.0 0.0 -160e-9 [Newton]
        Region B
    End
End
System
    Atoms
        C 1.32194823 1.26633023 1.67762819 region=A,free
        C 1.32194823 1.26633023 9.42762819 region=B,free
        C 1.32194823 3.79899068 1.67762819 region=A,free
        C 1.32194823 3.79899068 9.42762819 region=B,free
```

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```
        C 3.9658447 1.26633023 1.67762819 region=A,free
        C 3.9658447 1.26633023 9.42762819 region=B,free
        C 3.9658447 3.79899068 1.67762819 region=A,free
        C 3.9658447 3.79899068 9.42762819 region=B,free
        C 0.0 1.26633023 0.78253111 region=A,free
        C 0.0 1.26633023 8.532531110000001 region=B,free
        C 0.0 3.79899068 0.78253111 region=A,free
        C 0.0 3.79899068 8.532531110000001 region=B,free
        C 2.64389647 1.26633023 0.78253111 region=A,free
        C 2.64389647 1.26633023 8.532531110000001 region=B,free
        C 2.64389647 3.79899068 0.78253111 region=A,free
        C 2.64389647 3.79899068 8.532531110000001 region=B,free
        C 0.0 0.0 3.48183649 region=A,free
        C 0.0 0.0 11.23183649 region=B,free
        C 0.0 2.53266045 3.48183649 region=A,free
        C 0.0 2.53266045 11.23183649 region=B,free
        C 2.64389647 0.0 3.48183649 region=A,free
        C 2.64389647 0.0 11.23183649 region=B,free
        C 2.64389647 2.53266045 3.48183649 region=A,free
        C 2.64389647 2.53266045 11.23183649 region=B,free
        C 1.32194823 0.0 6.07181582 region=A,free
        C 1.32194823 0.0 13.82181582 region=B,free
        C 1.32194823 2.53266045 6.07181582 region=A,free
        C 1.32194823 2.53266045 13.82181582 region=B,free
        C 3.9658447 0.0 6.07181582 region=A,free
        C 3.9658447 0.0 13.82181582 region=B,free
        C 3.9658447 2.53266045 6.07181582 region=A,free
        C 3.9658447 2.53266045 13.82181582 region=B,free
        C 1.32194823 1.26633023 5.28928471 region=A,free
        C 1.32194823 1.26633023 13.03928471 region=B,free
        C 1.32194823 3.79899068 5.28928471 region=A,free
        C 1.32194823 3.79899068 13.03928471 region=B,free
        C 3.9658447 1.26633023 5.28928471 region=A,free
        C 3.9658447 1.26633023 13.03928471 region=B,free
        C 3.9658447 3.79899068 5.28928471 region=A,free
        C 3.9658447 3.79899068 13.03928471 region=B,free
        C 0.0 1.26633023 4.39418763 region=A,free
        C 0.0 1.26633023 12.14418763 region=B,free
        C 0.0 3.79899068 4.39418763 region=A,free
        C 0.0 3.79899068 12.14418763 region=B,free
        C 2.64389647 1.26633023 4.39418763 region=A,free
        C 2.64389647 1.26633023 12.14418763 region=B,free
        C 2.64389647 3.79899068 4.39418763 region=A,free
        C 2.64389647 3.79899068 12.14418763 region=B,free
        C 0.0 0.0 0.0 region=A,fixed
        C 0.0 0.0 7.75 region=B,free
        C 0.0 2.53266045 0.0 region=A,fixed
        C 0.0 2.53266045 7.75 region=B,free
        C 2.64389647 0.0 0.0 region=A,fixed
        C 2.64389647 0.0 7.75 region=B,free
        C 2.64389647 2.53266045 0.0 region=A,fixed
        C 2.64389647 2.53266045 7.75 region=B,free
        C 1.32194823 0.0 2.58997933 region=A,free
        C 1.32194823 0.0 10.33997933 region=B,free
        C 1.32194823 2.53266045 2.58997933 region=A,free
        C 1.32194823 2.53266045 10.33997933 region=B,free
        C 3.9658447 0.0 2.58997933 region=A,free
```

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```
        C 3.9658447 0.0 10.33997933 region=B,free
        C 3.9658447 2.53266045 2.58997933 region=A,free
        C 3.9658447 2.53266045 10.33997933 region=B,free
    End
    Lattice
        5.28779292 0.0 0.0
        0.0 5.06532092 0.0
    End
    BondOrders
         1 9 1.0
         1 13 1.0
         2 10 1.0
         2 14 1.0
         3 11 1.0
         3 15 1.0
         4 12 1.0
         4 16 1.0
         5 9 1.0 1 0
         5 13 1.0
         6 10 1.0 1 0
         6 14 1.0
         7 11 1.0 1 0
         7 15 1.0
         8 12 1.0 1 0
         8 16 1.0
         33 25 1.0
         33 27 1.0
         33 41 1.0
         33 45 1.0
         34 26 1.0
         34 28 1.0
         34 42 1.0
         34 46 1.0
         35 25 1.0 0 1
         35 27 1.0
         35 43 1.0
         35 47 1.0
         36 26 1.0 0 1
         36 28 1.0
         36 44 1.0
         36 48 1.0
         37 29 1.0
         37 31 1.0
         37 41 1.0 1 0
         37 45 1.0
         38 30 1.0
         38 32 1.0
         38 42 1.0 1 0
         38 46 1.0
         39 29 1.0 0 1
         39 31 1.0
         39 43 1.0 1 0
         39 47 1.0
         40 30 1.0 0 1
         40 32 1.0
         40 44 1.0 1 0
         40 48 1.0
```

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```
        41 17 1.0
        41 19 1.0
        42 18 1.0
        42 20 1.0
        43 17 1.0 0 1
        43 19 1.0
        44 18 1.0 0 1
        44 20 1.0
        45 21 1.0
        45 23 1.0
        46 22 1.0
        46 24 1.0
        47 21 1.0 0 1
        47 23 1.0
        48 22 1.0 0 1
        48 24 1.0
        49 9 1.0
        49 11 1.0 0 -1
        50 10 1.0
        50 12 1.0 0 -1
        51 9 1.0
        51 11 1.0
        52 10 1.0
        52 12 1.0
        53 13 1.0
        53 15 1.0 0 -1
        54 14 1.0
        54 16 1.0 0 -1
        55 13 1.0
        55 15 1.0
        56 14 1.0
        56 16 1.0
        57 1 1.0
        57 3 1.0 0 -1
        57 17 1.0
        57 21 1.0
        58 2 1.0
        58 4 1.0 0 -1
        58 18 1.0
        58 22 1.0
        59 1 1.0
        59 3 1.0
        59 19 1.0
        59 23 1.0
        60 2 1.0
        60 4 1.0
        60 20 1.0
        60 24 1.0
        61 5 1.0
        61 7 1.0 0 -1
        61 17 1.0 1 0
        61 21 1.0
        62 6 1.0
        62 8 1.0 0 -1
        62 18 1.0 1 0
        62 22 1.0
        63 5 1.0
```

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```
         63 7 1.0
         63 19 1.0 1 0
         63 23 1.0
         64 6 1.0
         64 8 1.0
         64 20 1.0 1 0
         64 24 1.0
    End
End
Constraints
    FixedRegion fixed
End

Engine ForceField
EndEngine
eor

"$AMSBIN/amspython" "${TEST_DIRECTORY:-.}/friction_coeff.py" --block 200 ams.results/
echo "END OF TEST"
```

11.7.7 Example: Measuring the viscosity using NEMD

Download MD_shear_viscosity.run

```
#!/bin/sh

# This example performs a NEMD simulation of a water box under a shear acceleration␣
↪profile.
# The acceleration profile is cosine-shaped and oriented along the Z axis (so that␣
↪atoms with Z=0 are
# pulled in one direction, atoms in the middle of the box are pulled the other way).␣
↪The flow direction
# is aligned with the X axis.
#
# This periodic perturbation induces a similarly cosine-shaped flow velocity profile␣
↪in the liquid.
# The steady-state average amplitude of the flow velocity is then used to calculate␣
↪the viscosity.

"$AMSBIN/ams" << eor
# Set the RNG seed to make results reproducible for regression testing, delete this␣
↪line for real simulations
RNGSeed 836841470 1678420146 -1718043284 -369569254 -2053894812 -1628712594 -
↪240676301 -356441007

Task MolecularDynamics
MolecularDynamics
    NSteps 24000
    TimeStep 1
    InitialVelocities
        Type Random
        Temperature 298.15
    End
    Thermostat
        Type NHC
```

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```
        Temperature 298.15
        Tau 1000
    End
    CosineShear
        Enabled Yes
        Acceleration 0.000004522108063030400
    End
End
System
    Atoms
        O 0.8244444545793177 4.544838021389278 7.080687151044827 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 0.3547827848924093 4.719510963847915 7.916536224904227 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 1.355721739229628 5.344893665481732 6.975525637919818 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 4.824211318207558 0.8069313216022225 7.759825120988862 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 4.514558713823999 1.280197293066311 8.558923240175481 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 4.033391063195659 0.7201928228115005 7.187127164561153 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 2.934572969015879 0.626831742380179 5.865967452739235 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 2.151893964459041 1.137329352693095 6.027000900498897 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 3.263433084806719 1.048186940192297 5.040531567587069 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 1.206430947463354 1.856002602957112 9.003428097539595 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 0.7495045796559563 2.685732546074114 9.186271372016726 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 0.5732201719526651 1.426252646404271 8.428676649867203 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 4.00858752820043 4.029996794081304 5.583951652401872 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 4.6767739512274 4.347838022636921 6.162932810282044 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 3.285915055183219 4.655218377978755 5.758534605518392 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 3.563629518129562 1.371347494469859 12.8855840322333 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 3.213171669104573 0.4819670684498465 12.77900015824002 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 3.044964414139814 1.734726370517266 13.59851543041306 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 0.3789251709796683 1.127496658856301 13.2115287736376 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 0.6813483419435356 1.239300575078584 14.13801389632943 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 5.369672396356584 1.083579289595597 13.29812675901156 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 5.466225740442832 5.993496838594383 3.826556322251799 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 4.698727888102344 0.3975271277797332 3.345862980059084 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 5.678590795097077 0.7684784866437412 4.409847532491263 ForceField.Type=HW␣
↪ForceField.Charge=0.417
```

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```
        O 5.308923379504553 4.019057754213824 12.30890772203438 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 4.947834409182614 3.130476283899112 12.54309710913415 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 4.507522419442757 4.539019535791192 12.2645840765018 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 0.5246189538877805 2.11444774753437 5.633847854203101 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 0.4798849442749721 2.981151461335371 6.079301327936341 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 0.1746402018766592 1.514431334250879 6.300570842670576 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 0.7532540279197091 1.724451179192218 15.61527324613631 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 1.102056945497837 1.316928430428979 16.4265184790613 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 0.7972987223637659 2.664620455755369 15.82837324135009 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 0.9018681569836331 3.656882816889424 3.402291999454496 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 0.4026827408969129 4.459281159084593 3.630496065021554 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 0.5526952071471827 3.010307298769798 4.02681327048169 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 4.863403687774274 0.9028609469360367 0.558021938995828 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 3.996919626672331 1.319885981099747 0.7021352725814224 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 4.689645967466681 5.893899093581502 0.6975454946677974 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 0.6125422333973695 4.471658272146462 15.20199530885226 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 5.757700386271314 4.628928071051244 14.72292292770029 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 0.4490343750054829 4.454474545873454 16.17738658790725 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 0.6366518329200573 4.752909677710202 9.952302751289087 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 0.9300822912913463 5.41930018832904 10.60529619335514 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 0.09536209451509015 4.185550544321785 10.53226705454537 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 1.973521991893519 4.136851000321193 0.9323878175561867 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 1.958801293505274 4.982561965771234 0.471890391343053 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 1.500116599864132 4.339560036883479 1.75645305944565 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 4.912922003545703 4.048464241294365 1.122473368577996 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 5.258380821455368 3.682506383808921 1.973193063451997 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 3.961611234368922 3.899191033445874 1.229424459523123 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 3.68652628868048 1.595323244715648 10.09294194440881 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 2.716738755606992 1.65284789480996 9.785054765941782 ForceField.Type=HW␣
↪ForceField.Charge=0.417
```

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```
        H 3.717820588318913 1.493830202223642 11.06393026159224 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 2.322791158566589 4.525494429167161 13.13712396271713 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 1.684244052546178 4.292584907055148 12.46669482040438 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 1.713022179274242 4.656194947137037 13.91280050486365 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 1.531573866397418 1.053168936091418 0.3718291838441352 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 1.522293261003647 2.011561261078512 0.5486474226338094 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 0.5646086101553838 0.8818604575421908 0.3306918436047358 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        O 3.418411885135323 2.370515151746976 3.6606774188027 ForceField.Type=OW␣
↪ForceField.Charge=-0.834
        H 2.581438388703135 2.63052383259613 3.242613350177665 ForceField.Type=HW␣
↪ForceField.Charge=0.417
        H 3.469669459117304 3.023705121589598 4.375706151452582 ForceField.Type=HW␣
↪ForceField.Charge=0.417
    End
    Lattice
        5.952918007318143 0.0 0.0
        0.0 5.952918007318143 0.0
        0.0 0.0 17.85875402195457
    End
    BondOrders
         1 2 1.0
         1 3 1.0
         4 5 1.0
         4 6 1.0
         7 8 1.0
         7 9 1.0
         10 11 1.0
         10 12 1.0
         13 14 1.0
         13 15 1.0
         16 17 1.0
         16 18 1.0
         19 20 1.0
         19 21 1.0 -1 0 0
         22 23 1.0 0 1 0
         22 24 1.0 0 1 0
         25 26 1.0
         25 27 1.0
         28 29 1.0
         28 30 1.0
         31 32 1.0
         31 33 1.0
         34 35 1.0
         34 36 1.0
         37 38 1.0
         37 39 1.0 0 -1 0
         40 41 1.0 -1 0 0
         40 42 1.0
         43 44 1.0
         43 45 1.0
```

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```
          46 47 1.0
          46 48 1.0
          49 50 1.0
          49 51 1.0
          52 53 1.0
          52 54 1.0
          55 56 1.0
          55 57 1.0
          58 59 1.0
          58 60 1.0
          61 62 1.0
          61 63 1.0
    End
End

Engine ForceField
    Type Amber95
EndEngine
eor

# The following script extracts the induced velocity amplitude and calculates the␣
↪corresponding viscosity
#
# The --test argument is only useful for regression testing
"$AMSBIN/amspython" "${TEST_DIRECTORY:-.}/analyze_cosine_shear.py" --test --from 41 --
↪block 100 ams.results/
echo "END OF TEST"
```

11.8 Trajectory replay

11.8.1 Example: Trajectory replays for PES scans, NEB and MD calculations

Download Replay.run

```
#!/bin/sh


# 1. Replay of PES scans
# ======================

AMS_JOBNAME=pesscan "$AMSBIN/ams" << eor

Task PESScan

PESScan
    ScanCoordinate
        nPoints 6
        Dihedral 5 1 2 6 0.0 50
        Dihedral 4 1 2 3 0.0 50
    End
    ScanCoordinate
        nPoints 7
        Distance 1 2 1.2 1.5
```

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```
    End
End

System
    Atoms
        C 0.0 -0.0 0.66687
        C 0.0 -0.0 -0.33313
        H 0.0 0.92974 -0.90538
        H 0.0 0.92974 1.23912
        H 0.0 -0.92974 1.23912
        H 0.0 -0.92974 -0.90538
    End
End

Engine ForceField
EndEngine

eor


AMS_JOBNAME=replay_pesscan "$AMSBIN/ams" << eor

Task Replay
Replay
   File pesscan.results
   StoreAllResultFiles Yes
End

Properties
   Gradients True
End

Engine DFTB
EndEngine

eor


echo "Start extracting data from ams.rkf ..."
echo "Number of frames on file:"
$AMSBIN/amsreport replay_pesscan.results/ams.rkf -r 'History%nEntries'
frame=1
while [ $frame -le 42 ]; do
   echo "Frame: $frame"
   $AMSBIN/amsreport replay_pesscan.results/ams.rkf -r "History%Energy($frame)"
   $AMSBIN/amsreport replay_pesscan.results/ams.rkf -r "History%Gradients($frame)"
   frame=$(expr $frame + 1)


done
echo "Data in PESScan section:"
$AMSBIN/amsreport replay_pesscan.results/ams.rkf -r 'PESScan%PESCoords'
$AMSBIN/amsreport replay_pesscan.results/ams.rkf -r 'PESScan%PES'
$AMSBIN/amsreport replay_pesscan.results/ams.rkf -r 'PESScan%HistoryIndices'
echo "Data extracted."
```

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```
# 2. Replay of NEB calculations
# ==============================

AMS_JOBNAME=neb "$AMSBIN/ams" << eor

Task NEB

NEB
    Images 16
End

GeometryOptimization
   Convergence
      Energy 1.0e-4
      Gradients 1.0e-2
   End
End

System
    Atoms
        C -0.04837097189972882 0.002828754545985427 1.099927275387085
        C -0.7231327687579711 -1.264630955508361 1.591341080262239
        C -0.7174118987979032 1.275587203448819 1.585489846719994
        H -1.758221225827696 -1.294861009536393 1.215612210647893
        H -0.7536609466556244 -1.286949469754588 2.689737906089842
        H 0.02700743800283175 0.0001348498227195367 0.004547638456250216
        H -0.7481941882345999 1.302956664081095 2.683766567353197
        H -0.1880537663322776 2.167332127899618 1.228056629315197
        H -1.752232117403696 1.308927696210993 1.209290912745431
        H -0.1979764470101184 -2.160385916691095 1.237731888775011
        Cl 1.710726893919094 4.005547128448699e-05 1.649098041095717
    End
End
System final
    Atoms
        C -0.8173023574499557 -0.01408167289928656 0.8544841004283144
        C -1.086263680920393 -1.14724517989661 1.518039806717775
        C -0.8990221290639472 1.362120508644236 1.43231282384412
        H -1.018446188967536 -2.121649215821082 1.03173453221026
        H -1.404982357822256 -1.129945575549278 2.563696578967125
        H -0.5085933307712909 -0.08344191227560969 -0.1948268157146379
        H -1.210244367762068 1.342173382164807 2.485525533439326
        H 0.07413947140246446 1.873805664554979 1.364278897383801
        H -1.616521025856608 1.9769362830809 0.8657976784252567
        H 1.044986335480545 -0.9543604705303219 1.922869894354733
        Cl 2.292729632733364 -1.053331811482705 2.350686966791855
    End
End

Engine DFTB
EndEngine

eor


AMS_JOBNAME=replay_neb "$AMSBIN/ams" << eor
```

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```
Task Replay
Replay File=neb.results/ams.rkf

Engine ADF
   NumericalQuality Basic
EndEngine

eor


echo "Start extracting data from ams.rkf ..."
echo "Number of frames on file:"
$AMSBIN/amsreport replay_neb.results/ams.rkf -r 'History%nEntries'
frame=1
while [ $frame -le 16 ]; do
   echo "Frame: $frame"
   $AMSBIN/amsreport replay_neb.results/ams.rkf -r "History%Energy($frame)"
   frame=$(expr $frame + 1)
done
echo "Data in NEB section:"
$AMSBIN/amsreport replay_neb.results/ams.rkf -r 'NEB%nebIterations'
$AMSBIN/amsreport replay_neb.results/ams.rkf -r 'NEB%historyIndex@dim'
$AMSBIN/amsreport replay_neb.results/ams.rkf -r 'NEB%historyIndex'
$AMSBIN/amsreport replay_neb.results/ams.rkf -r 'NEB%energy'
$AMSBIN/amsreport replay_neb.results/ams.rkf -r 'NEB%highestIndex'
$AMSBIN/amsreport replay_neb.results/ams.rkf -r 'NEB%LeftBarrier'
$AMSBIN/amsreport replay_neb.results/ams.rkf -r 'NEB%RightBarrier'
$AMSBIN/amsreport replay_neb.results/ams.rkf -r 'NEB%ReactionEnergy'
echo "Data extracted."


# 3. Replay of generic history (e.g. MD)
# ======================================

AMS_JOBNAME=md "$AMSBIN/ams" << eor

Task MolecularDynamics

MolecularDynamics
   nSteps 1000
   InitialVelocities Type=Zero
   Trajectory SamplingFreq=10
End

System
   Atoms
      O       5.84400000       0.31970000       0.89540000
      H       1.17000000       0.12750000      -2.13090000
      H      -0.61000000      -1.28280000      -1.84810000
      H      -0.57930000      -0.70680000       1.15800000
      C      -3.12520000       0.09550000       0.94430000
      C      -3.19980000      -1.42460000       1.23360000
      C      -2.05280000       0.23760000      -0.14210000
      C      -1.27100000       1.53130000      -0.13370000
      C      -0.13080000       1.46490000      -1.14670000
      C      -2.05030000      -2.08490000       0.42320000
      C      -1.08120000      -0.91390000       0.20520000
```

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```
      C      0.72590000       0.20890000      -1.09890000
      C     -0.07070000      -1.07000000      -0.90020000
      C      1.91880000       0.37840000      -0.17010000
      C      2.85070000       1.44940000      -0.76420000
      C      4.06090000       1.66070000       0.14280000
      C      0.79940000      -2.27110000      -0.66800000
      C      2.70610000      -0.90160000      -0.05510000
      C      4.70630000       0.33980000       0.46480000
      C      2.06470000      -2.18950000      -0.28730000
      C      4.02370000      -0.86790000       0.26480000
      C      1.49560000       0.82380000       1.22970000
      C     -2.72010000       0.03450000      -1.50220000
      C     -4.44990000       0.59620000       0.43260000
      O     -5.21170000      -0.16370000      -0.11570000
      C     -4.82510000       2.04560000       0.60460000
      H     -2.82710000       0.64000000       1.83720000
      H     -3.05600000      -1.60950000       2.29900000
      H     -4.16120000      -1.82340000       0.91220000
      H     -1.95080000       2.35390000      -0.41170000
      H     -0.90510000       1.74180000       0.87040000
      H     -0.54560000       1.56290000      -2.16020000
      H      0.51310000       2.34310000      -1.00320000
      H     -1.56740000      -2.86790000       1.01220000
      H     -2.40770000      -2.48600000      -0.52040000
      H      3.18420000       1.11610000      -1.74960000
      H      2.30420000       2.38610000      -0.86930000
      H      4.79290000       2.28810000      -0.38330000
      H      3.77550000       2.17310000       1.05860000
      H      0.36740000      -3.25490000      -0.82120000
      H      2.63690000      -3.09890000      -0.14660000
      H      4.55990000      -1.80060000       0.37040000
      H      0.83020000       0.07700000       1.66290000
      H      2.37890000       0.93230000       1.85900000
      H      0.97580000       1.77970000       1.16520000
      H     -3.42010000       0.84890000      -1.68870000
      H     -1.95890000       0.02380000      -2.28240000
      H     -3.25700000      -0.91410000      -1.50550000
      H     -4.48270000       2.61460000      -0.25970000
      H     -5.90820000       2.13270000       0.69120000
      H     -4.35580000       2.43770000       1.50690000
   End
End

Engine ReaxFF
   ForceField CHON-2019.ff
EndEngine

eor


AMS_JOBNAME=replay_md "$AMSBIN/ams" << eor

Task Replay
Replay
   File md.results/
   Frames 1:101:10
End
```

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```
Properties
   Gradients True
   BondOrders True
End

Engine DFTB
EndEngine

eor


echo "Start extracting data from ams.rkf ..."
echo "Number of frames on file:"
$AMSBIN/amsreport replay_md.results/ams.rkf -r 'History%nEntries'
frame=1
while [ $frame -le 11 ]; do
   echo "Frame: $frame"
   $AMSBIN/amsreport replay_md.results/ams.rkf -r "History%Energy($frame)"
   $AMSBIN/amsreport replay_md.results/ams.rkf -r "History%Bonds.Index($frame)"
   $AMSBIN/amsreport replay_md.results/ams.rkf -r "History%Bonds.Atoms($frame)"
   $AMSBIN/amsreport replay_md.results/ams.rkf -r "History%Bonds.Orders($frame)#8.2f"
   frame=$(expr $frame + 1)
done
echo "Data extracted."
```

11.9 Vibrational analysis

11.9.1 Example: Mode Refinement

Download VATools_dydrogesterone.run

```
#! /bin/sh

# This example shows a mode refinement of the band associated with the
# C=O and C=C stretch modes in the dydrogesterone molecule. This was one
# of the example calculations in the original paper on mode refinement:
#
#    J. Phys. Chem. Lett., 2018, 9 (23), pp 6878-6882


# Step 1: Get DFTB modes at the optimized DFT geometry
# ----------------------------------------------------

AMS_JOBNAME=FREQ_DFTB $AMSBIN/ams << EOF

   System
      Atoms
         # Dydrogesterone geometry already optimized with DFT (BP86/TZP).
         C 0.179402320119871 1.1462568499773749 -1.34045805553897
         C -1.0397129548582973 1.4038864822738149 -0.42742864655449175
         C -1.9187723039939633 0.15407663507305838 -0.2887082902723144
         C 5.26339021966562 -0.0803229279006518 0.15901574737297627
```

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```
        C 4.387948120190181 -1.2500901532169464 0.1985138671042922
        C 3.0305058270434313 -1.2006020082109579 0.06687676611264043
        C 2.2733069275281843 0.12162323554336309 -0.08656132560038762
        C 3.224495049036027 1.1562588842598234 -0.7427294996476081
        C 4.589580248129175 1.2673670000240371 -0.055599205726051454
        C -2.593712600512111 -0.1967276203097069 -1.6287069723510241
        C -2.011183672049868 -2.0904848406306247 0.6637924766824627
        C -3.24333170765593 -1.3040476226855777 1.1949612943873085
        C -2.9910039148987044 0.19289628304945772 0.8647395097635705
        C 1.8832501895313913 0.6066618903839885 1.3319251022509289
        C -1.021215985785471 -0.9883577256376227 0.2595406535945511
        C 0.950572917185341 -2.499497885394989 -0.17845795742396
        C 2.2618422613458535 -2.429295894019406 0.12998062227671012
        C 0.14931427176016024 -1.3398555308999998 -0.6810919840203331
        C 1.0424571714734645 -0.11148243146945544 -1.0381151732514977
        C -4.261014768367461 0.9709543041281233 0.5302962418813911
        C -4.2770282131623745 2.4457823410117943 0.8829249061723259
        O -5.23153866013212 0.4348316478674291 0.006835058476534351
        O 6.486629619384615 -0.1787206146841789 0.3101830744372818
        H 4.496419281348679 1.7413060958817603 0.9361407723186962
        H 4.889108126023183 -2.2103967123783246 0.34783394165927906
        H -2.5053803890738937 0.6948315694295174 1.7185731459759712
        H 2.747947397670055 2.147017249296297 -0.7608107343500633
        H 3.3788188981072294 0.8618896159833123 -1.7937886227370627
        H 5.278515387629924 1.9033945262275014 -0.6280820487414189
        H -0.313881863508176 -1.6818474813482587 -1.6263008186833716
        H 2.7970964757389787 -3.3338033858599037 0.4312075853898926
        H 0.4355882565839679 -3.460258453470549 -0.09628540747796212
        H 2.7788926695047853 0.7904363143118734 1.939504792825026
        H 1.3142558486724543 1.5445870277271823 1.281760102768146
        H 1.2817550339094792 -0.13839730232383732 1.865618408504196
        H 1.519857325493626 -0.37989780969443004 -1.9963570252289853
        H -3.35526145791249 2.9466219355670638 0.5538746959825623
        H -0.5844412872674496 -0.5966200898063014 1.193600037988863
        H 0.8128688006525261 2.043605920072621 -1.3496094336049678
        H -0.18858319204633375 1.0503960522723468 -2.3730012879550473
        H -1.6112343483079186 2.2461900431605373 -0.8495116990527544
        H -0.710640496667605 1.7174589936204205 0.5760379282354502
        H -1.5937002785491352 -2.7672883134736264 1.4205298630102559
        H -2.2836000112559893 -2.709635208733019 -0.2046201598348845
        H -3.3761548431942434 -1.4386051747789588 2.276540650869438
        H -4.174084527825135 -1.628156544022731 0.7132317870749941
        H -1.860827847389362 -0.4325042173503644 -2.4102132115597854
        H -3.2757258446436426 -1.0505046678063983 -1.5382984747892279
        H -3.1932088604642455 0.6502553019056425 -1.9892714020438331
        H -4.314908973244162 2.55066722711135 1.9790476680048945
        H -5.155478941054673 2.9311753898910595 0.44480850527661253
    End
End

Task SinglePoint

Properties
    NormalModes Yes
End

Engine DFTB
```

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```
       Model DFTB3
       ResourcesDir DFTB.org/3ob-freq-1-2
   EndEngine

EOF


# Step 2: Mode refinement of the DFTB C=O and C=C stretch bands at the DFT level
# ------------------------------------------------------------------------------

AMS_JOBNAME=ModeRefinement $AMSBIN/ams << EOF

   LoadSystem
      File FREQ_DFTB.results/dftb.rkf
   End

   Task VibrationalAnalysis

   VibrationalAnalysis
      Type ModeRefinement
      NormalModes
         ModeFile FREQ_DFTB.results/dftb.rkf
         ModeSelect
            FreqRange 1500 1800
         End
      End
   End

   Engine BAND
      # Settings from the paper:
      XC
         GGA BP86
      End
      Basis
         Type DZP
      End
      Relativity Level=None
      # Just to make this test run faster:
      NumericalQuality Basic
      Convergence Criterion=1e-6   # results quite sensitive to this
      SCF Method=DIIS  # slightly faster because mix is inherited with restarts, not␣
↪so for the MultiStepper.
   EndEngine

EOF
```

11.9.2 Example: Mode Tracking

Download VATools_cyclohexanone.run

```
#! /bin/sh

# This example demonstrates the usage of the AMS vibrational analysis tools
# on the cyclohexanone molecule.


# 1. Optimization with DFT
# ------------------------

AMS_JOBNAME=DFT $AMSBIN/ams << EOF

   System
      Atoms
        C          0.000000    0.000000    0.000000
        C          0.978606    1.950589   -1.251328
        C          0.978606    1.950589    1.251328
        C          0.812569    2.806732    0.000000
        C         -0.039622    0.802151    1.272926
        C         -0.039622    0.802151   -1.272926
        O          0.062619   -1.251283    0.000000
        H          0.123306    0.119861    2.122758
        H         -1.060012    1.229063    1.372200
        H          0.871524    2.560541    2.167037
        H          2.001065    1.521810    1.263746
        H         -0.196785    3.268312    0.000000
        H          1.549313    3.631809    0.000000
        H          0.871524    2.560541   -2.167037
        H          2.001065    1.521810   -1.263746
        H          0.123306    0.119861   -2.122758
        H         -1.060012    1.229063   -1.372200
      End
   End

   Task GeometryOptimization

   GeometryOptimization
      Convergence Gradients=1.0e-4
   End

   Engine BAND
   EndEngine

EOF


# 2. Obtain DFTB hessian and modes as preconditioner and guess
# ------------------------------------------------------------

AMS_JOBNAME=DFTB $AMSBIN/ams << EOF

   LoadSystem
      File DFT.results/ams.rkf
   End
```

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```
   Task GeometryOptimization

   GeometryOptimization
      Convergence Gradients=1.0e-4
   End

   Properties
      NormalModes Yes
   End

   Engine DFTB
      Model DFTB3
      ResourcesDir DFTB.org/3ob-freq-1-2
   EndEngine

EOF


# 3. ModeScanning of DFTB C=O stretch mode with DFT
# --------------------------------------------------

AMS_JOBNAME=ModeScanning $AMSBIN/ams << EOF

   LoadSystem
      File DFTB.results/ams.rkf
   End
   LoadEngine DFT.results/band.rkf

   Task VibrationalAnalysis

   VibrationalAnalysis
      Type ModeScanning
      NormalModes
         ModeFile DFTB.results/dftb.rkf
         ModeSelect
            HighIR 1 # This should select the C=O stretch
         End
      End
   End

EOF


# 4. Mode tracking with DFT starting from DFTB C=O stretch mode
# --------------------------------------------------------------

AMS_JOBNAME=ModeTracking $AMSBIN/ams << EOF

   LoadSystem
      File DFT.results/ams.rkf
   End
   LoadEngine DFT.results/band.rkf

   Task VibrationalAnalysis

   VibrationalAnalysis
      Type ModeTracking
```

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```
      ModeTracking
         HessianGuess File
         HessianPath DFTB.results
      End
      NormalModes
         ModeInputFormat File
         ModeFile DFTB.results/dftb.rkf
         ModeSelect
            HighIR 1 # This should select the C=O stretch
         End
      End
   End

EOF


# 5. Mode tracking with DFT starting from a pure C=O stretch
# ----------------------------------------------------------

AMS_JOBNAME=ModeTracking_COStretch $AMSBIN/ams << EOF

   LoadSystem
      File DFT.results/ams.rkf
   End
   LoadEngine DFT.results/band.rkf

   Task VibrationalAnalysis

   VibrationalAnalysis
      Type ModeTracking
      NormalModes
         ModeInputFormat Inline
         ModeInline
            0.0  0.0  0.7071 # This is the C attached to the O
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0 -0.7071 # This is the O
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0  0.0
            0.0  0.0  0.0
         End
         ModeSelect
            HighIR 1 # This should select the C=O stretch
         End
      End
      ModeTracking
         HessianGuess File
```

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```
         HessianPath DFTB.results
         TrackingMethod OverlapPrevious
                      #     ^-- Probably better than the default.
                      #         Our initial mode is not particularly close yet ...  ␣
↪
      End
   End

EOF
```

11.9.3 Example: Vibronic-Structure Tracking

Download VST_pyrene.run

```
#!/bin/sh

# This example demonstrates the usage of vibronic-structure tracking
# on the pyrene molecule. Excited state calculations are performed within AMS and
# at the DFTB level

# 1. Ground state optimization with DFTB
#----------------------------------------

AMS_JOBNAME=GroundState $AMSBIN/ams << eor

System
    Atoms
        C      -0.01654981       1.36506537       0.00802668
        C       0.00281590      -0.06808050       0.00051978
        C       1.19835953       2.08859192       0.00127327
        C      -1.25056871       2.05539572       0.02157814
        C       1.23682878      -0.75840671      -0.01375673
        C      -1.21209870      -0.79160461       0.00671225
        C       2.44308841       1.35898462      -0.01256813
        C       1.16450680       3.48665407       0.00772934
        C      -2.47512291       1.29231475       0.02824995
        C      -1.25452039       3.45386389       0.02759561
        C       2.46138768       0.00467142      -0.01984509
        C       1.24076149      -2.15686407      -0.02209661
        C      -2.45682219      -0.06199957       0.02121310
        C      -1.17826305      -2.18965609      -0.00177638
        C      -0.05432386       4.15935390       0.02049748
        C       0.04055488      -2.86234799      -0.01620562
        H       3.36596464       1.93801392      -0.01731234
        H       2.09583666       4.04986513       0.00239299
        H      -3.41330596       1.84611463       0.03902307
        H      -2.20073438       3.99162601       0.03767421
        H       3.39957176      -0.54912830      -0.03053168
        H       2.18696724      -2.69462025      -0.03320657
        H      -3.37969722      -0.64102946       0.02611688
        H      -2.10959908      -2.75286422       0.00274662
        H      -0.06904859       5.24837501       0.02503968
        H       0.05526108      -3.95135857      -0.02284989
    End
End
```

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```
Task GeometryOptimization

Engine DFTB
    Model DFTB3
    ResourcesDir DFTB.org/3ob-freq-1-2
EndEngine

eor

# 2. Get lowest singlet-singlet excitation of pyrene and
# compute the excited state gradient at the optimized GS geometry
#-----------------------------------------------------------------

AMS_JOBNAME=ExcitedState $AMSBIN/ams << eor

Task SinglePoint
LoadSystem
   File ./GroundState.results/dftb.rkf
End

Properties
    Gradients yes
End

Engine DFTB
    Model DFTB3
    ResourcesDir DFTB.org/3ob-freq-1-2
    Properties
        Excitations
            TDDFTB
                Calc Singlet
                Lowest 1
            End
            TDDFTBGradients
                Excitation 1
            End
        End
    End
EndEngine

eor

# 3. Vibronic-structure tracking for this excitation
# ---------------------------------------------------

AMS_JOBNAME=VibronicStructure $AMSBIN/ams << eor

LoadSystem
   File ./GroundState.results/dftb.rkf
End

Task VibrationalAnalysis

VibrationalAnalysis
   Type VibronicStructureTracking
   ExcitationSettings
```

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```
      ExcitationInputFormat File
      ExcitationFile ./ExcitedState.results/dftb.rkf
      Singlet
        A 1
      End
   End
   AbsorptionSpectrum
      AbsorptionRange -500.0 4000.0
      LineWidth 100
      FrequencyGridPoints 181
   End
End

Engine DFTB
    Model DFTB3
    ResourcesDir DFTB.org/3ob-freq-1-2
EndEngine

eor

# 4. Restart the VST run from the previous one
# We have changed our mind and we want
# the peaks to be a little sharper
# ----------------------------------------------------------

AMS_JOBNAME=VibronicStructureRestart $AMSBIN/ams << eor

LoadSystem
   File ./GroundState.results/dftb.rkf
End

Task VibrationalAnalysis

VibrationalAnalysis
   Type VibronicStructureTracking
   ExcitationSettings
      ExcitationInputFormat File
      ExcitationFile ./ExcitedState.results/dftb.rkf
      Singlet
        A 1
      End
   End
   VSTRestartFile ./VibronicStructure.results/ams.rkf
   AbsorptionSpectrum
      AbsorptionRange -500.0 4000.0
      LineWidth 50
      FrequencyGridPoints 181
   End
End

Engine DFTB
    Model DFTB3
    ResourcesDir DFTB.org/3ob-freq-1-2
EndEngine

eor
```

11.10 PES point properties

11.10.1 Example: Phonons for graphene

Download Phonons_Graphene.run

```
#!/bin/sh

AMS_JOBNAME=graphene $AMSBIN/ams << EOF

   Task GeometryOptimization

   GeometryOptimization
!       CoordinateType Cartesian
      OptimizeLattice True
      Convergence Gradients=1.0e-5
      Method Quasi-Newton
   End

   Properties
      Phonons True
   End

   NumericalPhonons
     SuperCell
       2  0
       0  2
     End
   End

   System
      Atoms
         C       0.000000000    -0.000000000     0.00000
         C       0.000000000    -1.420281662     0.00000
      End

      Lattice
         1.230000000    -2.130422493     0.000000000
         1.230000000     2.130422493     0.000000000
      End
   End

   Engine DFTB
      ResourcesDir Dresden
      Model DFTB0
      KSpace
        Type Symmetric
        Symmetric KInteg=9
      End
      Technical AnalyticalStressTensor=False # Not yet supported with symmetric k-
↪space grid ...
   EndEngine

EOF

echo ""
echo "Begin TOC of result file"
```

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```
$AMSBIN/dmpkf -n 1 graphene.results/dftb.rkf --toc

echo "End TOC of result file"
```

11.10.2 Example: Phonons with isotopes

Download Phonons_Isotopes.run

```
#! /bin/sh


# ====================================
# Phonons with default nuclear masses:
# ====================================

AMS_JOBNAME=defmasses $AMSBIN/ams << EOF

   Task SinglePoint

   Properties
      Phonons True
   End

   NumericalPhonons
      StepSize 0.01
      SuperCell
         4
      End
   End

   System
      Atoms
          C  -2.42906152   -0.3445528299    -0.1353492062
          C  -1.146891508  -1.134644249      0.1353492061
          H  -2.429062041   0.004468895147  -1.185797304
          H  -2.429062011   0.5753101439     0.4803683017
          H  -1.146891017  -2.054507222     -0.4803683019
          H  -1.146890987  -1.483665974      1.185797304
      End

      Lattice
          2.564338467 0.0 0.0
      End
   End

   Engine DFTB
      ResourcesDir QUASINANO2015
      Model DFTB0
      KSpace
        Type Symmetric
        Symmetric KInteg=9
      End
   EndEngine
```

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```
EOF

echo ""
echo "Begin TOC of result file"
$AMSBIN/dmpkf -n 1 defmasses.results/dftb.rkf --toc
echo "End TOC of result file"


# =================================
# Phonons with two deuterium atoms:
# =================================

AMS_JOBNAME=usermasses $AMSBIN/ams << EOF

   Task SinglePoint

   Properties
      Phonons true
   End

   NumericalPhonons
      StepSize 0.01
      SuperCell
         4
      End
   End

   System
       Atoms
           C   -2.42906152   -0.3445528299    -0.1353492062
           C   -1.146891508  -1.134644249      0.1353492061
           H   -2.429062041   0.004468895147  -1.185797304
           H   -2.429062011   0.5753101439     0.4803683017
           H   -1.146891017  -2.054507222     -0.4803683019    mass=2.014
           H   -1.146890987  -1.483665974      1.185797304     mass=2.014
       End
       Lattice
           2.564338467 0.0 0.0
       End
   End

   Engine DFTB
      ResourcesDir QUASINANO2015
      Model DFTB0
      KSpace
        Type Symmetric
        Symmetric KInteg=9
      End
   EndEngine

EOF

echo ""
echo "Begin TOC of result file"
$AMSBIN/dmpkf -n 1 usermasses.results/dftb.rkf --toc
echo "End TOC of result file"
```

11.10.3 Example: User-defined Brillouin zone for phonon dispersion

Download Phonons_UserBZPath.run

```
#!/bin/sh

# This example shows how to specify a user-defined path through the
# Brillouin zone (BZ) when computing the phonon dispersion curves.

# Note: when computing the phonons, you should first run a geometry
# optimization (including relaxation of lattice vectors).
# Here we use a pre-optimized structure.

AMS_JOBNAME=BoronNitrade $AMSBIN/ams << eor

Task SinglePoint

System
    Atoms
        B 0.0              0.0              0.0
        N 0.92538708336681 0.92538708336681 0.92538708336681
    End
    Lattice
        0.0              1.8507741667336 1.8507741667336
        1.8507741667336 0.0              1.8507741667336
        1.8507741667336 1.8507741667336 0.0
    End
End

Properties
    Phonons Yes
End

NumericalPhonons
    SuperCell
        2  0  0
        0  2  0
        0  0  2
    End

    # Disable the automatically generated path though the BZ

    AutomaticBZPath No

    BZPath
        # In each 'Path' block you should define the vertices of the path
        # in fractional coordinates (with respect to the reciprocal lattice
        # vectors)

        # First segment: Gamma-X-W-K
        Path
             0.0   0.0   0.0  G
             0.5   0.0   0.5  X
             0.5   0.25  0.75 W
             0.375 0.375 0.75 K
        End

        # Second segment: Gamma-SomeRandomPoint
```

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```
        Path
            0.0  0.0  0.0 G
            0.1  0.2  0.3 RandomPoint
        End
    End
End

Engine DFTB
    Model SCC-DFTB
    ResourcesDir DFTB.org/matsci-0-3
    KSpace Quality=Basic
EndEngine

eor

echo 'Content of phonon_curves section'
$AMSBIN/dmpkf BoronNitrade.results/dftb.rkf 'phonon_curves'
echo 'End content of phonon_curves section'
```

11.10.4 Example: Elastic tensor

Download ElasticTensor.run

```
#! /bin/sh


# === Diamond ===

AMS_JOBNAME=Diamond $AMSBIN/ams << EOF

   Task GeometryOptimization

   Properties
       ElasticTensor Yes
   End

   System
      Atoms
         C  0.44625  0.44625  2.23125
         C  2.23125  2.23125  2.23125
         C -2.23125 -2.23125 -2.23125
         C -0.44625 -0.44625 -2.23125
         C -0.44625 -2.23125 -0.44625
         C  1.33875 -0.44625 -0.44625
         C -2.23125 -0.44625 -0.44625
         C -0.44625  1.33875 -0.44625
         C -0.44625 -0.44625  1.33875
         C  1.33875  1.33875  1.33875
         C -1.33875 -1.33875 -1.33875
         C  0.44625  0.44625 -1.33875
         C  0.44625 -1.33875  0.44625
         C  2.23125  0.44625  0.44625
         C -1.33875  0.44625  0.44625
         C  0.44625  2.23125  0.44625
      End
```

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```
      Lattice
         0.0  3.57 3.57
         3.57 0.0  3.57
         3.57 3.57 0.0
      End
   End

   GeometryOptimization
       OptimizeLattice Yes
       Convergence Quality=Good
   End

   Symmetry Tolerance=1e-6

   Engine DFTB
       Model DFTB
       ResourcesDir DFTB.org/mio-1-1
       KSpace
           Type Symmetric
           Symmetric KInteg=3
       End
       Technical AnalyticalStressTensor=False # Not yet supported with symmetric k-
↪space grid.
   EndEngine

EOF


# === Boron-Nitride sheet ===

# 3x3 super-cell, default k-space sampling

AMS_JOBNAME=BN_sheet $AMSBIN/ams << EOF

   Task GeometryOptimization

   Properties
       ElasticTensor Yes
   End

   System
      Atoms
         N  3.76095075   0.723795     0.0
         N  5.01460112   2.89518114   0.0
         B -3.76095112  -2.17138614   0.0
         B -2.50730075   0.0          0.0
         B -1.25365038   2.17138614   0.0
         B -1.25365037  -2.17138614   0.0
         B  0.0          0.0          0.0
         B  1.25365037   2.17138614   0.0
         B  1.25365038  -2.17138614   0.0
         B  2.50730075   0.0          0.0
         B  3.76095112   2.17138614   0.0
         N -2.50730112  -1.44759114   0.0
         N -1.25365075   0.723795     0.0
         N  -3.8e-07      2.89518114 0.0
         N  -3.7e-07     -1.44759114 0.0
```

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```
         N  1.25365      0.723795     0.0
         N  2.50730037   2.89518114   0.0
         N  2.50730038  -1.44759114   0.0
      End
      Lattice
         7.52190225 0.0
         3.76095111 6.51415842
      End
   End

   GeometryOptimization
      OptimizeLattice Yes
      Convergence Quality=Good
   End

   Engine DFTB
      Model SCC-DFTB
      ResourcesDir DFTB.org/matsci-0-3
   EndEngine

EOF


# === Polyoxyethylene ===

# primitive cell with k-space sampling

AMS_JOBNAME=Polyoxyethylene $AMSBIN/ams << EOF

   Task GeometryOptimization

   Properties
      ElasticTensor Yes
   End

   ElasticTensor
      StrainStepSize 0.002
   End

   System
      Atoms
         C   -0.279368361   -0.125344097   -0.026221791
         O    0.840592835   -0.919621431   -0.193214154
         H   -0.279527057    0.337014408    0.997733792
         H   -0.281697417    0.707951120   -0.778297849
      End
      Lattice
         2.240292981
      End
   End

   GeometryOptimization
      OptimizeLattice Yes
      Convergence Quality=Good
   End

   Engine DFTB
```

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```
      Model SCC-DFTB
      ResourcesDir DFTB.org/3ob-3-1
      KSpace
          Type Symmetric
          Symmetric KInteg=5
      End
      Technical AnalyticalStressTensor=False # Not yet supported with symmetric k-
↪space grid.
   EndEngine

EOF


# Note: the elastic tensor is also printed to standard output.

echo ""
echo "Extract the elastic tensor of Diamond from the rkf file:"
$AMSBIN/amsreport Diamond.results/dftb.rkf -r "AMSResults%ElasticTensor#12.4f##6"

echo ""
echo "Extract the elastic tensor of Boron-Nitride from the rkf file:"
$AMSBIN/amsreport BN_sheet.results/dftb.rkf -r "AMSResults%ElasticTensor#12.4f##3"

echo ""
echo "Extract the elastic tensor of Polyoxyethylene from the rkf file:"
$AMSBIN/amsreport Polyoxyethylene.results/dftb.rkf -r "AMSResults%ElasticTensor#12.4f#
↪#1"
```

11.11 Pipe interface

11.11.1 Example: ASE calculator as a pipe worker

Download Pipe_ASEWorker.run

```
#!/bin/sh
# This example uses a Python pipe worker based on ASE to evaluate the Lennard-Jones␣
↪potential.
# First we do a single-point calculation including the gradients and the stress␣
↪tensor and then
# a short MD run similar to the Pipe_AMSonAMS example.

export SCM_DISABLE_MPI=1

AMS_JOBNAME=SP "$AMSBIN/ams" << eor
RNGSeed -538839488 972444872 -468448621 535232319 -953628259 777353319 -1036072␣
↪387155213

Task SinglePoint

Properties
    Gradients True
    StressTensor True
End
```

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```
System
    Atoms
        Ar     0.03374714    -0.02579634    -0.03864485
        Ar    -2.47202773    -2.57754100    -0.02505375
        Ar    -2.54465030    -0.00587811    -2.49637860
        Ar    -4.98237672    -2.60930954    -2.49495517
        Ar    -0.03221746    -2.51967081    -2.47883073
        Ar    -2.52675554    -5.12905072    -2.48152312
        Ar    -2.54445364    -2.45619404    -5.02601013
        Ar    -4.95645981    -5.14903666    -4.95752059
    End
    Lattice
              0.00000000     5.00000000     5.00000000
              5.00000000     0.00000000     5.00000000
              5.00000000     5.20000000     0.00000000
    End
End

Engine Pipe
    WorkerCommand "$AMSBIN/amspython" "$TEST_DIRECTORY/ASE-LJ-worker.py"
EndEngine

eor

AMS_JOBNAME=MD "$AMSBIN/ams" << eor
RNGSeed -538839488 972444872 -468448621 535232319 -953628259 777353319 -1036072␣
↪387155213

Task MolecularDynamics

MolecularDynamics
    nSteps 200
    TimeStep 5.0
    Thermostat Type=NHC Temperature=298.15 Tau=100
    Trajectory SamplingFreq=20
    InitialVelocities Type=random Temperature=200
End

System
    Atoms
        Ar 0.0 0.0 0.0
        Ar 1.605 0.9266471820493496 2.605
    End
    Lattice
        3.21 0.0 0.0
        1.605 2.779941546148048 0.0
        0.0 0.0 5.21
    End
    SuperCell 4 4 4
End

Engine Pipe
    WorkerCommand "$AMSBIN/amspython" "$TEST_DIRECTORY/ASE-LJ-worker.py"
EndEngine

eor
```

Download ASE-LJ-worker.py

```
from scm.amspipe import ASEPipeWorker
from ase.calculators.lj import LennardJones

calculator = LennardJones()
calculator.parameters.epsilon = 0.0102996
calculator.parameters.sigma = 3.4
calculator.parameters.rc = 12.0

engine = ASEPipeWorker(calculator=calculator)
engine.run()
```

11.11.2 Example: AMS as a pipe worker

Download Pipe_AMSonAMS.run

```
#!/bin/sh
# This example runs two separate AMS processes communicating over AMSPipe. One of␣
↪them is the PipeWorker
# calculating Lennard-Jones energies and the other as the PipeMaster drives the MD␣
↪simulation.

export SCM_DISABLE_MPI=1
export NSCM_AMSEXTERNAL=1

cat - > worker.in << eor
Task Pipe

Engine LennardJones
    Rmin 3.81637
    Eps 3.785e-4
    Cutoff 12.0
EndEngine
eor

"$AMSBIN/ams" << eor
RNGSeed -538839488 972444872 -468448621 535232319 -953628259 777353319 -1036072␣
↪387155213

Task MolecularDynamics

MolecularDynamics
    nSteps 200
    TimeStep 5.0
    Thermostat Type=NHC Temperature=298.15 Tau=100
    Trajectory SamplingFreq=20
    InitialVelocities Type=random Temperature=200
End

System
    Atoms
        Ar 0.0 0.0 0.0
        Ar 1.605 0.9266471820493496 2.605
    End
    Lattice
```

(continues on next page)

(continued from previous page)

```
        3.21 0.0 0.0
        1.605 2.779941546148048 0.0
        0.0 0.0 5.21
    End
    SuperCell 4 4 4
End

Engine Pipe
    WorkerCommand "$AMSBIN/ams" < ../../worker.in > worker.out 2>&1
EndEngine
eor

echo "Worker output:"
cat ams.results/*/worker.out
```

CHAPTER

TWELVE

APPENDICES

12.1 Extended XYZ file format

The `.xyz` file format is a simple text based format for molecular geometries. `.xyz` files have the number of atoms in the first line, followed by a comment line, followed by one line per atom, specifying the element as well as the x, y, and z coordinates of this atom.

However, the standard `.xyz` file format does not include lattice vectors. AMS therefore uses an extended `.xyz` file format which is also suitable for periodic systems. In this extended format the lattice vectors are specified at the end of the `.xyz` file via the keys `VEC1`, `VEC2` and `VEC3`. For 1D periodic systems (chains) only `VEC1` is needed. For 2D periodic systems (slabs) only `VEC1` and `VEC2` are needed. An example extended `.xyz` for graphene looks like this:

```
2

C     0.0   0.0       0.0
C     1.23  0.71014   0.0
VEC1  2.46  0.0       0.0
VEC2  1.23  2.13042   0.0
```

Note that the extended `.xyz` format is also understood by the AMS GUI for importing and exporting geometries from/to `.xyz` files.

12.2 Developer options

```
Print
   Timers [None | Normal | Detail | TooMuchDetail]
End
```

Print

Type Block

Description This block controls the printing of additional information to stdout.

Timers

Type Multiple Choice

Default value None

Options [None, Normal, Detail, TooMuchDetail]

Description Printing timing details to see how much time is spend in which part of the code.

```
EngineDebugging
   AlwaysClaimSuccess Yes/No
   CheckInAndOutput Yes/No
   ForceContinousPES Yes/No
   IgnoreGradientsRequest Yes/No
   IgnorePreviousResults Yes/No
   IgnoreStressTensorRequest Yes/No
   NeverQuiet Yes/No
   RandomFailureChance float
   RandomNoiseInEnergy float
   RandomNoiseInGradients float
   RandomStopChance float
End
```

`EngineDebugging`

Type Block

Description This block contains some options useful for debugging the computational engines.

`AlwaysClaimSuccess`

Type Bool

Default value No

Description If an engine fails, pretend that it worked. This can be useful when you know that an SCF might fail.

`CheckInAndOutput`

Type Bool

Default value No

Description Enables some additional checks on the input and output of an engine, e.g. for NaN values.

`ForceContinousPES`

Type Bool

Default value No

Description If this option is set, the engine will always run in continuous PES mode. For many engines this disables the use of symmetry, as this one always leads to a discontinuous PES around the symmetric points: Basically there is jump in the PES at the point where the symmetry detection starts classifying the system as symmetric. Normally the continuous PES mode of the engine (often disabling the symmetry) is only used when doing numerical derivatives, but this flag forces the engine to continuously run in this mode.

`IgnoreGradientsRequest`

Type Bool

Default value No

Description If this option is set, the engine will not do analytical gradients if asked for it, so that gradients will have to be evaluated numerically by AMS.

`IgnorePreviousResults`

Type Bool

Default value No

Description If this option is set, the engine will not receive information from previous calculations. Typically this information is used to restart the self consistent procedure of the engine.

`IgnoreStressTensorRequest`

Type Bool

Default value No

Description If this option is set, the engine will not calculate an analytical stress tensor if asked for it, so that the stress tensor will have to be evaluated numerically by AMS.

`NeverQuiet`

Type Bool

Default value No

Description Makes the engine ignore the request to work quietly.

`RandomFailureChance`

Type Float

Default value 0.0

Description Makes the engine randomly report failures, even though the results are actually fine. Useful for testing error handling on the application level.

`RandomNoiseInEnergy`

Type Float

Default value 0.0

Unit Hartree

Description Adds a random noise to the energy returned by the engine. The random contribution is drawn from [-r,r] where r is the value of this keyword.

`RandomNoiseInGradients`

Type Float

Default value 0.0

Unit Hartree/Angstrom

Description Adds a random noise to the gradients returned by the engine. A random number in the range [-r,r] (where r is the value of this keyword) is drawn and added separately to each component of the gradient.

`RandomStopChance`

Type Float

Default value 0.0

Description Makes the engine randomly stop. Can be used to simulate crashes.

12.3 Symmetry

12.3.1 Schönfliess symbols and symmetry labels

A survey of all molecular point groups that are recognized by AMS is given below. The table contains the Schönfliess symbols together with the names of the subspecies of the irreducible representations as they are used by AMS to label normal modes.

Table 12.1: Schönfliess symbols and the labels of the irreducible representations.

Point	Schönfliess	Irreducible representations
Group	Symbol in AMS	
C_1	NOSYM	A
$C_{\infty v}$	C(LIN)	Sigma Pi
$D_{\infty h}$	D(LIN)	Sigma.g Sigma.u Pi.g Pi.u
I	I	A T1 T2 G H
I_h	I(H)	A.g A.u T1.g T1.u T2.g T2.u G.g G.u H.g H.u
O	O	A1 A2 E T1 T2
O_h	O(H)	A1.g A1.u A2.g A2.u E.g E.u T1.g T1.u T2.g T2.u
T	T	A E T
T_h	T(H)	A.g A.u E.g E.u T.g T.u
T_d	T(D)	A1 A2 E T1 T2
C_i	C(I)	A.g A.u
S_n	S(N)	n=4: A B E
		n=6: A.g A.u E.g E.u
		n=8: A B E1 E2 E3
C_n	C(N)	n=2: A B
		n=4: A B E
		even n: A B E1 E2 …
		n=3: A E
		odd n: A E1 E2 …
C_{nv}	C(NV)	n=2: A1 A2 B1 B2
		n=4: A1 A2 B1 B2 E
		even n: A1 A2 B1 B2 E1 E2 …
		n=3: A1 A2 E
		odd n: A1 A2 E1 E2 …
C_s	C(S)	A' A”
C_{nh}	C(NH)	n=2: A.g A.u B.g B.u
		n=4: A.g A.u B.g B.u E.g E.u
		even n: A.g A.u B.g B.u E1.g E1.u E2.g E2.u …
		n=3: A' A” E' E”
		odd n: A' A” E1' E1” E2' E2” …
D_n	D(N)	n=2: A B1 B2 B3
		n=4: A1 A2 B1 B2 E
		even n A1 A2 B1 B2 E1 E2 …
		n=3: A1 A2 E
		odd n: A1 A2 E1 E2 …
D_{nd}	D(ND)	n=2: A1 A2 B1 B2 E
		even n: A1 A2 B1 B2 E1 E2 …
		n=3: A1.g A1.u A2.g A2.u E.g E.u

continues on next page

Table 12.1 – continued from previous page

		odd n: A1.g A1.u A2.g A2.u E1.g E1.u E2.g E2.u …
D_{nh}	D(NH)	n=2: A.g A.u B1.g B1.u B2.g B2.u B3.g B3.u
		n=4: A.g A.u B1.g B1.u B2.g B2.u B3.g B3.u E.g E.u
		even n: A.g A.u B1.g B1.u B2.g B2.u B3.g B3.u E1.g E1.u E2.g E2.u …
		n=3: A1' A1" A2' A2" E' E"
		odd n: A1' A1" A2' A2" E1' E1" E2' E2" …

The symmetry labeling may depend on the choice of coordinate system. For instance, B1 and B2 representations in C_{nv} are interchanged when you rotate the system by 90 degrees around the z-axis so that x-axis becomes y-axis and vice-versa (apart from sign).

12.3.2 Molecular orientation requirements

In order that AMS recognizes the (sub)symmetry of a molecule, the molecule has to have a specific orientation in space.

- The origin is a fixed point of the symmetry group.
- The z-axis is the main rotation axis.
- xy is the σ_h -plane (axial groups, C(s)).
- The x-axis is a C_2 axis (D symmetries).
- The xz-plane is a σ_v -plane (C_{nv} symmetries).
- In T_d and O_h the z-axis is a fourfold axis (S_4 and C_4 , respectively) and the (111)-direction is a threefold axis.

If the system is symmetrized (and no symmetry is given in the System block key) the molecular structure is rotranslated into this standard orientation.

Molecular orientation conventions

The molecular requirements for AMS may not fully determine the orientation of the molecule, like for D_{2h} molecules. See Mulliken[1] for standard conventions on the molecular orientation and notation. A few of these conventions are listed below:

- in planar C_{2v} molecules the x axis is perpendicular to the plane of the molecule.
- in planar D_{2h} molecules the x axis is perpendicular to the plane of the molecule and the z-axis passes through the greatest number of atoms. If the last condition is not decisive, the z-axis should pass through the greatest number of bonds.
- in planar D_{4h} and D_{6h} molecules the C_2-axis passes through the greatest number of atoms. If the last condition is not decisive, the C_2-axis should pass through the greatest number of bonds.

[1] R.S Mulliken, *Report on Notation for the Spectra of Polyatomic Molecules*, Journal of Chemical Physics 23, 1997 (1955) (https://doi.org/10.1063/1.1740655)

CHAPTER

THIRTEEN

REQUIRED CITATIONS

13.1 General references

When you publish results in the scientific literature that were obtained through the AMS driver program, you are required to include a reference to the program package with the appropriate release number:

AMS 2024.1, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com. Optionally, you may add the following list of authors and contributors: R. Rüger, M. Franchini, T. Trnka, A. Yakovlev, E. van Lenthe, P. Philipsen, T. van Vuren, B. Klumpers, T. Soini

The engine used for a particular calculation might require you to include other references. Please refer to the specific *engine manuals* (page 271) for required citations.

In addition to these general references, certain AMS features require additional citations, in case you have used them. An overview of these is given in the *Feature references* section below.

Note: If you have used a modified (by yourself, for instance) version of the code, you should mention in the citation that a modified version has been used.

13.2 Feature references

13.2.1 Frequencies, IR Intensities, Raman, VCD

Mode tracking M. Reiher, J. Neugebauer, *A mode-selective quantum chemical method for tracking molecular vibrations applied to functionalized carbon nanotubes*, Journal of Chemical Physics 118, 1634 (2003) (https://doi.org/10.1063/1.1523908)

M. Reiher, J. Neugebauer, *Convergence characteristics and efficiency of mode-tracking calculations on pre-selected molecular vibrations*, Physical Chemistry Chemical Physics 6, 4621 (2004) (http://dx.doi.org/10.1039/B406134A)

C. Herrmann, M. Reiher, J. Neugebauer, *Finding a needle in a haystack: direct determination of vibrational signatures in complex systems*, New Journal of Chemistry 31, 818 (2007) (http://dx.doi.org/10.1039/B618769M)

Mode tracking based on intensities M. Reiher, J. Neugebauer, *A mode-selective quantum chemical method for tracking molecular vibrations applied to functionalized carbon nanotubes*, Journal of Chemical Physics 118, 1634 (2003) (https://doi.org/10.1063/1.1523908)

S. Luber, J. Neugebauer, M. Reiher, *Intensity tracking for theoretical infrared spectroscopy of large molecules*, Journal of Chemical Physics 130, 064105 (2009) (https://doi.org/10.1063/1.3069834)

Mode refinement T.Q. Teodoro, M.A.J. Koenis, S.E. Galembeck, V.P. Nicu, W.J. Buma, L. Visscher, *A frequency range selection method for vibrational spectra*, J. Phys. Chem. Lett., 9 (23), 6878 (2018) (https://doi.org/10.1021/acs.jpclett.8b02963)

Mobile Block Hessian (MBH) A. Ghysels, D. Van Neck, V. Van Speybroeck, T. Verstraelen and M. Waroquier, *Vibrational Modes in partially optimized molecular systems* Journal of Chemical Physics 126, 224102 (2007) (https://doi.org/10.1063/1.2737444)

Raman scattering S.J.A. van Gisbergen, J.G. Snijders and E.J. Baerends, *Application of time-dependent density functional response theory to Raman scattering*, Chemical Physics Letters 259, 599 (1996) (https://doi.org/10.1016/0009-2614(96)00858-5)

Resonance Raman: excited-state finite lifetime L. Jensen, L. Zhao, J. Autschbach and G.C. Schatz, *Theory and method for calculating resonance Raman scattering from resonance polarizability derivatives*, Journal of Chemical Physics 123, 174110 (2005) (https://doi.org/10.1063/1.2046670)

Resonance Raman: excited-state gradient J. Neugebauer, E.J. Baerends, E. Efremov, F. Ariese and C. Gooijer, *Combined Theoretical and Experimental Deep-UV Resonance Raman Studies of Substituted Pyrenes*, Journal of Physical Chemistry A 109, 2100 (2005) (https://doi.org/10.1021/jp045360d)

VROA: (Resonance) vibrational Raman optical activity L. Jensen, J. Autschbach, M. Krykunov, and G.C. Schatz, *Resonance vibrational Raman optical activity: A time-dependent density functional theory approach*, Journal of Chemical Physics 127, 134101 (2007) (https://doi.org/10.1063/1.2768533)

Vibrational Circular Dichroism (VCD) V.P. Nicu J. Neugebauer S.K. Wolff and E.J. Baerends, *A vibrational circular dichroism implementation within a Slater-type-orbital based density functional framework and its application to hexa- and hepta-helicenes*, Theoretical Chemical Accounts 119, 245 (2008) (https://doi.org/10.1007/s00214-006-0234-x)

VCD analysis: VCDtools V.P. Nicu, J. Neugebauer and E.J. Baerends, *Effects of Complex Formation on Vibrational Circular Dichroism Spectra*, Journal of Physical Chemistry A 112, 6978 (2008) (https://doi.org/10.1021/jp710201q)

M.A.J. Koenis, O. Visser, L. Visscher, W.J. Buma, V.P. Nicu, *GUI Implementation of VCDtools, A Program to Analyze Computed Vibrational Circular Dichroism Spectra*, J. Chem. Inf. Model 60, 259 (2020) (https://pubs.acs.org/doi/abs/10.1021/acs.jcim.9b00956)

V.P. Nicu, *Revisiting an old concept: the coupled oscillator model for VCD. Part 1: the generalised coupled oscillator mechanism and its intrinsic connection to the strength of VCD signals*, Physical Chemistry Chemical Physics 18, 21202 (2016) (https://doi.org/10.1039/C6CP01282E).

Franck-Condon factors J.S. Seldenthuis, H.S.J. van der Zant, M.A. Ratner and J.M. Thijssen, *Vibrational Excitations in Weakly Coupled Single-Molecule Junctions: A Computational Analysis*, ACS Nano 2, 1445 (2008) (https://doi.org/10.1021/nn800170h)

13.2.2 PES Exploration

Samuel T Chill, Matthew Welborn, Rye Terrell, Liang Zhang, Jean-Claude Berthet, Andreas Pedersen, Hannes Jónsson and Graeme Henkelman *EON: software for long time simulations of atomic scale systems*, Modelling Simul. Mater. Sci. Eng. 22 055002 (2014) (https://doi.org/10.1088/0965-0393/22/5/055002)

CHAPTER

FOURTEEN

EXTERNAL PROGRAMS AND LIBRARIES

Click here for the list of programs and/or libraries used in the AMS package. On some platforms optimized libraries have been used and/or vendor specific MPI implementations.

CHAPTER

FIFTEEN

KEYWORDS

15.1 Links to manual entries

ams:

- *BondOrders* (page 266)
- *Constraints* (page 53)
- *ElasticTensor* (page 204)
- *Engine* (page 271)
- *EngineAddons* (page 284)
- *EngineDebugging* (page 488)
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- *GCMC* (page 164)
- *GeometryOptimization* (page 48)
- *IRC* (page 86)
- *LoadSystem* (page 40)
- *MolecularDynamics* (page 91)
- *Molecules* (page 267)
- *NEB* (page 79)
- *NormalModes* (page 211)
- *NumericalDifferentiation* (page 206)
- *NumericalPhonons* (page 234)
- *PESExploration* (page 172)
- *PESPointCharacter* (page 202)
- *PESScan* (page 73)
- *Print* (page 487)
- *Properties* (page 10)
- *Raman* (page 237)
- *Replay* (page 160)
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- *System* (page 31)
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- *Task* (page 10)
- *Thermo* (page 231)
- *TransitionStateSearch* (page 66)
- *UseSymmetry* (page 36)
- *VibrationalAnalysis > NormalModes > ModeSelect* (page 227)

ams_interactive:

- *Stop* (page 15)
- *StopProperties* (page 16)

amsbatch:

- *SystemsFromConformers* (page 293)
- *SystemsFromSMILES* (page 292)
- *SystemsFromTrajectory* (page 293)

analysis:

- *AutoCorrelation* (page 357)
- *AverageBinPlot* (page 371)
- *Histogram* (page 353)
- *Histogram > Axes > Axis > Atoms* (page 354)
- *Histogram > Axes > Axis > VecElements* (page 354)
- *MeanSquareDisplacement* (page 364)
- *RadialDistribution* (page 352)
- *Task* (page 350)
- *TrajectoryInfo* (page 348)

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- *InputMaxEnergy* (page 298)
- *Output* (page 304)
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- *Task* (page 297)

pipe:

- *WorkerCommand* (page 29)

15.2 Summary of all keywords

15.2.1 ams

`BondOrders`

Type Block

Description Configures details regarding the calculation/guessing of bond orders. To request the calculation of bond orders, use the 'Properties%BondOrders' key.

`Method`

Type Multiple Choice

Default value EngineWithGuessFallback

Options [Engine, Guess, EngineWithGuessFallback]

Description How to compute the bond orders when they are requested via the 'Properties%BondOrders' key.

'Engine': let the engine compute the bond orders. The specific method used to compute the bond orders depends on the engine selected, and it may be configurable in the engine's input. Note: the calculation may stop if the engine cannot compute bond orders.

'Guess': Use a bond guessing algorithm based on the system's geometry. This is the same algorithm that is used by the Graphical User Interface to guess bonds.

'EngineWithGuessFallback': let the engine compute the bond orders (same as in 'Engine' option) but if the engine did not produce any bond orders, use the bond guessing algorithm as a fallback opion.

`Constraints`

Type Block

Description The Constraints block allows geometry optimizations and potential energy surface scans with constraints. The constraints do not have to be satisfied at the start of the calculation.

`All`

Type String

Recurring True

Description Fix multiple distances using one the following formats: All [bondOrder] bonds at1 at2 [to distance] All triangles at1 at2 at3

The first option constrains all bonds between atoms at1 at2 to a certain length, while the second - bonds at1-at2 and at2-at3 as well as the angle between them.

The [bondOrder] can be a number or a string such as single, double, triple or aromatic. If it's omitted then any bond between specified atoms will be constrained. Atom names are case-sensitive and they must be as they are in the Atoms block, or an asterisk '*' denoting any atom. If the distance is omitted then the bond length from the initial geometry is used.

Important: only the bonds present in the system at the start of the simulation can be constrained, which means that the bonds may need to be specified in the System block.

Valid examples: All single bonds C C to 1.4 All bonds O H to 0.98 All bonds O H All bonds H * All triangles H * H

`Angle`

Type String

Recurring True

Description Fix the angle between three atoms. Three atom indices followed by an angle in degrees.

`Atom`

Type Integer

Recurring True

Description Fix the position of an atom. Just one integer referring to the index of the atom in the [System%Atoms] block.

`AtomList`

Type Integer List

Recurring True

Description Fix positions of the specified atoms. A list of integers referring to indices of atoms in the [System%Atoms] block.

`Block`

Type String

Recurring True

Description Name of the region to constrain as a rigid block. Regions are specified in the System%Atoms block.

`BlockAtoms`

Type Integer List

Recurring True

Description List of atom indices for a block constraint, where the internal degrees of freedom are frozen.

`Coordinate`

Type String

Recurring True

Description Fix a particular coordinate of an atom. Atom index followed by (x|y|z).

`DifDist`

Type String

Recurring True

Description Four atom indices i j k l followed by the distance in Angstrom. This will constrain the difference R(ij)-R(kl) at the given value.

`Dihedral`

Type String

Recurring True

Description Fix the dihedral angle between four atoms. Four atom indices followed by an angle in degrees.

`Distance`

Type String

Recurring True

Description Fix the distance between two atoms. Two atom indices followed by the distance in Angstrom.

`EqualStrain`

Type String

Description Exclusively for lattice optimizations:

Accepts a set of strain components [xx, xy, xz, yy, yz, zz] which are to be kept equal.

The applied strain will be determined by the average of the corresponding stress tensors components.

In AMSinput just check the corresponding check buttons.

`FixedRegion`

Type String

Recurring True

Description Fix positions of all atoms in a region.

`FreezeStrain`

Type String

Description Exclusively for lattice optimizations:

Freezes any lattice deformation corresponding to a particular component of the strain tensor.

Accepts a set of strain components [xx, xy, xz, yy, yz, zz] to be frozen.

In AMSinput just check the corresponding check buttons.

`SumDist`

Type String

Recurring True

Description Four atom indices i j k l followed by the distance in Angstrom. This will constrain the sum R(ij)+R(kl) at the given value.

ElasticTensor

Type Block

Description Options for numerical evaluation of the elastic tensor.

ConvergenceQuality

Type Multiple Choice

Default value Good

Options [Normal, Good, VeryGood]

GUI name Convergence

Description The tightness of the convergence of the geometry optimizations for each strain deformation. This should not be set higher than the overall convergence quality of the preceeding geometry optimization configured by the `GeometryOptimization%Convergence%Quality` keyword.

Parallel

Type Block

Description Options for double parallelization, which allows to split the available processor cores into groups working through all the available tasks in parallel, resulting in a better parallel performance. The keys in this block determine how to split the available processor cores into groups working in parallel.

nCoresPerGroup

Type Integer

GUI name Cores per group

Description Number of cores in each working group.

nGroups

Type Integer

GUI name Number of groups

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

nNodesPerGroup

Type Integer

GUI name Nodes per group

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

StrainStepSize

Type Float

Default value 0.001

Description Step size (relative) of strain deformations used for computing the elastic tensor numerically.

Engine

Type Block

Description The input for the computational engine. The header of the block determines the type of the engine.

`EngineAddons`

Type Block

Description This block configures all the engine add-ons.

`AtomEnergies`

Type Non-standard block

Description Add an element-dependent energy per atom. On each line, give the chemical element followed by the energy (in atomic units).

`D3Dispersion`

Type Block

Description This block configures the add-on that adds the Grimme D3 dispersion correction to the engine's energy, gradients, and stress tensor.

`Damping`

Type Multiple Choice

Default value BJ

Options [BJ, Zero]

Description Type of damping: BJ (Becke-Johnson) or Zero. BJ is recommended for most applications.

`Enabled`

Type Bool

Default value No

GUI name D3 dispersion

Description Enables the D3 dispersion correction addon.

`Functional`

Type String

Default value PBE

Description Use the D3 parameterization by Grimme for a given xc-functional. Accepts the same values as the –func command line option of the official dftd3 program. Note: the naming convention is different from elsewhere in the AMS suite. For example, BLYP should be called b-lyp.

`a1`

Type Float

Description The a1 parameter. Only used if Damping is set to BJ. If set, it overwrites the a1 value for the chosen functional.

`a2`

Type Float

Description The a2 parameter. Only used if Damping is set to BJ. If set, it overwrites the a2 value for the chosen functional.

`s6`

Type Float

Description The s6 parameter, global scaling parameter. If set, it overwrites the s6 value for the chosen functional.

`s8`

Type Float

Description The s8 parameter. If set, it overwrites the s8 value for the chosen functional.

`sr6`

Type Float

Description The sr6 parameter. Only used if Damping is set to Zero. If set, it overwrites the sr6 value for the chosen functional.

`D4Dispersion`

Type Block

Description This block configures the addon that adds the Grimme D4(EEQ) dispersion correction to the engine's energy, gradients, stress tensor and Hessian.

`Enabled`

Type Bool

Default value No

GUI name D4 dispersion

Description Enables the D4 dispersion correction addon.

`Functional`

Type Multiple Choice

Default value PBE

Options [HF, BLYP, BPBE, BP86, BPW, LB94, MPWLYP, MPWPW91, OLYP, OPBE, PBE, RPBE, REVPBE, PW86PBE, RPW86PBE, PW91, PW91P86, XLYP, B97, TPSS, REVTPSS, SCAN, B1LYP, B3LYP, BHLYP, B1P86, B3P86, B1PW91, B3PW91, O3LYP, REVPBE0, REVPBE38, PBE0, PWP1, PW1PW, MPW1PW91, MPW1LYP, PW6B95, TPSSH, TPSS0, X3LYP, M06L, M06, OMEGAB97, OMEGAB97X, CAM-B3LYP, LC-BLYP, LH07TSVWN, LH07SSVWN, LH12CTSSIRPW92, LH12CTSSIFPW92, LH14TCALPBE, B2PLYP, B2GPPLYP, MPW2PLYP, PWPB95, DSDBLYP, DSDPBE, DSDPBEB95, DSDPBEP86, DSDSVWN, DODBLYP, DODPBE, DODPBEB95, DODPBEP86, DODSVWN, PBE02, PBE0DH, DFTB(3ob), DFTB(mio), DFTB(pbc), DFTB(matsci), DFTB(ob2), B1B95, MPWB1K, REVTPSSH, GLYP, REVPBE0DH, REVTPSS0, REVDSDPBEP86, REVDSDPBEPBE, REVDSDBLYP, REVDODPBEP86, B97M, OMEGAB97M, R2SCAN]

Description Use the D4 parameterization by Grimme for a given xc-functional.

`Verbosity`

Type Multiple Choice

Default value Silent

Options [Silent, Normal, Verbose, VeryVerbose]

Description Controls the verbosity of the dftd4 code. Equivalent to the –silent and –verbose command line switches of the official dftd4 program.

`a1`

Type Float

Description The a1 parameter, see D4 article. The physically reasonable range for a1 is [0.0,1.0]. If set, it overwrites the a1 value for the chosen functional.

`a2`

Type Float

Description The a2 parameter, see D4 article. The physically reasonable range for a2 is [0.0,7.0]. If set, it overwrites the a2 value for the chosen functional.

`s6`

Type Float

Description The s6 parameter, see D4 article. The physically reasonable range for s6 is [0.0,1.0]. If set, it overwrites the s6 value for the chosen functional.

`s8`

Type Float

Description The s8 parameter, see D4 article. The physically reasonable range for s8 is [0.0,3.0]. If set, it overwrites the s8 value for the chosen functional.

`s9`

Type Float

Description The s9 parameter, see D4 article. If set, it overwrites the s9 value for the chosen functional.

`ExternalEngine`

Type Block

Description External engine as an addon

`Execute`

Type String

GUI name Execute

Description execute command

`ExternalStress`

Type Block

Description This block configures the addon that adds external stress term to the engine's energy and stress tensor.

`StressTensorVoigt`

Type Float List

Unit Hartree/Bohr^3

GUI name External stress tensor

Description The elements of the external stress tensor in Voigt notation. One should specify 6 numbers for 3D periodic system (order: xx,yy,zz,yz,xz,xy), 3 numbers for 2D periodic systems (order: xx,yy,xy) or 1 number for 1D periodic systems.

`UpdateReferenceCell`

Type Bool

Default value No

Description Whether ot not the reference cell should be updated every time the system changes (see documentation).

`PipeEngine`

Type Block

Description Pipe engine as an addon

`WorkerCommand`

Type String

GUI name Worker command

Description pipe worker command

`Pressure`

Type Float

Default value 0.0

Unit GPa

Description Add a hydrostatic pressure term to the engine's energy and stress tensor. Can only be used for 3D periodic boundary conditions.

`Repulsion`

Type Block

Description This block configures an addon that adds a repulsive Weeks-Chandler-Andersen potential to all atom pairs.

`Enabled`

Type Bool

Default value No

GUI name Repulsion

Description Enables the repulsive Weeks-Chandler-Andersen potential addon.

When enabled, all atom pairs will experience repulsion E = 4*epsilon*((sigma/r)^12 - (sigma/r)^6 + 1/4) at the distances shorter than about 1.12*sigma.

`Epsilon`

Type Float

Default value 0.01

Unit Hartree

Description The epsilon parameter in the potential equation. It is equal to the amount of energy added at r=sigma.

HydrogenSigmaScale

Type Float

Default value 0.75

Unit Angstrom

Description The sigma parameter for a pair of atoms where one of them is hydrogen is scaled with the given factor. For H-H interactions the sigma is scaled with this value squared.

Sigma

Type Float

Default value 0.55

Unit Angstrom

Description The sigma parameter in the potential equation. The potential is exactly zero at the distances larger than about 1.12*sigma

SkinLength

Type Float

Default value 2.0

Unit Angstrom

Description Technical parameter specifying skin length for the neighbor list generation. A larger value increases the neighbor list cutoff (and cost) but reduces the frequency it needs to be re-created.

WallPotential

Type Block

Description This block configures the addon that adds a spherical wall potential to the engine's energy and gradients.

Enabled

Type Bool

Default value No

Description Enables the wall potential addon. When enabled, a spherical wall of radius [Radius] around the origin will be added. The force due to the potential will decay exponentially inside the wall, will be close to [Prefactor*Gradient] outside and exactly half of that at the wall.

Gradient

Type Float

Default value 10.0

Unit 1/Angstrom

Description The radial gradient outside the sphere.

Prefactor

Type Float

Default value 0.01

Unit Hartree

Description The multiplier for the overall strength of the potential.

`Radius`

Type Float

Default value 30.0

Unit Angstrom

Value Range value > 0

Description The radius of the sphere, wherein the potential is close to zero.

`EngineDebugging`

Type Block

Description This block contains some options useful for debugging the computational engines.

`AlwaysClaimSuccess`

Type Bool

Default value No

Description If an engine fails, pretend that it worked. This can be useful when you know that an SCF might fail.

`CheckInAndOutput`

Type Bool

Default value No

Description Enables some additional checks on the input and output of an engine, e.g. for NaN values.

`ForceContinousPES`

Type Bool

Default value No

Description If this option is set, the engine will always run in continuous PES mode. For many engines this disables the use of symmetry, as this one always leads to a discontinuous PES around the symmetric points: Basically there is jump in the PES at the point where the symmetry detection starts classifying the system as symmetric. Normally the continuous PES mode of the engine (often disabling the symmetry) is only used when doing numerical derivatives, but this flag forces the engine to continuously run in this mode.

`IgnoreGradientsRequest`

Type Bool

Default value No

Description If this option is set, the engine will not do analytical gradients if asked for it, so that gradients will have to be evaluated numerically by AMS.

`IgnorePreviousResults`

Type Bool

Default value No

Description If this option is set, the engine will not receive information from previous calculations. Typically this information is used to restart the self consistent procedure of the engine.

IgnoreStressTensorRequest

Type Bool

Default value No

Description If this option is set, the engine will not calculate an analytical stress tensor if asked for it, so that the stress tensor will have to be evaluated numerically by AMS.

NeverQuiet

Type Bool

Default value No

Description Makes the engine ignore the request to work quietly.

RandomFailureChance

Type Float

Default value 0.0

Description Makes the engine randomly report failures, even though the results are actually fine. Useful for testing error handling on the application level.

RandomNoiseInEnergy

Type Float

Default value 0.0

Unit Hartree

Description Adds a random noise to the energy returned by the engine. The random contribution is drawn from [-r,r] where r is the value of this keyword.

RandomNoiseInGradients

Type Float

Default value 0.0

Unit Hartree/Angstrom

Description Adds a random noise to the gradients returned by the engine. A random number in the range [-r,r] (where r is the value of this keyword) is drawn and added separately to each component of the gradient.

RandomStopChance

Type Float

Default value 0.0

Description Makes the engine randomly stop. Can be used to simulate crashes.

EngineRestart

Type String

Description The path to the file from which to restart the engine.

Should be a proper engine result file (like adf.rkf, band.rkf etc), or the name of the results directory containing it.

ExitCondition

Type Block

Recurring True

Description If any of the specified exitconditions are met, the AMS driver will exit cleanly.

`AtomsTooClose`

Type Block

Description If any pair of atoms is closer than the specified minimum value, the program will exit cleanly.

`MinimumDistance`

Type Float

Default value 0.7

Unit Angstrom

Description Two atoms closer than this threshold value are considered too close.

`PairCalculation`

Type Multiple Choice

Default value NeighborList

Options [NeighborList, DistanceMatrix]

Description Two atoms closer than this threshold value are considered too close.

`EngineEnergyUncertainty`

Type Block

Description If the engine reports an uncertainty that is too high, the program will exit cleanly.

`MaxUncertainty`

Type Float

Default value 0.001

Unit Hartree

Description Threshold for Engine Energy Uncertainty divided by Normalization (by default the number of atoms)

`Normalization`

Type Float

Value Range value >= 0.0

Description Divide the reported Engine Energy Uncertainty by this normalization. Will divide by the number of atoms if unset.

`EngineGradientsUncertainty`

Type Block

Description If the engine reports an uncertainty in the magnitude of the nuclear gradient of any atom that is too high, the program will exit cleanly.

`MaxUncertainty`

Type Float

Default value 0.01580221

Unit Hartree/Angstrom

Description Threshold for Engine Gradients Uncertainty.

`Type`

Type Multiple Choice

Default value AtomsTooClose

Options [AtomsTooClose, EngineEnergyUncertainty, EngineGradientsUncertainty]

Description The type of exitcondition specified

`FallbackSolveAfterEngineFailure`

Type Bool

Default value Yes

Description If the engine fails to Solve, try to re-run the Solve without restarting the engine from the previous results. This generally decreases the engine falure rate. Only relevant certain tasks, such as GeometryOptimization, MolecularDynamics, Replay, IRC.

`GCMC`

Type Block

Description This block controls the Grand Canonical Monte Carlo (GCMC) task.

By default, molecules are added at random positions in the simulation box. The initial position is controlled by

`AccessibleVolume`

Type Float

Default value 0.0

Description Volume available to GCMC, in cubic Angstroms. AccessibleVolume should be specified for "Accessible" and "FreeAccessible" [VolumeOption].

`Box`

Type Block

Description Boundaries of the insertion space, i.e. coordinates of the origin of an inserted molecule (coordinates of an atom of the inserted system may fall outside the box).

For a periodic dimension it is given as a fraction of the simulation box (the full 0 to 1 range by default). For a non-periodic dimension it represents absolute Cartesian coordinates in Angstrom (the system's bounding box extended by the MaxDistance value by default).

`Amax`

Type Float

Description Coordinate of the upper bound along the first axis.

`Amin`

Type Float

Description Coordinate of the lower bound along the first axis.

`Bmax`

Type Float

Description Coordinate of the upper bound along the second axis.

Bmin

Type Float

Description Coordinate of the lower bound along the second axis.

Cmax

Type Float

Description Coordinate of the upper bound along the third axis.

Cmin

Type Float

Description Coordinate of the lower bound along the third axis.

Ensemble

Type Multiple Choice

Default value Mu-VT

Options [Mu-VT, Mu-PT]

Description Select the MC ensemble: Mu-VT for fixed volume or Mu-PT for variable volume. When the Mu-PT ensemble is selected the [Pressure] and [VolumeChangeMax] should also be specified.

Iterations

Type Integer

GUI name Number of GCMC iterations

Description Number of GCMC moves.

MapAtomsToOriginalCell

Type Bool

Default value Yes

Description Keeps the atom (mostly) in the original cell by mapping them back before the geometry optimizations.

MaxDistance

Type Float

Default value 3.0

Unit Angstrom

GUI name Add molecules within

Description The max distance to other atoms of the system when adding the molecule.

MinDistance

Type Float

Default value 0.3

Unit Angstrom

GUI name Add molecules not closer than

Description Keep the minimal distance to other atoms of the system when adding the molecule.

`Molecule`

Type Block

Recurring True

GUI name Molecules

Description This block defines the molecule (or atom) that can be inserted/moved/deleted with the MC method. The coordinates should form a reasonable structure. The MC code uses these coordinates during the insertion step by giving them a random rotation, followed by a random translation to generate a random position of the molecule inside the box. Currently, there is no check to make sure all atoms of the molecule stay inside the simulation box. The program does check that the MaxDistance/MinDistance conditions are satisfied.

`ChemicalPotential`

Type Float

Unit Hartree

Description Chemical potential of the molecule (or atom) reservoir.

It is used when calculating the Boltzmann accept/reject criteria after a MC move is executed. This value can be derived from first principles using statistical mechanics, or equivalently, it can be determined from thermochemical tables available in literature sources. For example, the proper chemical potential for a GCMC simulation in which single oxygen atoms are exchanged with a reservoir of O2 gas, should equal 1/2 the chemical potential of O2 at the temperature and pressure of the reservoir:

cmpot = Mu_O(T,P) = 1/2*Mu_O2(T,P) = 1/2 * [Mu_ref(T,P_ref) + kT*Log(P/Pref) - E_diss]

where the reference chemical potential [Mu_ref(T,P_ref)] is the experimentally determined chemical potential of O2 at T and Pref; kT*Log(P/Pref) is the pressure correction to the free energy, and E_diss is the dissociation energy of the O2 molecule.

`NoAddRemove`

Type Bool

Default value No

GUI name Fix molecule

Description Set to True to tell the GCMC code to keep the number of molecules/atoms of this type fixed.

It will thus disable Insert/Delete moves on this type, meaning it can only do a displacement move, or volume change move (for an NPT ensemble).

`SystemName`

Type String

GUI name Molecule

Description String ID of a named [System] to be inserted. The lattice specified with this System, if any, is ignored and the main system's lattice is used instead.

`NonAccessibleVolume`

Type Float

Default value 0.0

GUI name Non-accessible volume

Description Volume not available to GCMC, in cubic Angstroms. NonAccessibleVolume may be specified for the "Free" [VolumeOption] to reduce the accessible volume.

`NumAttempts`

Type Integer

Default value 1000

GUI name Max tries

Description Try inserting/moving the selected molecule up to the specified number of times or until all constraints are satisfied. If all attempts fail a message will be printed and the simulation will stop. If the MaxDistance-MinDistance interval is small this number may have to be large.

`Pressure`

Type Float

Default value 0.0

Unit Pascal

Description Pressure used to calculate the energy correction in the Mu-PT ensemble. Set it to zero for incompressible solid systems unless at very high pressures.

`Removables`

Type Non-standard block

Description The Removables can be used to specify a list of molecules that can be removed or moved during this GCMC calculation. Molecules are specified one per line in the format following format: MoleculeName atom1 atom2 … The MoleculeName must match a name specified in one of the [Molecule] blocks. The atom indices refer to the whole input System and the number of atoms must match that in the specified Molecule. A suitable Removables block is written to the standard output after each accepted MC move. If you do so then you should also replace the initial atomic coordinates with the ones found in the same file. If a [Restart] key is present then the Removables block is ignored.

`Restart`

Type String

Description Name of an RKF restart file. Upon restart, the information about the GCMC input parameters, the initial system (atomic coordinates, lattice, charge, etc.) and the MC molecules (both already inserted and to be inserted) are read from the restart file. The global GCMC input parameters and the MC Molecules can be modified from input. Any parameter not specified in the input will use its value from the restart file (i.e. not the default value). Molecules found in the restart file do not have to be present as named Systems in the input, however if there is a System present that matches the name of a molecule from restart then the System's geometry will replace that found in the restart file. It is also possible to specify new Molecules in the input, which will be added to the pool of the MC molecules from restart.

`SwapAtoms`

Type Block

Description Experimental: Occasionally swap the coordinates of a random pair of atoms from two regions.

`Probability`

Type Float

Default value 0.0

Description Probability of performing a swap move instead of any other GCMC move in a single GCMC iteration.

`Regions`

Type String

Description Names of two regions to swap between (separated by a space).

`Temperature`

Type Float

Default value 300.0

Unit Kelvin

Description Temperature of the simulation. Increase the temperature to improve the chance of accepting steps that result in a higher energy.

`UseGCPreFactor`

Type Bool

Default value Yes

GUI name Use GC prefactor

Description Use the GC pre-exponential factor for probability.

`VolumeChangeMax`

Type Float

Default value 0.05

Description Fractional value by which logarithm of the volume is allowed to change at each step. The new volume is then calculated as Vnew = exp(random(-1:1)*VolumeChangeMax)*Vold

`VolumeOption`

Type Multiple Choice

Default value Free

Options [Free, Total, Accessible, FreeAccessible]

GUI name Volume method

Description Specifies the method to calculate the volume used to calculate the GC pre-exponential factor and the energy correction in the Mu-PT ensemble: Free: V = totalVolume - occupiedVolume - NonAccessibleVolume; Total: V = totalVolume; Accessible: V = AccessibleVolume; FreeAccessible: V = AccessibleVolume - occupiedVolume. The AccessibleVolume and NonAccessibleVolume are specified in the input, the occupiedVolume is calculated as a sum of atomic volumes.

`GeometryOptimization`

Type Block

Description Configures details of the geometry optimization and transition state searches.

`CalcPropertiesOnlyIfConverged`

Type Bool

Default value Yes

Description Compute the properties requested in the 'Properties' block, e.g. Frequencies or Phonons, only if the optimization (or transition state search) converged. If False, the properties will be computed even if the optimization did not converge.

`Convergence`

Type Block

Description Convergence is monitored for up to 4 quantities: the energy change, the Cartesian gradients, the Cartesian step size, and for lattice optimizations the stress energy per atom. Convergence criteria can be specified separately for each of these items.

`Energy`

Type Float

Default value 1e-05

Unit Hartree

Value Range value > 0

GUI name Energy convergence

Description The criterion for changes in the energy. The energy is considered converged when the change in energy is smaller than this threshold times the number of atoms.

`Gradients`

Type Float

Default value 0.001

Unit Hartree/Angstrom

Value Range value > 0

GUI name Gradient convergence

Description Threshold for nuclear gradients.

`Quality`

Type Multiple Choice

Default value Custom

Options [VeryBasic, Basic, Normal, Good, VeryGood, Custom]

GUI name Convergence

Description A quick way to change convergence thresholds: 'Good' will reduce all thresholds by an order of magnitude from their default value. 'VeryGood' will tighten them by two orders of magnitude. 'Basic' and 'VeryBasic' will increase the thresholds by one or two orders of magnitude respectively.

`Step`

Type Float

Default value 0.01

Unit Angstrom

Value Range value > 0

GUI name Step convergence

Description The maximum Cartesian step allowed for a converged geometry.

`StressEnergyPerAtom`

Type Float

Default value 0.0005

Unit Hartree

Value Range value > 0

Description Threshold used when optimizing the lattice vectors. The stress is considered 'converged' when the maximum value of stress_tensor * cell_volume / number_of_atoms is smaller than this threshold (for 2D and 1D systems, the cell_volume is replaced by the cell_area and cell_length respectively).

`CoordinateType`

Type Multiple Choice

Default value Auto

Options [Auto, Delocalized, Cartesian]

GUI name Optimization space

Description Select the type of coordinates in which to perform the optimization. 'Auto' automatically selects the most appropriate CoordinateType for a given Method.

If 'Auto' is selected, Delocalized coordinates will be used for the Quasi-Newton method, while Cartesian coordinates will be used for all other methods.

`Dimer`

Type Block

Description Options for the Dimer method for transition state search.

`AngleThreshold`

Type Float

Default value 1.0

Unit Degree

Description The rotation is considered converged when the the rotation angle falls below the specified threshold.

`DimerDelta`

Type Float

Default value 0.01

Unit Angstrom

Description Eucledian distance between the midpoint and the endpoint.

`ExtrapolateForces`

Type Bool

Default value Yes

Description Set to false to call engine to calculate forces at the extrapolated rotation angle instead of extrapolating them.

`LBFGSMaxVectors`

Type Integer

Default value 10

Description Max number of vectors for the L-BFGS algorithm to save.

`MaxRotationIterations`

Type Integer

Default value 10

Description Maximum number of rotation iterations for a single translation step.

`Region`

Type String

Default value *

Description Include only atoms of the specified region(s) in the rotations, which allows searching for a transition state involving selected atoms only.

`RotationTrustRadius`

Type Float

Default value 0.1

Unit Angstrom

Description L-BFGS trust radius during rotation iterations.

`TranslationTrustRadius`

Type Float

Default value 0.1

Unit Angstrom

Description L-BFGS trust radius during translation iterations.

`EngineAutomations`

Type Block

Description The optimizer can change some settings of the engine, based for instance on the error. The idea is to allow the engine to be a bit quicker at the start, and more accurate towards the end. Automations are always engine specific.

`Enabled`

Type Bool

Default value Yes

Description Whether or not autotions are enabled at all.

`Gradient`

Type Block

Recurring True

Description A gradient-based automation.

`FinalValue`

Type Float

Description This value will be used whenever the gradient is less than GradientLow

`HighGradient`

Type Float

Default value 1.0

Unit Hartree/Angstrom

Description Defines a large gradient. When the actual gradient is between GradientHigh and GradientLow a linear interpolation scheme is used for kT (on a log scale).

`InitialValue`

Type Float

Description This value will be used at the first geometry, and whenever the gradient is higher than GradientHigh

`LowGradient`

Type Float

Default value 1.0

Unit Hartree/Angstrom

Description Defines a small gradient, see GradientHigh

`UseLogInterpolation`

Type Bool

Default value Yes

Description Whether to use interpolation on a log (y) scale or not

`Variable`

Type String

Default value

Description variable to be tweaked for the engine.

`Iteration`

Type Block

Recurring True

Description Geometry step based automation.

`FinalValue`

Type Float

Description

`FirstIteration`

Type Integer

Default value 1

Description When the actual gradient is between the first and last iteration, a linear interpolation is used.

`InitialValue`

Type Float

Description This value will be used when the iteration number is smaller or equal to FirstIteration

`LastIteration`

Type Integer

Default value 10

Description Where the automation should reach the FinalValue

`UseLogInterpolation`

Type Bool

Default value Yes

Description Whether to use interpolation on a log (y) scale or not

`Variable`

Type String

Default value

Description variable to be tweaked for the engine.

`FIRE`

Type Block

Description This block configures the details of the FIRE optimizer. The keywords name correspond the the symbols used in the article describing the method, see PRL 97, 170201 (2006).

`AllowOverallRotation`

Type Bool

Default value Yes

Description Whether or not the system is allowed to freely rotate during the optimization. This is relevant when optimizing structures in the presence of external fields.

`AllowOverallTranslation`

Type Bool

Default value No

Description Whether or not the system is allowed to translate during the optimization. This is relevant when optimizing structures in the presence of external fields.

`MapAtomsToUnitCell`

Type Bool

Default value No

Description Map the atoms to the central cell at each geometry step.

`NMin`

Type Integer

Default value 5

Description Number of steps after stopping before increasing the time step again.

`alphaStart`

Type Float

Default value 0.1

Description Steering coefficient.

`dtMax`

Type Float

Default value 1.0

Unit Femtoseconds

Description Maximum time step used for the integration. For ReaxFF and APPLE&P, this value is reduced by 50%.

`dtStart`

Type Float

Default value 0.25

Unit Femtoseconds

Description Initial time step for the integration.

`fAlpha`

Type Float

Default value 0.99

Description Reduction factor for the steering coefficient.

`fDec`

Type Float

Default value 0.5

Description Reduction factor for reducing the time step in case of uphill movement.

`fInc`

Type Float

Default value 1.1

Description Growth factor for the integration time step.

`strainMass`

Type Float

Default value 0.5

Description Fictitious relative mass of the lattice degrees of freedom. This controls the stiffness of the lattice degrees of freedom relative to the atomic degrees of freedom, with smaller values resulting in a more aggressive optimization of the lattice.

`HessianFree`

Type Block

Description Configures details of the Hessian-free (conjugate gradients or L-BFGS) geometry optimizer.

`Step`

Type Block

Description

`MaxCartesianStep`

Type Float

Default value 0.1

Unit Angstrom

Description Limit on a single Cartesian component of the step.

`MinRadius`

Type Float

Default value 0.0

Unit Angstrom

Description Minimum value for the trust radius.

`TrialStep`

Type Float

Default value 0.0005

Unit Angstrom

Description Length of the finite-difference step when determining curvature. Should be smaller than the step convergence criterion.

`TrustRadius`

Type Float

Default value 0.2

Unit Angstrom

Description Initial value of the trust radius.

`InitialHessian`

Type Block

Description Options for initial model Hessian when optimizing systems with the Quasi-Newton method.

`File`

Type String

GUI name Initial Hessian from

Description KF file containing the initial Hessian (or the results dir. containing it). This can be used to load a Hessian calculated in a previously with the [Properties%Hessian] keyword.

`Type`

Type Multiple Choice

Default value Auto

Options [Auto, UnitMatrix, Swart, FromFile, Calculate, CalculateWithFastEngine]

GUI name Initial Hessian

Description Select the type of initial Hessian. Auto: let the program pick an initial model Hessian. UnitMatrix: simplest initial model Hessian, just a unit matrix in the optimization coordinates. Swart: model Hessian from M. Swart. FromFile: load the Hessian from the results of a previous calculation (see InitialHessian%File). Calculate: compute the initial Hessian (this may be computationally expensive and it is mostly recommended for TransitionStateSearch calculations). CalculateWithFastEngine: compute the initial Hessian with a faster engine.

`KeepIntermediateResults`

Type Bool

Default value No

Description Whether the full engine result files of all intermediate steps are stored on disk. By default only the last step is kept, and only if the geometry optimization converged. This can easily lead to huge amounts of data being stored on disk, but it can sometimes be convenient to closely monitor a tricky optimization, e.g. excited state optimizations going through conical intersections, etc. …

`MaxIterations`

Type Integer

Value Range value >= 0

GUI name Maximum number of iterations

Description The maximum number of geometry iterations allowed to converge to the desired structure.

`MaxRestarts`

Type Integer

Default value 0

Description If a geometry optimization of a system with no symmetry operators (or with explicitly disabled symmetry: `UseSymmetry False`) and enabled PES point characterization converges to a transition state (or higher order saddle point), it can be restarted automatically after a small displacement along the imaginary vibrational mode. In case the restarted optimization again does not find a minimum, this can happen multiple times in succession. This keyword sets the maximum number of restarts. The default value is 0, so the automatic restarting is disabled by default.

`Method`

Type Multiple Choice

Default value Auto

Options [Auto, Quasi-Newton, FIRE, L-BFGS, ConjugateGradients, Dimer]

GUI name Optimization method

Description Select the optimization algorithm employed for the geometry relaxation. Currently supported are:

the Hessian-based Quasi-Newton-type BFGS algorithm, the fast inertial relaxation method (FIRE),

the limited-memory BFGS method,

and the conjugate gradients method. The default is to choose an appropriate method automatically based on the engine's speed, the system size and the supported optimization options.

`OptimizeLattice`

Type Bool

Default value No

Description Whether to also optimize the lattice for periodic structures. This is currently supported with the Quasi-Newton, FIRE, and L-BFGS optimizers.

`PretendConverged`

Type Bool

Default value No

Description Normally a non-converged geometry optimization is considered an error. If this keyword is set to True, the optimizer will only produce a warning and still claim that the optimization is converged. (This is mostly useful for scripting applications, where one might want to consider non-converged optimizations still successful jobs.)

`Quasi-Newton`

Type Block

Description Configures details of the Quasi-Newton geometry optimizer.

`MaxGDIISVectors`

Type Integer

Default value 0

Description Sets the maximum number of GDIIS vectors. Setting this to a number >0 enables the GDIIS method.

`Step`

Type Block

Description

`TrustRadius`

Type Float

Description Initial value of the trust radius.

`VaryTrustRadius`

Type Bool

Description Whether to allow the trust radius to change during optimization. By default True during energy minimization and False during transition state search.

`UpdateTSVectorEveryStep`

Type Bool

Default value Yes

GUI name Update TSRC vector every step

Description Whether to update the TS reaction coordinate at each step with the current eigenvector.

RestartDisplacement

Type Float

Default value 0.05

Unit Angstrom

Description If a geometry optimization of a system with no symmetry operators (or with explicitly disabled symmetry: `UseSymmetry False`) and enabled PES point characterization converges to a transition state (or higher order saddle point), it can be restarted automatically after a small displacement along the imaginary vibrational mode. This keywords sets the size of the displacement for the furthest moving atom.

IRC

Type Block

Description Configures details of the Intrinsic Reaction Coordinate optimization.

Convergence

Type Block

Description Convergence at each given point is monitored for two items: the Cartesian gradient and the calculated step size. Convergence criteria can be specified separately for each of these items. The same criteria are used both in the inner IRC loop and when performing energy minimization at the path ends.

Gradients

Type Float

Default value 0.001

Unit Hartree/Angstrom

GUI name Gradient convergence

Description Convergence criterion for the max component of the residual energy gradient.

Step

Type Float

Default value 0.001

Unit Angstrom

GUI name Step convergence

Description Convergence criterion for the max component of the step in the optimization coordinates.

CoordinateType

Type Multiple Choice

Default value Cartesian

Options [Cartesian, Delocalized]

GUI name Coordinates used for optimization

Description Select the type of coordinates in which to perform the optimization. Note that the Delocalized option should be considered experimental.

`Direction`

Type Multiple Choice

Default value Both

Options [Both, Forward, Backward]

Description Select direction of the IRC path. The difference between the Forward and the Backward directions is determined by the sign of the largest component of the vibrational normal mode corresponding to the reaction coordinate at the transition state geometry. The Forward path correspond to the positive sign of the component. If Both is selected then first the Forward path is computed followed by the Backward one.

`InitialHessian`

Type Block

Description Options for initial Hessian at the transition state. The first eigenvalue of the initial Hessian defines direction of the first forward or backward step. This block is ignored when restarting from a previous IRC calculation because the initial Hessian found in the restart file is used.

`File`

Type String

GUI name File

Description If 'Type' is set to 'FromFile' then in this key you should specify the RKF file containing the initial Hessian (or the ams results dir. containing it). This can be used to load a Hessian calculated previously with the 'Properties%Hessian' keyword. If you want to also use this file for the initial geometry then also specify it in a 'LoadSystem' block.

`Type`

Type Multiple Choice

Default value Calculate

Options [Calculate, FromFile]

GUI name Initial Hessian

Description Calculate the exact Hessian for the input geometry or load it from the results of a previous calculation.

`KeepConvergedResults`

Type Bool

Default value Yes

Description Keep the binary RKF result file for every converged IRC point. These files may contain more information than the main ams.rkf result file.

`MaxIRCSteps`

Type Integer

GUI name Maximum IRC steps

Description Soft limit on the number of IRC points to compute in each direction. After the specified number of IRC steps the program will switch to energy minimization and complete the path. This option should be used when you are interested only in the reaction path area near the transition state. Note that even if the soft limit has been hit and the calculation has completed, the IRC can still be restarted with a 'RedoBackward' or 'RedoForward' option.

`MaxIterations`

Type Integer

Default value 300

GUI name Maximum iterations

Description The maximum number of geometry iterations allowed to converge the inner IRC loop. If optimization does not converge within the specified number of steps, the calculation is aborted.

`MaxPoints`

Type Integer

Default value 100

GUI name Maximum points

Description Hard limit on the number of IRC points to compute in each direction. After the specified number of IRC steps the program will stop with the current direction and switch to the next one. If both 'MaxPoints' and 'MaxIRCSteps' are set to the same value then 'MaxPoints' takes precedence, therefore this option should be used to set a limit on the number of IRC steps if you intend to use the results later for a restart.

`MinEnergyProfile`

Type Bool

Default value No

GUI name Minimum energy profile

Description Calculate minimum energy profile (i.e. no mass-weighting) instead of the IRC.

`MinPathLength`

Type Float

Default value 0.1

Unit Angstrom

Description Minimum length of the path required before switching to energy minimization. Use this to overcome a small kink or a shoulder on the path.

`Restart`

Type Block

Description Restart options. Upon restart, the information about the IRC input parameters and the initial system (atomic coordinates, lattice, charge, etc.) is read from the restart file. The IRC input parameters can be modified from input. Except for 'MaxPoints' and 'Direction' all parameters not specified in the input will use their values from the restart file. The 'MaxPoints' and 'Direction' will be reset to their respective default values if not specified in the input. By default, the IRC calculation will continue from the point where it left off. However, the 'RedoForward' and/or 'RedoBackward' option can be used to enforce recalculation of a part of the reaction path, for example, using a different 'Step' value.

`File`

Type String

GUI name Restart

Description Name of an RKF restart file generated by a previous IRC calculation. Do not use this key to provide an RKF file generated by a TransitionStateSearch or a SinglePoint calculation, use the 'LoadSystem' block instead.

`RedoBackward`

Type Integer

Default value 0

Description IRC step number to start recalculating the backward path from. By default, if the backward path has not been completed then start after the last completed step. If the backward path has been completed and the 'RedoBackward' is omitted then no point on the backward path will be recomputed.

`RedoForward`

Type Integer

Default value 0

Description IRC step number to start recalculating the forward path from. By default, if the forward path has not been completed then start after the last completed step. If the forward path has been completed and the 'RedoForward' is omitted then no point on the forward path will be recomputed.

`Step`

Type Float

Default value 0.2

GUI name Step size

Description IRC step size in mass-weighted coordinates, sqrt(amu)*bohr. One may have to increase this value when heavy atoms are involved in the reaction, or decrease it if the reactant or products are very close to the transition state.

`LoadEngine`

Type String

Description The path to the file from which to load the engine configuration. Replaces the Engine block.

`LoadSystem`

Type Block

Recurring True

Description Block that controls reading the chemical system from a KF file instead of the [System] block.

`File`

Type String

Description The path of the KF file from which to load the system. It may also be the results directory containing it.

Section

Type String

Default value Molecule

Description The section on the KF file from which to load the system.

Log

Type Non-standard block

Description Configures the debugging loggers. Syntax: 'Level LoggerName'. Possible Levels: All, Debug, Info, Warning, Error, Fatal.

MolecularDynamics

Type Block

Description Configures molecular dynamics (with the velocity-Verlet algorithm) with and without thermostats. This block allows to specify the details of the molecular dynamics calculation.

AddMolecules

Type Block

Recurring True

GUI name Add molecules

Description This block controls adding molecules to the system (a.k.a. the Molecule Gun). Multiple occurrences of this block are possible.

By default, molecules are added at random positions in the simulation box with velocity matching the current system temperature. The initial position can be modified using one of the following keywords: Coords, CoordsBox, FractionalCoords, FractionalCoordsBox. The Coords and FractionalCoords keys can optionally be accompanied by CoordsSigma or FractionalCoordsSigma, respectively.

AtomTemperature

Type Float

Default value 0.0

Unit Kelvin

Description Add random velocity corresponding to the specified temperature to individual atoms of the molecule. This only affects rotational and internal degrees of freedom, not the net translational velocity of the inserted molecule as set by the other options.

ContactDistance

Type Float

Default value 0.0

Unit Angstrom

Description Translate the bullet along the velocity vector until it comes within ContactDistance of any other atom.

Coords

Type Float List

Unit Angstrom

Description Place molecules at or around the specified Cartesian coordinates.

This setting takes precedence over other ways to specify initial coordinates of the molecule: [CoordsBox], [FractionalCoords], and [FractionalCoordsBox].

`CoordsBox`

Type Float List

Unit Angstrom

Description Place molecules at random locations inside the specified box in Cartesian coordinates.

Coordinates of the box corners are specified as: Xmin, Xmax, Ymin, Ymax, Zmin, Zmax. This setting is ignored if Coords is used.

In AMSinput, if this field is not empty it will be used instead of the default Coords.

`CoordsSigma`

Type Float List

Unit Angstrom

Description Sigma values (one per Cartesian axis) for a Gauss distribution of the initial coordinates. Can only be used together with Coords.

`DeviationAngle`

Type Float

Default value 0.0

Unit Degree

Description Randomly tilt the shooting direction up to this angle away from the VelocityDirection vector.

`Energy`

Type Float

Unit Hartree

Description Initial kinetic energy of the molecule in the shooting direction.

`EnergySigma`

Type Float

Default value 0.0

Unit Hartree

Description Sigma value for the Gauss distribution of the initial kinetic energy around the specified value. Should only be used together with Energy.

`FractionalCoords`

Type Float List

Description Place molecules at or around the specified fractional coordinates in the main system's lattice. For non-periodic dimensions a Cartesian value in Angstrom is expected. This setting is ignored if [Coords] or [CoordsBox] is used.

`FractionalCoordsBox`

Type Float List

Description Place molecules at random locations inside the box specified as fractional coordinates in the main system's lattice.

Coordinates of the box corners are specified as: Xmin, Xmax, Ymin, Ymax, Zmin, Zmax.

For non-periodic dimensions the Cartesian value in Angstrom is expected.

This setting is ignored if [Coords], [CoordsBox], or [FractionalCoords] is used.

`FractionalCoordsSigma`

Type Float List

Description Sigma values (one per axis) for a Gauss distribution of the initial coordinates. For non-periodic dimensions the Cartesian value in Angstrom is expected. Can only be used together with FractionalCoords.

`Frequency`

Type Integer

Default value 0

Description A molecule is added every [Frequency] steps after the StartStep.

There is never a molecule added at step 0.

`MinDistance`

Type Float

Default value 0.0

Unit Angstrom

Description Keep the minimal distance to other atoms of the system when adding the molecule.

`MoleFraction`

Type Float

Description Defines a mixture to be deposited using one AddMolecules block per component.

AMS will randomly alternate between any guns that have MoleFraction set. These need to all have the same settings for StartStep, StopStep and Frequency. Any additional AddMolecules blocks without MoleFraction will remain completely independent.

`NumAttempts`

Type Integer

Default value 10

Description Try adding the molecule up to the specified number of times or until the MinDistance constraint is satisfied. If all attempts fail a message will be printed and the simulation will continue normally.

`Rotate`

Type Bool

Default value No

Description Rotate the molecule randomly before adding it to the system.

`StartStep`

Type Integer

Default value 0

Description Step number when the first molecule should be added. After that, molecules are added every Frequency steps.

For example, ff StartStep=99 and Frequency=100 then a molecule will be added at steps 99, 199, 299, etc…

No molecule will be added at step 0, so if StartStep=0 the first molecule is added at the step number equal to [Frequency].

`StopStep`

Type Integer

Description Do not add this molecule after the specified step.

`System`

Type String

Description String ID of the [System] that will be added with this 'gun'.

The lattice specified with this System is ignored and the main system's lattice is used instead.

AMSinput adds the system at the coordinates of the System (thus setting Coords to the center of the System).

`Temperature`

Type Float

Unit Kelvin

Description Initial energy of the molecule in the shooting direction will correspond to the given temperature.

`TemperatureSigma`

Type Float

Default value 0.0

Unit Kelvin

Description Sigma value for the Gauss distribution of the initial temperature the specified value. Should only be used together with Temperature.

`Velocity`

Type Float

Unit Angstrom/fs

Description Initial velocity of the molecule in the shooting direction.

`VelocityDirection`

Type Float List

Description Velocity direction vector for aimed shooting. It will be random if not specified.

In AMSinput add one or two atoms (which may be dummies).

One atom: use vector from center of the system to add to that atom.

Two atoms: use vector from the first to the second atom.

`VelocitySigma`

Type Float

Default value 0.0

Unit Angstrom/fs

Description Sigma value for the Gauss distribution of the initial velocity around the specified value. Should only be used together with Velocity.

`ApplyForce`

Type Block

Recurring True

Description The ApplyForce keyword can be used to apply an arbitrary constant force to a certain (subgroups of) atoms in the system

`Force`

Type Float List

Unit Hartree/Bohr

Description Defines the constant force vector

`PerAtom`

Type Bool

Default value No

Description If enabled, the Force vector is applied separately to every atom in the selected Region, so that the total net force on the Region equals the value of Force times the number of atoms in Region. This was the behaviour of ApplyForce in AMS2022. By default, with PerAtom disabled, the Force vector defines the total net force on the Region, so the force applied to each atom equals the value of Force divided by the number of atoms in Region.

`Region`

Type String

Recurring True

Description Apply the constant force to all atoms in this region.

`ApplyVelocity`

Type Block

Recurring True

Description The ApplyVelocity keyword can be used to move an arbitrary group of atoms in the system with a constant net velocity

`Components`

Type Multiple Choice

Default value XY

Options [X, Y, Z, XY, YZ, XZ, XYZ]

Description Select which components of the Velocity vector are used to set the corresponding components of the net velocity of the specified set of atoms. Any other components of Velocity are ignored and the motion of the selected atoms in those directions is unaffected by ApplyVelocity.

`Region`

Type String

Recurring True

Description Applies the defined velocity to all atoms in this region.

`Velocity`

Type Float List

Unit Angstrom/fs

Recurring False

Description The constant velocity that will be applied to the specified atoms.

`Barostat`

Type Block

Description This block allows to specify the use of a barostat during the simulation.

`BulkModulus`

Type Float

Default value 2200000000.0

Unit Pascal

Description An estimate of the bulk modulus (inverse compressibility) of the system for the Berendsen barostat.

This is only used to make Tau correspond to the true observed relaxation time constant. Values are commonly on the order of 10-100 GPa (1e10 to 1e11) for solids and 1 GPa (1e9) for liquids (2.2e9 for water). Use 1e9 to match the behavior of standalone ReaxFF.

`ConstantVolume`

Type Bool

Default value No

Description Keep the volume constant while allowing the box shape to change.

This is currently supported only by the MTK barostat.

`Duration`

Type Integer List

Description Specifies how many steps should a transition from a particular pressure to the next one in sequence take.

`Equal`

Type Multiple Choice

Default value None

Options [None, XYZ, XY, YZ, XZ]

Description Enforce equal scaling of the selected set of dimensions. They will be barostatted as one dimension according to the average pressure over the components.

`Pressure`

Type Float List

Unit Pascal

Description Specifies the target pressure.

You can specify multiple pressures (separated by spaces). In that case the Duration field specifies how many steps to use for the transition from one p to the next p (using a linear ramp).

`Scale`

Type Multiple Choice

Default value XYZ

Options [XYZ, Shape, X, Y, Z, XY, YZ, XZ]

Description Dimensions that should be scaled by the barostat to maintain pressure. Selecting Shape means that all three dimensions and also all the cell angles are allowed to change.

`Tau`

Type Float

Unit Femtoseconds

GUI name Damping constant

Description Specifies the time constant of the barostat.

`Type`

Type Multiple Choice

Default value None

Options [None, Berendsen, MTK]

GUI name Barostat

Description Selects the type of the barostat.

`BinLog`

Type Block

Description This block controls writing the BinLog section in ams.rkf, which contains the selected MD state scalars and tensors from every MD step. No per-atom data is written. If you need the per-atom data then you can set the sampling frequency to 1 and get the required data from the MDHistory section. The tensors are written per component, that is, the pressure tensor is written as six variables: PressureTensor_xx, PressureTensor_yy, etc.. To reduce the file size, all data is written in blocks.

`BiasEnergy`

Type Bool

Default value No

Description Write the CVDH bias energy.

`BoostFactor`

Type Bool

Default value No

Description Write the CVDH boost factor.

`ConservedEnergy`

Type Bool

Default value No

Description Write the conserved energy value.

`Density`

Type Bool

Default value No

Description Write the density.

`DipoleMoment`

Type Bool

Default value No

Description Write the dipole moment. Each component of the tensor is written in its own variable.

`Hypertime`

Type Bool

Default value No

Description Write the CVDH hypertime.

`KineticEnergy`

Type Bool

Default value No

Description Write the kinetic energy value.

`MaxBiasEnergy`

Type Bool

Default value No

Description Write the max CVDH bias energy.

`MaxBoostFactor`

Type Bool

Default value No

Description Write the max CVDH boost factor.

`PotentialEnergy`

Type Bool

Default value No

Description Write the potential energy value.

`Pressure`

Type Bool

Default value No

Description Write the pressure.

`PressureTensor`

Type Bool

Default value No

Description Write the pressure tensor in Voigt notation. Each component of the tensor is written in its own variable.

`Step`

Type Bool

Default value No

Description Write the step index during the simulation.

`Temperature`

Type Bool

Default value No

Description Write the temperature.

`Time`

Type Bool

Default value No

Description Write the simulation time (fs).

`TotalEnergy`

Type Bool

Default value No

Description Write the total energy value.

`Volume`

Type Bool

Default value No

Description Write the simulation cell volume, area or length, depending on the system periodicity.

`BondBoost`

Type Block

Recurring True

Description Forced reaction (bond boost) definitions. Multiple BondBoost blocks may be specified, which will be treated independently.

`Chain`

Type Block

Description Specifications of a chain of atoms. When a chain is detected the distance restraints will be activated. No other chain of this type will be detected while any restraints for this chain is active.

`AtomNames`

Type String

Description Atom names specifying the chain. An atom name can optionally be followed by '@' and a region name, in this case only atoms of this type from the given region will be matched. A leading '@' followed by a number indicates that this position in the chain must be occupied by the atom found earlier at the specified position in the chain. For example "O H N C @1" indicates that the last atom in the chain of the five atoms must be the first oxygen, thus defining a 4-membered ring. This is the only way to define a ring because implicit rings will not be detected. For example, "O H N C O" does not include rings.

`MaxDistances`

Type Float List

Unit Angstrom

Description Maximum distances for each pair of atoms in the chain. The number of distances must be one less than the number of AtomNames.

`MinDistances`

Type Float List

Unit Angstrom

Description Minimum distances for each pair of atoms in the chain. The number of distances must be one less than the number of AtomNames.

`DistanceRestraint`

Type String

Recurring True

Description Specify two atom indices followed by the optimum distance in Angstrom, the first parameter and, optionally, the profile type and the second parameter.

This restraint will try to keep the distance between the two specified atoms at the given value. For periodic systems this restraint follows the minimum image convention.

Each atom index indicates a position of the corresponding atom in the AtomNames key. Currently recognized restraint profile types: Harmonic (default), Hyperbolic, Erf, GaussianWell. The first parameter is the force constant for the Harmonic, Hyperbolic, and Erf profiles, or well depth for GaussianWell. The second parameter is the asymptotic force value F(Inf) for Hyperbolic and Erf profiles, or the factor before x^2 in the exponent for GaussianWell.

Note: the GaussianWell restraint should be used with the Moving flag.

`Moving`

Type Bool

Default value No

GUI name Move restraint

Description Move the restraints created with this BondBoost. The restraint value will start at the currect coordinate's value and will move towards the optimum during the restraint's lifetime. The increment is calculated from the initial deviation and the [NSteps] parameter.

This feature should be used with the GaussianWell restraint types.

`NSteps`

Type Integer

GUI name Boost lifetime

Description Number of steps the restraints will remain active until removed. Atoms participating in one reaction are not available for the given number of steps.

NumInstances

Type Integer

Default value 1

GUI name Number of instances

Description Number of reactions of this type taking place simultaneously.

Units

Type Multiple Choice

Default value Default

Options [Default, MD]

GUI name Restr. parameter units

Description Change energy, force and force constant units in the DistanceRestraint key from the default (atomic units) to those often used in the MD community (based on kcal/mol and Angstrom). Units for the optimum distances are not affected.

CRESTMTD

Type Block

GUI name CREST_MTD

Description Input for CREST metadynamics simulation.

AddEnergy

Type Bool

Default value No

Description Add the bias energy to the potential energy (to match the gradients)

GaussianScaling

Type Block

Description Options for gradual introduction of the Gaussians

ScaleGaussians

Type Bool

Default value Yes

Description Introduce the Gaussians gradually, using a scaling function

ScalingSlope

Type Float

Default value 0.03

Description Slope of the scaling function for the Gaussians with respect to time

Height

Type Float

Unit Hartree

Description The height of the Gaussians added

`NGaussiansMax`

Type Integer

Description Maximum number of Gaussians stored

`NSteps`

Type Integer

Description Interval of Gaussian placement

`Region`

Type String

Default value *

Description Restrict the range of atoms for RMSD calculation to the specified region.

`RestartFile`

Type String

Description Filename for file from which to read data on Gaussians placed previously.

`Width`

Type Float

Unit Bohr

Description The width of the Gaussians added in terms of the RMSD

`CVHD`

Type Block

Recurring True

GUI name CVHD

Description Input for the Collective Variable-driven HyperDynamics (CVHD).

`Bias`

Type Block

Description The bias is built from a series of Gaussian peaks deposited on the collective variable axis every [Frequency] steps during MD. Each peak is characterized by its (possibly damped) height and the RMS width (standard deviation).

`DampingTemp`

Type Float

Default value 0.0

Unit Kelvin

GUI name Bias damping T

Description During well-tempered hyperdynamics the height of the added bias is scaled down with an exp(-E/kT) factor [PhysRevLett 100, 020603 (2008)], where E is the current value of the bias at the given CV value and T is the damping temperature DampingTemp. If DampingTemp is zero then no damping is applied.

`Delta`

Type Float

Description Standard deviation parameter of the Gaussian bias peak.

`Height`

Type Float

Unit Hartree

Description Height of the Gaussian bias peak.

`ColVarBB`

Type Block

Recurring True

GUI name Collective Variable

Description Description of a bond-breaking collective variable (CV) as described in [Bal & Neyts, JCTC, 11 (2015)]. A collective variable may consist of multiple ColVar blocks.

`at1`

Type Block

Description Specifies the first bonded atom in the collective variable.

`region`

Type String

Default value *

Description Restrict the selection of bonded atoms to a specific region. If this is not set, atoms anywhere in the system will be selected.

`symbol`

Type String

Description Atom type name of the first atom of the bond. The name must be as it appears in the System block. That is, if the atom name contains an extension (e.g C.1) then the full name including the extension must be used here.

`at2`

Type Block

Description Specifies the second bonded atom in the collective variable.

`region`

Type String

Default value *

Description Restrict the selection of bonded atoms to a specific region. If this is not set, atoms anywhere in the system will be selected.

`symbol`

Type String

Description Atom type name of the second atom of the bond. The value is allowed to be the same as [at1], in which case bonds between atoms of the same type will be included.

`cutoff`

Type Float

Default value 0.3

GUI name Bond order cutoff

Description Bond order cutoff. Bonds with BO below this value are ignored when creating the initial bond list for the CV. The bond list does not change during lifetime of the variable even if some bond orders drop below the cutoff.

`p`

Type Integer

Default value 6

GUI name Exponent p

Description Exponent value p used to calculate the p-norm for this CV.

`rmax`

Type Float

Unit Angstrom

GUI name R max

Description Max bond distance parameter Rmax used for calculating the CV. It should be close to the transition-state distance for the corresponding bond.

`rmin`

Type Float

Unit Angstrom

GUI name R min

Description Min bond distance parameter Rmin used for calculating the CV. It should be close to equilibrium distance for the corresponding bond.

`ColVarBM`

Type Block

Recurring True

GUI name Collective Variable

Description Description of a bond-making collective variable (CV). A collective variable may consist of multiple ColVar blocks.

`at1`

Type Block

Description Specifies selection criteria for the first atom of a pair in the collective variable.

`region`

Type String

Default value *

Description Restrict the selection to a specific region. If this is not set, atoms anywhere in the system will be selected.

`symbol`

Type String

Description Atom type name of the first atom of the pair. The name must be as it appears in the System block. That is, if the atom name contains an extension (e.g C.1) then the full name including the extension must be used here.

at2

Type Block

Description Specifies selection criteria for the second atom of a pair in the collective variable.

region

Type String

Default value *

Description Restrict the selection to a specific region. If this is not set, atoms anywhere in the system will be selected.

symbol

Type String

Description Atom type name of the second atom of the pair. The value is allowed to be the same as [at1], in which case pairs of atoms of the same type will be included.

cutoff

Type Float

Default value 0.3

GUI name Bond order cutoff

Description Bond order cutoff. Bonds with BO above this value are ignored when creating the initial atom-pair list for the CV. The list does not change during lifetime of the variable even if some bond orders rise above the cutoff.

p

Type Integer

Default value 6

GUI name Exponent p

Description Exponent value p used to calculate the p-norm for this CV.

rmax

Type Float

Unit Angstrom

GUI name R max

Description Max bond distance parameter Rmax used for calculating the CV. It should be much larger than the corresponding Rmin.

rmin

Type Float

Unit Angstrom

GUI name R min

Description Min bond distance parameter Rmin used for calculating the CV. It should be close to the transition-state distance for the corresponding bond.

`Frequency`

Type Integer

Description Frequency of adding a new bias peak, in steps. New bias is deposited every [Frequency] steps after [StartStep] if the following conditions are satisfied: the current CV value is less than 0.9 (to avoid creating barriers at the transition state), the step number is greater than or equal to [StartStep], and the step number is less than or equal to [StopStep].

`MaxEvents`

Type Integer

Default value 0

Description Max number of events to allow during dynamics. When this number is reached no new bias will be added for this input block.

`StartStep`

Type Integer

Description If this key is specified, the first bias will be deposited at this step. Otherwise, the first bias peak is added at the step number equal to the Frequency parameter. The bias is never deposited at step 0.

`StopStep`

Type Integer

Description No bias will be deposited after the specified step. The already deposited bias will continue to be applied until the reaction event occurs. After that no new CVHD will be started. By default, the CVHD runs for the whole duration of the MD calculation.

`WaitSteps`

Type Integer

Description If the CV value becomes equal to 1 and remains at this value for this many steps then the reaction event is considered having taken place. After this, the collective variable will be reset and the bias will be removed.

`CalcPressure`

Type Bool

Default value No

GUI name Calculate pressure

Description Calculate the pressure in periodic systems.

This may be computationally expensive for some engines that require numerical differentiation.

Some other engines can calculate the pressure for negligible additional cost and will always do so, even if this option is disabled.

`Checkpoint`

Type Block

Description Sets the frequency for storing the entire MD state necessary for restarting the calculation.

`Frequency`

Type Integer

Default value 1000

GUI name Checkpoint frequency

Description Write the MD state and engine-specific data to the respective .rkf files once every N steps.

`WriteProperties`

Type Bool

Default value No

Description Write the properties from the properties section to the ChecoPoint file once every N steps.

`CopyRestartTrajectory`

Type Bool

Default value No

Description If the keyword Restart is present, the content of the restartfile is copied to the ams.rkf file.

`CosineShear`

Type Block

Description Apply an external acceleration to all atoms of a fluid using a periodic (cosine) function along a selected coordinate axis. This induces a periodic shear flow profile which can be used to determine the viscosity.

`Acceleration`

Type Float

Default value 5e-06

Unit Angstrom/fs^2

Description Amplitude of the applied cosine shear acceleration profile. The default value should be a rough first guess for water and it needs to be adjusted by experimentation for other systems.

`Enabled`

Type Bool

Default value No

GUI name Enable cosine shear

Description Apply a cosine shear acceleration profile for a NEMD calculation of viscosity.

`FlowDirection`

Type Float List

Default value [1.0, 0.0, 0.0]

Description The direction in which to apply the shear acceleration, in Cartesian coordinates. The magnitude of this vector is ignored (AMS will normalize it internally). FlowDirection has to be perpendicular to ProfileAxis.

`ProfileAxis`

Type Multiple Choice

Default value Z

Options [X, Y, Z]

Description The Cartesian coordinate axis along which the cosine wave runs

`Deformation`

Type Block

Recurring True

Description Deform the periodic lattice of the system during the simulation.

`LatticeVelocity`

Type Non-standard block

Description Velocity of individual lattice vector components in Angstrom/fs. The format is identical to the System%Lattice block. For Type Sine and Cosine, this defines the maximum velocity (at the inflection point).

`LengthRate`

Type Float List

Default value [0.0, 0.0, 0.0]

Description Relative rate of change of each lattice vector per step.

`LengthVelocity`

Type Float List

Default value [0.0, 0.0, 0.0]

Unit Angstrom/fs

Description Change the length of each lattice vector with this velocity. With Type=Exponential, LengthVelocity is divided by the current lattice vector lengths on StartStep to determine a LengthRate, which is then applied on all subsequent steps. For Type Sine and Cosine, this defines the maximum velocity (at the inflection point).

`Period`

Type Float

Unit Femtoseconds

Description Period of oscillation for Type Sine and Cosine.

`ScaleAtoms`

Type Bool

Default value Yes

Description Scale the atomic positions together with the lattice vectors. Disable this to deform only the lattice, keeping the coordinates of atoms unchanged.

`StartStep`

Type Integer

Default value 1

Description First step at which the deformation will be applied.

`StopStep`

Type Integer

Default value 0

Description Last step at which the deformation will be applied. If unset or zero, nSteps will be used instead.

`StrainRate`

Type Non-standard block

Description Strain rate matrix to be applied on every step. The format is identical to the System%Lattice block.

`TargetLattice`

Type Non-standard block

Description Target lattice vectors to be achieved by StopStep. The format is identical to the System%Lattice block.

`TargetLength`

Type Float List

Default value [0.0, 0.0, 0.0]

Unit Angstrom

Description Target lengths of each lattice vector to be achieved by StopStep. The number of values should equal the periodicity of the system. If a value is zero, the corresponding lattice vector will not be modified.

`Type`

Type Multiple Choice

Default value Linear

Options [Linear, Exponential, Sine, Cosine]

Description Function defining the time dependence of the deformed lattice parameters.

Linear increments the lattice parameters by the same absolute amount every timestep. Exponential multiplies the lattice parameters by the same factor every timestep. Only StrainRate, LengthRate, and LengthVelocity are supported for Type=Exponential. Sine deforms the system from the starting lattice to TargetLattice/TargetLength and then by the same amount to the opposite direction, while Cosine deforms the system from the starting lattice to the target and back.

`Gravity`

Type Block

Description Apply a constant acceleration in -z.

`Acceleration`

Type Float

Default value 0.0

Unit Angstrom/fs^2

Description Magnitude of the applied acceleration.

`HeatExchange`

Type Block

Recurring True

GUI name Heat exchange

Description Input for the heat-exchange non-equilibrium MD (T-NEMD).

`HeatingRate`

Type Float

Unit Hartree/fs

Description Rate at which the energy is added to the Source and removed from the Sink. A heating rate of 1 Hartree/fs equals to about 0.00436 Watt of power being transferred through the system.

`Method`

Type Multiple Choice

Default value Simple

Options [Simple, HEX, eHEX]

Description Heat exchange method used.

Simple: kinetic energy of the atoms of the source and sink regions is modified irrespective of that of the center of mass (CoM) of the region (recommended for solids).

HEX: kinetic energy of the atoms of these regions is modified keeping that of the corresponding CoM constant.

eHEX: an enhanced version of HEX that conserves the total energy better (recommended for gases and liquids).

`Sink`

Type Block

Description Defines the heat sink region (where the heat will be removed).

`AtomList`

Type Integer List

GUI name Sink region

Description The atoms that are part of the sink.

This key is ignored if the [Box] block or [Region] key is present.

`Box`

Type Block

Description Part of the simulation box (in fractional cell coordinates) defining the heat sink. If this block is specified, then by default, the whole box in each of the three dimensions is used, which usually does not make much sense. Normally, you will want to set the bounds along one of the axes.

`Amax`

Type Float

Default value 1.0

Description Coordinate of the upper bound along the first axis.

`Amin`

Type Float

Default value 0.0

Description Coordinate of the lower bound along the first axis.

`Bmax`

Type Float

Default value 1.0

Description Coordinate of the upper bound along the second axis.

`Bmin`

Type Float

Default value 0.0

Description Coordinate of the lower bound along the second axis.

`Cmax`

Type Float

Default value 1.0

Description Coordinate of the upper bound along the third axis.

`Cmin`

Type Float

Default value 0.0

Description Coordinate of the lower bound along the third axis.

`Region`

Type String

GUI name Sink region

Description The region that is the sink.

This key is ignored if the [Box] block is present.

`Source`

Type Block

Description Defines the heat source region (where the heat will be added).

`AtomList`

Type Integer List

GUI name Source region

Description The atoms that are part of the source.

This key is ignored if the [Box] block or [Region] key is present.

`Box`

Type Block

Description Part of the simulation box (in fractional cell coordinates) defining the heat source. If this block is specified, then by default, the whole box in each of the three dimensions is used, which usually does not make much sense. Normally, you will want to set the bounds along one of the axes. This block is mutually exclusive with the FirstAtom/LastAtom setting.

`Amax`

Type Float

Default value 1.0

Description Coordinate of the upper bound along the first axis.

`Amin`

Type Float

Default value 0.0

Description Coordinate of the lower bound along the first axis.

`Bmax`

Type Float

Default value 1.0

Description Coordinate of the upper bound along the second axis.

`Bmin`

Type Float

Default value 0.0

Description Coordinate of the lower bound along the second axis.

`Cmax`

Type Float

Default value 1.0

Description Coordinate of the upper bound along the third axis.

`Cmin`

Type Float

Default value 0.0

Description Coordinate of the lower bound along the third axis.

`Region`

Type String

GUI name Source region

Description The region that is the source.

This key is ignored if the [Box] block is present.

`StartStep`

Type Integer

Default value 0

Description Index of the MD step at which the heat exchange will start.

`StopStep`

Type Integer

Description Index of the MD step at which the heat exchange will stop.

`InitialVelocities`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`File`

Type String

Description AMS RKF file containing the initial velocities.

`RandomVelocitiesMethod`

Type Multiple Choice

Default value Exact

Options [Exact, Boltzmann, Gromacs]

GUI name Velocity randomization method

Description Specifies how are random velocities generated. Three methods are available.

Exact: Velocities are scaled to exactly match set random velocities temperature.

Boltzmann: Velocities are not scaled and sample Maxwell-Boltzmann distribution. However, the distribution is not corrected for constraints.

Gromacs: Velocities are scaled to match set random velocities temperature, but removal of net momentum is performed only after the scaling. Resulting kinetic energy is lower based on how much net momentum the system had.

`Temperature`

Type Float

Unit Kelvin

GUI name Initial temperature

Description Sets the temperature for the Maxwell-Boltzmann distribution when the type of the initial velocities is set to random, in which case specifying this key is mandatory.

AMSinput will use the first temperature of the first thermostat as default.

`Type`

Type Multiple Choice

Default value Random

Options [Zero, Random, FromFile, Input]

GUI name Initial velocities

Description Specifies the initial velocities to assign to the atoms. Three methods to assign velocities are available.

Zero: All atom are at rest at the beginning of the calculation.

Random: Initial atom velocities follow a Maxwell-Boltzmann distribution for the temperature given by the [MolecularDynamics%InitialVelocities%Temperature] keyword.

FromFile: Load the velocities from a previous ams result file.

Input: Atom's velocities are set to the values specified in the [MolecularDynamics%InitialVelocities%Values] block, which can be accessed via the Expert AMS panel in AMSinput.

`Values`

Type Non-standard block

Description This block specifies the velocity of each atom, in Angstrom/fs, when [MolecularDynamics%InitialVelocities%Type] is set to Input. Each row must contain three floating point values (corresponding to the x,y,z component of the velocity vector) and a number of rows equal to the number of atoms must be present, given in the same order as the [System%Atoms] block.

`MovingRestraints`

Type Block

Recurring True

Description Define a set of moving restraints.

`Change`

Type Multiple Choice

Default value Linear

Options [Linear, Sine, Cosine]

GUI name Move type

Description Type of function defining how the target restraint value will change over time:

Linear - linearly between the StartValue and EndValue. Sine - oscillating around StartValue with an amplitude equal to the difference between EndValue and StartValue. Cosine - oscillating between StartValue and EndValue.

`Distance`

Type Block

Recurring True

Description Define a distance restraint between pair of atoms. For linear-type

`Atom1`

Type Integer

Description First atom of the distance restraint.

`Atom2`

Type Integer

Description Second atom of the distance restraint.

`EndValue`

Type Float

Unit Angstrom

Description Linear: final target distance. Sine: target distance at 1/4 of the period. Cosine: target distance at 1/2 of the period.

`StartValue`

Type Float

Unit Angstrom

Description Initial target distance.

`Erf`

Type Block

Description Define parameters for the Int(erf) restraint potential V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI)). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

GUI name Erf force constant

Description The force constant (second derivative of the potential) at the optimum point.

`MaxForce`

Type Float

Default value 0.05

Unit Hartree/Bohr

GUI name Erf F(Inf)

Description Asymptotic value of the force at the infinity.

`GaussianWell`

Type Block

Description Define parameters in the Gaussian well restraint potential V=-WellDepth*exp(-Sigma*(r-r0)^2).

`Sigma`

Type Float

Default value 1.0

Unit 1/Bohr^2

GUI name Gaussian well sigma

Description Sigma parameter in the potential expression.

`WellDepth`

Type Float

Default value 1.0

Unit Hartree

GUI name Gaussian well depth

Description WellDepth parameter in the potential expression.

`Harmonic`

Type Block

Description Define parameters for the harmonic potential V=0.5*FC*(r-r0)^2.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

GUI name Harmonic force constant

Description The FC parameter of the harmonic potential.

`Hyperbolic`

Type Block

Description Define parameters for the hyperbolic restraint potential V=alpha*(sqrt(1 + beta*x^2) - 1). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce: beta=ForceConstant/MaxForce, alpha=MaxForce/beta

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

GUI name Hyperbolic force constant

Description The force constant (second derivative of the potential) at the optimum point.

`MaxForce`

Type Float

Default value 0.05

Unit Hartree/Bohr

GUI name Hyperbolic F(Inf)

Description Asymptotic value of the force at the infinity.

`Name`

Type String

GUI name Name

Description Optional name to be used for plotting.

`Period`

Type Float

Default value 0.0

Unit Femtoseconds

Description Period of oscillation for Sine and Cosine change types.

`RestraintType`

Type Multiple Choice

Default value None

Options [None, Harmonic, Hyperbolic, Erf, GaussianWell]

GUI name Restraint type

Description Select type of the moving restraint profile. The force for Hyperbolic and Erf is bounded by a user-defined value, the latter converging to it faster than the former. The GaussianWell has a finite depth so it is suitable for cases when crossing a high reaction barrier is not desirable.

`StartStep`

Type Integer

Default value 1

GUI name Start step

Description First step number at which the restraints will be applied.

`StopStep`

Type Integer

Default value 0

GUI name End step

Description Last step number at which the restraints will be applied.

`NSteps`

Type Integer

Default value 1000

GUI name Number of steps

Description The number of steps to be taken in the MD simulation.

`Plumed`

Type Block

Description Input for PLUMED. The parallel option is still experimental.

`Input`

Type Non-standard block

Description Input for PLUMED. Contents of this block is passed to PLUMED as is.

`Parallel`

Type Block

Description Options for double parallelization, which allows to split the available processor cores into groups working through all the available tasks in parallel, resulting in a better parallel performance. The keys in this block determine how to split the available processor cores into groups working in parallel.

`nCoresPerGroup`

Type Integer

GUI name Cores per group

Description Number of cores in each working group.

`nGroups`

Type Integer

GUI name Number of groups

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

`nNodesPerGroup`

Type Integer

GUI name Nodes per group

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

`Preserve`

Type Block

Description Periodically remove numerical drift accumulated during the simulation to preserve different whole-system parameters.

`AngularMomentum`

Type Bool

Default value Yes

GUI name : Angular momentum

Description Remove overall angular momentum of the system. This option is ignored for 2D and 3D-periodic systems, and disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

`CenterOfMass`

Type Bool

Default value No

GUI name : Center of mass

Description Translate the system to keep its center of mass at the coordinate origin. This option is not very useful for 3D-periodic systems.

`Momentum`

Type Bool

Default value Yes

GUI name Preserve: Total momentum

Description Remove overall (linear) momentum of the system. This is disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

`Print`

Type Block

Description This block controls the printing of additional information to stdout.

System

Type Bool

Default value No

Description Print the chemical system before and after the simulation.

Velocities

Type Bool

Default value No

Description Print the atomic velocities before and after the simulation.

ReactionBoost

Type Block

GUI name Reaction Boost

Description Define a series of transitions between different states of the system.

Each transition is defined by a TargetSystem and by a set of restraints that force the transition.

BondBreakingRestraints

Type Block

Description Define parameters for moving restraints that are added for pairs of atoms that become disconnected during the transition.

It is intended to make sure the corresponding bonds get broken, although this may not always be required because forming other bonds will likely get these bonds broken.

Erf

Type Block

Description Define parameters for the Int(erf) potential V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI)). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce.

ForceConstant

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

MaxForce

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

GaussianWell

Type Block

Description Define parameters in the Gaussian well potential V=-WellDepth*exp(-Sigma*(r-r0)^2).

Sigma

Type Float

Default value 1.0

Unit 1/Bohr^2

Description Sigma parameter in the potential expression.

WellDepth

Type Float

Default value 1.0

Unit Hartree

Description WellDepth parameter in the potential expression.

Harmonic

Type Block

Description Define parameters for the harmonic potential V=0.5*FC*(r-r0)^2.

ForceConstant

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The FC parameter of the harmonic potential.

Hyperbolic

Type Block

Description Define parameters for the hyperbolic potential V=alpha*(sqrt(1 + beta*x^2) - 1). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce: beta=ForceConstant/MaxForce, alpha=MaxForce/beta

ForceConstant

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

MaxForce

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

Taper

Type Block

Description

Enabled

Type Bool

Default value No

GUI name Tapering

Description Enable tapering of the restraint potential and force between the given range of bond distances. A 7-th order tapering function on the actual (not target!) distance will be used. The MaxDistance must be greater than MinDistance.

`MaxDistance`

Type Float

Default value 0.0

Unit Angstrom

GUI name End tapering at

Description Bond length at which the restraint potential and force decays to zero.

`MinDistance`

Type Float

Default value 0.0

Unit Angstrom

GUI name Start tapering at

Description Bond length at which the restraint potential and force will start decaying to zero.

`Type`

Type Multiple Choice

Default value Erf

Options [None, Harmonic, Hyperbolic, Erf, GaussianWell]

GUI name Bond breaking restraints

Description Select type of the moving restraint profile.

Harmonic: V=0.5*FC*(r-r0)^2

Hyperbolic: V=alpha*(sqrt(1 + beta*x^2) - 1)

Erf: V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI))

GaussianWell: V=-WellDepth*exp(-Sigma*(r-r0)^2)

Here beta=ForceConstant/MaxForce, alpha=MaxForce/beta.

The force for Hyperbolic and Erf is bounded by a user-defined value, the latter converging to it faster than the former. The GaussianWell has a finite depth so it is suitable for cases when crossing a high reaction barrier is not desirable.

Moving restraints are added for pairs of atoms that become disconnected during the transition.

It is intended to make sure the corresponding bonds get broken, although this may not always be required because forming other bonds will likely get these bonds broken.

`BondMakingRestraints`

Type Block

Description Define parameters for moving restraints that are added for pairs of atoms that become connected during the transition.

It is intended to make sure the bonds are created as required.

`Erf`

Type Block

Description Define parameters for the Int(erf) potential V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI)). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

`MaxForce`

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

`GaussianWell`

Type Block

Description Define parameters in the Gaussian well potential V=-WellDepth*exp(-Sigma*(r-r0)^2).

`Sigma`

Type Float

Default value 1.0

Unit 1/Bohr^2

Description Sigma parameter in the potential expression.

`WellDepth`

Type Float

Default value 1.0

Unit Hartree

Description WellDepth parameter in the potential expression.

`Harmonic`

Type Block

Description Define parameters for the harmonic potential V=0.5*FC*(r-r0)^2.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The FC parameter of the harmonic potential.

`Hyperbolic`

Type Block

Description Define parameters for the hyperbolic potential V=alpha*(sqrt(1 + beta*x^2) - 1). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce: beta=ForceConstant/MaxForce, alpha=MaxForce/beta

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

`MaxForce`

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

`Type`

Type Multiple Choice

Default value Erf

Options [None, Harmonic, Hyperbolic, Erf, GaussianWell]

GUI name Bond making restraints

Description Select type of the moving restraint profile.

Harmonic: V=0.5*FC*(r-r0)^2

Hyperbolic: V=alpha*(sqrt(1 + beta*x^2) - 1)

Erf: V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI))

GaussianWell: V=-WellDepth*exp(-Sigma*(r-r0)^2)

Here beta=ForceConstant/MaxForce, alpha=MaxForce/beta.

The force for Hyperbolic and Erf is bounded by a user-defined value. The GaussianWell has a finite depth so it is suitable for cases when crossing a high reaction barrier is not desirable.

Moving restraints are added for pairs of atoms that become connected during the transition.

It is intended to make sure the bonds are created as required.

`BondedRestraints`

Type Block

Description Define parameters for bonded restraints. A bonded restraint is added for each pair of atoms that are bonded both in the current and in the final state.

It is intended to make sure they remain bonded during simulation.

`Harmonic`

Type Block

Description Define parameters for the harmonic potential V=0.5*FC*(r-r0)^2.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The FC parameter of the harmonic potential.

`Type`

Type Multiple Choice

Default value None

Options [None, Harmonic]

GUI name Bonded restraints

Description Select type of the bonded restraints:

Harmonic: V=0.5*FC*(r-r0)^2

A bonded restraint is added for each pair of atoms that are bonded both in the current and in the final state.

It is intended to make sure they remain bonded during simulation.

`Change`

Type Multiple Choice

Default value TargetCoordinate

Options [TargetCoordinate, Force, LogForce]

GUI name Move type

Description Select what to change during dynamics.

By default, once the restraints are switched on, AMS will change the restraint's target coordinate towards its final value.

If the [Force] or [LogForce] option is selected then the target coordinate is set to its final value immediately and instead the restraint force is gradually scaled from 0 to 1. The scaling is either linear (Force) or logarithmic (LogForce).

`InitialFraction`

Type Float

Default value 0.0

Description Initial fraction of the boost variable.

At the first boosting step, the restraint's target value (or force or log(force)) is equal to InitialFraction + 1/NSteps.

InterEquilibrationSteps

Type Integer

Default value 0

Description Number of equilibration steps after reaching a target before setting up restraints for the next one.

MinBondChange

Type Float

Default value 1.0

Unit Bohr

Description Minimal change in the distance for an individual restraint to be considered bond-breaking/making vs bonded.

MinBondStrength

Type Float

Default value 0.5

Description Minimum strength (usually ranges from 0 to 1) for a bond to be considered.

NSteps

Type Integer

Default value 500

GUI name Steps per target

Description Number of steps per target the restraints should be active for.

NonBondedRestraints

Type Block

Description Define parameters for non-bonded restraints. A non-bonded restraint is added for each pair of atoms that are bonded neither in the current nor in the final state.

It is intended to keep them from forming a bond unintentionally. They are represented by a repulsive potential

Exponential

Type Block

Description Define parameters for the repulsive potential V=Epsilon*exp(-Sigma*r).

Epsilon

Type Float

Default value 1.0

Unit Hartree

Description Epsilon parameter in the repulsive potential expression.

Sigma

Type Float

Default value 1.0

Unit 1/Bohr

Description Sigma parameter in the repulsive potential expression.

`Type`

Type Multiple Choice

Default value None

Options [None, Exponential]

GUI name Non-bonded restraints

Description Select type of the non-bonded restraints:

Exponential: V=Epsilon*exp(-Sigma*r)

A non-bonded restraint is added for each pair of atoms that are bonded neither in the current nor in the final state.

It is intended to keep them from forming a bond unintentionally. They are represented by a repulsive potential.

`PreEquilibrationSteps`

Type Integer

Default value 0

Description Number of steps before enabling the first set of restraints.

`RMSDRestraint`

Type Block

GUI name RMSD restraint

Description Define a static restraint that pulls each atom to its position in the target system, but in contrast to the individual restraints, the force for this one depends on the total mass-weighted root-mean-squared distance (RMSD) between the two structures.

`Erf`

Type Block

Description Define parameters for the Int(erf) potential V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI)). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

`MaxForce`

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

`GaussianWell`

Type Block

Description Define parameters in the Gaussian well potential V=-WellDepth*exp(-Sigma*(r-r0)^2).

`Sigma`

Type Float

Default value 1.0

Unit 1/Bohr^2

Description Sigma parameter in the potential expression.

`WellDepth`

Type Float

Default value 1.0

Unit Hartree

Description WellDepth parameter in the potential expression.

`Harmonic`

Type Block

Description Define parameters for the harmonic potential V=0.5*FC*(r-r0)^2.

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The FC parameter of the harmonic potential.

`Hyperbolic`

Type Block

Description Define parameters for the hyperbolic potential V=alpha*(sqrt(1 + beta*x^2) - 1). The alpha and beta parameters are computed from the user-defined ForceConstant and MaxForce: beta=ForceConstant/MaxForce, alpha=MaxForce/beta

`ForceConstant`

Type Float

Default value 0.5

Unit Hartree/Bohr^2

Description The force constant (second derivative of the potential) at the optimum point.

`MaxForce`

Type Float

Default value 0.05

Unit Hartree/Bohr

Description Asymptotic value of the force at the infinity.

`Type`

Type Multiple Choice

Default value None

Options [None, Harmonic, Hyperbolic, Erf, GaussianWell]

GUI name Type

Description Select type of the RMSD restraint profile:

Harmonic: V=0.5*FC*(r-r0)^2

Hyperbolic: V=alpha*(sqrt(1 + beta*x^2) - 1)

Erf: V = alpha*(beta*x*erf(beta*x) + (exp(-(beta*x)**2) - 1)/sqrt(PI),

GaussianWell: V=-WellDepth*exp(-Sigma*(r-r0)^2)

Here beta=ForceConstant/MaxForce, alpha=MaxForce/beta.

The Harmonic profile can be problematic at large deviations as it may result in large forces. The force for Hyperbolic and Erf is bounded by a user-defined value. The GaussianWell has a finite depth so it is suitable for cases when crossing a high reaction barrier is not desirable.

`Region`

Type String

Default value *

GUI name Region

Description Region to which the restraints should be limited.

`TargetSystem`

Type String

Recurring True

GUI name Target system

Description The target system's name for this transition. Multiple targets can be specified to request multiple transitions in one simulation.

Note that only the lattice and the atomic coordinates of the target system are used and other properties (bonds, charge, etc.) are ignored. The target system's lattice is used only to determine connections and it cannot be restrainted.

`Type`

Type Multiple Choice

Default value None

Options [None, Pair, RMSD]

GUI name Restraint set type

Description Reaction Boost uses a series of transitions between different states of the system. Each transition is defined by a TargetSystem and by a set of restraints that force the transition.

Select the type of the restraint set: -None: no Reaction Boost - Pair: use pair restraints - RMSD: use RMSD restraints.

Pair restraints are defined per atom pair while the RMSD defines one collective restraint for all atoms and is thus suitable for very large systems.

The pair restraints are further divided into four sub-types: bonding, non-bonding, bond-breaking and bond-making. The sub-type of restraints for each pair is determined automatically depending on whether the two atoms are bonded in the initial/final state.

Parameters of the pair restraints are defined by [NonBondedRestraints], [BondedRestraints], [BondBreakingRestraints] and [BondMakingRestraints] blocks, while those of the RMSD restraint by the [RMSDRestraint] block.

`Reactor`

Type Block

Recurring True

Description Define one phase of the nanoreactor. A reactor is a region of space surrounded by an elastic wall. Atoms inside the region are not affected. Atoms outside it will be pushed back with force depending on the [ForceConstant] and the [MassScaled] flag.

`ForceConstant`

Type Float

GUI name Reactor force constant

Description Force constant of the reactor wall in Hartree/Bohr^2 (or Hartree/Bohr^2/Dalton if [MassScaled] is true).

`MassScaled`

Type Bool

Default value Yes

GUI name Scale force by mass

Description If this flag is disabled the force on an atom outside of the reactor depends only on the atomic coordinates and the force constant. Otherwise, the force is also multiplied by the mass of the atom. This means that atoms at the same distance from the wall will receive the same accelerate due to the wall potential.

`NSteps`

Type Integer

GUI name Reactor lifetime

Description Number of steps for which the reactor will remain active until disabled. The next reactor will be activated immediately after this. After the last reactor is disabled the cycle will repeat.

`Radius`

Type Float

Unit Angstrom

GUI name Reactor radius

Description Radius of the reactor sphere.

`ReflectiveWall`

Type Block

Recurring True

Description Apply a reflective wall in space

Axis

Type Float List

Unit Angstrom

Description Defines the normal vector perpendicular to the plane of the reflective wall. Any particle moving in this direction will be reflected back.

Region

Type String

Recurring True

Description Apply the reflective wall to all atoms in this region.

Threshold

Type Float

Unit Angstrom

Description Defines the threshold value determining the position of the reflective wall. If the dot product of a position of a particle with Axis exceeds Threshold, the particle will be reflected. This means that the plane of the wall passes through a point given by Axis times Threshold.

Remap

Type Block

Description Control periodic remapping (backtranslation) of atoms into the PBC box.

Type

Type Multiple Choice

Default value Atoms

Options [None, Atoms]

Description Select the method used to remap atoms into the unit cell.

None: Disable remapping completely.

Atoms: Remap any atoms that leave the unit cell.

RemoveMolecules

Type Block

Recurring True

GUI name Remove molecules

Description This block controls removal of molecules from the system. Multiple occurrences of this block are possible.

Formula

Type String

Description Molecular formula of the molecules that should be removed from the system.

The order of elements in the formula is very important and the correct order is: C, H, all other elements in the strictly alphabetic order. Element names are case-sensitive, spaces in the formula are not allowed. Digit '1' must be omitted.

Valid formula examples: C2H6O, H2O, O2S. Invalid formula examples: C2H5OH, H2O1, OH, SO2. Invalid formulas are silently ignored.

Use * to remove any molecule, which must be combined with SinkBox or SafeBox.

Frequency

Type Integer

Default value 0

Description The specified molecules are removed every so many steps after the StartStep. There is never a molecule removed at step 0.

SafeBox

Type Block

Description Part of the simulation box where molecules may not be removed. Only one of the SinkBox or SafeBox blocks may be present. If this block is present the molecule will not be removed if any of its atoms is within the box. For a periodic dimension it is given as a fraction of the simulation box (the full 0 to 1 range by default). For a non-periodic dimension it represents absolute Cartesian coordinates in Angstrom.

Amax

Type Float

Description Coordinate of the upper bound along the first axis.

Amin

Type Float

Description Coordinate of the lower bound along the first axis.

Bmax

Type Float

Description Coordinate of the upper bound along the second axis.

Bmin

Type Float

Description Coordinate of the lower bound along the second axis.

Cmax

Type Float

Description Coordinate of the upper bound along the third axis.

Cmin

Type Float

Description Coordinate of the lower bound along the third axis.

FractionalCoordsBox

Type Float List

GUI name Safe box

Description Do not remove molecules that are (partly) inside the safe box.

Borders of the safe box specified as: Amin, Amax, Bmin, Bmax, Cmin, Cmax.

For periodic dimensions fractional coordinates between 0 and 1 and for non-periodic dimensions Cartesian values in Angstrom are expected.

`SinkBox`

Type Block

Description Part of the simulation box where matching molecules will be removed. By default, molecules matching the formula will be removed regardless of their location. If this block is present then such a molecule will only be removed if any of its atoms is within the box. For a periodic dimension it is given as a fraction of the simulation box (the full 0 to 1 range by default). For a non-periodic dimension it represents absolute Cartesian coordinates in Angstrom.

`Amax`

Type Float

Description Coordinate of the upper bound along the first axis.

`Amin`

Type Float

Description Coordinate of the lower bound along the first axis.

`Bmax`

Type Float

Description Coordinate of the upper bound along the second axis.

`Bmin`

Type Float

Description Coordinate of the lower bound along the second axis.

`Cmax`

Type Float

Description Coordinate of the upper bound along the third axis.

`Cmin`

Type Float

Description Coordinate of the lower bound along the third axis.

`FractionalCoordsBox`

Type Float List

GUI name Sink box

Description Remove molecules that are (partly) inside the sink box.

Borders of the sink box specified as: Amin, Amax, Bmin, Bmax, Cmin, Cmax.

For periodic dimensions fractional coordinates between 0 and 1 and for non-periodic dimensions Cartesian values in Angstrom are expected.

`StartStep`

Type Integer

Default value 0

Description Step number when molecules are removed for the first time. After that, molecules are removed every [Frequency] steps.

For example, if StartStep=99 and Frequency=100 then molecules will be removed at steps 99, 199, 299, etc…

No molecule will be removed at step 0, so if StartStep=0 the first molecules are removed at the step number equal to [Frequency].

`StopStep`

Type Integer

Description Do not remove the specified molecules after this step.

`ReplicaExchange`

Type Block

Description This block is used for (temperature) Replica Exchange MD (Parallel Tempering) simulations.

`AllowWrongResults`

Type Bool

Default value No

Description Allow combining Replica Exchange with other features when the combination is known to produce physically incorrect results.

`EWMALength`

Type Integer

Default value 10

Description Length of the exponentially weighted moving average used to smooth swap probabilities for monitoring.

This value is equal to the inverse of the EWMA mixing factor.

`SwapFrequency`

Type Integer

Default value 100

Description Attempt an exchange every N steps.

`TemperatureFactors`

Type Float List

Description This is the ratio of the temperatures of two successive replicas.

The first value sets the temperature of the second replica with respect to the first replica, the second value sets the temperature of the third replica with respect to the second one, and so on. If there are fewer values than nReplicas, the last value of TemperatureFactor is used for all the remaining replicas.

`Temperatures`

Type Float List

Description List of temperatures for all replicas except for the first one.

This is mutually exclusive with TemperatureFactors. Exactly nReplicas-1 temperature values need to be specified, in increasing order. The temperature of the first replica is given by [Thermostat%Temperature].

`nReplicas`

Type Integer

Default value 1

GUI name Number of replicas

Description Number of replicas to run in parallel.

`Restart`

Type String

GUI name Restart from

Description The path to the ams.rkf file from which to restart the simulation.

`Shake`

Type Block

Description Parameters of the Shake/Rattle algorithm.

`All`

Type String

Recurring True

GUI name Constrain all

Description Constraint description in one the following formats: All [bondOrder] bonds at1 at2 [to distance] All triangles at1 at2 at3

The first option constrains all bonds between atoms at1 at2 to a certain length, while the second - bonds at1-at2 and at2-at3 and the angle between them.

The [bondOrder] can be a number or a string such as single, double, triple or aromatic. If it's omitted then all bonds between specified atoms will be constrained. Atom names are case-sensitive and they must be as they are in the Atoms block, or an asterisk '*' denoting any atom. The distance, if present, must be in Angstrom. If it is omitted then the bond length from the initial geometry is used.

Important: only the bonds present in the system at certain points of the simulation (at the start or right after adding/removing atoms) can be constrained, which means that the bonds may need to be specified in the System block.

Warning: the triangles constraint should be used with care because each constrained bond or angle means removing one degree of freedom from the dynamics. When there are too many constraints (for example, "All triangles H C H" in methane) some of them may be linearly dependent, which will lead to an error in the temperature computation.

Valid examples: All single bonds C C to 1.4 All bonds O H to 0.98 All bonds O H All bonds H * All triangles H * H

`ConvergeR2`

Type Float

Default value 1e-08

Description Convergence criterion on the max squared difference, in atomic units.

`ConvergeRV`

Type Float

Default value 1e-08

Description Convergence criterion on the orthogonality of the constraint and the relative atomic velocity, in atomic units.

`Iterations`

Type Integer

Default value 100

Description Number of iterations.

`ShakeInitialCoordinates`

Type Bool

Default value Yes

Description Apply constraints before computing the first energy and gradients.

`Thermostat`

Type Block

Recurring True

Description This block allows to specify the use of a thermostat during the simulation. Depending on the selected thermostat type, different additional options may be needed to characterize the specific thermostat' behavior.

`BerendsenApply`

Type Multiple Choice

Default value Global

Options [Local, Global]

GUI name Apply Berendsen

Description Select how to apply the scaling correction for the Berendsen thermostat:

- per-atom-velocity (Local) - on the molecular system as a whole (Global).

`ChainLength`

Type Integer

Default value 10

GUI name NHC chain length

Description Number of individual thermostats forming the NHC thermostat

`Duration`

Type Integer List

GUI name Duration(s)

Description Specifies how many steps should a transition from a particular temperature to the next one in sequence take.

`Region`

Type String

Default value *

Description The identifier of the region to thermostat. The default '*' applies the thermostat to the entire system. The value can by a plain region name, or a region expression, e.g. '*-myregion' to thermostat all atoms that are not in myregion, or 'regionA+regionB' to thermostat the union of the 'regionA' and 'regionB'. Note that if multiple thermostats are used, their regions may not overlap.

`Tau`

Type Float

Unit Femtoseconds

GUI name Damping constant

Description The time constant of the thermostat.

`Temperature`

Type Float List

Unit Kelvin

GUI name Temperature(s)

Description The target temperature of the thermostat.

You can specify multiple temperatures (separated by spaces). In that case the Duration field specifies how many steps to use for the transition from one T to the next T (using a linear ramp). For NHC thermostat, the temperature may not be zero.

`Type`

Type Multiple Choice

Default value None

Options [None, Berendsen, NHC]

GUI name Thermostat

Description Selects the type of the thermostat.

`TimeStep`

Type Float

Default value 0.25

Unit Femtoseconds

Description The time difference per step.

`Trajectory`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`ExitConditionFreq`

Type Integer

GUI name Exit condition frequency

Description Check the exit conditions every N steps. By default this is done every SamplingFreq steps.

`PrintFreq`

Type Integer

GUI name Printing frequency

Description Print current thermodynamic properties to the output every N steps. By default this is done every SamplingFreq steps.

`SamplingFreq`

Type Integer

Default value 100

GUI name Sample frequency

Description Write the the molecular geometry (and possibly other properties) to the .rkf file once every N steps.

`TProfileGridPoints`

Type Integer

Default value 0

Description Number of points in the temperature profile. If TProfileGridPoints > 0, a temperature profile along each of the three lattice axes will be written to the .rkf file. The temperature at a given profile point is calculated as the total temperature of all atoms inside the corresponding slice of the simulation box, time-averaged over all MD steps since the previous snapshot. By default, no profile is generated.

`WriteBonds`

Type Bool

Default value Yes

Description Write detected bonds to the .rkf file.

`WriteCharges`

Type Bool

Default value Yes

Description Write current atomic point charges (if available) to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze charges.

`WriteCoordinates`

Type Bool

Default value Yes

Description Write atomic coordinates to the .rkf file.

`WriteEngineGradients`

Type Bool

Default value No

Description Write atomic gradients (negative of the atomic forces, as calculated by the engine) to the History section of ams.rkf.

WriteMolecules

Type Bool

Default value Yes

Description Write the results of molecule analysis to the .rkf file.

WriteVelocities

Type Bool

Default value Yes

Description Write velocities to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze the velocities.

fbMC

Type Block

Recurring True

GUI name fbMC

Description This block sets up force bias Monte Carlo interleaved with the molecular dynamics simulation.

Frequency

Type Integer

Default value 1

Description Run the fbMC procedure every Frequency MD steps.

MassRoot

Type Float

Default value 2.0

Description Inverse of the exponent used to mass-weight fbMC steps.

MolecularMoves

Type Block

Description Move molecules as rigid bodies in addition to normal atomic moves.

Enabled

Type Bool

Default value No

GUI name Enable molecular moves

Description Enable moving molecules as rigid bodies based on net forces and torques. Ordinary per-atom displacements will then be based on residual atomic forces.

RotationStepAngle

Type Float

Default value 0.1

Unit Radian

Description Maximum allowed angle of rotation of each molecule in one fbMC step.

`TranslationStepLength`

Type Float

Default value 0.1

Unit Angstrom

Description Maximum allowed displacement of each molecule in each Cartesian coordinate in one fbMC step.

`NSteps`

Type Integer

GUI name Number of steps

Description Number of fbMC steps to perform on every invocation of the procedure.

`PrintFreq`

Type Integer

GUI name Printing frequency

Description Print current thermodynamic properties to the output every N fbMC steps. This defaults to the PrintFreq set in the Trajectory block. Setting this to zero disables printing fbMC steps.

`StartStep`

Type Integer

Default value 1

Description First step at which the fbMC procedure may run.

`StepLength`

Type Float

Default value 0.1

Unit Angstrom

Description Maximum allowed displacement of the lightest atom in the system in each Cartesian coordinate in one fbMC step.

`StopStep`

Type Integer

Default value 0

Description Last step at which the fbMC procedure may run. If unset or zero, there is no limit.

`Temperature`

Type Float

Unit Kelvin

Description Temperature used for fbMC.

`Molecules`

Type Block

Description Configures details of the molecular composition analysis enabled by the Properties%Molecules block.

`AdsorptionSupportRegion`

Type String

GUI name Adsorption support region

Description Select region that will represent a support for adsorption analysis. Adsorbed molecules will receive an '(ads)' suffix after name of the element bonded to the support. Such elements will be listed separate from atoms of the same element not bonded to the support, for example, HOH(ads) for a water molecule bonded to a surface via one of its H atoms.

`BondOrderCutoff`

Type Float

Default value 0.5

Description Bond order cutoff for analysis of the molecular composition. Bonds with bond order smaller than this value are neglected when determining the molecular composition.

`NEB`

Type Block

Description Configures details of the Nudged Elastic Band optimization.

`Climbing`

Type Bool

Default value Yes

GUI name Climb highest image to TS

Description Use the climbing image algorithm to drive the highest image to the transition state.

`ClimbingThreshold`

Type Float

Default value 0.0

Unit Hartree/Bohr

GUI name CI force threshold

Description Climbing image force threshold. If ClimbingThreshold > 0 and the max perpendicular force component is above the threshold then no climbing is performed at this step. This entry can be used to get a better approximation for the reaction path before starting the search for the transition state. A typical value is 0.01 Hartree/Bohr.

`Images`

Type Integer

Default value 8

GUI name Number of images

Description Number of NEB images (not counting the chain ends). Using more images will result in a smoother reaction path and can help with convergence problems, but it will also increase the computation time.

`InterpolateInternal`

Type Bool

Default value Yes

GUI name Interpolate in Internal coordinates

Description The initial NEB image geometries are calculated by interpolating between the initial and the final state. By default, for non-periodic systems the interpolation is performed in internal coordinates but the user can choose to do it in the Cartesian ones. For periodic systems the interpolation is always done in Cartesian coordinates. If PreOptimizeWithIDPP is set then the path may be further refined using the image-dependent pair potential (IDPP).

`InterpolateShortest`

Type Bool

Default value Yes

GUI name Interpolate across cell boundary

Description Allow interpolation across periodic cell boundaries. Set to false if an atom is intended to move more than half across the simulation box during reaction.

`Iterations`

Type Integer

GUI name Maximum number of iterations

Description Maximum number of NEB iterations. The default value depends on the number of degrees of freedom (number of images, atoms, periodic dimensions).

`Jacobian`

Type Float

GUI name Jacobian value

Description Scaling factor used to convert the lattice strain to a NEB coordinate value. Default value: sqrt(N)*(V/N)^(1/d), where V - lattice volume (area for 2D, length for 1D), N - number of atoms, and d - number of periodic dimensions.

`LoadPath`

Type Block

Description Provide details about the trajectory to get the initial NEB path from. PESScan and NEB trajectories are supported. Only the last geometry for each point on the trajectory is considered.

`File`

Type String

GUI name Initial path file

Description Provide an ams.rkf file to load the initial path from. All geometries of this calculation, including initial and final, will be taken from the History section of the file.

Note that for a PESScan it should be a 1D path.

`Geometries`

Type Integer List

GUI name Raw geometry indices

Description Raw indices of the geometries from the History section. By default the last geometry of each path point is used.

`Points`

Type Integer List

GUI name Path points

Description By default the whole path is used, which may sometimes be not desirable. For example when a PESScan revealed multiple barriers. In this case one can specify indices of the path points to be used. The last geometry of the specified path point will be loaded.

`MapAtomsToCell`

Type Bool

Default value Yes

GUI name Map atoms to cell

Description Translate atoms to the [-0.5,0.5] cell before every step. This option cannot be disabled for SS-NEB.

`OldTangent`

Type Bool

Default value No

GUI name Use old tangent

Description Turn on the old central difference tangent.

`OptimizeEnds`

Type Bool

Default value Yes

GUI name Optimize reactants/products

Description Start the NEB with optimization of the reactant and product geometries.

`OptimizeLattice`

Type Bool

Default value No

GUI name Optimize lattice

Description Turn on the solid-state NEB (SS-NEB).

`Parallel`

Type Block

Description Options for double parallelization, which allows to split the available processor cores into groups working through all the available tasks in parallel, resulting in a better parallel performance. The keys in this block determine how to split the available processor cores into groups working in parallel.

`nCoresPerGroup`

Type Integer

GUI name Cores per group

Description Number of cores in each working group.

`nGroups`

Type Integer

GUI name Number of groups

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

`nNodesPerGroup`

Type Integer

GUI name Nodes per group

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

`PreOptimizeWithIDPP`

Type Bool

Default value No

GUI name Use IDPP

Description (Experimental) When there is only initial and final system available, the image-dependent pair potential (IDPP, doi: 10.1063/1.4878664) can be used to determine the initial NEB path by interpolating all interatomic distances between the two points and optimizing intermediate images towards them. The optimization starts from the geometries obtained using the selected interpolation options.

`ReOptimizeEnds`

Type Bool

Default value No

GUI name Re-optimize reactants/products

Description Re-optimize reactant and product geometries upon restart.

`Restart`

Type String

GUI name Restart from

Description Provide an ams.rkf file from a previous NEB calculation to restart from. It can be an unfinished NEB calculation or one performed with different engine parameters.

`Skewness`

Type Float

Default value 1.0

GUI name Skewness

Description Degree of how much images are shifted towards or away from the TS, which may help tackle problems with a long reaction path (for example involving a loose adsorption complex) without needing too many images. A value greater than 1 will make sure that images are concentrated near the transition state. The optimal value depends on the path length, the number of images (larger [Skewness] may be needed for a longer path and fewer images). Technically

[Skewness] is equal to the ratio between the optimized distances to the lower and the higher neighbor image on the path.

Spring

Type Float

Default value 1.0

Unit Hartree/Bohr^2

GUI name Spring value

Description Spring force constant in atomic units.

NormalModes

Type Block

Description Configures details of a normal modes calculation.

BlockDisplacements

Type Block

Description Configures details of a Block Normal Modes (a.k.a. Mobile Block Hessian, or MBH) calculation.

AngularDisplacement

Type Float

Default value 0.5

Unit Degree

Description Relative step size for rotational degrees of freedom during Block Normal Modes finite difference calculations. It will be scaled with the characteristic block size.

BlockAtoms

Type Integer List

Recurring True

Description List of atoms belonging to a block. You can have multiple BlockAtoms.

BlockRegion

Type String

Recurring True

Description The region to to be considered a block. You can have multiple BlockRegions, also in combination with BlockAtoms.

Parallel

Type Block

Description Configuration for how the individual displacements are calculated in parallel.

nCoresPerGroup

Type Integer

Description Number of cores in each working group.

nGroups

Type Integer

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

nNodesPerGroup

Type Integer

GUI name Cores per task

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

RadialDisplacement

Type Float

Default value 0.005

Unit Angstrom

Description Step size for translational degrees of freedom during Block Normal Modes finite difference calculations.

Displacements

Type Multiple Choice

Default value Cartesian

Options [Cartesian, Symmetric, Block]

GUI name Displacements

Description Type of displacements.

In case of symmetric displacements it is possible to choose only the modes that have non-zero IR or Raman intensity.

Block displacements take rigid blocks into account.

Hessian

Type Multiple Choice

Default value Auto

Options [Auto, Analytical, Numerical]

Description Default Auto means that if possible by the engine the Hessian will be calculated analytically, else the Hessian will be calculated numerically by AMS.

ReScanFreqRange

Type Float List

Default value [-10000000.0, 10.0]

Unit cm-1

Recurring True

GUI name Re-scan range

Description Specifies a frequency range within which all modes will be scanned. 2 numbers: an upper and a lower bound.

ReScanModes

Type Bool

Default value Yes

GUI name Re-scan modes

Description Whether or not to scan imaginary modes after normal modes calculation has concluded.

`SymmetricDisplacements`

Type Block

Description Configures details of the calculation of the frequencies and normal modes of vibration in symmetric displacements.

`Type`

Type Multiple Choice

Default value All

Options [All, Infrared, Raman, InfraredAndRaman]

GUI name Symm Frequencies

Description For symmetric molecules it is possible to choose only the modes that have non-zero IR or Raman intensity (or either of them) by symmetry.

In order to calculate the Raman intensities the Raman property must be requested.

`NumericalDifferentiation`

Type Block

Description Define options for numerical differentiations, that is the numerical calculation of gradients, Hessian and the stress tensor for periodic systems.

`NuclearStepSize`

Type Float

Default value 0.005

Unit Bohr

Description Step size for numerical nuclear gradient calculation.

`Parallel`

Type Block

Description Options for double parallelization, which allows to split the available processor cores into groups working through all the available tasks in parallel, resulting in a better parallel performance. The keys in this block determine how to split the available processor cores into groups working in parallel.

`nCoresPerGroup`

Type Integer

GUI name Cores per group

Description Number of cores in each working group.

`nGroups`

Type Integer

GUI name Number of groups

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

nNodesPerGroup

Type Integer

GUI name Nodes per group

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

StrainStepSize

Type Float

Default value 0.001

Description Step size (relative) for numerical stress tensor calculation.

NumericalPhonons

Type Block

Description Configures details of a numerical phonons calculation.

AutomaticBZPath

Type Bool

Default value Yes

GUI name Automatic BZ path

Description If True, compute the phonon dispersion curve for the standard path through the Brillouin zone. If False, you must specify your custom path in the [BZPath] block.

BZPath

Type Block

Description If [NumericalPhonons%AutomaticBZPath] is false, the phonon dispersion curve will be computed for the user-defined path in the [BZPath] block. You should define the vertices of your path in fractional coordinates (with respect to the reciprocal lattice vectors) in the [Path] sub-block. If you want to make a jump in your path (i.e. have a discontinuous path), you need to specify a new [Path] sub-block.

Path

Type Non-standard block

Recurring True

Description A section of a k space path. This block should contain multiple lines, and in each line you should specify one vertex of the path in fractional coordinates. Optionally, you can add text labels for your vertices at the end of each line.

BornEffCharge

Type Float

Default value 0.0

Description Input option to give the Born effective charges of the species.

DielectricConst

Type Float

Default value 1.0

Description Input option to give the static dielectric constant of the species.

`DoubleSided`

Type Bool

Default value Yes

Description By default a two-sided (or quadratic) numerical differentiation of the nuclear gradients is used. Using a single-sided (or linear) numerical differentiation is computationally faster but much less accurate. Note: In older versions of the program only the single-sided option was available.

`Interpolation`

Type Integer

Default value 100

Description Use interpolation to generate smooth phonon plots.

`NDosEnergies`

Type Integer

Default value 1000

Description Nr. of energies used to calculate the phonon DOS used to integrate thermodynamic properties. For fast compute engines this may become time limiting and smaller values can be tried.

`Parallel`

Type Block

Description Options for double parallelization, which allows to split the available processor cores into groups working through all the available tasks in parallel, resulting in a better parallel performance. The keys in this block determine how to split the available processor cores into groups working in parallel.

`nCoresPerGroup`

Type Integer

GUI name Cores per group

Description Number of cores in each working group.

`nGroups`

Type Integer

GUI name Number of groups

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

`nNodesPerGroup`

Type Integer

GUI name Nodes per group

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

`StepSize`

Type Float

Default value 0.04

Unit Angstrom

Description Step size to be taken to obtain the force constants (second derivative) from the analytical gradients numerically.

`SuperCell`

Type Non-standard block

Description Used for the phonon run. The super lattice is expressed in the lattice vectors. Most people will find a diagonal matrix easiest to understand.

`PESExploration`

Type Block

Description Configures details of the automated PES exploration methods.

`BasinHopping`

Type Block

Description Configures the details of the Basin Hopping subtask.

`DisplaceAtomsInRegion`

Type String

Default value

Description If you specify a region name here, only the atoms belonging to this region will be displaced during the basin hopping procedure. For more details on regions, see the documentation on the System definition.

`Displacement`

Type Float

Default value 0.5

Unit Angstrom

Description Displacement in each degree of freedom.

`MainSystemAsSeed`

Type Bool

Default value No

Description If true, only the main system will be used as a seed state. The main system is not added to the database.

`PESPointCharacterization`

Type Bool

Default value Yes

Description If true, a PES point characterization based on a vibrational analysis is carried out to confirm each detected state is an actual local minimum (no imaginary frequencies). Conversely, if this option is false, the PES point characterization is avoided, which will assume that all located states are local minima (zero gradients). Enabling this option is very useful for large systems. It circumvents the need for computing and diagonalizing the Hessian matrix, a typically expensive computational process.

`PushApartDistance`

Type Float

Default value 0.4

Unit Angstrom

Description Push atoms apart until no atoms are closer than this distance. This criterion is enforced for the initial structure and all those generated by random displacements.

`Steps`

Type Integer

Default value 20

Description Number of displace & optimize Monte-Carlo steps to take.

`BindingSites`

Type Block

Description Options related to the calculation of binding sites.

`Calculate`

Type Bool

Default value No

Description Calculate binding sites at the end of a job. Not needed for Binding Sites job.

`DistanceDifference`

Type Float

Default value -1.0

Unit Angstrom

Description If the distance between two mapped binding-sites is larger than this threshold, the binding-sites are considered different. If not specified, its value will set equal to [PESExploration%StructureComparison%DistanceDifference]

`MaxCoordinationShellsForLabels`

Type Integer

Default value 3

Description The binding site labels are given based on the coordination numbers of shells in the reference region, using the following format: N<int><int>…, e.g., the label 'N334' means 3 atoms in the first coordination shell, 3 in the second one, and 4 in the third one. This parameter controls the maximum number of shells to include.

`NeighborCutoff`

Type Float

Default value -1.0

Unit Angstrom

Description Atoms within this distance of each other are considered neighbors for the calculation of the binding sites. If not specified, its value will set equal to [PESExploration%StructureComparison%NeighborCutoff]

`ReferenceRegion`

Type String

Default value

Description Defines the region that is considered as the reference for binding sites detection. Binding sites are projected on this region using the geometry from the reference system. If not specified, its value will set equal to [PESExploration%StatesAlignment%ReferenceRegion]

`CalculateEnergyReferences`

Type Bool

Default value No

Description Calculates the energy references.

`CalculateFragments`

Type Bool

Default value No

Description Must be used together with an adsorbent set as the StatesAlignment%ReferenceRegion. Runs a final calculation of the adsorbate and adsorbent (marked by the ReferenceRegion) individually. The fragmented state is included in the energy landscape.

`Debug`

Type Block

Description ???.

`DynamicSeedStates`

Type Bool

Default value Yes

Description Whether subsequent expeditions may start from states discovered by previous expeditions. This should lead to a more comprehensive exploration of the potential energy surface. Disabling this will focus the PES exploration around the initial seed states.

`Dynamics`

Type Block

Description ???.

`Andersen`

Type Block

Description ???.

`Alpha`

Type Float

Default value 1.0

Description ???.

`CollisionPeriod`

Type Float

Default value 100.0

Description ???.

`Langevin`

Type Block

Description ???.

`Friction`

Type Float

Default value 0.01

Description ???.

`Nose`

Type Block

Description ???.

`Mass`

Type Float

Default value 1.0

Description ???.

`Thermostat`

Type Multiple Choice

Default value none

Options [andersen, nose_hoover, langevin, none]

Description ???.

`Time`

Type Float

Default value 1000.0

Description ???.

`TimeStep`

Type Float

Default value 1.0

Description ???.

`FiniteDifference`

Type Float

Default value 0.0026458861

Unit Angstrom

Description The finite difference distance to use for Dimer, Hessian, Lanczos, and optimization methods.

`Hessian`

Type Block

Description ???.

`AtomList`

Type String

Default value all

Description ???.

`ZeroFreqValue`

Type Float

Default value 1e-06

Description ???.

`Job`

Type Multiple Choice

Options [ProcessSearch, BasinHopping, SaddleSearch, LandscapeRefinement, BindingSites]

Description Specify the PES exploration job to perform.

`LandscapeRefinement`

Type Block

Description Configures details of the energy landscape refinement job.

`CalculateOnlyEnergies`

Type Bool

Default value No

Description If true, the states' geometry is not optimized, and the final PES point characterization is ignored [PESExploration%LandscapeRefinement%IgnoreFinalPESPointCharacter]. Only energy values are updated using the specified engine. Furthermore, normal modes and associated properties are copied from the previous calculation to avoid the typically high computational effort of the Hessian matrix calculation. Enabling this option implies that RunInitialSinglePoints='F', IgnoreFinalPESPointCharacter='T'.

`IgnoreFinalPESPointCharacter`

Type Bool

Default value No

Description At the end of the energy landscape refinement job, each state is assigned a PES point character (MIN or TS) based on its vibrational frequencies before being included in the final database. States are only added if the PES point character after refinement remains unchanged. However, states are added without verifying if this option is `true`. Nonetheless, vibrational frequencies are calculated and stored for future analysis. This option is especially useful when using computationally demanding engines. Because in those cases, precision and computational effort must be balanced, resulting in significant vibrational frequencies inaccuracies.

`IgnoreFinalPESPointCharacterForFragments`

Type Bool

Default value No

Description Same as `LandscapeRefinement%IgnoreFinalPESPointCharacter` but regarding the Fragments calculations, see option `LandscapeRefinement%CalculateFragments`.

`RelaxFromSaddlePoint`

Type Bool

Default value No

Description Relaxes the saddle point geometries following the imaginary mode to get both reactants and products.

`RunInitialSinglePoints`

Type Bool

Default value Yes

Description If it is `true`, just after loading the energy landscape to refine, the single energy point computations are disabled. Be aware that if you enable this, the output file's 'Initial Energy Landscape' section will display incorrect states' energy values. If the engine requires too much processing power, this option can help you save a small amount of time.

`TransitionStateSearchMethod`

Type Multiple Choice

Default value Auto

Options [Auto, Dimer]

Description Sets the method to refine transition states.

`LoadEnergyLandscape`

Type Block

Description Options related to the loading of an Energy Landscape from a previous calculation.

`GenerateSymmetryImages`

Type Bool

Default value No

Description By activating this option, after loading the energy landscape, it will create the complete set of symmetry-related copies by using the symmetry operators of the reference structure. Be aware that rkf result files of the generated symmetry images are copies from the parent structures but only atomic coordinates are updated.

`KeepOnly`

Type Integer List

GUI name List of states to keep

Description Upon loading the Energy Landscape, only keep the states specified here. The states should be specified via a list of integers referring to the indices of the states you want to keep.

`Path`

Type String

GUI name Load energy landscape from

Description AMS results folder to load an energy landscape from. In the text input file, you may alternatively specify a `.con` file in the native EON format.

`Remove`

Type Integer List

GUI name List of states to remove

Description Upon loading the Energy Landscape, remove (i.e. do not load) the states specified here. The states should be specified via a list of integers referring to the indices of the states you want to remove (i.e. the states you don't want to load).

`RemoveWithNoBindingSites`

Type Bool

Default value No

Description Upon loading the Energy Landscape, it removes states with no associated binding sites. Associated transition states are also removed. This is an advantageous option to remove physisorbed states automatically. Notice that it requires that the previous calculation was executed, enabling the option [BindingSites%Calculate].

`SeedStates`

Type Integer List

GUI name List of seed states

Description By default when you start a new PES Exploration from a loaded Energy Landscape, expeditions can start from any of the loaded minima. By using this input option, you can instruct the program to only use some of the states as 'expedition starting point'. The states that serve as 'expedition starting points' should be specified via a list of integers referring to the indices of the states.

`NegativeEigenvalueTolerance`

Type Float

Default value -0.0005

Unit Hartree/Bohr^2

Description The threshold in Hessian eigenvalue below which a mode is considered imaginary, i.e. indicating a transition state. This is a small negative number, as very small negative eigenvalues may be due to numerical noise on an essentially flat PES and do not indicate true transition states. We need a more flexible value for this parameter in PESExploration because the high computational cost of the task typically forces us to reduce the engine precision, which increases the noise in the vibrational frequencies evaluation. [PESPointCharacter%NegativeEigenvalueTolerance] is overridden by this parameter.

`NudgedElasticBand`

Type Block

Description Options for the Nudged Elastic Band (NEB) method.

`ClimbingImageMethod`

Type Bool

Default value Yes

Description Use the climbing image algorithm to drive the highest image to the transition state.

`ConvergedForce`

Type Float

Default value -1.0

Unit eV/Angstrom

Description Convergence threshold for nuclear gradients. Note: Special value of -1.0 means using the same convergence criterion as the PES explorer's geometry optimizer.

`Images`

Type Integer

Default value 5

Description Number of NEB images between the two endpoints.

`MaxIterations`

Type Integer

Default value 500

Description Maximum number of NEB iterations.

`OldTangent`

Type Bool

Default value No

Description Use the old central difference tangent.

`Spring`

Type Float

Default value 5.0

Unit eV/Ang^2

Description Spring force constant.

`NumExpeditions`

Type Integer

Default value 1

Description Sets the number of subsequent expeditions our job will consist of. Larger values result in a more comprehensive exploration of the potential energy surface, but will take more computational time.

`NumExplorers`

Type Integer

Default value 1

Description Sets the number of independent PES explorers dispatched as part of each expedition. Larger values will result in a more comprehensive exploration of the potential energy surface, but will take more computational time. By default an appropriate number of explorers are executed in parallel.

OptTSMethod

Type Multiple Choice

Default value SaddleSearch

Options [SaddleSearch, NudgedElasticBand]

Description When the full set of states in the energy landscape are optimized (see PESExploration%Job = GeometryOptimization), transition states can be optimized using either SaddleSearch or NudgedElasticBand methods. SaddleSearch uses information only from the current geometry of the TS; contrary, NudgedElasticBand ignores the current geometry and runs a Nudged-Elastic-Band calculation trying to connect the associated reactants and products if they are available.

Optimizer

Type Block

Description Configures the details of the geometry optimizers used by the PES explorers.

ConvergedForce

Type Float

Default value 0.005

Unit eV/Angstrom

Description Convergence threshold for nuclear gradients.

MaxIterations

Type Integer

Default value 400

Description Maximum number of iterations allowed for optimizations.

Method

Type Multiple Choice

Default value CG

Options [CG, QM, LBFGS, FIRE, SD]

Description Select the method for geometry optimizations.

Parallel

Type Block

Description Options for double parallelization, which allows to split the available processor cores into groups working through all the available tasks in parallel, resulting in a better parallel performance. The keys in this block determine how to split the available processor cores into groups working in parallel.

nCoresPerGroup

Type Integer

GUI name Cores per group

Description Number of cores in each working group.

nGroups

Type Integer

GUI name Number of groups

Description Total number of processor groups. This is the number of tasks that will be executed in parallel.

nNodesPerGroup

Type Integer

GUI name Nodes per group

Description Number of nodes in each group. This option should only be used on homogeneous compute clusters, where all used compute nodes have the same number of processor cores.

ParallelReplica

Type Block

Description ???.

DephaseLoopMax

Type Integer

Default value 5

Description ???.

DephaseLoopStop

Type Bool

Default value No

Description ???.

DephaseTime

Type Float

Default value 1000.0

Description ???.

PostTransitionTime

Type Float

Default value 1000.0

Description ???.

RefineTransition

Type Bool

Default value Yes

Description ???.

StateCheckInterval

Type Float

Default value 1000.0

Description ???.

StateSaveInterval

Type Float

Default value -1.0

Description ???.

`StopAfterTransition`

Type Bool

Default value No

Description ???.

`Prefactor`

Type Block

Description ???.

`Rate`

Type Multiple Choice

Default value HTST

Options [HTST, QQHTST]

Description Calculates the pre-exponential factors of the Reaction Rates using either Harmonic Transition State Theory (HTST) or quasi-quantum HTST (QQHTST).

`ProcessSearch`

Type Block

Description Input options specific to the process search procedure.

`MinimizationOffset`

Type Float

Default value 0.2

Description After a saddle is found, images are placed on either side of the saddle along the mode and minimized to ensure that the saddle is connected to the original minimum and to locate the product state. MinimizationOffset is the distance those images are displaced from the saddle.

`RandomSeed`

Type Integer

Description Number used to initialize both the EON clients random number generators as well as the AMS global RNG. The latter is normally initialized with the RNGSeed keyword at the root level. Should be used by developers only. May or may not help to make more reproducible regression tests …

`SaddleSearch`

Type Block

Description Configuration for the Saddle Search procedure (used in SaddleSearch and ProcessSearch Jobs).

`ConvergedForce`

Type Float

Default value -1.0

Unit eV/Angstrom

Description Convergence threshold for nuclear gradients. Note: Special value of -1.0 means using the same convergence criterion as the PES explorer's geometry optimizer.

`DisplaceAlongNormalModesActiveModes`

Type String

Default value

Description Sets the active modes to be used when the option [SaddleSearch%DisplaceAlongNormalModesWeight] is enabled. e.g. 1,2,3,5. By default, all normal modes are considered active.

`DisplaceAlongNormalModesWeight`

Type Float

Default value 0.0

Description The probability of generating a displacement resulting in a random linear combination of the normal modes specified in [SaddleSearch%DisplaceAlongNormalModesActiveModes]. This parameter is a numeric value that should fall within the interval [0.0, 1.0].

`DisplaceAtomsInRegion`

Type String

Default value

Description A string corresponding to the name of a region. When performing the initial random displacement, only displace atoms in the specified region.

`DisplaceAtomsInRegionWeight`

Type Float

Default value 0.0

Description The probability of generating a displacement involving only atoms from the region specified in [SaddleSearch%DisplaceAtomsInRegion]. This parameter is a numeric value that should fall within the interval [0.0, 1.0].

`DisplaceListedAtoms`

Type String

Default value

Description Sets the active atoms to be used when the option [SaddleSearch%DisplaceAlongNormalModesWeight] is enabled. e.g. 1,2,3,5. By default, all normal modes are considered active.

`DisplaceListedTypes`

Type String

Default value

Description ???.

`DisplaceMagnitude`

Type Float

Default value 0.1

Unit Angstrom

Description The standard deviation of the Gaussian displacement in each degree of freedom for the selected atoms.

`DisplaceRadius`

Type Float

Default value 4.0

Unit Angstrom

Description Atoms within this distance of the epicenter will be displaced.

`MaxEnergy`

Type Float

Default value 20.0

Unit eV

Description The energy (relative to the starting point of the saddle search) at which a saddle search explorer considers the search bad and terminates it.

`MaxIterations`

Type Integer

Default value 400

Description Maximum number of iterations for each saddle search run.

`MinEnergyBarrier`

Type Float

Default value 0.001

Unit eV

Description Minimum energy barrier to accept a new transition state.

`MinModeMethod`

Type Multiple Choice

Default value dimer

Options [dimer, lanczos]

Description The minimum-mode following method to use.

`RelaxFromSaddlePoint`

Type Bool

Default value No

Description Relaxes the saddle point geometries following the imaginary mode to get both reactants and products.

`ZeroModeAbortCurvature`

Type Float

Default value 0.01

Unit eV/Angstrom^2

Description The threshold in the frequency below which the minimum mode is considered zero. The calculation is aborted if the negative mode becomes zero.

`StatesAlignment`

Type Block

Description Configures details of how the energy landscape configurations are aligned respect to the main chemical system [System].

`DistanceDifference`

Type Float

Default value -1.0

Unit Angstrom

Description If the distance between two mapped atoms is larger than this threshold, the configuration is considered not aligned. If not specified, its value will set equal to [PESExploration%StructureComparison%DistanceDifference]

`ReferenceRegion`

Type String

Default value

Description Defines the region that is considered as the reference for alignments. Atoms outside this region are ignored in the alignments.

`StructureComparison`

Type Block

Description Settings for structure comparison.

`CheckRotation`

Type Bool

Description Rotates the system optimally before comparing structures. The default is to do this only for molecular systems when there are no fixed atom constraints.

`CheckSymmetry`

Type Bool

Default value No

Description Considers that two systems are equal if they are equivalent by symmetry.

`DistanceDifference`

Type Float

Default value 0.1

Unit Angstrom

Description If the distance between two mapped atoms is larger than this threshold, the two configurations are considered different structures.

`EnergyDifference`

Type Float

Default value 0.01

Unit eV

Description If the energy difference between two configurations is larger than this threshold, the two configurations are considered to be different structures.

`IndistinguishableAtoms`

Type Bool

Default value Yes

Description If yes, the order of the atoms does not affect the structural comparison. Atoms of the same element are then indistinguishable.

`NeighborCutoff`

Type Float

Default value 3.3

Unit Angstrom

Description Atoms within this distance of each other are considered neighbors.

`RemoveTranslation`

Type Bool

Description Translates the system optimally before comparing structures. The default is to do this only when there are no fixed atom constraints.

`Temperature`

Type Float

Default value 300.0

Unit Kelvin

Description The temperature that the job will run at. This may be used in different ways depending on the job, e.g. acceptance probabilities for Monte-Carlo based jobs, thermostatting for dynamics based jobs, kinetic prefactors for jobs that find transition states. Some jobs may not use this temperature at all.

`WriteEngineGradients`

Type Bool

Default value No

Description Write atomic gradients (negative of the atomic forces, as calculated by the engine) to the History section of ams.rkf.

`WriteHistory`

Type Multiple Choice

Default value Converged

Options [None, Converged, All]

Description When to write the molecular geometry (and possibly other properties) to the history on the ams.rkf file. The default is to only write the converged geometries to the history. Can be changed to write no frames at all to the history, or write all frames (should only be used when testing because of the performance impact). Note that for parallel calculations, only the first group of processes writes to ams.rkf.

`PESPointCharacter`

Type Block

Description Options for the characterization of PES points.

`Displacement`

Type Float

Default value 0.04

Description Controls the size of the displacements used for numerical differentiation: The displaced geometries are calculated by taking the original coordinates and adding the mass-weighted mode times the reduced mass of the mode times the value of this keyword.

`NegativeEigenvalueTolerance`

Type Float

Default value -0.0001

Unit Hartree/Bohr^2

Description The threshold in Hessian eigenvalue below which a mode is considered imaginary, i.e. indicating a transition state. This is a small negative number, as very small negative eigenvalues may be due to numerical noise on an essentially flat PES and do not indicate true transition states.

`NumberOfModes`

Type Integer

Default value 2

Description The number of (lowest) eigenvalues that should be checked.

`Tolerance`

Type Float

Default value 0.016

Description Convergence tolerance for residual in iterative Davidson diagonalization.

`PESScan`

Type Block

Description Configures the details of the potential energy surface scanning task.

`CalcPropertiesAtPESPoints`

Type Bool

Default value No

Description Whether to perform an additional calculation with properties on all the sampled points of the PES. If this option is enabled AMS will produce a separate engine output file for every sampled PES point.

`FillUnconvergedGaps`

Type Bool

Default value Yes

Description After the initial pass over the PES, restart the unconverged points from converged neighboring points.

`ScanCoordinate`

Type Block

Recurring True

Description Specifies a coordinate along which the potential energy surface is scanned. If this block contains multiple entries, these coordinates will be varied and scanned together as if they were one. Note that there can be only one ScanCoordinate containing a lattice scan in any PES scan job.

`Angle`

Type String

Recurring True

Description Scan the angle between three atoms. Three atom indices followed by two real numbers delimiting the transit range in degrees.

`CellVolumeRange`

Type Float List

Unit Angstrom^3

Description Two numbers for the initial and final cell volume. The cell is scaled isotropically between these values. Can not be used together with any other coordinate within the same ScanCoordinate block.

`CellVolumeScalingRange`

Type Float List

Description Two scaling factors for the initial and final cell volume. A value of '0.9 1.1' would result in an isotropic scaling between 90% and 110% of the cell volume of the input system. Can not be used together with any other coordinate within the same ScanCoordinate block.

`Coordinate`

Type String

Recurring True

Description Scan a particular coordinate of an atom. Atom index followed by (x|y|z) followed by two real numbers delimiting the transit range.

`DifDist`

Type String

Recurring True

Description Scan the difference distance between two pairs of atoms, R(12)-R(34). Four atom indices followed by two real numbers delimiting the transit range in Angstrom.

`Dihedral`

Type String

Recurring True

Description Scan the dihedral angle between four atoms. Four atom indices followed by two real numbers delimiting the transit angle in degrees.

`Distance`

Type String

Recurring True

Description Scan the distance between two atoms. Two atom indices followed by two real numbers delimiting the transit distance in Angstrom.

`FromLattice`

Type Non-standard block

Description Up to three lattice vectors to start the scan at. Has to be used in combination with the ToLattice keyword and no other coordinate within the same ScanCoordinate block. Unit can be specified in the header. Default unit is Angstrom.

`FromStrainVoigt`

Type Float List

Description The elements of the initial lattice strain in Voigt notation. One should specify 6 numbers for 3D periodic system (order: xx,yy,zz,yz,xz,xy), 3 numbers for 2D periodic systems (order: xx,yy,xy) or 1 number for 1D periodic systems. Has to be used in combination with the ToStrainVoigt keyword and no other coordinate within the same ScanCoordinate block.

`LatticeARange`

Type Float List

Unit Angstrom

Description Scans the length of the first lattice vector. Can be combined with the LatticeBRange and LatticeCRange keywords, but no other coordinates within the same ScanCoordinate.

`LatticeBRange`

Type Float List

Unit Angstrom

Description Scans the length of the second lattice vector. Can be combined with the LatticeARange and LatticeCRange keyword, but no other coordinates within the same ScanCoordinate..

`LatticeCRange`

Type Float List

Unit Angstrom

Description Scans the length of the third lattice vector. Can be combined with the LatticeARange and LatticeBRange keyword, but no other coordinates within the same ScanCoordinate..

`SumDist`

Type String

Recurring True

Description Scan the sum of distances between two pairs of atoms, R(12)+R(34). Four atom indices followed by two real numbers delimiting the transit range in Angstrom.

`ToLattice`

Type Non-standard block

Description Up to three lattice vectors to end the scan at. Unit can be specified in the header. Default unit is Angstrom.

`ToStrainVoigt`

Type Float List

Description The elements of the final lattice strain in Voigt notation. One should specify 6 numbers for 3D periodic system (order: xx,yy,zz,yz,xz,xy), 3 numbers for 2D periodic systems (order: xx,yy,xy) or 1 number for 1D periodic systems.

`nPoints`

Type Integer

Default value 10

Description The number of points along the scanned coordinate. Must be greater or equal 2.

`Print`

Type Block

Description This block controls the printing of additional information to stdout.

`Timers`

Type Multiple Choice

Default value None

Options [None, Normal, Detail, TooMuchDetail]

Description Printing timing details to see how much time is spend in which part of the code.

`Properties`

Type Block

Description Configures which AMS level properties to calculate for SinglePoint calculations or other important geometries (e.g. at the end of an optimization).

`BondOrders`

Type Bool

Default value No

Description Requests the engine to calculate bond orders.

For MM engines these might just be the defined bond orders that go into the force-field, while for QM engines, this might trigger a bond order analysis based on the electronic structure. For engines that do not have a bond order analysis method, a bond guessing algorithm will be used. See also the input options in the BondOrders block.

`Charges`

Type Bool

Default value No

Description Requests the engine to calculate the atomic charges.

`DipoleGradients`

Type Bool

Default value No

Description Requests the engine to calculate the nuclear gradients of the electric dipole moment of the molecule. This can only be requested for non-periodic systems.

`DipoleMoment`

Type Bool

Default value No

Description Requests the engine to calculate the electric dipole moment of the molecule. This can only be requested for non-periodic systems.

`ElasticTensor`

Type Bool

Default value No

Description Calculate the elastic tensor.

`GSES`

Type Bool

Default value No

Description Requests the engine to calculate the gradients of ground to excited state properties.

`Gradients`

Type Bool

Default value No

GUI name Nuclear gradients

Description Calculate the nuclear gradients.

`Hessian`

Type Bool

Default value No

Description Whether or not to calculate the Hessian.

`Molecules`

Type Bool

Default value No

Description Requests an analysis of the molecular components of a system, based on the bond orders calculated by the engine.

`NormalModes`

Type Bool

Default value No

GUI name Frequencies

Description Calculate the frequencies and normal modes of vibration, and for molecules also the corresponding IR intensities if the engine supports the calculation of dipole moments.

`OrbitalsInfo`

Type Bool

Default value No

Description Basic molecular orbitals information: orbital energies, occupations, HOMO, LUMO and HOMO-LUMO gap.

`Other`

Type Bool

Default value Yes

Description Other (engine specific) properties. Details are configured in the engine block.

`PESPointCharacter`

Type Bool

Default value No

GUI name Characterize PES point

Description Determine whether the sampled PES point is a minimum or saddle point. Note that for large systems this does not entail the calculation of the full Hessian and can therefore be used to quickly confirm the success of a geometry optimization or transition state search.

`Phonons`

Type Bool

Default value No

Description Calculate the phonons (for periodic systems).

`Polarizability`

Type Bool

Default value No

Description Requests the engine to calculate the polarizability tensor of the system.

`Raman`

Type Bool

Default value No

Description Requests calculation of Raman intensities for vibrational normal modes.

`SelectedRegionForHessian`

Type String

GUI name Hessian only for

Description Compute the Hessian matrix elements only for the atoms in a particular region. If not specified, the Hessian will be computed for all atoms.

`StressTensor`

Type Bool

Default value No

GUI name Stress tensor

Description Calculate the stress tensor.

`VCD`

Type Bool

Default value No

Description Requests calculation of VCD for vibrational normal modes.

VROA

Type Bool

Default value No

Description Requests calculation of VROA for vibrational normal modes.

Raman

Type Block

Description Configures details of the Raman or VROA calculation.

FreqRange

Type Float List

Unit cm-1

Recurring True

GUI name Frequency range

Description Specifies a frequency range within which all modes will be scanned. 2 numbers: an upper and a lower bound.

IncidentFrequency

Type Float

Default value 0.0

Unit eV

Description Frequency of incident light.

LifeTime

Type Float

Default value 0.0

Unit hartree

Description Specify the resonance peak width (damping) in Hartree units. Typically the lifetime of the excited states is approximated with a common phenomenological damping parameter. Values are best obtained by fitting absorption data for the molecule, however, the values do not vary a lot between similar molecules, so it is not hard to estimate values. A typical value is 0.004 Hartree.

Replay

Type Block

Description Configures the details of the Replay task.

File

Type String

GUI name Restart from

Description Provide an ams.rkf file (or a .results folder) from a previously run job to replay. The file needs to contain a History section.

Frames

Type Integer List

Description List of frames from the History section to recompute.

If not specified the recomputed frames are determined automatically based on the task of the job that is being replayed: PES scans and NEB calculations will only have the converged points replayed, while all other tasks will have all frames recomputed.

Specifying the frames to recompute in the input is probably only useful when replaying trajectories from MolecularDynamics calculations.

`StoreAllResultFiles`

Type Bool

Default value No

Description If this option is enabled AMS will produce a separate engine output file for every replayed frame.

While basic properties like energy, gradients, stress tensor, etc. are stored anyway on the History section in the AMS driver output file (if they were requested in the Properties block), engine specific properties (e.g. excitations energies from ADF) will only be available if the full result files are stored.

`Restraints`

Type Block

Description The Restraints block allows to add soft constraints to the system. A restraint is a potential energy function (a spring) attached to a certain coordinate, for example, an interatomic distance, with its minimum at the specified optimal value. A restraint is defined using one or two parameters: the ForceConstant and, for some types, the F(Inf) value. The ForceConstant parameter corresponds to second derivative of the restraint potential energy d2V(x)/dx^2 for any x (harmonic restraints) or only at at x=0 (other restraints). Here, x is a deviation from the restraint's optimal value.

`Angle`

Type String

Recurring True

Description Specify three atom indices i j k followed by an angle in degrees and, optionally, by the ForceConstant (default is 0.3 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the i-j-k angle at the given value. For periodic systems this restraint follows the minimum image convention.

`DifDist`

Type String

Recurring True

Description Specify four atom indices i j k l followed by the distance in Angstrom and, optionally, by the ForceConstant (default is 1.0 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the difference R(ij)-R(kl) at the given value. For periodic systems this restraint follows the minimum image convention.

`Dihedral`

Type String

Recurring True

Description Specify four atom indices i j k l followed by an angle in degrees and, optionally, by the ForceConstant (default is 0.1 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the i-j-k-l dihedral angle at the given value. For periodic systems this restraint follows the minimum image convention.

`Distance`

Type String

Recurring True

Description Specify two atom indices followed by the distance in Angstrom and, optionally, by the ForceConstant (default is 1.0 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the distance between the two specified atoms at the given value. For periodic systems this restraint follows the minimum image convention.

`FInfinity`

Type Float

Default value 1.0

GUI name Default F(inf)

Description Specify the default asymptotic value for the restraint force for the Hyperbolic and Erf profiles, in Hartree/Bohr or Hartree/radian.

A per-restraint value can be specified after the profile type on the corresponding restraint line.

`Profile`

Type Multiple Choice

Default value Harmonic

Options [Harmonic, Hyperbolic, Erf, GaussianWell]

GUI name Default restraint profile

Description Select the default type of restraint profile.

The harmonic profile is most suitable for geometry optimizations but may result is very large forces that can be problematic in molecular dynamic.

For MD simulations the Hyperbolic or Erf may be more suitable because the restraint force is bounded by a user-defined value.

A per-restraint profile type can be specified after the ForceConstant value on the corresponding restraint line.

`SumDist`

Type String

Recurring True

Description Specify four atom indices i j k l followed by the distance in Angstrom and, optionally, by the ForceConstant (default is 1.0 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the sum R(ij)+R(kl) at the given value. For periodic systems this restraint follows the minimum image convention.

`Units`

Type Multiple Choice

Default value Default

Options [Default, MD]

GUI name Units

Description Change units for energy, force and force constant values from the default (atomic units) to those often used in the MD community (based on kcal/mol and Angstrom). Units for the optimal distances are not affected and are always Angstrom.

`RigidMotions`

Type Block

Description Specify which rigid motions of the total system are allowed. An external field is not considered part of the system. Normally the automatic option is doing what you want. However this feature can be used as a means of geometry constraint.

`AllowRotations`

Type Multiple Choice

Default value Auto

Options [Auto, None, All, X, Y, Z, XY, XZ, YZ]

Description Which overall rotations of the system are allowed

`AllowTranslations`

Type Multiple Choice

Default value Auto

Options [Auto, None, All, X, Y, Z, XY, XZ, YZ]

Description Which overall transitions of the system are allowed

`Tolerance`

Type Float

Default value 1e-06

Description Tolerance for detecting linear molecules. A large value means larger deviation from linearity is permitted.

`RNGSeed`

Type Integer List

Description Initial seed for the (pseudo)random number generator. This should be omitted in most calculations to avoid introducing bias into the results. If this is unset, the generator will be seeded randomly from external sources of entropy. If you want to exactly reproduce an older calculation, set this to the numbers printed in its output.

`SCMMatrix`

Type Block

Description Technical settings for programs using the AMT matrix system. Currently this is only used by DFTB

`DistributedMatrix`

Type Block

Description Technical settings for Distributed matrices

`ColBlockSize`

Type Integer

Default value 64

Description See comment of RowBlockSize.

`RowBlockSize`

Type Integer

Default value 64

Description The matrix is divided into blocks of size RowBlockSize x ColBlockSize. The smaller the blocks the better the distribution, but at the expense of increased communication overhead

`Type`

Type Multiple Choice

Default value Elpa

Options [Auto, Reference, ScaLapack, Elpa]

Description Determines which implementation is used to support the AbstractMatrixType.

`Symmetry`

Type Block

Description Specifying details about the details of symmetry detection and usage.

`SymmetrizeTolerance`

Type Float

Default value 0.05

Description Tolerance used to detect symmetry in case symmetrize is requested.

`Tolerance`

Type Float

Default value 1e-07

Description Tolerance used to detect symmetry in the system.

`System`

Type Block

Recurring True

Description Specification of the chemical system. For some applications more than one system may be present in the input. In this case, all systems except one must have a non-empty string ID specified after the System keyword. The system without an ID is considered the main one.

`AllowCloseAtoms`

Type Bool

Default value No

Description If AllowCloseAtoms is set to False, the AMS driver will stop with an error if it detects almost-coinciding atomic coordinates. If set to True, the AMS driver will try to carry on with the calculation.

`Atoms`

Type Non-standard block

Description The atom types and coordinates. Unit can be specified in the header. Default unit is Angstrom.

`BondOrders`

Type Non-standard block

Description Defined bond orders. Each line should contain two atom indices, followed by the bond order (1, 1.5, 2, 3 for single, aromatic, double and triple bonds) and (optionally) the cell shifts for periodic systems. May be used by MM engines and for defining constraints. If the system is periodic and none of the bonds have the cell shift defined then AMS will attempt to determine them following the minimum image convention.

`Charge`

Type Float

Default value 0.0

GUI name Total charge

Description The system's total charge in atomic units.

`ElectrostaticEmbedding`

Type Block

Description Container for electrostatic embedding options, which can be combined.

`ElectricField`

Type Float List

Unit V/Angstrom

Description External homogeneous electric field with three Cartesian components: ex, ey, ez, the default unit being V/Å.

In atomic units: Hartree/(e bohr) = 14.39964 V/Angstrom; the relation to SI units is: 1 Hartree/(e bohr) = 5.14 … e11 V/m.

Supported by the engines adf, band, dftb and mopac.

For periodic systems the field may only have nonzero components orthogonal to the direction(s) of periodicity (i.e. for 1D periodic system the x-component of the electric field should be zero, while for 2D periodic systems both the x and y components should be zero. This options cannot be used for 3D periodic systems.

`MultipolePotential`

Type Block

Description External point charges (and dipoles).

`ChargeModel`

Type Multiple Choice

Default value Point

Options [Point, Gaussian]

Description A multipole may be represented by a point (with a singular potential at its location) or by a spherical Gaussian distribution.

`ChargeWidth`

Type Float

Default value -1.0

Description The width parameter in a.u. in case a Gaussian charge model is chosen. A negative value means that the width will be chosen automatically.

Coordinates

Type Non-standard block

Description Positions and values of the multipoles, one per line. Each line has the following format:

x y z q, or x y z q μx μy μz.

Here x, y, z are the coordinates in Å, q is the charge (in atomic units of charge) and μx, μy, μz are the (optional) dipole moment components (in atomic units, i.e. e*Bohr).

Periodic systems are not supported.

FractionalCoords

Type Bool

Default value No

Description Whether the atomic coordinates in the Atoms block are given in fractional coordinates of the lattice vectors. Requires the presence of the Lattice block.

GeometryFile

Type String

Description Read the geometry from a file (instead of from Atoms and Lattice blocks). Supported formats: .xyz

GuessBonds

Type Bool

Default value No

Description Whether or not UFF bonds should be guessed.

Lattice

Type Non-standard block

Description Up to three lattice vectors. Unit can be specified in the header. Default unit is Angstrom.

LatticeStrain

Type Float List

Description Deform the input system by the specified strain. The strain elements are in Voigt notation, so one should specify 6 numbers for 3D periodic system (order: xx,yy,zz,yz,xz,xy), 3 numbers for 2D periodic systems (order: xx,yy,xy) or 1 number for 1D periodic systems.

LoadForceFieldAtomTypes

Type Block

Description This is a mechanism to set the ForceField.Type attribute in the input. This information is currently only used by the ForceField engine.

File

Type String

Description Name of the (kf) file. It needs to be the result of a forcefield calculation.

`LoadForceFieldCharges`

Type Block

Recurring True

Description This is a mechanism to set the ForceField.Charge attribute in the input. This information is currently only used by the ForceField engine.

`CheckGeometryRMSD`

Type Bool

Default value No

Description Whether the geometry RMSD test should be performed, see MaxGeometryRMSD. Otherwise only basic tests are performed, such as number and atom types. Not doing the RMSD test allows you to load molecular charges in a periodic system.

`File`

Type String

Description Name of the (kf) file

`MaxGeometryRMSD`

Type Float

Default value 0.1

Unit Angstrom

Description The geometry of the charge producing calculation is compared to the one of the region, and need to be the same within this tolerance.

`Region`

Type String

Default value *

Description Region for which the charges should be loaded

`Section`

Type String

Default value AMSResults

Description Section name of the kf file

`Variable`

Type String

Default value Charges

Description Variable name of the kf file

`MapAtomsToUnitCell`

Type Bool

Default value No

Description For periodic systems the atoms will be moved to the central cell.

`ModifyAlternativeElements`

Type Bool

Default value No

Description When using alternative elements (using the nuclear_charge attribute) set the element to the nearest integer Z. If you specify an H atom with a nuclear_charge of 2.9 it is replaced by a Li atom with the same nuclear charge.

`PerturbCoordinates`

Type Float

Default value 0.0

Unit Angstrom

Description Perturb the atomic coordinates by adding random numbers between [-PerturbCoordinates,PerturbCoordinates] to each Cartesian component. This can be useful if you want to break the symmetry of your system (e.g. for a geometry optimization).

`PerturbLattice`

Type Float

Default value 0.0

Description Perturb the lattice vectors by applying random strain with matrix elements between [-PerturbLattice,PerturbLattice]. This can be useful if you want to deviate from an ideal symmetric geometry, for example if you look for a phase change due to high pressure.

`RandomizeAtomOrder`

Type Bool

Default value No

Description Whether or not the order of the atoms should be randomly changed. Intended for some technical testing purposes only. Does not work with bond information.

`Region`

Type Block

Recurring True

Description Properties for each region specified in the Atoms block.

`Properties`

Type Non-standard block

Description Properties for each region specified in the Atoms block.

`ShiftCoordinates`

Type Float List

Unit Bohr

Description Translate the atoms by the specified shift (three numbers).

`SuperCell`

Type Integer List

Description Create a supercell of the input system (only possible for periodic systems). The integer numbers represent the diagonal elements of the supercell transformation; you should specify as many numbers as lattice vectors (i.e. 1 number for 1D, 2 numbers for 2D and 3 numbers for 3D periodic systems).

`SuperCellTrafo`

Type Integer List

Description Create a supercell of the input system (only possible for periodic systems) $\vec{a}'_i = \sum_j T_{ij} \vec{a}_j$. The integer numbers represent the supercell transformation T_{ij}: 1 number for 1D PBC, 4 numbers for 2D PBC corresponding to a 2x2 matrix (order: (1,1),(1,2),(2,1),(2,2)) and 9 numbers for 3D PBC corresponding to a 3x3 matrix (order: (1,1),(1,2),(1,3),(2,1),(2,2),(2,3),(3,1),(3,2),(3,3)).

`Symmetrize`

Type Bool

Default value No

Description Whether to symmetrize the input structure. This might also rototranslate the structure into a standard orientation. This will symmetrize the atomic coordinates to machine precision. Useful if the system is almost symmetric or to rototranslate a symmetric molecule into a standard orientation.

`Symmetry`

Type Multiple Choice

Default value AUTO

Options [AUTO, NOSYM, C(LIN), D(LIN), C(I), C(S), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(2V), C(3V), C(4V), C(5V), C(6V), C(7V), C(8V), C(2H), C(3H), C(4H), C(5H), C(6H), C(7H), C(8H), D(2), D(3), D(4), D(5), D(6), D(7), D(8), D(2D), D(3D), D(4D), D(5D), D(6D), D(7D), D(8D), D(2H), D(3H), D(4H), D(5H), D(6H), D(7H), D(8H), I, I(H), O, O(H), T, T(D), T(H), S(4), S(6), S(8)]

Description Use (sub)symmetry with this Schoenflies symbol. Can only be used for molecules. Orientation should be correct for the (sub)symmetry. If used icw Symmetrize, the symmetrization will not reorient the molecule.

`Task`

Type Multiple Choice

Options [GCMC, GeometryOptimization, IRC, MolecularDynamics, NEB, PESExploration, PESScan, Replay, SinglePoint, TransitionStateSearch, VibrationalAnalysis]

Description Specify the computational task to perform:

• Single Point: keep geometry as is • Geometry Optimization: minimize energy • Transition State: search for a transition state • IRC: intrinsic reaction coordinate • PES Scan: scan the potential energy surface • NEB: Nudged elastic band for reaction path optimization • Vibrational Analysis: perform one of the analysis types selected on the options page • Molecular Dynamics: perform MD simulation • GCMC: Grand Canonical Monte Carlo simulation • PES Exploration: automated potential energy surface exploration • Replay: recompute frames from the trajectory of a previously run job

`Thermo`

Type Block

Description Options for thermodynamic properties (assuming an ideal gas). The properties are computed for all specified temperatures.

`LowFrequencyCorrector`

Type Block

Description Options for the dampener-powered free rotor interpolator that corrects thermodynamic quantities for low frequencies. See DOI:10.1021/jp509921r and DOI:10.1002/chem.201200497.

`Alpha`

Type Float

Default value 4.0

Description The exponent term used in the dampener.

`Frequency`

Type Float

Default value 100.0

Unit cm-1

Description The frequency around which the dampener interpolates between harmonic oscillator and free rotor quantities.

`MomentOfInertia`

Type Float

Default value 1e-44

Unit kg m^2

GUI name Averaging Moment of Inertia

Description The moment of inertia used to restrict entropy results for very small frequencies (generally around less than 1 cm-1).

`Pressure`

Type Float

Default value 1.0

Unit atm

Description The pressure at which the thermodynamic properties are computed.

`Temperatures`

Type Float List

Default value [298.15]

Unit Kelvin

Value Range value >= 0

Description List of temperatures at which the thermodynamic properties will be calculated.

`TransitionStateSearch`

Type Block

Description Configures some details of the transition state search.

ModeToFollow

Type Integer

Default value 1

Description In case of Transition State Search, here you can specify the index of the normal mode to follow (1 is the mode with the lowest frequency).

ReactionCoordinate

Type Block

Description Specify components of the transition state reaction coordinate (TSRC) as a linear combination of internal coordinates (distances or angles).

Angle

Type String

Recurring True

Description The TSRC contains the valence angle between the given atoms. Three atom indices followed by the weight.

Block

Type String

Recurring True

Description Name of the region. Only atoms of the region will be included in the TSRC. It is useful when computing the reaction coordinate from the initial Hessian, in which case only part of the Hessian will be analyzed.

BlockAtoms

Type Integer List

Value Range value > 0

Recurring True

Description List of atom indices. Only the listed atoms will be included in the TSRC. It is useful when computing the reaction coordinate from the initial Hessian, in which case only part of the Hessian will be analyzed.

Coordinate

Type String

Recurring True

Description The TSRC contains Cartesian displacement of an atom: atom index followed by [x|y|z] and the weight.

Dihedral

Type String

Recurring True

Description The TSRC contains the dihedral angle between the given atoms. Four atom indices followed by the weight.

Distance

Type String

Recurring True

Description The TSRC contains the distance between the given atoms. Two atom indices followed by the weight.

UseSymmetry

Type Bool

Default value Yes

Description Whether to use the system's symmetry in AMS. Symmetry is recognized within a tolerance as given in the Symmetry key.

VibrationalAnalysis

Type Block

Description Input data for all vibrational analysis utilities in the AMS driver.

AbsorptionSpectrum

Type Block

Description Settings related to the integration of the spectrum for vibronic tasks.

AbsorptionRange

Type Float List

Default value [-200.0, 4000.0]

Unit cm-1

Recurring True

Description Specifies frequency range of the vibronic absorption spectrum to compute. 2 numbers: an upper and a lower bound.

FrequencyGridPoints

Type Integer

Default value 400

Description Number of grid points to use for the spectrum

LineWidth

Type Float

Default value 200.0

Unit cm-1

Description Lorentzian line-width.

SpectrumOffset

Type Multiple Choice

Default value relative

Options [absolute, relative]

Description Specifies whether provided frequency range are absolute frequencies or frequencies relative to computed 0-0 excitation energy.

Displacement

Type Float

Unit Bohr

Description Step size for finite difference calculations.

`ExcitationSettings`

Type Block

Description Block that contains settings related to the excitation for vibronic tasks.

`EnergyInline`

Type Float

Unit hartree

Description Vertical excitation energy, used when [ExcitationInfo] = [Inline].

`ExcitationFile`

Type String

Description Path to a .rkf/.t21 file containing the excited state information (gradients, transition dipoles and energies).

`ExcitationInputFormat`

Type Multiple Choice

Default value File

Options [File, Inline]

Description Select how the application should retrieve the excited state information (energy, gradient).

`GradientInline`

Type Non-standard block

Description Excited state gradient at ground state equilibrium geometry, used when [ExcitationInfo] = [Inline].

`Singlet`

Type Non-standard block

Description Symmetry labels + integer indices of desired singlet transitions (VG-FC absorption spectra support only 1 at a time)

`Triplet`

Type Non-standard block

Description Symmetry labels + integer indices of desired triplet transitions (VG-FC absorption spectra support only 1 at a time)

`ModeTracking`

Type Block

Description Input data for Mode Tracking.

`HessianGuess`

Type Multiple Choice

Default value CalculateWithFastEngine

Options [Unit, File, CalculateWithFastEngine]

GUI name Guess Hessian

Description Sets how to obtain the guess for the Hessian used in the preconditioner (if one is to be used).

`HessianInline`

Type Non-standard block

Description Initial guess for the (non-mass-weighted) Hessian in a 3N x 3N block, used when [HessianGuess] = [Inline].

`HessianPath`

Type String

Description Path to a .rkf file containing the initial guess for the Hessian, used when [HessianGuess] = [File]. It may also be the name of the results folder containing the engine file.

`ToleranceForBasis`

Type Float

Default value 0.0001

Description Convergence tolerance for the contribution of the newest basis vector to the tracked mode.

`ToleranceForNorm`

Type Float

Default value 0.0005

Description Convergence tolerance for residual RMS value.

`ToleranceForResidual`

Type Float

Default value 0.0005

Description Convergence tolerance for the maximum component of the residual vector.

`ToleranceForSpectrum`

Type Float

Default value 0.01

Description Convergence tolerance for the spectrum in Vibronic Structure Tracking.

`TrackingMethod`

Type Multiple Choice

Default value OverlapInitial

Options [OverlapInitial, DifferenceInitial, FreqInitial, IRInitial, OverlapPrevious, DifferencePrevious, FreqPrevious, IRPrevious, HighestFreq, HighestIR, LowestFreq, LowestResidual]

Description Set the tracking method that will be used. Vibronic Structure Tracking uses Largest Displacement.

`UpdateMethod`

Type Multiple Choice

Options [JD, D, I]

Description Chooses the method for expanding the Krylov subspace: (I) No preconditioner (VST default), (D) Davidson or (JD) vdVorst-Sleijpen variant of Jacobi-Davidson (Mode tracking default).

`NormalModes`

Type Block

Description All input related to processing of normal modes. Not available for vibronic structure tracking (as no modes are required there).

`MassWeightInlineMode`

Type Bool

Default value Yes

Description MODE TRACKING ONLY: The supplied modes must be mass-weighted. This tells the program to mass-weight the supplied modes in case this has not yet been done. (True means the supplied modes will be mass-weighted by the program, e.g. the supplied modes are non-mass-weighted.)

`ModeFile`

Type String

Description Path to a .rkf or .t21 file containing the modes which are to be scanned. Which modes will be scanned is selected using the criteria from the [ModeSelect] block.) This key is optional for Resonance Raman and Vibronic Structure. These methods can also calculate the modes using the engine.

`ModeInline`

Type Non-standard block

Recurring True

Description MODE TRACKING ONLY: Coordinates of the mode which will be tracked in a N x 3 block (same as for atoms), used when [ModeInputFormat] = [Inline]. Rows must be ordered in the same way as in the [System%Atoms] block. Mode Tracking only.

`ModeInputFormat`

Type Multiple Choice

Default value File

Options [File, Inline, Hessian]

GUI name Tracked mode source

Description Set how the initial guesses for the modes are supplied. Only mode tracking supports the Inline and Hessian options.

`ModeSelect`

Type Block

Description Pick which modes to read from file.

`DisplacementBound`

Type Float

Description Vibronic Structure (Refinement), Resonance Raman: Select all modes with a dimensionless oscillator displacement greater than the specified value.

`FreqAndIRRange`

Type Float List

Recurring True

Description Specifies a combined frequency and IR intensity range within which all modes will be selected. First 2 numbers are the frequency range in cm-1, last 2 numbers are the IR intensity range in km/mol.

`FreqRange`

Type Float List

Unit cm-1

Recurring True

Description Specifies a frequency range within which all modes will be selected. 2 numbers: an upper and a lower bound. Calculating all modes higher than some frequency can be achieved by making the upper bound very large.

`Full`

Type Bool

Default value No

GUI name All modes

Description Select all modes. This only make sense for Mode Scanning calculations.

`HighFreq`

Type Integer

GUI name # High frequencies

Description Select the N modes with the highest frequencies.

`HighIR`

Type Integer

GUI name # High IR

Description Select the N modes with the largest IR intensities.

`IRRange`

Type Float List

Unit km/mol

Recurring True

Description Specifies an IR intensity range within which all modes will be selected. 2 numbers: an upper and a lower bound.

`ImFreq`

Type Bool

Default value No

GUI name All imaginary frequencies

Description Select all modes with imaginary frequencies.

`LargestDisplacement`

Type Integer

Description Vibronic Structure (Refinement), Resonance Raman: Select the N modes with the largest VG-FC displacement.

`LowFreq`

Type Integer

GUI name # Low frequencies

Description Select the N modes with the lowest frequencies. Includes imaginary modes which are recorded with negative frequencies.

`LowFreqNoIm`

Type Integer

GUI name # Low positive frequencies

Description Select the N modes with the lowest non-negative frequencies. Imaginary modes have negative frequencies and are thus omitted here.

`LowIR`

Type Integer

GUI name # Low IR

Description Select the N modes with the smallest IR intensities.

`ModeNumber`

Type Integer List

GUI name Mode numbers

Description Indices of the modes to select.

`ScanModes`

Type Bool

Default value No

GUI name Scan after refining

Description Supported by: Mode Tracking, Mode Refinement, Vibronic Structure Refinement: If enabled an additional displacement will be performed along the new modes at the end of the calculation to obtain refined frequencies and IR intensities. Equivalent to running the output file of the mode tracking calculation through the AMS ModeScanning task.

`ResonanceRaman`

Type Block

Description Block that contains settings for the calculation of Resonance Raman calculations

`IncidentFrequency`

Type Float

Unit cm-1

Description Frequency of incident light. Also used to determine most important excitation in case more than one is provided.

`LifeTime`

Type Float

Default value 0.00045

Unit hartree

Description Lifetime of Raman excited state.

`RamanOrder`

Type Integer

Default value 2

Description Order up to which to compute Raman transitions

`RamanRange`

Type Float List

Default value [0.0, 2000.0]

Unit cm-1

Recurring True

Description Specifies frequency range of the Raman spectrum to compute. 2 numbers: an upper and a lower bound.

`Type`

Type Multiple Choice

Options [ModeScanning, ModeTracking, ModeRefinement, VibronicStructure, VibronicStructureTracking, VibronicStructureRefinement, ResonanceRaman]

Description Specifies the type of vibrational analysis that should be performed

`VSTRestartFile`

Type String

Description Path to a .rkf file containing restart information for VST.

15.2.2 analysis

`AutoCorrelation`

Type Block

Recurring True

Description All input related to auto correlation functions.

`Atoms`

Type Block

Description Relevant if Property is set to Velocities, DipoleMomentFromCharges, DipoleDerivativeFromCharges, or DiffusionCoefficient. Atom numbers or elements for the set of atoms for which the property is read/computed. By default all atoms are used.

`Atom`

Type Integer

Recurring True

Description Atom number.

`Element`

Type String

Recurring True

Description Element Symbol Atom.

`Region`

Type String

Recurring True

Description Region name.

`DataReading`

Type Multiple Choice

Default value Auto

Options [Auto, AtOnce, BlockWise]

Description The KF data can be read in and handled once, or blockwise. The former is memory intensive, but mostly faster. If Auto is selected, the data is read at once if it is less than 1 GB, and blockwise if it is more.

`InputValues`

Type Block

Description Relevant if Property is set to InputValues. All input values (a vector on each line) need to be provided in this block, using the keyword Values (possibly multiple times).

`Values`

Type Float List

Recurring True

Description The values at each step (on a single line)

`MaxFrame`

Type Integer

Description The maximum number of frames for which the autocorrelation function will be computed. The default is half of the number of provided frames.

`NPointsHighestFreq`

Type Integer

Default value 4

Description The number of points (timesteps) used for the highest frequency displayed in spectrum. This determines up to which frequency the spectrum is displayed. If the spacing between time-steps used for the ACF is 1 fs, then by default the maximum frequency displayed is 0.25 fs-1 (or 8339 cm-1). This corresponds to a (default) value of NPointsHighestFreq of 4. A higher number selected here, will result in a lower maximum frequency returned by the program. The lowest possible value (spectrum up to highest possible frequency) is 2.

`PerElement`

Type Bool

Default value No

Description Compute ACF for all elements in the system. Any other settings in the block will be used.

`Property`

Type Multiple Choice

Default value DipoleDerivativeFromCharges

Options [Velocities, DipoleMomentFromCharges, DiffusionCoefficient, DipoleDerivativeFromCharges, PressureTensor, Viscosity, DipoleMomentFromBinLog, ViscosityFromBinLog]

Description Compute the ACF either from velocities (from rkf), the dipole moment (from coordinates and atomic charges in rkf), the dipole moment derivative (from velocities and atomic charges in rkf), from the pressure tensor (from rkf), or from values specified in input. Selecting DiffusionCoefficient is equivalent to selecting Velocities. The default, DipoleDerivativeFromCharges, results in the computation of an IR spectrum.DipoleMomentFromBinLog and ViscosityFromBinLog allow the relevant properties (dipole moment and pressure tensor respectively) to be read from the BinLog section of the trajectory file. In the BinLog section requested properties are stored every step (even if SamplingFreq was set to a higher number than 1) but only if this was specifically requested at the start of the MD simulation.

`TimeStep`

Type Float

Description Relevant if Property is set to InputValues. The time separating the entries (in fs). If Property is set to any of the other quantities, it can be read from an RKF file, and the timestep is read from the RKF file as well. The read value then overrides this keyword.

`UnwrapCoordinates`

Type Multiple Choice

Default value Auto

Options [Auto, Yes, No]

Description If the coordinates are involved in the requested property, those coordinates are wrapped into the box at each time step. If set to true, this keyword unwraps those coordinates so that the trajectory is continuous. If not provided the code uses automatic defaults.

`UseAllValues`

Type Bool

Default value No

Description By default the same number of values are used for each t-step in the ACF. This has the advantage that all values in the ACF are equally reliable, but it does mean that for the smaller timesteps much of the data is not used. To switch this off and use all data, UseAllValues can be set to true

`UseTimeDerivative`

Type Block

Description Possibly use the time derivative of the selected property (e.g. velocity or dipole moments).

`Enabled`

Type Bool

Default value No

Description Enable the use of the time derivative of the property.

`VecElements`

Type Block

Description A set of indices referring to a subset of the property vector. Works in combination with the atoms block. For example, in combination with the property Velocities, the Atoms block allows the selection of a subset of atoms, while the VecElelements block allows the selection of a subset of vector elements (e.g. 1 and 2 for the elements x and y). Currently not implemented with InputValues.

`Index`

Type Integer

Recurring True

Description Element of the property vector.

`WritePropertyToKF`

Type Bool

Default value No

Description Write the selected property to the KF files for every requested frame

`AverageBinPlot`

Type Block

Recurring True

Description All input related to velocity profile

`Atoms`

Type Block

Description Relevant if Properties are atom dependent. Atom numbers or elements for the set of atoms for which the property is read/computed. By default all atoms are used.

`Atom`

Type Integer

Recurring True

Description Atom number.

`Element`

Type String

Recurring True

Description Element Symbol Atom.

`Region`

Type String

Recurring True

Description Region name.

`Nbins`

Type Integer

Default value 10

Description Number of bins that are plotted

`Property`

Type Block

Description Property to be plotted along the Y-axis

`Axis`

Type Float List

Description If defined the dot_product along this axis will be taken. Otherwise, the length of the property vector will be used.

`Name`

Type Multiple Choice

Options [FrictionCoefficient, Viscosity, Velocities, EngineGradients]

Description Name of the property

`XProperty`

Type Block

Description Property to be plotted along the Y-axis

`Name`

Type Multiple Choice

Default value Time

Options [Time, Coords]

Description Timestep used for the plotting

`VecElements`

Type Block

Description A set of indices referring to a subset of the property vector. Works in combination with the atoms block. For example, in combination with the property Velocities, the Atoms block allows the selection of a subset of atoms, while the VecElelements block allows the selection of a subset of vector elements (e.g. 1 and 2 for the elements x and y). Currently not implemented with InputValues.

`Index`

Type Integer

Default value 3

Description Element of the x_property, in case it is a vector (For Coords: 1 for X, 2 for Y, 3 for Z).

`Histogram`

Type Block

Recurring True

Description All input related to histograms.

`Axes`

Type Block

Description Specifications for the histogram axes.

`Axis`

Type Block

Recurring True

Description Specifications for a single histogram axis.

`Atoms`

Type Block

Description Relevant if variable has a value per atom (e.g. Coords, Velocities). This block specifies indices or elements for the set of atoms for which the variable is to be read. By default all atoms are used.

`Atom`

Type Integer

Recurring True

Description Atom index.

`Element`

Type String

Recurring True

Description Element Symbol Atom.

`Region`

Type String

Recurring True

Description Region name

`NBins`

Type Integer

Default value 100

Description The number of bins along the histogram axis.

`Range`

Type Float List

Description Either one, two, or three real values. If one it is the stepsize. If two, it is the minimum value and the maximum value. If three, it is the minimum value, the maximum value, and the stepsize. The stepsize overrides NBins.

`Variable`

Type String

Description The quantity along the histogram axis.

`VecElements`

Type Block

Description A set of indices referring to a subset of a vector. If the variable to be plotted has non-scalar values per step, then this block allows the selection of a subset of vector elements (e.g. 1 and 2 for the x and y values). Can be used in combination with the Atoms block.

`Index`

Type Integer

Recurring True

Description Element of the property vector.

`KeepRemainder`

Type Bool

Default value No

Description Place the values that fall outside the range in an extra bin (on the right).

`Normalized`

Type Bool

Default value No

Description Give the normalized histogram.

`MeanSquareDisplacement`

Type Block

Recurring True

Description All input related to auto correlation functions.

`Atoms`

Type Block

Description Relevant if Property is set to any quantity that is available per atom (Coords, DiffusionCoefficient). Atom numbers or elements for the set of atoms for which the property is read/computed are provided here. By default all atoms are used.

`Atom`

Type Integer

Recurring True

Description Atom number.

`Element`

Type String

Recurring True

Description Element Symbol Atom.

`Region`

Type String

Recurring True

Description Region name.

`DataReading`

Type Multiple Choice

Default value Auto

Options [Auto, AtOnce, BlockWise]

Description The KF data can be read in and handled once, or blockwise. The former is memory intensive, but mostly faster. If Auto is selected, the data is read at once if it is less than 1 GB, and blockwise if it is more.

`InputValues`

Type Block

Description Relevant if Property is set to InputValues. All input values (a vector on each line) need to be provided in this block, using the keyword Values (possibly multiple times).

`Values`

Type Float List

Recurring True

Description The values at each step (on a single line)

`MaxFrame`

Type Integer

Description The maximum number of frames for which the mean square displacement function will be computed. The default is half of the number of provided frames.

`PerElement`

Type Bool

Default value No

Description Compute MSD for all elements in the system. Any other settings in thie block will be used.

`Property`

Type Multiple Choice

Default value Coords

Options [Coords, DiffusionCoefficient, Conductivity]

Description Compute the MSD from the property selected here (from rkf). Selecting Diffusion-Coefficient is equivalent to selecting the property Coords.

`StartTimeSlope`

Type Float

Default value 0.0

Description The MSD has a nonlinear regime at short timescales, and a linear regime at long timescales. To determine the slope, the starting point for the linear regime has to be determined. This keyword sets the starting time in fs. If set to zero, the starttime will be automatically determined.

`TimeStep`

Type Float

Description Relevant if Property is set to InputValues. The time separating the entries (in fs). If Property is set to any of the other quantities, it can be read from an RKF file, and the timestep is read from the RKF file as well. The read value then overrides this keyword.

`UnwrapCoordinates`

Type Multiple Choice

Default value Auto

Options [Auto, Yes, No]

Description If the coordinates are involved in the requested property, those coordinates are wrapped into the box at each time step. If seti to true, this keyword unwraps those coordinates so that the trajectory is continuous. If not provided the code uses automatic defaults.

`UseAllValues`

Type Bool

Default value No

Description By default the same number of values are used for each t-step in the MSD. This has the advantage that all values in the MSD are equally reliable, but it does mean that for the smaller timesteps much of the data is not used. To switch this off and use all data, UseAllValues can be set to true

`VecElements`

Type Block

Description A set of indices referring to a subset of the property vector. Works in combination with the atoms block. For example, in combination with the property Coords, the Atoms block allows the selection of a subset of atoms, while the VecElelements block allows the selection of a subset of vector elements (e.g. 1 and 2 for the elements x and y). Currently not implemented with InputValues.

`Index`

Type Integer

Recurring True

Description Element of the property vector.

`WritePropertyToKF`

Type Bool

Default value No

Description Write the selected property to the KF files for every requested frame

`Print`

Type Block

Description This block controls the printing of additional information to stdout.

`Timers`

Type Multiple Choice

Default value None

Options [None, Normal, Detail, TooMuchDetail]

Description Printing timing details to see how much time is spend in which part of the code.

`RadialDistribution`

Type Block

Recurring True

Description All input related to radial distribution functions.

`AtomsFrom`

Type Block

Description Atom numbers or elements for the first set of atoms in the radial distribution.

`Atom`

Type Integer

Default value 0

Recurring True

Description Atom number.

`Element`

Type String

Recurring True

Description Element Symbol Atom.

`Region`

Type String

Recurring True

Description Region name.

`AtomsTo`

Type Block

Description Atom numbers or elements for the second set of atoms in the radial distribution.

`Atom`

Type Integer

Default value 0

Recurring True

Description Atom number.

`Element`

Type String

Recurring True

Description Element Symbol Atom.

`Region`

Type String

Recurring True

Description Region name.

`DistanceTypeSelection`

Type Multiple Choice

Default value All

Options [All, InterMolecular, IntraMolecular]

Description Select only a certain type of interatomic distances.

`KeepRemainder`

Type Bool

Default value No

Description Place the values that fall outside the range in an extra bin (on the right).

`NBins`

Type Integer

Default value 1000

Description The number of bins in the histogram.

`PairwisePerElement`

Type Bool

Default value No

Description Compute RDF for all element pairs (for all atoms in the system). Any other settings in the block will be used.

`Range`

Type Float List

Description Either one, two, or three real values. If one it is the stepsize. If two, it is the minimum value and the maximum value. If three, it is the minimum value, the maximum value, and the stepsize. The stepsize overrides NBins.

`Task`

Type Multiple Choice

Options [RadialDistribution, Histogram, AutoCorrelation, MeanSquareDisplacement, AverageBinPlot]

Description The analysis task.

`TrajectoryInfo`

Type Block

Description All the info regarding the reading of the trajectory files.

`NBlocksToCompare`

Type Integer

Default value 1

Description Get an error estimate by comparing histograms for NBLocks time blocks of the trajectory.

`Trajectory`

Type Block

Recurring True

Description All info regarding the reading of a single trajectory file.

`KFFilename`

Type String

Default value ams.rkf

Description The name of the AMS trajectory file.

`Range`

Type Integer List

Description One or two values: start frame, and optionally end frame. By default the first and last frame are read.

`StepSize`

Type Integer

Default value 1

Description The step size at which frames are read from the RKF (default 1, every frame is read).

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`Analysis`

Type Block

Description Statistical post-detection analysis, includes reaction coefficients calculation.

`PerformAnalysis`

Type Bool

Default value Yes

Description Determine the reaction rate coefficients and statistical errors for the detected reactions.

`RateConfidence`

Type Float

Default value 0.9

Description Upper and lower bounds to the rate coefficients will be calculated for this confidence ($0 < \text{confidence} < 1$), assuming a Poisson distribution of the number of reactive events. A value of 0.9 means that the kinetics of 90% of events of one reaction can be described by a coefficient between the bounds.

`MoleculeIdentifier`

Type Block

Description Settings for the subgraph identification of molecules and reactions.

`MaxDepth`

Type Integer

Default value 2

Description The maximum number of layers the algorithm goes along bonds, starting from one atom when generating hashes for one atom. The entire molecule hash is built from the atom hashes, so this setting influences the identification of atom neighborhoods.

`UseBondOrders`

Type Bool

Default value No

Description Consider bond orders in the identifier.

`UseHs`

Type Bool

Default value No

GUI name Use Hs

Description Consider number of hydrogens of atoms in the identifier.

`UseRings`

Type Bool

Default value Yes

Description Consider ring membership of atoms in the identifier.

`WindowDepth`

Type Integer

Default value 5

Description The maximum number of layers the algorithm goes along bonds starting from the reactive atoms when generating hashes for the entire molecule. With this setting, the identifier can be limited to only a part of the molecule.

`Output`

Type Block

Description Settings for program output and output file generation.

`CreateLegacyOutput`

Type Bool

Default value No

Description Whether to save the reactions, species, and rates as 'reac.reac.tab', 'reac.spec.tab', and 'reac.rate.tab' in the same format as ChemTraYzer 1.

`ShowReactionGraph`

Type Bool

Default value No

Description Whether or not to show the reaction graph at the end of the calculation. Requires the python library matplotlib to be installed.

`WriteEventsPerTime`

Type Bool

Default value No

Description Write two .csv files that contain the number of reactions in every frame (reaction_events_per_time.csv) and the number of bond changes in every frame(bond_change_events_per_time.csv)

`WriteKF`

Type Bool

Default value No

Description Whether to write output to KF

`WriteMolPopulation`

Type Bool

Default value No

Description Write two .csv files: (1) mol_statistics.csv, which contains basic population statistics (counts, averages) for each unique species over the entire trajectory; and (2) mol_population.csv, which provides the count of each unique species in every frame.

`WriteReactions`

Type Bool

Default value Yes

Description Write two .csv files that contain information about (1) all unique reactions (reactions.csv); and (2) all individual reaction events (reaction_events.csv).

`WriteXYZFiles`

Type Bool

Default value No

Description Write XYZ files (geometries) for detected species and XYZ movies for detected reactions into a subfolder named ‘xyz’.

`PrintDebug`

Type Bool

Default value No

Description Print extra debug information to the terminal.

`ReactionDetection`

Type Block

Description Parameters for the the reaction detection algorithm.

`BondBreakingThreshold`

Type Float

Default value 0.3

Description The bond-order threshold for bond breaking. If the bond order of a bond goes below this value, the bond is considered broken.

`BondFormationThreshold`

Type Float

Default value 0.8

Description The bond-order threshold for bond formation. If the bond order between two atoms goes above this value, then this will be considered to be a new bond.

`InitialBondThreshold`

Type Float

Description The bond-order threshold for determining the connectivity for the first frame of the simulation. If not specified, the value in BondFormationThreshold will be used instead.

`TStable`

Type Float

Default value 10.0

Unit fs

GUI name T stable

Description The minimum time for a molecule to be considered stable.

`Trajectory`

Type Block

Description Info regarding the trajectory to analyze.

`FinalFrame`

Type Integer

Default value -1

Description Last frame of the trajectory to analyze.

`FirstFrame`

Type Integer

Default value 1

Description First frame of the trajectory to analyze.

`Path`

Type String

Description The path to ams results dir of an AMS calculation. This folder must contain a ams.rkf file.

15.2.4 conformers

`Constraints`

Type Block

Description The Constraints block allows geometry optimizations and potential energy surface scans with constraints. The constraints do not have to be satisfied at the start of the calculation.

`All`

Type String

Recurring True

Description Fix multiple distances using one the following formats: All [bondOrder] bonds at1 at2 [to distance] All triangles at1 at2 at3

The first option constrains all bonds between atoms at1 at2 to a certain length, while the second - bonds at1-at2 and at2-at3 as well as the angle between them.

The [bondOrder] can be a number or a string such as single, double, triple or aromatic. If it's omitted then any bond between specified atoms will be constrained. Atom names are case-sensitive and they must be as they are in the Atoms block, or an asterisk '*' denoting any atom. If the distance is omitted then the bond length from the initial geometry is used.

Important: only the bonds present in the system at the start of the simulation can be constrained, which means that the bonds may need to be specified in the System block.

Valid examples: All single bonds C C to 1.4 All bonds O H to 0.98 All bonds O H All bonds H * All triangles H * H

`Angle`

Type String

Recurring True

Description Fix the angle between three atoms. Three atom indices followed by an angle in degrees.

`Atom`

Type Integer

Recurring True

Description Fix the position of an atom. Just one integer referring to the index of the atom in the [System%Atoms] block.

`AtomList`

Type Integer List

Recurring True

Description Fix positions of the specified atoms. A list of integers referring to indices of atoms in the [System%Atoms] block.

`Block`

Type String

Recurring True

Description Name of the region to constrain as a rigid block. Regions are specified in the System%Atoms block.

BlockAtoms

Type Integer List

Recurring True

Description List of atom indices for a block constraint, where the internal degrees of freedom are frozen.

Coordinate

Type String

Recurring True

Description Fix a particular coordinate of an atom. Atom index followed by (x|y|z).

DifDist

Type String

Recurring True

Description Four atom indices i j k l followed by the distance in Angstrom. This will constrain the difference R(ij)-R(kl) at the given value.

Dihedral

Type String

Recurring True

Description Fix the dihedral angle between four atoms. Four atom indices followed by an angle in degrees.

Distance

Type String

Recurring True

Description Fix the distance between two atoms. Two atom indices followed by the distance in Angstrom.

EqualStrain

Type String

Description Exclusively for lattice optimizations:

Accepts a set of strain components [xx, xy, xz, yy, yz, zz] which are to be kept equal.

The applied strain will be determined by the average of the corresponding stress tensors components.

In AMSinput just check the corresponding check buttons.

FixedRegion

Type String

Recurring True

Description Fix positions of all atoms in a region.

FreezeStrain

Type String

Description Exclusively for lattice optimizations:

Freezes any lattice deformation corresponding to a particular component of the strain tensor.

Accepts a set of strain components [xx, xy, xz, yy, yz, zz] to be frozen.

In AMSinput just check the corresponding check buttons.

`SumDist`

Type String

Recurring True

Description Four atom indices i j k l followed by the distance in Angstrom. This will constrain the sum R(ij)+R(kl) at the given value.

`Engine`

Type Block

Description The input for the computational engine used to compute energy and forces.

`EngineAddons`

Type Block

Description This block configures all the engine add-ons.

`AtomEnergies`

Type Non-standard block

Description Add an element-dependent energy per atom. On each line, give the chemical element followed by the energy (in atomic units).

`D3Dispersion`

Type Block

Description This block configures the add-on that adds the Grimme D3 dispersion correction to the engine's energy, gradients, and stress tensor.

`Damping`

Type Multiple Choice

Default value BJ

Options [BJ, Zero]

Description Type of damping: BJ (Becke-Johnson) or Zero. BJ is recommended for most applications.

`Enabled`

Type Bool

Default value No

GUI name D3 dispersion

Description Enables the D3 dispersion correction addon.

`Functional`

Type String

Default value PBE

Description Use the D3 parameterization by Grimme for a given xc-functional. Accepts the same values as the –func command line option of the official dftd3 program. Note: the naming convention is different from elsewhere in the AMS suite. For example, BLYP should be called b-lyp.

`a1`

Type Float

Description The a1 parameter. Only used if Damping is set to BJ. If set, it overwrites the a1 value for the chosen functional.

`a2`

Type Float

Description The a2 parameter. Only used if Damping is set to BJ. If set, it overwrites the a2 value for the chosen functional.

`s6`

Type Float

Description The s6 parameter, global scaling parameter. If set, it overwrites the s6 value for the chosen functional.

`s8`

Type Float

Description The s8 parameter. If set, it overwrites the s8 value for the chosen functional.

`sr6`

Type Float

Description The sr6 parameter. Only used if Damping is set to Zero. If set, it overwrites the sr6 value for the chosen functional.

`D4Dispersion`

Type Block

Description This block configures the addon that adds the Grimme D4(EEQ) dispersion correction to the engine's energy, gradients, stress tensor and Hessian.

`Enabled`

Type Bool

Default value No

GUI name D4 dispersion

Description Enables the D4 dispersion correction addon.

`Functional`

Type Multiple Choice

Default value PBE

Options [HF, BLYP, BPBE, BP86, BPW, LB94, MPWLYP, MPWPW91, OLYP, OPBE, PBE, RPBE, REVPBE, PW86PBE, RPW86PBE, PW91, PW91P86, XLYP, B97, TPSS, REVTPSS, SCAN, B1LYP, B3LYP, BHLYP, B1P86, B3P86, B1PW91, B3PW91, O3LYP, REVPBE0, REVPBE38, PBE0, PWP1, PW1PW, MPW1PW91, MPW1LYP, PW6B95, TPSSH, TPSS0, X3LYP, M06L, M06, OMEGAB97, OMEGAB97X, CAM-B3LYP, LC-BLYP, LH07TSVWN, LH07SSVWN, LH12CTSSIRPW92, LH12CTSSIFPW92, LH14TCALPBE, B2PLYP, B2GPPLYP, MPW2PLYP, PWPB95, DSDBLYP, DS-DPBE, DSDPBEB95, DSDPBEP86, DSDSVWN, DODBLYP, DODPBE, DODPBEB95, DODPBEP86, DODSVWN, PBE02, PBE0DH, DFTB(3ob), DFTB(mio), DFTB(pbc), DFTB(matsci), DFTB(ob2), B1B95, MPWB1K, REVTPSSH, GLYP, REVPBE0DH, REVTPSS0, REVDSDPBEP86, REVDSDPBEPBE, REVDSDBLYP, REVDODPBEP86, B97M, OMEGAB97M, R2SCAN]

Description Use the D4 parameterization by Grimme for a given xc-functional.

`Verbosity`

Type Multiple Choice

Default value Silent

Options [Silent, Normal, Verbose, VeryVerbose]

Description Controls the verbosity of the dftd4 code. Equivalent to the –silent and –verbose command line switches of the official dftd4 program.

`a1`

Type Float

Description The a1 parameter, see D4 article. The physically reasonable range for a1 is [0.0,1.0]. If set, it overwrites the a1 value for the chosen functional.

`a2`

Type Float

Description The a2 parameter, see D4 article. The physically reasonable range for a2 is [0.0,7.0]. If set, it overwrites the a2 value for the chosen functional.

`s6`

Type Float

Description The s6 parameter, see D4 article. The physically reasonable range for s6 is [0.0,1.0]. If set, it overwrites the s6 value for the chosen functional.

`s8`

Type Float

Description The s8 parameter, see D4 article. The physically reasonable range for s8 is [0.0,3.0]. If set, it overwrites the s8 value for the chosen functional.

`s9`

Type Float

Description The s9 parameter, see D4 article. If set, it overwrites the s9 value for the chosen functional.

`ExternalEngine`

Type Block

Description External engine as an addon

`Execute`

Type String

GUI name Execute

Description execute command

`ExternalStress`

Type Block

Description This block configures the addon that adds external stress term to the engine's energy and stress tensor.

`StressTensorVoigt`

Type Float List

Unit Hartree/Bohr^3

GUI name External stress tensor

Description The elements of the external stress tensor in Voigt notation. One should specify 6 numbers for 3D periodic system (order: xx,yy,zz,yz,xz,xy), 3 numbers for 2D periodic systems (order: xx,yy,xy) or 1 number for 1D periodic systems.

`UpdateReferenceCell`

Type Bool

Default value No

Description Whether ot not the reference cell should be updated every time the system changes (see documentation).

`PipeEngine`

Type Block

Description Pipe engine as an addon

`WorkerCommand`

Type String

GUI name Worker command

Description pipe worker command

`Pressure`

Type Float

Default value 0.0

Unit GPa

Description Add a hydrostatic pressure term to the engine's energy and stress tensor. Can only be used for 3D periodic boundary conditions.

`Repulsion`

Type Block

Description This block configures an addon that adds a repulsive Weeks-Chandler-Andersen potential to all atom pairs.

`Enabled`

Type Bool

Default value No

GUI name Repulsion

Description Enables the repulsive Weeks-Chandler-Andersen potential addon.

When enabled, all atom pairs will experience repulsion E = 4*epsilon*((sigma/r)^12 - (sigma/r)^6 + 1/4) at the distances shorter than about 1.12*sigma.

`Epsilon`

Type Float

Default value 0.01

Unit Hartree

Description The epsilon parameter in the potential equation. It is equal to the amount of energy added at r=sigma.

`HydrogenSigmaScale`

Type Float

Default value 0.75

Unit Angstrom

Description The sigma parameter for a pair of atoms where one of them is hydrogen is scaled with the given factor. For H-H interactions the sigma is scaled with this value squared.

`Sigma`

Type Float

Default value 0.55

Unit Angstrom

Description The sigma parameter in the potential equation. The potential is exactly zero at the distances larger than about 1.12*sigma

`SkinLength`

Type Float

Default value 2.0

Unit Angstrom

Description Technical parameter specifying skin length for the neighbor list generation. A larger value increases the neighbor list cutoff (and cost) but reduces the frequency it needs to be re-created.

`WallPotential`

Type Block

Description This block configures the addon that adds a spherical wall potential to the engine's energy and gradients.

`Enabled`

Type Bool

Default value No

Description Enables the wall potential addon. When enabled, a spherical wall of radius [Radius] around the origin will be added. The force due to the potential will decay exponentially inside the wall, will be close to [Prefactor*Gradient] outside and exactly half of that at the wall.

`Gradient`

Type Float

Default value 10.0

Unit 1/Angstrom

Description The radial gradient outside the sphere.

`Prefactor`

Type Float

Default value 0.01

Unit Hartree

Description The multiplier for the overall strength of the potential.

`Radius`

Type Float

Default value 30.0

Unit Angstrom

Value Range value > 0

Description The radius of the sphere, wherein the potential is close to zero.

`Equivalence`

Type Block

Description Options for the procedure determining whether two structures are equivalent or distinct conformers.

`AMS`

Type Block

Description Options for the AMS method of checking equivalence. This method uses the atomic distance matrices and the torsion angles between heavy atoms to determine if conformer candidates are duplicates.

`DihedralThreshold`

Type Float

Default value 30.0

Description Maximum difference a dihedral can have for a conformer to be considered a duplicate.

`DistanceThreshold`

Type Float

Default value 0.1

Description Maximum difference a distance between two atoms can have for a conformer to be considered a duplicate.

`EnergyThreshold`

Type Float

Default value 0.2

Unit kcal/mol

Description The energy difference beyond which two conformers are always considered distinct.

`IrrelevantAtoms`

Type Integer List

Description To detect equivalence, only a subset of atoms is used. The atoms that are excluded from equivalence comparison should be specified here. By default only non-hydrogen atoms will be used for the comparison. Numbering starts at 0.

`AcceptAll`

Type Bool

Default value No

Description If set to True, add any candidate to the set without checks of connectivity changes, stereo- or cis/trans isomerization, or duplication.

`AcceptIsomers`

Type Bool

Default value No

Description If set to True, perform all checks of a new conformer candidate, except for the stereo- or cis/trans isomerization check.

`CREST`

Type Block

Description Options for the CREST method of checking equivalence. This method uses the rotational constants of conformer candidates to determine if they are duplicates.

`EnergyThreshold`

Type Float

Default value 0.05

Unit kcal/mol

Description The energy difference beyond which two conformers are always considered distinct.

`RMSDThreshold`

Type Float

Default value 0.125

Description Threshold for the RMSD between two conformers that determines if they are duplicates or rotamers (according to the CREST rotamer definition.)

`ScaledRotationalConstantSettings`

Type Block

Description By default, the equivalence of two geometries is determined mainly by comparing the rotational constants, and weighing the difference based on the average anisotropy of the two systems. This procedure has several settings that can be user defined.

`RotationalConstantThreshold`

Type Float

Default value 0.003

Description Threshold for the difference in rotational constants that determines if two geometries are duplicates. The threshold is weighed by the anisotropy of the systems. Note: in the grimme code they use 0.01 as bconst_threshold, but this leads to a lot of misclassifications (i.e. different conformers are classified as equivalent rotamers) So, here we use a smaller default value.

`CheckForDuplicates`

Type Bool

Default value Yes

Description If set to True, check any new conformer candidate for duplication, and only accept unique conformers. If set to False, accept duplicates into the set.

`Method`

Type Multiple Choice

Default value CREST

Options [AMS, TFD, RMSD, CREST]

GUI name Equivalence method

Description Method used to determine (and filter out) equivalent conformers.

The CREST equivalence method relies on rotational constants comparisons. For this reason, conformers with the same rotational constants (such as mirror images) will be considered equivalent conformers.

The AMS equivalence method uses a distance matrix and dihedrals to compare conformers. This equivalence method can be computationally expensive for large molecules.

The TFD equivalence method uses the Torsion Fingerprint Difference as implemented in RDKit.

The RMSD equivalence method uses the RDKit GetBestRMS implementation.

`RMSD`

Type Block

Description Options for the RMSD method of checking equivalence. This method uses the RDKit implementation of GetBestRMS, which enumerates over atomic permutations for pairs of geometries to detect duplicates based on the RMSD value.

`EnergyThreshold`

Type Float

Default value 0.05

Unit kcal/mol

Description The energy difference beyond which two conformers are always considered distinct.

`RMSDThreshold`

Type Float

Default value 0.125

Description Threshold on the RMSD difference to determine if two geometries represent the same conformer. This value is in Angstrom.

`Reorder`

Type Bool

Default value Yes

Description Reorder conformers based on energy, whenever a new conformer is added.

`TFD`

Type Block

Description Options for the TFD method of checking equivalence. This method uses the Torsion Finger Print method to determine if two conformer candidates are duplicates.

`EnergyThreshold`

Type Float

Default value 0.05

Unit kcal/mol

Description The energy difference beyond which two conformers are always considered distinct.

`TFDThreshold`

Type Float

Default value 0.05

Description Threshold on the torsion fingerprint difference to determine if two geometries represent the same conformer. This value is unit-less.

`Expander`

Type Block

Description Options for the conformer expander. The Expander expands an existing conformer set, by adding new conformers to it. The new conformers are generated from the original conformers in the set. Unlike the generators, the outcome of an expander is therefore very dependent on the input conformations.

The GC generator uses a genetic algorithm to create a combinatorial expansion by combining local substructures. The MD expander start MD simulations from the conformers in the set, and extracts snapshots to create new conformers. Both these expanders are part of the CREST generator.

`GC`

Type Block

Description Options for the genetic algorithm for combinatorial expansion of conformer geometries. This generator only works if a non-zero set of conformers is already provided.

`MaxGCenergy`

Type Float

Default value 6.0

Description The maximum energy (relative to the lowest in the set) of the conformers we are going to use for expansion. The default is 6.0 kcal/mol, but if MaxEnergy was set, then that value is used.

`Parallel`

Type Bool

Default value Yes

Description Determines if the combinatorial expansion of conformers should be performed in parallel or not (default: True).

`RMSDThreshold`

Type Float

Default value 0.25

Description Newly generated geometries are only considered unique if their RMSD from all other newly generated geometries is larger than this threshold.

`MD`

Type Block

Description Produces conformers by running a set of MD simulations at different elevated temperatures, etracting snapshots, and optimizing those.

`MolecularDynamics`

Type Block

Description Configures molecular dynamics (with the velocity-Verlet algorithm) with and without thermostats. This block allows to specify the details of the molecular dynamics calculation. Default values will be ignored.

`Checkpoint`

Type Block

Description Sets the frequency for storing the entire MD state necessary for restarting the calculation.

`Frequency`

Type Integer

Default value 1000

GUI name Checkpoint frequency

Description Write the MD state and engine-specific data to the respective .rkf files once every N steps.

`WriteProperties`

Type Bool

Default value No

Description Write the properties from the properties section to the ChecoPoint file once every N steps.

`InitialVelocities`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`File`

Type String

Description AMS RKF file containing the initial velocities.

`RandomVelocitiesMethod`

Type Multiple Choice

Default value Exact

Options [Exact, Boltzmann, Gromacs]

GUI name Velocity randomization method

Description Specifies how are random velocities generated. Three methods are available.

Exact: Velocities are scaled to exactly match set random velocities temperature.

Boltzmann: Velocities are not scaled and sample Maxwell-Boltzmann distribution. However, the distribution is not corrected for constraints.

Gromacs: Velocities are scaled to match set random velocities temperature, but removal of net momentum is performed only after the scaling. Resulting kinetic energy is lower based on how much net momentum the system had.

`Temperature`

Type Float

Unit Kelvin

GUI name Initial temperature

Description Sets the temperature for the Maxwell-Boltzmann distribution when the type of the initial velocities is set to random, in which case specifying this key is mandatory.

AMSinput will use the first temperature of the first thermostat as default.

`Type`

Type Multiple Choice

Default value Random

Options [Zero, Random, FromFile, Input]

GUI name Initial velocities

Description Specifies the initial velocities to assign to the atoms. Three methods to assign velocities are available.

Zero: All atom are at rest at the beginning of the calculation.

Random: Initial atom velocities follow a Maxwell-Boltzmann distribution for the temperature given by the [MolecularDynamics%InitialVelocities%Temperature] keyword.

FromFile: Load the velocities from a previous ams result file.

Input: Atom's velocities are set to the values specified in the [MolecularDynamics%InitialVelocities%Values] block, which can be accessed via the Expert AMS panel in AMSinput.

`Values`

Type Non-standard block

Description This block specifies the velocity of each atom, in Angstrom/fs, when [MolecularDynamics%InitialVelocities%Type] is set to Input. Each row must contain three floating point values (corresponding to the x,y,z component of the velocity vector) and a number of rows equal to the number of atoms must be present, given in the same order as the [System%Atoms] block.

NSteps

Type Integer

Default value 1000

GUI name Number of steps

Description The number of steps to be taken in the MD simulation.

Preserve

Type Block

Description Periodically remove numerical drift accumulated during the simulation to preserve different whole-system parameters.

AngularMomentum

Type Bool

Default value Yes

GUI name : Angular momentum

Description Remove overall angular momentum of the system. This option is ignored for 2D and 3D-periodic systems, and disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

CenterOfMass

Type Bool

Default value No

GUI name : Center of mass

Description Translate the system to keep its center of mass at the coordinate origin. This option is not very useful for 3D-periodic systems.

Momentum

Type Bool

Default value Yes

GUI name Preserve: Total momentum

Description Remove overall (linear) momentum of the system. This is disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

Print

Type Block

Description This block controls the printing of additional information to stdout.

System

Type Bool

Default value No

Description Print the chemical system before and after the simulation.

`Velocities`

Type Bool

Default value No

Description Print the atomic velocities before and after the simulation.

`Restart`

Type String

GUI name Restart from

Description The path to the ams.rkf file from which to restart the simulation.

`Shake`

Type Block

Description Parameters of the Shake/Rattle algorithm.

`All`

Type String

Recurring True

GUI name Constrain all

Description Constraint description in one the following formats: All [bondOrder] bonds at1 at2 [to distance] All triangles at1 at2 at3

The first option constrains all bonds between atoms at1 at2 to a certain length, while the second - bonds at1-at2 and at2-at3 and the angle between them.

The [bondOrder] can be a number or a string such as single, double, triple or aromatic. If it's omitted then all bonds between specified atoms will be constrained. Atom names are case-sensitive and they must be as they are in the Atoms block, or an asterisk '*' denoting any atom. The distance, if present, must be in Angstrom. If it is omitted then the bond length from the initial geometry is used.

Important: only the bonds present in the system at certain points of the simulation (at the start or right after adding/removing atoms) can be constrained, which means that the bonds may need to be specified in the System block.

Warning: the triangles constraint should be used with care because each constrained bond or angle means removing one degree of freedom from the dynamics. When there are too many constraints (for example, "All triangles H C H" in methane) some of them may be linearly dependent, which will lead to an error in the temperature computation.

Valid examples: All single bonds C C to 1.4 All bonds O H to 0.98 All bonds O H All bonds H * All triangles H * H

`ConvergeR2`

Type Float

Default value 1e-08

Description Convergence criterion on the max squared difference, in atomic units.

`ConvergeRV`

Type Float

Default value 1e-08

Description Convergence criterion on the orthogonality of the constraint and the relative atomic velocity, in atomic units.

`Iterations`

Type Integer

Default value 100

Description Number of iterations.

`ShakeInitialCoordinates`

Type Bool

Default value Yes

Description Apply constraints before computing the first energy and gradients.

`Thermostat`

Type Block

Recurring True

Description This block allows to specify the use of a thermostat during the simulation. Depending on the selected thermostat type, different additional options may be needed to characterize the specific thermostat' behavior.

`BerendsenApply`

Type Multiple Choice

Default value Global

Options [Local, Global]

GUI name Apply Berendsen

Description Select how to apply the scaling correction for the Berendsen thermostat:

- per-atom-velocity (Local) - on the molecular system as a whole (Global).

`ChainLength`

Type Integer

Default value 10

GUI name NHC chain length

Description Number of individual thermostats forming the NHC thermostat

`Duration`

Type Integer List

GUI name Duration(s)

Description Specifies how many steps should a transition from a particular temperature to the next one in sequence take.

`Region`

Type String

Default value *

Description The identifier of the region to thermostat. The default '*' applies the thermostat to the entire system. The value can by a plain region name, or a region expression, e.g. '*-myregion' to thermostat all atoms that are not in myregion, or 'regionA+regionB' to thermostat the union of the 'regionA' and 'regionB'. Note that if multiple thermostats are used, their regions may not overlap.

`Tau`

Type Float

Unit Femtoseconds

GUI name Damping constant

Description The time constant of the thermostat.

`Temperature`

Type Float List

Unit Kelvin

GUI name Temperature(s)

Description The target temperature of the thermostat.

You can specify multiple temperatures (separated by spaces). In that case the Duration field specifies how many steps to use for the transition from one T to the next T (using a linear ramp). For NHC thermostat, the temperature may not be zero.

`Type`

Type Multiple Choice

Default value None

Options [None, Berendsen, NHC]

GUI name Thermostat

Description Selects the type of the thermostat.

`TimeStep`

Type Float

Default value 0.25

Unit Femtoseconds

Description The time difference per step.

`Trajectory`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`ExitConditionFreq`

Type Integer

GUI name Exit condition frequency

Description Check the exit conditions every N steps. By default this is done every SamplingFreq steps.

`PrintFreq`

Type Integer

GUI name Printing frequency

Description Print current thermodynamic properties to the output every N steps. By default this is done every SamplingFreq steps.

`SamplingFreq`

Type Integer

Default value 100

GUI name Sample frequency

Description Write the the molecular geometry (and possibly other properties) to the .rkf file once every N steps.

`TProfileGridPoints`

Type Integer

Default value 0

Description Number of points in the temperature profile. If TProfileGridPoints > 0, a temperature profile along each of the three lattice axes will be written to the .rkf file. The temperature at a given profile point is calculated as the total temperature of all atoms inside the corresponding slice of the simulation box, time-averaged over all MD steps since the previous snapshot. By default, no profile is generated.

`WriteBonds`

Type Bool

Default value Yes

Description Write detected bonds to the .rkf file.

`WriteCharges`

Type Bool

Default value Yes

Description Write current atomic point charges (if available) to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze charges.

`WriteCoordinates`

Type Bool

Default value Yes

Description Write atomic coordinates to the .rkf file.

`WriteEngineGradients`

Type Bool

Default value No

Description Write atomic gradients (negative of the atomic forces, as calculated by the engine) to the History section of ams.rkf.

`WriteMolecules`

Type Bool

Default value Yes

Description Write the results of molecule analysis to the .rkf file.

`WriteVelocities`

Type Bool

Default value Yes

Description Write velocities to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze the velocities.

`Ngeoms`

Type Integer

Default value 4

Description At each temperature, MD simulations are started from Ngeoms different starting geometries. The starting geometries are extracted from the provided conformer set. If the conformer set is empty, then no more than a single geometry per temperature can be provided, limiting the total number of MD simulations.

`Temperatures`

Type Float List

Default value [400.0, 500.0]

Unit Kelvin

Description The list of different temperatures at which MD simulations are run.

`UseShake`

Type Bool

Default value No

Description Constrain all -H bonds with shake. If turned on, the MD timestep is automatically increased.

`MaxEnergy`

Type Float

Unit kcal/mol

Description Threshold for filtering out high-energy conformers. If the relative energy of a conformer with respect to the lowest conformer is larger than this value, the conformer will be discarded.

`Method`

Type Multiple Choice

Default value GC

Options [MD, GC]

GUI name Generator method

Description Method used to generate the conformers.

`Preoptimization`

Type Block

Description If this block is enabled geometries will be preoptimized. After preoptimization the high energy conformers will be discarded, and then from the remaining set the unoptimized geometries will be optimized at higher level. This is to prevent the preoptimizer from collapsing different conformers into a single false minimum. As a result, preoptimization is only useful if MaxEnergy is chosen low.

`Enable`

Type Bool

Default value No

Description Perform preoptimization at a low level of accuracy.

`Engine`

Type Block

Description The engine specifics to be used for preoptimization.

`PreoptFactor`

Type Integer

Default value 2

Description This factor is multiplied with MaxEnergy, to determine which high energy conformers can be discarded after preoptimization.

`RDKitETKDG`

Type Block

Description Settings for the call to RDKits ETKDG conformer generator tool.

`BestRMSDThreshold`

Type Float

Default value -1.0

Description After ETKDG conformer generation by RDKit, RDKit can be used to remove duplicates via the BestRMS algorithm. This filter does exactly the same as the RMSD equivalence detector in the Equivalence block.

`Forcefield`

Type Multiple Choice

Default value None

Options [None, UFF, MMFF]

Description The name of the RDKit forcefield to use for geometry optimization at the end of ETKDG conformer generation (by default no geometry optimization is performed). Using the RDKit internal optimization may make the subsequent geometry optimizations with AMS faster.

`Parallel`

Type Bool

Default value No

Description Experimental: Parallelize the RDKit generation step by calling the RDKit conformer generation method in parallel from multiple processes.

`RMSDThreshold`

Type Float

Default value -1.0

Description Root Mean Square deviation threshold for removing similar/equivalent conformations during the RDKit ETKDG procedure. By default there is no pruning (value: -1).

UseExpTorsionAnglePrefs

Type String

Default value default

Description Impose experimental torsion angle preferences in RDKit ETKDG conformer generation. By default the RDKit version determines wether or not to switch this on.

RNGSeed

Type Integer

Description Initial guesses for conformers can be randomly generated by RDKit, using the ETKDG algorithm. For reproducability, a random number seed can be provided here.

Filter

Type Block

Description Options for the conformer filtering.

MaxEnergy

Type Float

Unit kcal/mol

Description Threshold for filtering out high-energy conformers. If the relative energy of a conformer with respect to the lowest conformer is larger than this value, the conformer will be discarded.

RemoveNonMinima

Type Bool

Default value No

Description For the final set of conformers, explicitly check that the geometry corresponds to a local minimum, and remove it if it does not. Note: this will run a PES point characterization, which can be computationally expensive!

Generator

Type Block

Description Options for the conformer generator.

ANNEALING

Type Block

Description Options for the annealing generator. This generator creates conformers by performing a simulated annealing simulation.

MolecularDynamics

Type Block

Description Configures molecular dynamics (with the velocity-Verlet algorithm) with and without thermostats. This block allows to specify the details of the molecular dynamics calculation. Default values will be ignored.

Checkpoint

Type Block

Description Sets the frequency for storing the entire MD state necessary for restarting the calculation.

Frequency

Type Integer

Default value 1000

GUI name Checkpoint frequency

Description Write the MD state and engine-specific data to the respective .rkf files once every N steps.

WriteProperties

Type Bool

Default value No

Description Write the properties from the properties section to the ChecoPoint file once every N steps.

InitialVelocities

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

File

Type String

Description AMS RKF file containing the initial velocities.

RandomVelocitiesMethod

Type Multiple Choice

Default value Exact

Options [Exact, Boltzmann, Gromacs]

GUI name Velocity randomization method

Description Specifies how are random velocities generated. Three methods are available.

Exact: Velocities are scaled to exactly match set random velocities temperature.

Boltzmann: Velocities are not scaled and sample Maxwell-Boltzmann distribution. However, the distribution is not corrected for constraints.

Gromacs: Velocities are scaled to match set random velocities temperature, but removal of net momentum is performed only after the scaling. Resulting kinetic energy is lower based on how much net momentum the system had.

Temperature

Type Float

Unit Kelvin

GUI name Initial temperature

Description Sets the temperature for the Maxwell-Boltzmann distribution when the type of the initial velocities is set to random, in which case specifying this key is mandatory.

AMSinput will use the first temperature of the first thermostat as default.

`Type`

Type Multiple Choice

Default value Random

Options [Zero, Random, FromFile, Input]

GUI name Initial velocities

Description Specifies the initial velocities to assign to the atoms. Three methods to assign velocities are available.

Zero: All atom are at rest at the beginning of the calculation.

Random: Initial atom velocities follow a Maxwell-Boltzmann distribution for the temperature given by the [MolecularDynamics%InitialVelocities%Temperature] keyword.

FromFile: Load the velocities from a previous ams result file.

Input: Atom's velocities are set to the values specified in the [MolecularDynamics%InitialVelocities%Values] block, which can be accessed via the Expert AMS panel in AMSinput.

`Values`

Type Non-standard block

Description This block specifies the velocity of each atom, in Angstrom/fs, when [MolecularDynamics%InitialVelocities%Type] is set to Input. Each row must contain three floating point values (corresponding to the x,y,z component of the velocity vector) and a number of rows equal to the number of atoms must be present, given in the same order as the [System%Atoms] block.

`NSteps`

Type Integer

Default value 1000

GUI name Number of steps

Description The number of steps to be taken in the MD simulation.

`Preserve`

Type Block

Description Periodically remove numerical drift accumulated during the simulation to preserve different whole-system parameters.

`AngularMomentum`

Type Bool

Default value Yes

GUI name : Angular momentum

Description Remove overall angular momentum of the system. This option is ignored for 2D and 3D-periodic systems, and disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

`CenterOfMass`

Type Bool

Default value No

GUI name : Center of mass

Description Translate the system to keep its center of mass at the coordinate origin. This option is not very useful for 3D-periodic systems.

`Momentum`

Type Bool

Default value Yes

GUI name Preserve: Total momentum

Description Remove overall (linear) momentum of the system. This is disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

`Print`

Type Block

Description This block controls the printing of additional information to stdout.

`System`

Type Bool

Default value No

Description Print the chemical system before and after the simulation.

`Velocities`

Type Bool

Default value No

Description Print the atomic velocities before and after the simulation.

`Restart`

Type String

GUI name Restart from

Description The path to the ams.rkf file from which to restart the simulation.

`Shake`

Type Block

Description Parameters of the Shake/Rattle algorithm.

`All`

Type String

Recurring True

GUI name Constrain all

Description Constraint description in one the following formats: All [bondOrder] bonds at1 at2 [to distance] All triangles at1 at2 at3

The first option constrains all bonds between atoms at1 at2 to a certain length, while the second - bonds at1-at2 and at2-at3 and the angle between them.

The [bondOrder] can be a number or a string such as single, double, triple or aromatic. If it's omitted then all bonds between specified atoms will be constrained. Atom names are case-sensitive and they must be as they are in the Atoms block, or an asterisk '*' denoting any atom. The distance, if present, must be in Angstrom. If it is omitted then the bond length from the initial geometry is used.

Important: only the bonds present in the system at certain points of the simulation (at the start or right after adding/removing atoms) can be constrained, which means that the bonds may need to be specified in the System block.

Warning: the triangles constraint should be used with care because each constrained bond or angle means removing one degree of freedom from the dynamics. When there are too many constraints (for example, "All triangles H C H" in methane) some of them may be linearly dependent, which will lead to an error in the temperature computation.

Valid examples: All single bonds C C to 1.4 All bonds O H to 0.98 All bonds O H All bonds H * All triangles H * H

`ConvergeR2`

Type Float

Default value 1e-08

Description Convergence criterion on the max squared difference, in atomic units.

`ConvergeRV`

Type Float

Default value 1e-08

Description Convergence criterion on the orthogonality of the constraint and the relative atomic velocity, in atomic units.

`Iterations`

Type Integer

Default value 100

Description Number of iterations.

`ShakeInitialCoordinates`

Type Bool

Default value Yes

Description Apply constraints before computing the first energy and gradients.

`Thermostat`

Type Block

Recurring True

Description This block allows to specify the use of a thermostat during the simulation. Depending on the selected thermostat type, different additional options may be needed to characterize the specific thermostat' behavior.

`BerendsenApply`

Type Multiple Choice

Default value Global

Options [Local, Global]

GUI name Apply Berendsen

Description Select how to apply the scaling correction for the Berendsen thermostat:

- per-atom-velocity (Local) - on the molecular system as a whole (Global).

`ChainLength`

Type Integer

Default value 10

GUI name NHC chain length

Description Number of individual thermostats forming the NHC thermostat

`Duration`

Type Integer List

GUI name Duration(s)

Description Specifies how many steps should a transition from a particular temperature to the next one in sequence take.

`Region`

Type String

Default value *

Description The identifier of the region to thermostat. The default '*' applies the thermostat to the entire system. The value can by a plain region name, or a region expression, e.g. '*-myregion' to thermostat all atoms that are not in myregion, or 'regionA+regionB' to thermostat the union of the 'regionA' and 'regionB'. Note that if multiple thermostats are used, their regions may not overlap.

`Tau`

Type Float

Unit Femtoseconds

GUI name Damping constant

Description The time constant of the thermostat.

`Temperature`

Type Float List

Unit Kelvin

GUI name Temperature(s)

Description The target temperature of the thermostat.

You can specify multiple temperatures (separated by spaces). In that case the Duration field specifies how many steps to use for the transition from one T to the next T (using a linear ramp). For NHC thermostat, the temperature may not be zero.

`Type`

Type Multiple Choice

Default value None

Options [None, Berendsen, NHC]

GUI name Thermostat

Description Selects the type of the thermostat.

`TimeStep`

Type Float

Default value 0.25

Unit Femtoseconds

Description The time difference per step.

`Trajectory`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`ExitConditionFreq`

Type Integer

GUI name Exit condition frequency

Description Check the exit conditions every N steps. By default this is done every SamplingFreq steps.

`PrintFreq`

Type Integer

GUI name Printing frequency

Description Print current thermodynamic properties to the output every N steps. By default this is done every SamplingFreq steps.

`SamplingFreq`

Type Integer

Default value 100

GUI name Sample frequency

Description Write the the molecular geometry (and possibly other properties) to the .rkf file once every N steps.

`TProfileGridPoints`

Type Integer

Default value 0

Description Number of points in the temperature profile. If TProfileGridPoints > 0, a temperature profile along each of the three lattice axes will be written to the .rkf file. The temperature at a given profile point is calculated as the total temperature of all atoms inside the corresponding slice of the simulation box, time-averaged over all MD steps since the previous snapshot. By default, no profile is generated.

WriteBonds

Type Bool

Default value Yes

Description Write detected bonds to the .rkf file.

WriteCharges

Type Bool

Default value Yes

Description Write current atomic point charges (if available) to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze charges.

WriteCoordinates

Type Bool

Default value Yes

Description Write atomic coordinates to the .rkf file.

WriteEngineGradients

Type Bool

Default value No

Description Write atomic gradients (negative of the atomic forces, as calculated by the engine) to the History section of ams.rkf.

WriteMolecules

Type Bool

Default value Yes

Description Write the results of molecule analysis to the .rkf file.

WriteVelocities

Type Bool

Default value Yes

Description Write velocities to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze the velocities.

Temperatures

Type Float List

Default value [298.0, 798.0]

Unit Kelvin

Description The minimum and maximum temperature of the annealing simulation. The simulation will start at the highest temperature, and cool down to the lowest.

UseShake

Type Bool

Default value No

Description Constrain all -H bonds with shake. If turned on, the MD timestep is automatically increased.

CREST

Type Block

Description Options for the CREST generator. The CREST generator performs a set of metadynamics simulations (using the METADYNAMICS generator), then a set of MD simulations (using the MD expander), and finally it does a combinatorial expansion of the generated conformers using the GC expander. This sequence is repeated in an iterative fashion until the lowest energy conformer no longer changes.

ConvergenceQualityCrude

Type Multiple Choice

Default value None

Options [Normal, Good, VeryGood, Excellent, None]

Description The tightness of the convergence of the crude geometry pre-optimizations. If set to none it will be selected two levels below ConvergenceQuality.

ConvergenceQualityTight

Type Multiple Choice

Default value None

Options [Normal, Good, VeryGood, Excellent, None]

Description The tightness of the convergence of the final geometry optimizations. If set to none it will be selected the same as ConvergenceQuality.

GCStep

Type Bool

Default value Yes

Description Wether or not to include the combinatorial expansion of the conformers using the GC Generator. For big systems this step can be very time consuming. By default it is set to True.

NCycles

Type Integer

Default value 10

Description The maximum number of CREST cycles (by default the number is 10). If the lowest conformer energy converges before then, Crest exits.

UseShake

Type Bool

Default value Yes

Description Wether or not SHAKE should be turned on in the MD and Metadynamics simulations. If this is turned on, the MD timestep is automatically increased (from 2 to 5 fs).

METADYNAMICS

Type Block

Description Produces conformers by running a set of CREST-RMSD metadynamics simulations with different biases, extracting snapshots, and optimizing those.

ConvergenceQualityCrude

Type Multiple Choice

Default value none

Options [normal, good, verygood, excellent, none]

Description The tightness of the convergence of the crude geometry pre-optimizations. If set to none it will be selected two levels below ConvergenceQuality.

`MolecularDynamics`

Type Block

Description Configures molecular dynamics (with the velocity-Verlet algorithm) with and without thermostats. This block allows to specify the details of the molecular dynamics calculation. Default values will be ignored.

`Checkpoint`

Type Block

Description Sets the frequency for storing the entire MD state necessary for restarting the calculation.

`Frequency`

Type Integer

Default value 1000

GUI name Checkpoint frequency

Description Write the MD state and engine-specific data to the respective .rkf files once every N steps.

`WriteProperties`

Type Bool

Default value No

Description Write the properties from the properties section to the ChecoPoint file once every N steps.

`InitialVelocities`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`File`

Type String

Description AMS RKF file containing the initial velocities.

`RandomVelocitiesMethod`

Type Multiple Choice

Default value Exact

Options [Exact, Boltzmann, Gromacs]

GUI name Velocity randomization method

Description Specifies how are random velocities generated. Three methods are available.

Exact: Velocities are scaled to exactly match set random velocities temperature.

Boltzmann: Velocities are not scaled and sample Maxwell-Boltzmann distribution. However, the distribution is not corrected for constraints.

Gromacs: Velocities are scaled to match set random velocities temperature, but removal of net momentum is performed only after the scaling. Resulting kinetic energy is lower based on how much net momentum the system had.

`Temperature`

Type Float

Unit Kelvin

GUI name Initial temperature

Description Sets the temperature for the Maxwell-Boltzmann distribution when the type of the initial velocities is set to random, in which case specifying this key is mandatory.

AMSinput will use the first temperature of the first thermostat as default.

`Type`

Type Multiple Choice

Default value Random

Options [Zero, Random, FromFile, Input]

GUI name Initial velocities

Description Specifies the initial velocities to assign to the atoms. Three methods to assign velocities are available.

Zero: All atom are at rest at the beginning of the calculation.

Random: Initial atom velocities follow a Maxwell-Boltzmann distribution for the temperature given by the [MolecularDynamics%InitialVelocities%Temperature] keyword.

FromFile: Load the velocities from a previous ams result file.

Input: Atom's velocities are set to the values specified in the [MolecularDynamics%InitialVelocities%Values] block, which can be accessed via the Expert AMS panel in AMSinput.

`Values`

Type Non-standard block

Description This block specifies the velocity of each atom, in Angstrom/fs, when [MolecularDynamics%InitialVelocities%Type] is set to Input. Each row must contain three floating point values (corresponding to the x,y,z component of the velocity vector) and a number of rows equal to the number of atoms must be present, given in the same order as the [System%Atoms] block.

`NSteps`

Type Integer

Default value 1000

GUI name Number of steps

Description The number of steps to be taken in the MD simulation.

`Preserve`

Type Block

Description Periodically remove numerical drift accumulated during the simulation to preserve different whole-system parameters.

`AngularMomentum`

Type Bool

Default value Yes

GUI name : Angular momentum

Description Remove overall angular momentum of the system. This option is ignored for 2D and 3D-periodic systems, and disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

`CenterOfMass`

Type Bool

Default value No

GUI name : Center of mass

Description Translate the system to keep its center of mass at the coordinate origin. This option is not very useful for 3D-periodic systems.

`Momentum`

Type Bool

Default value Yes

GUI name Preserve: Total momentum

Description Remove overall (linear) momentum of the system. This is disabled by default for systems which are not translationally invariant (for example when frozen atoms are present).

`Print`

Type Block

Description This block controls the printing of additional information to stdout.

`System`

Type Bool

Default value No

Description Print the chemical system before and after the simulation.

`Velocities`

Type Bool

Default value No

Description Print the atomic velocities before and after the simulation.

`Restart`

Type String

GUI name Restart from

Description The path to the ams.rkf file from which to restart the simulation.

`Shake`

Type Block

Description Parameters of the Shake/Rattle algorithm.

`All`

Type String

Recurring True

GUI name Constrain all

Description Constraint description in one the following formats: All [bondOrder] bonds at1 at2 [to distance] All triangles at1 at2 at3

The first option constrains all bonds between atoms at1 at2 to a certain length, while the second - bonds at1-at2 and at2-at3 and the angle between them.

The [bondOrder] can be a number or a string such as single, double, triple or aromatic. If it's omitted then all bonds between specified atoms will be constrained. Atom names are case-sensitive and they must be as they are in the Atoms block, or an asterisk '*' denoting any atom. The distance, if present, must be in Angstrom. If it is omitted then the bond length from the initial geometry is used.

Important: only the bonds present in the system at certain points of the simulation (at the start or right after adding/removing atoms) can be constrained, which means that the bonds may need to be specified in the System block.

Warning: the triangles constraint should be used with care because each constrained bond or angle means removing one degree of freedom from the dynamics. When there are too many constraints (for example, "All triangles H C H" in methane) some of them may be linearly dependent, which will lead to an error in the temperature computation.

Valid examples: All single bonds C C to 1.4 All bonds O H to 0.98 All bonds O H All bonds H * All triangles H * H

`ConvergeR2`

Type Float

Default value 1e-08

Description Convergence criterion on the max squared difference, in atomic units.

`ConvergeRV`

Type Float

Default value 1e-08

Description Convergence criterion on the orthogonality of the constraint and the relative atomic velocity, in atomic units.

`Iterations`

Type Integer

Default value 100

Description Number of iterations.

`ShakeInitialCoordinates`

Type Bool

Default value Yes

Description Apply constraints before computing the first energy and gradients.

`Thermostat`

Type Block

Recurring True

Description This block allows to specify the use of a thermostat during the simulation. Depending on the selected thermostat type, different additional options may be needed to characterize the specific thermostat' behavior.

`BerendsenApply`

Type Multiple Choice

Default value Global

Options [Local, Global]

GUI name Apply Berendsen

Description Select how to apply the scaling correction for the Berendsen thermostat:

- per-atom-velocity (Local) - on the molecular system as a whole (Global).

`ChainLength`

Type Integer

Default value 10

GUI name NHC chain length

Description Number of individual thermostats forming the NHC thermostat

`Duration`

Type Integer List

GUI name Duration(s)

Description Specifies how many steps should a transition from a particular temperature to the next one in sequence take.

`Region`

Type String

Default value *

Description The identifier of the region to thermostat. The default '*' applies the thermostat to the entire system. The value can by a plain region name, or a region expression, e.g. '*-myregion' to thermostat all atoms that are not in myregion, or 'regionA+regionB' to thermostat the union of the 'regionA' and 'regionB'. Note that if multiple thermostats are used, their regions may not overlap.

`Tau`

Type Float

Unit Femtoseconds

GUI name Damping constant

Description The time constant of the thermostat.

`Temperature`

Type Float List

Unit Kelvin

GUI name Temperature(s)

Description The target temperature of the thermostat.

You can specify multiple temperatures (separated by spaces). In that case the Duration field specifies how many steps to use for the transition from one T to the next T (using a linear ramp). For NHC thermostat, the temperature may not be zero.

`Type`

Type Multiple Choice

Default value None

Options [None, Berendsen, NHC]

GUI name Thermostat

Description Selects the type of the thermostat.

`TimeStep`

Type Float

Default value 0.25

Unit Femtoseconds

Description The time difference per step.

`Trajectory`

Type Block

Description Sets the frequency for printing to stdout and storing the molecular configuration on the .rkf file.

`ExitConditionFreq`

Type Integer

GUI name Exit condition frequency

Description Check the exit conditions every N steps. By default this is done every SamplingFreq steps.

`PrintFreq`

Type Integer

GUI name Printing frequency

Description Print current thermodynamic properties to the output every N steps. By default this is done every SamplingFreq steps.

`SamplingFreq`

Type Integer

Default value 100

GUI name Sample frequency

Description Write the the molecular geometry (and possibly other properties) to the .rkf file once every N steps.

`TProfileGridPoints`

Type Integer

Default value 0

Description Number of points in the temperature profile. If TProfileGridPoints > 0, a temperature profile along each of the three lattice axes will be written to the .rkf file. The temperature at a given profile point is calculated as the total temperature of all atoms inside the corresponding slice of the simulation box, time-averaged over all MD steps since the previous snapshot. By default, no profile is generated.

`WriteBonds`

Type Bool

Default value Yes

Description Write detected bonds to the .rkf file.

`WriteCharges`

Type Bool

Default value Yes

Description Write current atomic point charges (if available) to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze charges.

`WriteCoordinates`

Type Bool

Default value Yes

Description Write atomic coordinates to the .rkf file.

`WriteEngineGradients`

Type Bool

Default value No

Description Write atomic gradients (negative of the atomic forces, as calculated by the engine) to the History section of ams.rkf.

`WriteMolecules`

Type Bool

Default value Yes

Description Write the results of molecule analysis to the .rkf file.

`WriteVelocities`

Type Bool

Default value Yes

Description Write velocities to the .rkf file. Disable this to reduce trajectory size if you do not need to analyze the velocities.

`NCycles`

Type Integer

Default value 5

Description The maximum number of cycles of metadynamics simulations. The generator stops when either this number is reached, or the conformer set is stable.

`NWidthsHeights`

Type Integer List

Default value [4, 3]

Description The number of different Gaussian widths and heights respectively used in the metadynamics simulations. By default 4 different widths are used and 3 different heights, resulting in 12 different metadynamics simulations.

`SimulationSuccessFraction`

Type Float

Default value 0.4

Description The fraction of planned metadynamics steps that has to have succeeded in order for the metadynamics iteration to be considered a success.

`UseShake`

Type Bool

Default value No

Description Constrain all -H bonds with shake. If turned on, the MD timestep is automatically increased.

`MaxEnergy`

Type Float

Unit kcal/mol

Description Threshold for filtering out high-energy conformers. If the relative energy of a conformer with respect to the lowest conformer is larger than this value, the conformer will be discarded.

`Method`

Type Multiple Choice

Default value RDKit

Options [RDKit, CREST, ANNEALING]

GUI name Generator method

Description Method used to generate the conformers.

The RDKit generator is based on random distance matrix method. This is the recommended (and default) method.

The CREST Generator uses a multi-step workflow with meta-dynamics simulations to explore the conformers space of a molecule. This can be a powerful conformer search method, but it is generally computationally expensive compared to the RDKit generator.

THe ANNEALING generator performs a simulated annealing simulation to explore conformer space.

`Preoptimization`

Type Block

Description If this block is enabled geometries will be preoptimized. After preoptimization the high energy conformers will be discarded, and then from the remaining set the unoptimized geometries will be optimized at higher level. This is to prevent the preoptimizer from collapsing different conformers into a single false minimum. As a result, preoptimization is only useful if MaxEnergy is chosen low.

`Enable`

Type Bool

Default value No

Description Perform preoptimization at a low level of accuracy.

`Engine`

Type Block

Description The engine specifics to be used for preoptimization.

`PreoptFactor`

Type Integer

Default value 2

Description This factor is multiplied with MaxEnergy, to determine which high energy conformers can be discarded after preoptimization.

`RDKit`

Type Block

Description Options for the RDKit generator. This generator produces initial guesses for conformers using the RDKit ETKDG method, followed by AMS geometry optimizations.

`InitialNConformers`

Type Integer

GUI name Initial no. of conformers

Description Number of geometries initially created by RDKit, before AMS geometry optimization and filtering. If not set, the number will be automatically set, based on the number of rotational bonds.

`MaxConfs`

Type Integer

Default value 5000

Description If InitialNConformers is not set, then the number of conformers will be automatically set, with a maximum of MaxConfs.

`MinConfs`

Type Integer

Default value 10

Description If InitialNConformers is not set, then the number of conformers will be automatically set, with a minimum of MinConfs.

`NconfsEstimationFactor`

Type Integer

Default value 100

Description If InitialNConformers is not set, then the number of conformers will be automatically set based on the number of rotational bonds. The resulting number is then multiplied by this factor (default: 100), to ensure that enough conformers will be created.

`RDKitETKDG`

Type Block

Description Settings for the call to RDKits ETKDG conformer generator tool.

`BestRMSDThreshold`

Type Float

Default value -1.0

Description After ETKDG conformer generation by RDKit, RDKit can be used to remove duplicates via the BestRMS algorithm. This filter does exactly the same as the RMSD equivalence detector in the Equivalence block.

`ConstrainedAtoms`

Type Integer List

Description The indices of the atoms to constrain during ETKDG conformer generation.

`Forcefield`

Type Multiple Choice

Default value None

Options [None, UFF, MMFF]

Description The name of the RDKit forcefield to use for geometry optimization at the end of ETKDG conformer generation (by default no geometry optimization is performed). Using the RDKit internal optimization may make the subsequent geometry optimizations with AMS faster.

`Parallel`

Type Bool

Default value No

Description Experimental: Parallelize the RDKit generation step by calling the RDKit conformer generation method in parallel from multiple processes.

`RMSDThreshold`

Type Float

Default value -1.0

Description Root Mean Square deviation threshold for removing similar/equivalent conformations during the RDKit ETKDG procedure. By default there is no pruning (value: -1).

`UseExpTorsionAnglePrefs`

Type String

Default value default

Description Impose experimental torsion angle preferences in RDKit ETKDG conformer generation. By default the RDKit version determines wether or not to switch this on.

`RNGSeed`

Type Integer

Description Initial guesses for conformers can be randomly generated by RDKit, using the ETKDG algorithm. For reproducability, a random number seed can be provided here.

`TORSION`

Type Block

Description Options for the TorsionGenerator, which generates geometries by enumerative rotation around rotatable bonds. This is the slowest of all generator, and quickly becomes infeasible for large systems. Currently does not work for systems with interconnected rings.

`Dtheta`

Type Float

Default value 60.0

Description The angle over which the bonds are rotated, in order to create a new conformer.

`GeometryOptimization`

Type Block

Description Some options / details regarding the optimization procedure.

`ConvergenceQuality`

Type Multiple Choice

Default value VeryGood

Options [Normal, Good, VeryGood, Excellent]

GUI name Convergence

Description The tightness of the convergence of the geometry optimizations. Lower quality levels may lead to badly converged geometries being classified as distinct conformers.

`GeometryOptimization`

Type Block

Description Configures details of the geometry optimization and transition state searches.

`CalcPropertiesOnlyIfConverged`

Type Bool

Default value Yes

Description Compute the properties requested in the 'Properties' block, e.g. Frequencies or Phonons, only if the optimization (or transition state search) converged. If False, the properties will be computed even if the optimization did not converge.

`Convergence`

Type Block

Description Convergence is monitored for up to 4 quantities: the energy change, the Cartesian gradients, the Cartesian step size, and for lattice optimizations the stress energy per atom. Convergence criteria can be specified separately for each of these items.

`Energy`

Type Float

Default value 1e-05

Unit Hartree

Value Range value > 0

GUI name Energy convergence

Description The criterion for changes in the energy. The energy is considered converged when the change in energy is smaller than this threshold times the number of atoms.

`Gradients`

Type Float

Default value 0.001

Unit Hartree/Angstrom

Value Range value > 0

GUI name Gradient convergence

Description Threshold for nuclear gradients.

`Quality`

Type Multiple Choice

Default value Custom

Options [VeryBasic, Basic, Normal, Good, VeryGood, Custom]

GUI name Convergence

Description A quick way to change convergence thresholds: 'Good' will reduce all thresholds by an order of magnitude from their default value. 'VeryGood' will tighten them by two orders of magnitude. 'Basic' and 'VeryBasic' will increase the thresholds by one or two orders of magnitude respectively.

`Step`

Type Float

Default value 0.01

Unit Angstrom

Value Range value > 0

GUI name Step convergence

Description The maximum Cartesian step allowed for a converged geometry.

`StressEnergyPerAtom`

Type Float

Default value 0.0005

Unit Hartree

Value Range value > 0

Description Threshold used when optimizing the lattice vectors. The stress is considered 'converged' when the maximum value of stress_tensor * cell_volume / number_of_atoms is smaller than this threshold (for 2D and 1D systems, the cell_volume is replaced by the cell_area and cell_length respectively).

CoordinateType

Type Multiple Choice

Default value Auto

Options [Auto, Delocalized, Cartesian]

GUI name Optimization space

Description Select the type of coordinates in which to perform the optimization. 'Auto' automatically selects the most appropriate CoordinateType for a given Method.

If 'Auto' is selected, Delocalized coordinates will be used for the Quasi-Newton method, while Cartesian coordinates will be used for all other methods.

Dimer

Type Block

Description Options for the Dimer method for transition state search.

AngleThreshold

Type Float

Default value 1.0

Unit Degree

Description The rotation is considered converged when the the rotation angle falls below the specified threshold.

DimerDelta

Type Float

Default value 0.01

Unit Angstrom

Description Eucledian distance between the midpoint and the endpoint.

ExtrapolateForces

Type Bool

Default value Yes

Description Set to false to call engine to calculate forces at the extrapolated rotation angle instead of extrapolating them.

LBFGSMaxVectors

Type Integer

Default value 10

Description Max number of vectors for the L-BFGS algorithm to save.

MaxRotationIterations

Type Integer

Default value 10

Description Maximum number of rotation iterations for a single translation step.

Region

Type String

Default value *

Description Include only atoms of the specified region(s) in the rotations, which allows searching for a transition state involving selected atoms only.

`RotationTrustRadius`

Type Float

Default value 0.1

Unit Angstrom

Description L-BFGS trust radius during rotation iterations.

`TranslationTrustRadius`

Type Float

Default value 0.1

Unit Angstrom

Description L-BFGS trust radius during translation iterations.

`EngineAutomations`

Type Block

Description The optimizer can change some settings of the engine, based for instance on the error. The idea is to allow the engine to be a bit quicker at the start, and more accurate towards the end. Automations are always engine specific.

`Enabled`

Type Bool

Default value Yes

Description Whether or not autotions are enabled at all.

`Gradient`

Type Block

Recurring True

Description A gradient-based automation.

`FinalValue`

Type Float

Description This value will be used whenever the gradient is less than GradientLow

`HighGradient`

Type Float

Default value 1.0

Unit Hartree/Angstrom

Description Defines a large gradient. When the actual gradient is between GradientHigh and GradientLow a linear interpolation scheme is used for kT (on a log scale).

`InitialValue`

Type Float

Description This value will be used at the first geometry, and whenever the gradient is higher than GradientHigh

`LowGradient`

Type Float

Default value 1.0

Unit Hartree/Angstrom

Description Defines a small gradient, see GradientHigh

`UseLogInterpolation`

Type Bool

Default value Yes

Description Whether to use interpolation on a log (y) scale or not

`Variable`

Type String

Default value

Description variable to be tweaked for the engine.

`Iteration`

Type Block

Recurring True

Description Geometry step based automation.

`FinalValue`

Type Float

Description

`FirstIteration`

Type Integer

Default value 1

Description When the actual gradient is between the first and last iteration, a linear interpolation is used.

`InitialValue`

Type Float

Description This value will be used when the iteration number is smaller or equal to FirstIteration

`LastIteration`

Type Integer

Default value 10

Description Where the automation should reach the FinalValue

`UseLogInterpolation`

Type Bool

Default value Yes

Description Whether to use interpolation on a log (y) scale or not

`Variable`

Type String

Default value

Description variable to be tweaked for the engine.

`FIRE`

Type Block

Description This block configures the details of the FIRE optimizer. The keywords name correspond the the symbols used in the article describing the method, see PRL 97, 170201 (2006).

`AllowOverallRotation`

Type Bool

Default value Yes

Description Whether or not the system is allowed to freely rotate during the optimization. This is relevant when optimizing structures in the presence of external fields.

`AllowOverallTranslation`

Type Bool

Default value No

Description Whether or not the system is allowed to translate during the optimization. This is relevant when optimizing structures in the presence of external fields.

`MapAtomsToUnitCell`

Type Bool

Default value No

Description Map the atoms to the central cell at each geometry step.

`NMin`

Type Integer

Default value 5

Description Number of steps after stopping before increasing the time step again.

`alphaStart`

Type Float

Default value 0.1

Description Steering coefficient.

`dtMax`

Type Float

Default value 1.0

Unit Femtoseconds

Description Maximum time step used for the integration. For ReaxFF and APPLE&P, this value is reduced by 50%.

`dtStart`

Type Float

Default value 0.25

Unit Femtoseconds

Description Initial time step for the integration.

`fAlpha`

Type Float

Default value 0.99

Description Reduction factor for the steering coefficient.

`fDec`

Type Float

Default value 0.5

Description Reduction factor for reducing the time step in case of uphill movement.

`fInc`

Type Float

Default value 1.1

Description Growth factor for the integration time step.

`strainMass`

Type Float

Default value 0.5

Description Fictitious relative mass of the lattice degrees of freedom. This controls the stiffness of the lattice degrees of freedom relative to the atomic degrees of freedom, with smaller values resulting in a more aggressive optimization of the lattice.

`HessianFree`

Type Block

Description Configures details of the Hessian-free (conjugate gradients or L-BFGS) geometry optimizer.

`Step`

Type Block

Description

`MaxCartesianStep`

Type Float

Default value 0.1

Unit Angstrom

Description Limit on a single Cartesian component of the step.

`MinRadius`

Type Float

Default value 0.0

Unit Angstrom

Description Minimum value for the trust radius.

`TrialStep`

Type Float

Default value 0.0005

Unit Angstrom

Description Length of the finite-difference step when determining curvature. Should be smaller than the step convergence criterion.

`TrustRadius`

Type Float

Default value 0.2

Unit Angstrom

Description Initial value of the trust radius.

`InitialHessian`

Type Block

Description Options for initial model Hessian when optimizing systems with the Quasi-Newton method.

`File`

Type String

GUI name Initial Hessian from

Description KF file containing the initial Hessian (or the results dir. containing it). This can be used to load a Hessian calculated in a previously with the [Properties%Hessian] keyword.

`Type`

Type Multiple Choice

Default value Auto

Options [Auto, UnitMatrix, Swart, FromFile, Calculate, CalculateWithFastEngine]

GUI name Initial Hessian

Description Select the type of initial Hessian. Auto: let the program pick an initial model Hessian. UnitMatrix: simplest initial model Hessian, just a unit matrix in the optimization coordinates. Swart: model Hessian from M. Swart. FromFile: load the Hessian from the results of a previous calculation (see InitialHessian%File). Calculate: compute the initial Hessian (this may be computationally expensive and it is mostly recommended for TransitionStateSearch calculations). CalculateWithFastEngine: compute the initial Hessian with a faster engine.

`KeepIntermediateResults`

Type Bool

Default value No

Description Whether the full engine result files of all intermediate steps are stored on disk. By default only the last step is kept, and only if the geometry optimization converged. This can easily lead to huge amounts of data being stored on disk, but it can sometimes be convenient to closely monitor a tricky optimization, e.g. excited state optimizations going through conical intersections, etc. …

`MaxIterations`

Type Integer

Value Range value >= 0

GUI name Maximum number of iterations

Description The maximum number of geometry iterations allowed to converge to the desired structure.

`MaxRestarts`

Type Integer

Default value 0

Description If a geometry optimization of a system with no symmetry operators (or with explicitly disabled symmetry: `UseSymmetry False`) and enabled PES point characterization converges to a transition state (or higher order saddle point), it can be restarted automatically after a small displacement along the imaginary vibrational mode. In case the restarted optimization again does not find a minimum, this can happen multiple times in succession. This keyword sets the maximum number of restarts. The default value is 0, so the automatic restarting is disabled by default.

`Method`

Type Multiple Choice

Default value Auto

Options [Auto, Quasi-Newton, FIRE, L-BFGS, ConjugateGradients, Dimer]

GUI name Optimization method

Description Select the optimization algorithm employed for the geometry relaxation. Currently supported are:

the Hessian-based Quasi-Newton-type BFGS algorithm,

the fast inertial relaxation method (FIRE),

the limited-memory BFGS method,

and the conjugate gradients method. The default is to choose an appropriate method automatically based on the engine's speed, the system size and the supported optimization options.

`OptimizeLattice`

Type Bool

Default value No

Description Whether to also optimize the lattice for periodic structures. This is currently supported with the Quasi-Newton, FIRE, and L-BFGS optimizers.

`PretendConverged`

Type Bool

Default value No

Description Normally a non-converged geometry optimization is considered an error. If this keyword is set to True, the optimizer will only produce a warning and still claim that the optimization is converged. (This is mostly useful for scripting applications, where one might want to consider non-converged optimizations still successful jobs.)

`Quasi-Newton`

Type Block

Description Configures details of the Quasi-Newton geometry optimizer.

`MaxGDIISVectors`

Type Integer

Default value 0

Description Sets the maximum number of GDIIS vectors. Setting this to a number >0 enables the GDIIS method.

`Step`

Type Block

Description

`TrustRadius`

Type Float

Description Initial value of the trust radius.

`VaryTrustRadius`

Type Bool

Description Whether to allow the trust radius to change during optimization. By default True during energy minimization and False during transition state search.

`UpdateTSVectorEveryStep`

Type Bool

Default value Yes

GUI name Update TSRC vector every step

Description Whether to update the TS reaction coordinate at each step with the current eigenvector.

`RestartDisplacement`

Type Float

Default value 0.05

Unit Angstrom

Description If a geometry optimization of a system with no symmetry operators (or with explicitly disabled symmetry: `UseSymmetry False`) and enabled PES point characterization converges to a transition state (or higher order saddle point), it can be restarted automatically after a small displacement along the imaginary vibrational mode. This keywords sets the size of the displacement for the furthest moving atom.

Keep

Type Multiple Choice

Default value None

Options [None, all]

Description Keep all the output files of the geometry optimizations. If set to 'all', must be used in combination with Output%KeepWorkDir.

MaxConvergenceTime

Type Multiple Choice

Default value Default

Options [Default, High]

Description The number of iterations for the geometry optimization, based on the number of atoms in the system. The default value is the general AMS value for geometry optimization. Often, for conformer generation, it needs to be set higher.

MaxOptimizations

Type Integer

Default value 1000

Description Set a maximum to the number of geometries accepted for optimization at once, per AMSWorker (so should be multiplied by the number of cores used). If not set, the disc size requirements can become too large.

OptimizationMethod

Type Multiple Choice

Default value Quasi-Newton

Options [Auto, Quasi-Newton, FIRE, L-BFGS, ConjugateGradients, Dimer]

Description Select the optimization algorithm employed for the geometry relaxation. Currently supported are:

the Hessian-based Quasi-Newton-type BFGS algorithm,

the fast inertial relaxation method (FIRE),

the limited-memory BFGS method,

and the conjugate gradients method. The default is Quasi-Newton, which gives the most reliable results for conformers. The Auto method leaves it to the AMS GeometryOptimization task to select a method.

UseAMSWorker

Type Bool

Default value Yes

Description Whether the set of optimizations should be run via the AMSWorkerPool or via regular AMSJobs.

WriteGeometries

Type Block

Description Determines if and where optimized geometries will be written to file during optimization. When the AMSWorker is used, then the write interval depends on MaxOptimizations. If enabled, must be used in combination with Output%KeepWorkDir.

`Dirname`

Type String

Default value conf_tmpdir

Description The name of the folder that should contain the optimized geometries.

`Enabled`

Type Bool

Default value No

Description Enables or disables the periodic writing of optimized geometries to file

`InputConformersSet`

Type String

Recurring True

Description The path to a file containing a set of conformers.

The file should be either an 'conformers.rkf' file (i.e. the results file of conformers) or a concatenated .xyz file.

You can specify multiple input conformers sets by including the InputConformersSet keyword multiple times.

`InputMaxConfs`

Type Integer

Description The maximum number of conformers to carry forward when loading conformer sets. If this input is not specified, this limit will not be imposed.

`InputMaxEnergy`

Type Float

Unit kcal/mol

Description Threshold for filtering out high-energy conformers when loading conformers sets using the InputConformerSet keyword. Conformers with an larger relative energy will not be loaded.

`LoadSystem`

Type Block

Recurring True

Description Block that controls reading the chemical system from a KF file instead of the [System] block.

`File`

Type String

Description The path of the KF file from which to load the system. It may also be the results directory containing it.

`Section`

Type String

Default value Molecule

Description The section on the KF file from which to load the system.

`Output`

Type Block

Description Options regarding the output and result files.

`KeepWorkDir`

Type Bool

Default value No

Description Do not remove the working directories after the conformer generation is finished.

`rkf`

Type Bool

Default value Yes

Description Save the final conformers in .rkf format. The file 'conformers.rkf' will be located in the results directory. You can visualize this file using the AMSMovie GUI module.

`sdf`

Type Bool

Default value Yes

Description Save the final conformers in .sdf format. The file 'conformers.sdf' will be located in the results directory.

`xyz`

Type Bool

Default value Yes

Description Save the final conformers in .xyz format. The file 'conformers.xyz' will be located in the results directory.

`Restraints`

Type Block

Description The Restraints block allows to add soft constraints to the system. A restraint is a potential energy function (a spring) attached to a certain coordinate, for example, an interatomic distance, with its minimum at the specified optimal value. A restraint is defined using one or two parameters: the ForceConstant and, for some types, the F(Inf) value. The ForceConstant parameter corresponds to second derivative of the restraint potential energy d2V(x)/dx^2 for any x (harmonic restraints) or only at at x=0 (other restraints). Here, x is a deviation from the restraint's optimal value.

`Angle`

Type String

Recurring True

Description Specify three atom indices i j k followed by an angle in degrees and, optionally, by the ForceConstant (default is 0.3 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the i-j-k angle at the given value. For periodic systems this restraint follows the minimum image convention.

`DifDist`

Type String

Recurring True

Description Specify four atom indices i j k l followed by the distance in Angstrom and, optionally, by the ForceConstant (default is 1.0 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the difference R(ij)-R(kl) at the given value. For periodic systems this restraint follows the minimum image convention.

`Dihedral`

Type String

Recurring True

Description Specify four atom indices i j k l followed by an angle in degrees and, optionally, by the ForceConstant (default is 0.1 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the i-j-k-l dihedral angle at the given value. For periodic systems this restraint follows the minimum image convention.

`Distance`

Type String

Recurring True

Description Specify two atom indices followed by the distance in Angstrom and, optionally, by the ForceConstant (default is 1.0 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the distance between the two specified atoms at the given value. For periodic systems this restraint follows the minimum image convention.

`FInfinity`

Type Float

Default value 1.0

GUI name Default F(inf)

Description Specify the default asymptotic value for the restraint force for the Hyperbolic and Erf profiles, in Hartree/Bohr or Hartree/radian.

A per-restraint value can be specified after the profile type on the corresponding restraint line.

`Profile`

Type Multiple Choice

Default value Harmonic

Options [Harmonic, Hyperbolic, Erf, GaussianWell]

GUI name Default restraint profile

Description Select the default type of restraint profile.

The harmonic profile is most suitable for geometry optimizations but may result is very large forces that can be problematic in molecular dynamic.

For MD simulations the Hyperbolic or Erf may be more suitable because the restraint force is bounded by a user-defined value.

A per-restraint profile type can be specified after the ForceConstant value on the corresponding restraint line.

`SumDist`

Type String

Recurring True

Description Specify four atom indices i j k l followed by the distance in Angstrom and, optionally, by the ForceConstant (default is 1.0 in a.u.), profile type and F(Inf) (in a.u.). This restraint will try to keep the sum R(ij)+R(kl) at the given value. For periodic systems this restraint follows the minimum image convention.

`Units`

Type Multiple Choice

Default value Default

Options [Default, MD]

GUI name Units

Description Change units for energy, force and force constant values from the default (atomic units) to those often used in the MD community (based on kcal/mol and Angstrom). Units for the optimal distances are not affected and are always Angstrom.

`RNGSeed`

Type Integer

Description Initial seed for the (pseudo)random number generator. If this is unset, the generator will be seeded randomly from external sources of entropy and the generated conformers will be non-deterministic.

`System`

Type Block

Recurring True

Description Specification of the chemical system. For some applications more than one system may be present in the input. In this case, all systems except one must have a non-empty string ID specified after the System keyword. The system without an ID is considered the main one.

`AllowCloseAtoms`

Type Bool

Default value No

Description If AllowCloseAtoms is set to False, the AMS driver will stop with an error if it detects almost-coinciding atomic coordinates. If set to True, the AMS driver will try to carry on with the calculation.

`Atoms`

Type Non-standard block

Description The atom types and coordinates. Unit can be specified in the header. Default unit is Angstrom.

`BondOrders`

Type Non-standard block

Description Defined bond orders. Each line should contain two atom indices, followed by the bond order (1, 1.5, 2, 3 for single, aromatic, double and triple bonds) and (optionally) the cell shifts for periodic systems. May be used by MM engines and for defining constraints. If the system is periodic and none of the bonds have the cell shift defined then AMS will attempt to determine them following the minimum image convention.

`Charge`

Type Float

Default value 0.0

GUI name Total charge

Description The system's total charge in atomic units.

`ElectrostaticEmbedding`

Type Block

Description Container for electrostatic embedding options, which can be combined.

`ElectricField`

Type Float List

Unit V/Angstrom

Description External homogeneous electric field with three Cartesian components: ex, ey, ez, the default unit being V/Å.

In atomic units: Hartree/(e bohr) = 14.39964 V/Angstrom; the relation to SI units is: 1 Hartree/(e bohr) = 5.14 … e11 V/m.

Supported by the engines adf, band, dftb and mopac.

For periodic systems the field may only have nonzero components orthogonal to the direction(s) of periodicity (i.e. for 1D periodic system the x-component of the electric field should be zero, while for 2D periodic systems both the x and y components should be zero. This options cannot be used for 3D periodic systems.

`MultipolePotential`

Type Block

Description External point charges (and dipoles).

`ChargeModel`

Type Multiple Choice

Default value Point

Options [Point, Gaussian]

Description A multipole may be represented by a point (with a singular potential at its location) or by a spherical Gaussian distribution.

`ChargeWidth`

Type Float

Default value -1.0

Description The width parameter in a.u. in case a Gaussian charge model is chosen. A negative value means that the width will be chosen automatically.

`Coordinates`

Type Non-standard block

Description Positions and values of the multipoles, one per line. Each line has the following format:

x y z q, or x y z q μx μy μz.

Here x, y, z are the coordinates in Å, q is the charge (in atomic units of charge) and μx, μy, μz are the (optional) dipole moment components (in atomic units, i.e. e*Bohr).

Periodic systems are not supported.

`FractionalCoords`

Type Bool

Default value No

Description Whether the atomic coordinates in the Atoms block are given in fractional coordinates of the lattice vectors. Requires the presence of the Lattice block.

`GeometryFile`

Type String

Description Read the geometry from a file (instead of from Atoms and Lattice blocks). Supported formats: .xyz

`GuessBonds`

Type Bool

Default value No

Description Whether or not UFF bonds should be guessed.

`Lattice`

Type Non-standard block

Description Up to three lattice vectors. Unit can be specified in the header. Default unit is Angstrom.

`LatticeStrain`

Type Float List

Description Deform the input system by the specified strain. The strain elements are in Voigt notation, so one should specify 6 numbers for 3D periodic system (order: xx,yy,zz,yz,xz,xy), 3 numbers for 2D periodic systems (order: xx,yy,xy) or 1 number for 1D periodic systems.

`LoadForceFieldAtomTypes`

Type Block

Description This is a mechanism to set the ForceField.Type attribute in the input. This information is currently only used by the ForceField engine.

`File`

Type String

Description Name of the (kf) file. It needs to be the result of a forcefield calculation.

`LoadForceFieldCharges`

Type Block

Recurring True

Description This is a mechanism to set the ForceField.Charge attribute in the input. This information is currently only used by the ForceField engine.

`CheckGeometryRMSD`

Type Bool

Default value No

Description Whether the geometry RMSD test should be performed, see MaxGeometryRMSD. Otherwise only basic tests are performed, such as number and atom types. Not doing the RMSD test allows you to load molecular charges in a periodic system.

`File`

Type String

Description Name of the (kf) file

`MaxGeometryRMSD`

Type Float

Default value 0.1

Unit Angstrom

Description The geometry of the charge producing calculation is compared to the one of the region, and need to be the same within this tolerance.

`Region`

Type String

Default value *

Description Region for which the charges should be loaded

`Section`

Type String

Default value AMSResults

Description Section name of the kf file

`Variable`

Type String

Default value Charges

Description Variable name of the kf file

`MapAtomsToUnitCell`

Type Bool

Default value No

Description For periodic systems the atoms will be moved to the central cell.

`ModifyAlternativeElements`

Type Bool

Default value No

Description When using alternative elements (using the nuclear_charge attribute) set the element to the nearest integer Z. If you specify an H atom with a nuclear_charge of 2.9 it is replaced by a Li atom with the same nuclear charge.

PerturbCoordinates

Type Float

Default value 0.0

Unit Angstrom

Description Perturb the atomic coordinates by adding random numbers between [-PerturbCoordinates,PerturbCoordinates] to each Cartesian component. This can be useful if you want to break the symmetry of your system (e.g. for a geometry optimization).

PerturbLattice

Type Float

Default value 0.0

Description Perturb the lattice vectors by applying random strain with matrix elements between [-PerturbLattice,PerturbLattice]. This can be useful if you want to deviate from an ideal symmetric geometry, for example if you look for a phase change due to high pressure.

RandomizeAtomOrder

Type Bool

Default value No

Description Whether or not the order of the atoms should be randomly changed. Intended for some technical testing purposes only. Does not work with bond information.

Region

Type Block

Recurring True

Description Properties for each region specified in the Atoms block.

Properties

Type Non-standard block

Description Properties for each region specified in the Atoms block.

ShiftCoordinates

Type Float List

Unit Bohr

Description Translate the atoms by the specified shift (three numbers).

SuperCell

Type Integer List

Description Create a supercell of the input system (only possible for periodic systems). The integer numbers represent the diagonal elements of the supercell transformation; you should specify as many numbers as lattice vectors (i.e. 1 number for 1D, 2 numbers for 2D and 3 numbers for 3D periodic systems).

SuperCellTrafo

Type Integer List

Description Create a supercell of the input system (only possible for periodic systems) $\vec{a}'_i = \sum_j T_{ij}\vec{a}_j$. The integer numbers represent the supercell transformation T_{ij}: 1 number for 1D PBC, 4 numbers for 2D PBC corresponding to a 2x2 matrix (order: (1,1),(1,2),(2,1),(2,2)) and 9 numbers for 3D PBC corresponding to a 3x3 matrix (order: (1,1),(1,2),(1,3),(2,1),(2,2),(2,3),(3,1),(3,2),(3,3)).

`Symmetrize`

Type Bool

Default value No

Description Whether to symmetrize the input structure. This might also rototranslate the structure into a standard orientation. This will symmetrize the atomic coordinates to machine precision. Useful if the system is almost symmetric or to rototranslate a symmetric molecule into a standard orientation.

`Symmetry`

Type Multiple Choice

Default value AUTO

Options [AUTO, NOSYM, C(LIN), D(LIN), C(I), C(S), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(2V), C(3V), C(4V), C(5V), C(6V), C(7V), C(8V), C(2H), C(3H), C(4H), C(5H), C(6H), C(7H), C(8H), D(2), D(3), D(4), D(5), D(6), D(7), D(8), D(2D), D(3D), D(4D), D(5D), D(6D), D(7D), D(8D), D(2H), D(3H), D(4H), D(5H), D(6H), D(7H), D(8H), I, I(H), O, O(H), T, T(D), T(H), S(4), S(6), S(8)]

Description Use (sub)symmetry with this Schoenflies symbol. Can only be used for molecules. Orientation should be correct for the (sub)symmetry. If used icw Symmetrize, the symmetrization will not reorient the molecule.

`Task`

Type Multiple Choice

Default value Generate

Options [Generate, Optimize, Filter, Score, Expand]

Description The task to be performed by the Conformers tool.

'Generate': given a molecule, generate a set of conformers. Note: this task will automatically optimize, filter and score the conformers.

'Optimize': given a previously generated set of conformers, optimize, filter and score the structures using the specified engine.

'Filter': given one or more previously generated set of conformers, merge them into a single conformer set and filter out duplicate conformers. Note: this will not optimize or re-score the conformers.

'Score' given one or more previously generated set of conformers, re-score them by computing the energy using the specified engine. Note: this will only do a single point calculation, and will not optimize the structures.

In case of 'Optimize', 'Filter' and 'Score' you can specify the input conformer set(s) using the 'InputConformersSet' keyword.

15.2.5 fcf

See *FCF manual page* (page 247)

15.2.6 oled-deposition

`Box`

Type Block

Description Specifications of the box into which the material is deposited.

`Size`

Type Float List

Default value [60.0, 60.0, 120.0]

Unit Angstrom

GUI name Box size

Description Specify the desired size of the box. The final deposited box may have a different size. The x- and y-axis are perpendicular to the direction of deposition, so these may be regarded as the width of the growing layer. The z-axis is the direction along which the deposition happens, so this determines the thickness of the deposited layer. Note that the x- and y-axis will be ignored if a custom substrate is used: the are of the box is then determined by the lattice of the substrate. The z-axis can still be freely chosen, but should be large enough that there is enough space for the substrate itself and to deposit more molecules on top of it.

`Substrate`

Type Multiple Choice

Default value Graphene

Options [Graphene, Custom]

Description The substrate on which to grow the layer.

`SubstrateSystem`

Type String

GUI name Custom substrate

Description String ID of a named [System] to be used as a substrate. (This is only used when the Substrate key is set to Custom.)

`Deposition`

Type Block

Description Specifies the details of how molecules are deposited.

`ConstrainHXBonds`

Type Bool

Default value Yes

GUI name Constrain H-* bonds

Description Constrain the bond length for all H-* bonds (i.e. any bond to a hydrogen atom). Doing this allows choosing a larger time step. If this option is disabled, the TimeStep needs to be reduced manually.

`Frequency`

Type Integer

Default value 10000

Description The frequency in MD steps at which new molecules will be added to the system.

`NumMolecules`

Type Integer

Description The number of molecules that we will try to deposit. If not specified the number will be determined automatically such that the box becomes approximately full.

`Temperature`

Type Float

Default value 600.0

Description The temperature at which the deposition happens.

`TimeStep`

Type Float

Default value 1.0

Unit Femtoseconds

Description The time difference per step.

`LAMMPSOffload`

Type Block

Description Offload the calculation to LAMMPS via AMSPipe.

`Enabled`

Type Bool

Default value No

Description Enable offloading the force field evaluation to LAMMPS instead of handling it internally in AMS.

`UseGPU`

Type Bool

Default value No

GUI name Use GPU

Description Accelerate LAMMPS calculations using a GPU. Requires a LAMMPS library built with the GPU package.

`UseOpenMP`

Type Bool

Default value No

GUI name Use OpenMP

Description Parallelize LAMMPS calculations using OpenMP threading. Requires a LAMMPS library built with the OMP package.

`LoadSystem`

Type Block

Recurring True

Description Block that controls reading the chemical system from a KF file instead of the [System] block.

`File`

Type String

Description The path of the KF file from which to load the system. It may also be the results directory containing it.

`Section`

Type String

Default value Molecule

Description The section on the KF file from which to load the system.

`Molecule`

Type Block

Recurring True

GUI name Molecules

Description Specification of the molecule to be deposited.

`MoleFraction`

Type Float

Default value 1.0

GUI name Molar fraction

Description The relative occurrence of the molecule with regard to other deposited species. Only relevant for mixed molecule depositions.

`SystemName`

Type String

GUI name Molecule

Description String ID of a named [System] to be inserted. The lattice specified with this System, if any, is ignored and the main system's lattice is used instead.

`RestartWorkdir`

Type String

Description Uses the data from the working directory of a previously run deposition workflow for restarting. Under the hood this uses the normal rerun-prevention available in PLAMS: it may reuse results from old jobs instead of running them again.

`System`

Type Block

Recurring True

Description Specification of the chemical system. For some applications more than one system may be present in the input. In this case, all systems except one must have a non-empty string ID specified after the System keyword. The system without an ID is considered the main one.

`AllowCloseAtoms`

Type Bool

Default value No

Description If AllowCloseAtoms is set to False, the AMS driver will stop with an error if it detects almost-coinciding atomic coordinates. If set to True, the AMS driver will try to carry on with the calculation.

`Atoms`

Type Non-standard block

Description The atom types and coordinates. Unit can be specified in the header. Default unit is Angstrom.

`BondOrders`

Type Non-standard block

Description Defined bond orders. Each line should contain two atom indices, followed by the bond order (1, 1.5, 2, 3 for single, aromatic, double and triple bonds) and (optionally) the cell shifts for periodic systems. May be used by MM engines and for defining constraints. If the system is periodic and none of the bonds have the cell shift defined then AMS will attempt to determine them following the minimum image convention.

`Charge`

Type Float

Default value 0.0

GUI name Total charge

Description The system's total charge in atomic units.

`ElectrostaticEmbedding`

Type Block

Description Container for electrostatic embedding options, which can be combined.

`ElectricField`

Type Float List

Unit V/Angstrom

Description External homogeneous electric field with three Cartesian components: ex, ey, ez, the default unit being V/Å.

In atomic units: Hartree/(e bohr) = 14.39964 V/Angstrom; the relation to SI units is: 1 Hartree/(e bohr) = 5.14 … e11 V/m.

Supported by the engines adf, band, dftb and mopac.

For periodic systems the field may only have nonzero components orthogonal to the direction(s) of periodicity (i.e. for 1D periodic system the x-component of the electric field should be zero, while for 2D periodic systems both the x and y components should be zero. This options cannot be used for 3D periodic systems.

`MultipolePotential`

Type Block

Description External point charges (and dipoles).

`ChargeModel`

Type Multiple Choice

Default value Point

Options [Point, Gaussian]

Description A multipole may be represented by a point (with a singular potential at its location) or by a spherical Gaussian distribution.

`ChargeWidth`

Type Float

Default value -1.0

Description The width parameter in a.u. in case a Gaussian charge model is chosen. A negative value means that the width will be chosen automatically.

`Coordinates`

Type Non-standard block

Description Positions and values of the multipoles, one per line. Each line has the following format:

x y z q, or x y z q µx µy µz.

Here x, y, z are the coordinates in Å, q is the charge (in atomic units of charge) and µx, µy, µz are the (optional) dipole moment components (in atomic units, i.e. e*Bohr).

Periodic systems are not supported.

`FractionalCoords`

Type Bool

Default value No

Description Whether the atomic coordinates in the Atoms block are given in fractional coordinates of the lattice vectors. Requires the presence of the Lattice block.

`GeometryFile`

Type String

Description Read the geometry from a file (instead of from Atoms and Lattice blocks). Supported formats: .xyz

`GuessBonds`

Type Bool

Default value No

Description Whether or not UFF bonds should be guessed.

`Lattice`

Type Non-standard block

Description Up to three lattice vectors. Unit can be specified in the header. Default unit is Angstrom.

`LatticeStrain`

Type Float List

Description Deform the input system by the specified strain. The strain elements are in Voigt notation, so one should specify 6 numbers for 3D periodic system (order: xx,yy,zz,yz,xz,xy), 3 numbers for 2D periodic systems (order: xx,yy,xy) or 1 number for 1D periodic systems.

`LoadForceFieldAtomTypes`

Type Block

Description This is a mechanism to set the ForceField.Type attribute in the input. This information is currently only used by the ForceField engine.

`File`

Type String

Description Name of the (kf) file. It needs to be the result of a forcefield calculation.

`LoadForceFieldCharges`

Type Block

Recurring True

Description This is a mechanism to set the ForceField.Charge attribute in the input. This information is currently only used by the ForceField engine.

`CheckGeometryRMSD`

Type Bool

Default value No

Description Whether the geometry RMSD test should be performed, see MaxGeometryRMSD. Otherwise only basic tests are performed, such as number and atom types. Not doing the RMSD test allows you to load molecular charges in a periodic system.

`File`

Type String

Description Name of the (kf) file

`MaxGeometryRMSD`

Type Float

Default value 0.1

Unit Angstrom

Description The geometry of the charge producing calculation is compared to the one of the region, and need to be the same within this tolerance.

`Region`

Type String

Default value *

Description Region for which the charges should be loaded

`Section`

Type String

Default value AMSResults

Description Section name of the kf file

`Variable`

Type String

Default value Charges

Description Variable name of the kf file

`MapAtomsToUnitCell`

Type Bool

Default value No

Description For periodic systems the atoms will be moved to the central cell.

`ModifyAlternativeElements`

Type Bool

Default value No

Description When using alternative elements (using the nuclear_charge attribute) set the element to the nearest integer Z. If you specify an H atom with a nuclear_charge of 2.9 it is replaced by a Li atom with the same nuclear charge.

`PerturbCoordinates`

Type Float

Default value 0.0

Unit Angstrom

Description Perturb the atomic coordinates by adding random numbers between [-PerturbCoordinates,PerturbCoordinates] to each Cartesian component. This can be useful if you want to break the symmetry of your system (e.g. for a geometry optimization).

`PerturbLattice`

Type Float

Default value 0.0

Description Perturb the lattice vectors by applying random strain with matrix elements between [-PerturbLattice,PerturbLattice]. This can be useful if you want to deviate from an ideal symmetric geometry, for example if you look for a phase change due to high pressure.

`RandomizeAtomOrder`

Type Bool

Default value No

Description Whether or not the order of the atoms should be randomly changed. Intended for some technical testing purposes only. Does not work with bond information.

`Region`

Type Block

Recurring True

Description Properties for each region specified in the Atoms block.

`Properties`

Type Non-standard block

Description Properties for each region specified in the Atoms block.

`ShiftCoordinates`

Type Float List

Unit Bohr

Description Translate the atoms by the specified shift (three numbers).

`SuperCell`

Type Integer List

Description Create a supercell of the input system (only possible for periodic systems). The integer numbers represent the diagonal elements of the supercell transformation; you should specify as many numbers as lattice vectors (i.e. 1 number for 1D, 2 numbers for 2D and 3 numbers for 3D periodic systems).

`SuperCellTrafo`

Type Integer List

Description Create a supercell of the input system (only possible for periodic systems) $\vec{a}_i' = \sum_j T_{ij}\vec{a}_j$. The integer numbers represent the supercell transformation T_{ij}: 1 number for 1D PBC, 4 numbers for 2D PBC corresponding to a 2x2 matrix (order: (1,1),(1,2),(2,1),(2,2)) and 9 numbers for 3D PBC corresponding to a 3x3 matrix (order: (1,1),(1,2),(1,3),(2,1),(2,2),(2,3),(3,1),(3,2),(3,3)).

`Symmetrize`

Type Bool

Default value No

Description Whether to symmetrize the input structure. This might also rototranslate the structure into a standard orientation. This will symmetrize the atomic coordinates to machine precision. Useful if the system is almost symmetric or to rototranslate a symmetric molecule into a standard orientation.

`Symmetry`

Type Multiple Choice

Default value AUTO

Options [AUTO, NOSYM, C(LIN), D(LIN), C(I), C(S), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(2V), C(3V), C(4V), C(5V), C(6V), C(7V), C(8V), C(2H), C(3H), C(4H), C(5H), C(6H), C(7H), C(8H), D(2), D(3), D(4), D(5), D(6), D(7), D(8), D(2D), D(3D), D(4D), D(5D), D(6D), D(7D), D(8D), D(2H), D(3H), D(4H), D(5H), D(6H), D(7H), D(8H), I, I(H), O, O(H), T, T(D), T(H), S(4), S(6), S(8)]

Description Use (sub)symmetry with this Schoenflies symbol. Can only be used for molecules. Orientation should be correct for the (sub)symmetry. If used icw Symmetrize, the symmetrization will not reorient the molecule.

15.2.7 oled-properties

CoresPerJob

Type Integer

Default value 8

Description The number of CPU cores used for each job in the workflow. Combined with the total number of cores used (set by the `NSCM` environment variable or the `-n` command line argument), this indirectly determines the number of simultaneously running jobs. The default value should usually be a good choice. When changing this value, make sure you are using all allocated cores by setting a value that divides the total number of cores, as well as the number of cores on each node.

Embedding

Type Block

Description Configures details of how the environment is taken into account.

Charges

Type Multiple Choice

Default value DFT

Options [DFTB, DFT]

Description Which atomic charges to use for the DRF embedding.

• DFTB: Use the self-consistent Mulliken charges from a quick DFTB calculation with the GFN1-xTB model.

• DFT: Use the MDC-D charges from a relatively quick DFT calculation using LDA and a DZP basis set.

Cutoff

Type Float

Default value 15.0

Unit Angstrom

Description The cutoff distance determining which molecules will be considered the environment of the central molecule. The maximum possible cutoff distance is half the length of the smallest lattice vector. The distance can be measured using different metrics, see the `Metric` keyword.

Metric

Type Multiple Choice

Default value Atoms

Options [CoM, Atoms, Atoms_noH]

Description The metric used to calculate the distance between two molecules.

• CoM: use the distance between the centers of mass of the two molecules.

• Atoms: Use the distance between the two closest atoms of two molecules.

• Atoms_noH: Use the distance between the closest non-hydrogen atoms of the two molecules.

Type

Type Multiple Choice

Default value DRF

Options [None, DRF]

Description The type of embedding used to simulate the molecular environment.

GW

Type Block

Description Instruct ADF to perform a G0W0 calculation.

AdaptiveMixing

Type Float List

Description Requests to use adaptive mixing instead of DIIS and sets the staring mixing parameter for mixing of Green's function in case of self-consistency.

Adapative mixing is recommenened in case a qsGW calculation does not converge with DIIS.

It is ignored in non-selfconsistent calculation and overwritten by DIIS when DIIS is also present.

AnalyticalIntegration

Type Block

Description Use analytical integration to calculate the self-energy. Very slow, unless the system is very small but useful to check the accuracy of the frequency integration

Enabled

Type Bool

Default value No

GUI name analytical integration

Description Enable the calculation of the GW quasi-particle energies via analytical integration.

Polarizability

Type Multiple Choice

Default value RPA

Options [RPA, BSE]

Description Sets the expression for the Polarizability used in the GW calculation.

RPA is the Default and amounts to a standard GW calculation.

BSE denotes screening in the Bethe-Salpeter-equation formalism.

PrintSpectralFunction

Type Bool

Default value No

Description Plot the self-energy as a function of freuency. Aotumatically done in case of analytical continuation. However, this is expensive in the analytical integration formalism.

SpectralFunctionResolution

Type Integer

Default value 800

Description Number of points at which spectral function is evaluated.

TDA

Type Bool

Default value No

Description Solve the linear reponse equations in the Tamm-Dancoff approximation.

eta

Type Float

Default value 0.001

Description Artificial (positive) broadening parameter for evaluation of self-energy in analytical integration.

Ideally should be as small as possible but this might lead to convergence issues in partially self-consistent approaches.

In this case, a value of up to 0.1 is possible.

Converge

Type Block

Description Sets convergence criteria for the GW calculation in self-consistent case

Density

Type Float List

Default value [1e-08, 1e-05]

Description First Criterion for self-consistency procedure to terminate.

Criterion is the trace of the density matrix. Ignored in non-selfconsistent Calculation and in eigenvalue self-consistent GW

It is possible to run a qsGW calculation with an inner SCF loop which updates the static part of the elf-energy only. This can be useful to accelerate the convergence in case linear mixing is used. It is not recommended to use linear mixing, so it is also not recommened to use that inner loop as well. The second number in this list specifies the convergence criterion for the inner SCF loop.

HOMO

Type Float

Default value 0.003

Unit eV

GUI name HOMO energy convergence

Description Criterion for self-consistency procedure to terminate.

The self-consistent GW calculation terminates, when the difference between the HOMO QP energies between 2 consecutive iterations is below this number.

The LUMO energy converged faster than the HOMO energy so when the HOMO energy is converged according to this criterion, the LUMO energy will be converged as well.

In non-selfconsistent Calculation, this criterion is ignored.

DIIS

Type Integer

Default value 10

Description Requests to use DIIS. This is the Default. Number of expansion coefficients can be requested as well. Ignored in non-selfconsistent calculation

Enabled

Type Bool

Default value No

GUI name Calculate GW quasi-particle energies

Description Enable the calculation of the GW quasi-particle energies.

FixedGrids

Type Bool

Default value No

Description In a self-consistent GW calculation, do not recalculate Grids. Can be useful in case of convergence problems. Only relevant for qsGW and qsGW0. In case of evGW and evGW0, the grids are always kept fixed.

LinearMixing

Type Float List

Description Requests to use linear mixing instead of DIIS and sets the mixing parameter for linear mixing of Green's function in case of self-consistency.

It is ignored in non-selfconsistent calculation and overwritten by DIIS when DIIS is also present.

LinearizeQPequations

Type Bool

Default value No

Description Instead of solving the non-linear QP equations in a G0W0 (or evGW calculation) by bisection exacly, linearize them by first-order Taylor expansion.

This is not recommended since it does not save computational time when used together with analytical continuation (as implemented in AMS). It might however be useful for benchmarking or for validating results.

If the results os the linearization differ by a lot (for instance, more than 0.1 eV in frontier QP energies) from the non-linearized results, this might indicate that the GW calculation is not reliable.

OffDiagonalEFermi

Type Bool

Default value No

Description Analytically continue the off-diagonal elements of the KSF2 qsGW Hamiltonian at the Fermi-energy instead of omega=0. Typically leads to slightly lower QP energies, i.e. higher ionization potentials. The HOMO-LUMO gaps are typically not affected.

PrintAllSolutions

Type Bool

Default value No

Description Print out all solutions for all requested states. Detects multiple solutions of the QP equations.

`QPHamiltonian`

Type Multiple Choice

Default value KSF2

Options [KSF1, KSF2, SRG, LQSGW]

Description The quasi-particle Hamiltonian can be constructed in different ways.

KSF1 refers to the original construction by Kotani, Van Schilfgaarde anf Faleev (KSF) which is also implemented in TURBOMOLE.

KSF2 refers to an alternative construction by KSF.

KSF1 is not recommended since it is numerically less stable than KSF2. The results are typically very similar.

The QP energies at which the matrix elements are evaluated can be tweaked further, see the two subsequent keys: However, KSF2 is recommended since it typically leads to QP energies with the best agreement with experiment.

Ignored when not a quasi-particle self-consistent GW calculation is performed

`ScissorShift`

Type Bool

Default value No

Description Only calculate the HOMO and LUMO QP energies and shift the remaining QP energies by the same amount.

This is a rather crude approximaiton and not recommended.

It might again be useful for benchmarking purposes.

`SelfConsistency`

Type Multiple Choice

Default value G0W0

Options [G0W0, EVGW0, EVGW, QSGW0, QSGW]

Description Sets the level of self-consistency in a GW calculation.

G0W0 calculates a one-shot, perturbative correction to the KS eigenvalues.

In evGW and evGW0, the quasi-particle energies are updated until self-consistency is reached.

evGW0 requests that the Green's function is evaluated self-consistently but not the screened interaction.

In qsGW, the density is updated as well, however, the self-energy is mapped to a static effective potential and the Dyson equation is solved by diagonalization instead of inversion. The results of a qsGW are independent of the choice of the underlying exchange-correlation functional and are usually the most accurate ones.

The same is done in qsGW0, but the screened interaction is not updated.

`SelfEnergy`

Type Multiple Choice

Default value GW

Options [HF, GW, G3W2, SOSEX, GWGamma, G3W2dynamic]

Description Controls the form of the self-energy.

GW is the default and corresponds to the standard GW calculation.

G3W2 is a GW calculation plus a perturbative second-order statically screened exchange correction (second order expansion in the self-energy). Note, that there the self-energy is always static.

`nIterations`

Type Integer List

Default value [10]

GUI name Number of iterations

Description The maximum number of iterations within the (partially or fully) self-consistent GW calculation has to converge.

Ignored when Formalism is set to G0W0

`nLowest`

Type Integer

Default value 1

GUI name N Lowest

Description Number of lowest occupied QP levels to be evaluated, overwrites nStates'

`nStates`

Type Integer

Default value 5

GUI name N states

Description Number of Quasiparticle States to be printed to output.

The default is 5 states which in this case means that min(5, Number of particle states) occupied and min(5, Number of hole states) hole states are printed. The whole list of states can be printed by setting this parameter to -1'

`preconditionQSGW`

Type Bool

Default value No

Description If true, the QSGW equations are solved but prior to each diagonalization, i.e. a G0W0 calculation is performed to find the optimal QP energies at which to analytically continue the self-energy.

This is in principle a more consistent construction than KSF1 or KSF2 since the diagonal elements are consistent with G0W0.

In KSF1 and KSF2, the diagonal elements are evaluated at the QP energies from the previous iteration which is equivalent to a zeroth-order Taylor expansion of the diaognal elements around the previous QP energies.Enabling this option typically leads to slightly lower QP energies.

`LoadSystem`

Type Block

Recurring True

Description Block that controls reading the chemical system from a KF file instead of the [System] block.

`File`

Type String

Description The path of the KF file from which to load the system. It may also be the results directory containing it.

`Section`

Type String

Default value Molecule

Description The section on the KF file from which to load the system.

`LogProgressEvery`

Type Float

Default value 600.0

Unit Seconds

Description How often to print progress information to the logfile.

`NumAdditionalOrbitalEnergies`

Type Integer

Default value 1

Description The number of additional orbital energies to write to the HDF5 file. A value of N means to write everything up to HOMO-N and LUMO+N.

`NumExcitations`

Type Integer

Default value 1

Description The number of exited states to calculate. By default the S_1 and T_1 states will be calculated. The calculation of excited states is currently only supported for systems with a closed-shell ground state.

`OccupationSmearing`

Type Multiple Choice

Default value Ions

Options [None, Ions, All]

Description Determines for which systems the electron smearing feature in ADF will be used. If enabled, the molecular orbital occupations will be smeared out with a 300K Fermi-Dirac distribution. This makes SCF convergence easier, as the occupation of energetically close orbitals does not jump when their energetic order flips. See the ADF manual for details. It is recommended to keep this option enabled for the ionic systems, which are more likely to suffer from difficult SCF convergence.

`Relax`

Type Multiple Choice

Default value All

Options [None, Neutral, All]

Description Which geometries to relax prior to taking the energy differences for the calculation of ionization potential and electron affinity. The relaxation is done at the DFTB level using the GFN1-xTB model Hamiltonian with electrostatic embedding in a UFF environment.

• None: Use the geometries directly from the input.

• Neutral: Relax the uncharged molecule and use its optimized geometry for the neutral as well as the ionic systems. This gives (approximately) the vertial ionization potential and electron affinity.

• All: Individually relax the neutral systems and the ions before calculating the total energies. This gives (approximately) the adiabatic ionization potential and electron affinity.

`Restart`

Type String

Description The HDF5 file from a previous calculation on the same morphology. Data already calculated on the restart file will just be copied over and not be recalculated.

`SelectedMolecules`

Type Integer List

Description Indices of the molecules to calculate properties for. If not present, all molecules will be used. Note that indexing starts at 0.

`StoreResultFiles`

Type Multiple Choice

Default value Failed

Options [None, Failed, All]

Description Whether to keep the full result files from all the individual jobs. By default the result files from all jobs for a particular molecule will be deleted after all relevant results have been extracted and stored on the HDF5 file. Note that keeping the full results for all molecules can easily require hundreds of gigabytes of storage space.

`System`

Type Block

Recurring True

Description Specification of the chemical system. For some applications more than one system may be present in the input. In this case, all systems except one must have a non-empty string ID specified after the System keyword. The system without an ID is considered the main one.

`AllowCloseAtoms`

Type Bool

Default value No

Description If AllowCloseAtoms is set to False, the AMS driver will stop with an error if it detects almost-coinciding atomic coordinates. If set to True, the AMS driver will try to carry on with the calculation.

`Atoms`

Type Non-standard block

Description The atom types and coordinates. Unit can be specified in the header. Default unit is Angstrom.

`BondOrders`

Type Non-standard block

Description Defined bond orders. Each line should contain two atom indices, followed by the bond order (1, 1.5, 2, 3 for single, aromatic, double and triple bonds) and (optionally) the cell shifts for periodic systems. May be used by MM engines and for defining constraints. If the system is periodic and none of the bonds have the cell shift defined then AMS will attempt to determine them following the minimum image convention.

`Charge`

Type Float

Default value 0.0

GUI name Total charge

Description The system's total charge in atomic units.

`ElectrostaticEmbedding`

Type Block

Description Container for electrostatic embedding options, which can be combined.

`ElectricField`

Type Float List

Unit V/Angstrom

Description External homogeneous electric field with three Cartesian components: ex, ey, ez, the default unit being V/Å.

In atomic units: Hartree/(e bohr) = 14.39964 V/Angstrom; the relation to SI units is: 1 Hartree/(e bohr) = 5.14 … e11 V/m.

Supported by the engines adf, band, dftb and mopac.

For periodic systems the field may only have nonzero components orthogonal to the direction(s) of periodicity (i.e. for 1D periodic system the x-component of the electric field should be zero, while for 2D periodic systems both the x and y components should be zero. This options cannot be used for 3D periodic systems.

`MultipolePotential`

Type Block

Description External point charges (and dipoles).

`ChargeModel`

Type Multiple Choice

Default value Point

Options [Point, Gaussian]

Description A multipole may be represented by a point (with a singular potential at its location) or by a spherical Gaussian distribution.

`ChargeWidth`

Type Float

Default value -1.0

Description The width parameter in a.u. in case a Gaussian charge model is chosen. A negative value means that the width will be chosen automatically.

`Coordinates`

Type Non-standard block

Description Positions and values of the multipoles, one per line. Each line has the following format:

x y z q, or x y z q µx µy µz.

Here x, y, z are the coordinates in Å, q is the charge (in atomic units of charge) and µx, µy, µz are the (optional) dipole moment components (in atomic units, i.e. e*Bohr).

Periodic systems are not supported.

`FractionalCoords`

Type Bool

Default value No

Description Whether the atomic coordinates in the Atoms block are given in fractional coordinates of the lattice vectors. Requires the presence of the Lattice block.

`GeometryFile`

Type String

Description Read the geometry from a file (instead of from Atoms and Lattice blocks). Supported formats: .xyz

`GuessBonds`

Type Bool

Default value No

Description Whether or not UFF bonds should be guessed.

`Lattice`

Type Non-standard block

Description Up to three lattice vectors. Unit can be specified in the header. Default unit is Angstrom.

`LatticeStrain`

Type Float List

Description Deform the input system by the specified strain. The strain elements are in Voigt notation, so one should specify 6 numbers for 3D periodic system (order: xx,yy,zz,yz,xz,xy), 3 numbers for 2D periodic systems (order: xx,yy,xy) or 1 number for 1D periodic systems.

`LoadForceFieldAtomTypes`

Type Block

Description This is a mechanism to set the ForceField.Type attribute in the input. This information is currently only used by the ForceField engine.

`File`

Type String

Description Name of the (kf) file. It needs to be the result of a forcefield calculation.

`LoadForceFieldCharges`

Type Block

Recurring True

Description This is a mechanism to set the ForceField.Charge attribute in the input. This information is currently only used by the ForceField engine.

`CheckGeometryRMSD`

Type Bool

Default value No

Description Whether the geometry RMSD test should be performed, see MaxGeometryRMSD. Otherwise only basic tests are performed, such as number and atom types. Not doing the RMSD test allows you to load molecular charges in a periodic system.

`File`

Type String

Description Name of the (kf) file

`MaxGeometryRMSD`

Type Float

Default value 0.1

Unit Angstrom

Description The geometry of the charge producing calculation is compared to the one of the region, and need to be the same within this tolerance.

`Region`

Type String

Default value *

Description Region for which the charges should be loaded

`Section`

Type String

Default value AMSResults

Description Section name of the kf file

`Variable`

Type String

Default value Charges

Description Variable name of the kf file

`MapAtomsToUnitCell`

Type Bool

Default value No

Description For periodic systems the atoms will be moved to the central cell.

`ModifyAlternativeElements`

Type Bool

Default value No

Description When using alternative elements (using the nuclear_charge attribute) set the element to the nearest integer Z. If you specify an H atom with a nuclear_charge of 2.9 it is replaced by a Li atom with the same nuclear charge.

`PerturbCoordinates`

Type Float

Default value 0.0

Unit Angstrom

Description Perturb the atomic coordinates by adding random numbers between [-PerturbCoordinates,PerturbCoordinates] to each Cartesian component. This can be useful if you want to break the symmetry of your system (e.g. for a geometry optimization).

`PerturbLattice`

Type Float

Default value 0.0

Description Perturb the lattice vectors by applying random strain with matrix elements between [-PerturbLattice,PerturbLattice]. This can be useful if you want to deviate from an ideal symmetric geometry, for example if you look for a phase change due to high pressure.

`RandomizeAtomOrder`

Type Bool

Default value No

Description Whether or not the order of the atoms should be randomly changed. Intended for some technical testing purposes only. Does not work with bond information.

`Region`

Type Block

Recurring True

Description Properties for each region specified in the Atoms block.

`Properties`

Type Non-standard block

Description Properties for each region specified in the Atoms block.

`ShiftCoordinates`

Type Float List

Unit Bohr

Description Translate the atoms by the specified shift (three numbers).

`SuperCell`

Type Integer List

Description Create a supercell of the input system (only possible for periodic systems). The integer numbers represent the diagonal elements of the supercell transformation; you should specify as many numbers as lattice vectors (i.e. 1 number for 1D, 2 numbers for 2D and 3 numbers for 3D periodic systems).

`SuperCellTrafo`

Type Integer List

Description Create a supercell of the input system (only possible for periodic systems) $\vec{a}'_i = \sum_j T_{ij}\vec{a}_j$. The integer numbers represent the supercell transformation T_{ij}: 1 number for 1D PBC, 4 numbers for 2D PBC corresponding to a 2x2 matrix (order: (1,1),(1,2),(2,1),(2,2)) and 9 numbers for 3D PBC corresponding to a 3x3 matrix (order: (1,1),(1,2),(1,3),(2,1),(2,2),(2,3),(3,1),(3,2),(3,3)).

`Symmetrize`

Type Bool

Default value No

Description Whether to symmetrize the input structure. This might also rototranslate the structure into a standard orientation. This will symmetrize the atomic coordinates to machine precision. Useful if the system is almost symmetric or to rototranslate a symmetric molecule into a standard orientation.

`Symmetry`

Type Multiple Choice

Default value AUTO

Options [AUTO, NOSYM, C(LIN), D(LIN), C(I), C(S), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(2V), C(3V), C(4V), C(5V), C(6V), C(7V), C(8V), C(2H), C(3H), C(4H), C(5H), C(6H), C(7H), C(8H), D(2), D(3), D(4), D(5), D(6), D(7), D(8), D(2D), D(3D), D(4D), D(5D), D(6D), D(7D), D(8D), D(2H), D(3H), D(4H), D(5H), D(6H), D(7H), D(8H), I, I(H), O, O(H), T, T(D), T(H), S(4), S(6), S(8)]

Description Use (sub)symmetry with this Schoenflies symbol. Can only be used for molecules. Orientation should be correct for the (sub)symmetry. If used icw Symmetrize, the symmetrization will not reorient the molecule.

`TransferIntegrals`

Type Block

Description Configures the details of the calculation of electron and hole transfer integrals.

`Exclude`

Type Block

Description Configures which dimers NOT to calculate transfer integrals for.

`Cutoff`

Type Float

Default value 4.0

Unit Angstrom

GUI name Exclude beyond

Description Exclude dimers for which the distance is larger than this threshold. Acts as a quick pre-screening to reduce the number of dimers to calculate transfer integrals for.

`Metric`

Type Multiple Choice

Default value Atoms

Options [CoM, Atoms, Atoms_noH]

Description The metric used to calculate the distance between two molecules.

- CoM: use the distance between the centers of mass of the two molecules.
- Atoms: Use the distance between the two closest atoms of two molecules.
- Atoms_noH: Use the distance between the closest non-hydrogen atoms of the two molecules.

`Include`

Type Block

Description Configures which dimers transfer integrals are calculated for.

`Cutoff`

Type Float

Default value 4.0

Unit Angstrom

GUI name Include within

Description Transfer integrals will be calculated for all molecule pairs within a cutoff distance from each other. This distance can be measured using different metrics, see the corresponding `Metric` keyword.

`Metric`

Type Multiple Choice

Default value Atoms

Options [CoM, Atoms, Atoms_noH]

Description The metric used to calculate the distance between two molecules.

- CoM: use the distance between the centers of mass of the two molecules.
- Atoms: Use the distance between the two closest atoms of two molecules.
- Atoms_noH: Use the distance between the closest non-hydrogen atoms of the two molecules.

`Type`

Type Multiple Choice

Default value Fast

Options [None, Fast, Full]

Description The method used for the calculation of the transfer integrals.

CHAPTER

SIXTEEN

KF OUTPUT FILES

16.1 Accessing KF files

KF files are Direct Access binary files. KF stands for Keyed File: KF files are keyword oriented, which makes them easy to process by simple procedures. Internally all the data on KF files is organized into sections containing variables, so each datum on the file can be identified by the combination of section and variable.

All KF files can be opened using the KFbrowser GUI program:

```
$AMSBIN/kfbrowser path/to/ams.rkf
```

By default KFbrowser shows a just a curated summary of the results on the file, but you can make it show the raw section and variable structure by switching it to expert mode. To do this, click on **File → Expert Mode** or press **ctrl/cmd + e**.

KF files can be opened and read with Command line tools.

For working with the data from KF files, it is often useful to be able to read them from Python. Using the AMS Python Stack, this can easily be done with the AKFReader class:

```
>>> from scm.akfreader import AKFReader
>>> kf = AKFReader("path/to/ams.rkf")
>>> "Molecule%Coords" in kf
True
>>> kf.description("Molecule%Coords")
{
    '_type': 'float_array',
    '_shape': [3, 'nAtoms'],
    '_comment': 'Coordinates of the nuclei (x,y,z)',
    '_unit': 'Bohr'
}
>>> kf.read("Molecule%Coords")
array([[-11.7770694 ,  -4.19739597,   0.04934546],
       [ -9.37471321,  -2.63234227,  -0.13448698],
        ...
       [ 10.09508738,  -1.06191208,   1.45286913],
       [ 10.11689333,  -1.5080196 ,  -1.87916127]])
```

Tip: For a full overview of the available methods in AKFReader, see the AKFReader API documentation.

16.2 Sections and variables on ams.rkf

Note: The AMS driver creates an entire directory full of result files. Often there are multiple `.rkf` files in that directory. This page only documents the sections and variables in the `ams.rkf` file.

BindingSites **Section content:** Information on binding sites for a adsorbate.

`BindingSites%AdsorbateLabel`

Type string

Description Label for the adsorbate.

`BindingSites%AverEnergy`

Type float_array

Description The average energy per site. The energy of all stationary states that at least has an atom attached to the given site contributes to this average.

Unit hartree

Shape [nSites]

`BindingSites%Coords`

Type float_array

Description The coordinates of the sites.

Unit bohr

Shape [3, nSites]

`BindingSites%CoordsFrac`

Type float_array

Description The fractional coordinates of the sites.

Shape [3, nSites]

`BindingSites%FromSites`

Type int_array

Description Sites from where the connections start.

Shape [nConnections]

`BindingSites%Labels`

Type lchar_string_array

Description Arbitrary labels for the binding sites. They are assigned according to the number of atom neighbors.

`BindingSites%LatticeDisplacements`

Type int_array

Description Links between neighbouring sites across the periodic boundary conditions.

Shape [:, nConnections]

`BindingSites%nConnections`

Type int

Description The number of connections between sites.

`BindingSites%nParentStates`

Type int_array

Description The number of stationary states contributing to the average and standard deviation of the energy. See AverEnergy and StdevEnergy.

Shape [nSites]

`BindingSites%nSites`

Type int

Description The number of sites.

`BindingSites%ParentAtoms`

Type int_array

Description Atom id that is attached to the site in the corresponding parent state. See ParentStates.

Shape [:]

`BindingSites%ParentStates`

Type int_array

Description Stationary states ids contributing to the average and standard deviation of the energy. See AverEnergy and StdevEnergy.

Shape [:]

`BindingSites%ReferenceRegionLabel`

Type string

Description Label for the reference region.

`BindingSites%StdevEnergy`

Type float_array

Description Std. deviation for energy per site. The energy of all stationary states that at least has an atom attached to the given site contributes to this std. deviation.

Unit hartree

Shape [nSites]

`BindingSites%ToSites`

Type int_array

Description Sites to where the connections end up.

Shape [nConnections]

BinLog Section content:

`BinLog%Area(#)`

Type float_array

Description The area of the cell (only for 2D PBC). This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit bohr^2

BinLog%BiasEnergy(#)

Type float_array

Description ? This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

BinLog%blockSize

Type int

Description Explain the block-system… ?

BinLog%BoostFactor(#)

Type float_array

Description The boost factor for hyper-dynamics. Expand? This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

BinLog%ConservedEnergy(#)

Type float_array

Description The conserved energy…? Some MD person, please fix. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

BinLog%currentEntryOpen

Type bool

Description ?

BinLog%Density(#)

Type float_array

Description The density of the system (mass/simulation_cell_volume). Only for 3D PBC. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit dalton/bohr^3

BinLog%DipoleMoment_*(#)

Type float_array

Description The dipolemoment of the full system. For periodic systems this value will often not make sense, because molecules are not mapped together

BinLog%Hypertime(#)

Type float_array

Description Hyper time for hyper-dynamics. Expand? This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit femtosecond

BinLog%ItemName(#)

Type string

Description ?

BinLog%KineticEnergy(#)

Type float_array

Description The kinetic energy of the system. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

BinLog%Length(#)

Type float_array

Description The length of the cell (only for 1D PBC). This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit bohr

BinLog%MaxBiasEnergy(#)

Type float_array

Description ? This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

BinLog%MaxBoostFactor(#)

Type float_array

Description The maximum boost factor for hyper-dynamics. Expand? This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

BinLog%nBlocks

Type int

Description Explain the block-system… ?

BinLog%nEntries

Type int

Description Number of MD history entries.

BinLog%PotentialEnergy(#)

Type float_array

Description The potential energy, i.e. the energy as computed by the engine. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

BinLog%Pressure(#)

Type float_array

Description The pressure of the system (only for 3D PBC). This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree/bohr^3

BinLog%PressureTensor_*(#)

Type float_array

Description ?

`BinLog%Step(#)`

Type int_array

Description The step number of the MD calculation. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

`BinLog%Temperature(#)`

Type float_array

Description The temperature of the system, computed from the kinetic energy?. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit kelvin

`BinLog%Time(#)`

Type float_array

Description The MD simulation time. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit femtosecond

`BinLog%TotalEnergy(#)`

Type float_array

Description The total energy of the system: potential energy (as computed by the engine) + kinetic energy. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

`BinLog%Volume(#)`

Type float_array

Description The volume of the cell (only for 3D PBC). This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit bohr^3

ChemicalSystem(#) **Section content:** Various 'versions' of the chemical system. See also the 'SystemVersionHistory' section.

`ChemicalSystem(#)%AtomicNumbers`

Type int_array

Description Atomic number 'Z' of the atoms in the system

Shape [nAtoms]

`ChemicalSystem(#)%AtomMasses`

Type float_array

Description Masses of the atoms

Unit a.u.

Values range [0, '\infinity']

Shape [nAtoms]

`ChemicalSystem(#)%AtomSymbols`

Type string

Description The atom's symbols (e.g. 'C' for carbon)

Shape [nAtoms]

`ChemicalSystem(#)%bondOrders`

Type float_array

Description The bond orders for the bonds in the system. The indices of the two atoms participating in the bond are defined in the arrays 'fromAtoms' and 'toAtoms'. e.g. bondOrders[1]=2, fromAtoms[1]=4 and toAtoms[1]=7 means that there is a double bond between atom number 4 and atom number 7

`ChemicalSystem(#)%Charge`

Type float

Description Net charge of the system

Unit e

`ChemicalSystem(#)%Coords`

Type float_array

Description Coordinates of the nuclei (x,y,z)

Unit bohr

Shape [3, nAtoms]

`ChemicalSystem(#)%eeAttachTo`

Type int_array

Description A multipole may be attached to an atom. This influences the energy gradient.

`ChemicalSystem(#)%eeChargeWidth`

Type float

Description If charge broadening was used for external charges, this represents the width of the charge distribution.

`ChemicalSystem(#)%eeEField`

Type float_array

Description The external homogeneous electric field.

Unit hartree/(e*bohr)

Shape [3]

`ChemicalSystem(#)%eeLatticeVectors`

Type float_array

Description The lattice vectors used for the external point- or multipole- charges.

Unit bohr

Shape [3, eeNLatticeVectors]

`ChemicalSystem(#)%eeMulti`

Type float_array

Description The values of the external point- or multipole- charges.

Unit a.u.

Shape [eeNZlm, eeNMulti]

`ChemicalSystem(#)%eeNLatticeVectors`

Type int

Description The number of lattice vectors for the external point- or multipole- charges.

`ChemicalSystem(#)%eeNMulti`

Type int

Description The number of external point- or multipole- charges.

`ChemicalSystem(#)%eeNZlm`

Type int

Description When external point- or multipole- charges are used, this represents the number of spherical harmonic components. E.g. if only point charges were used, eeNZlm=1 (s-component only). If point charges and dipole moments were used, eeNZlm=4 (s, px, py and pz).

`ChemicalSystem(#)%eeUseChargeBroadening`

Type bool

Description Whether or not the external charges are point-like or broadened.

`ChemicalSystem(#)%eeXYZ`

Type float_array

Description The position of the external point- or multipole- charges.

Unit bohr

Shape [3, eeNMulti]

`ChemicalSystem(#)%EngineAtomicInfo`

Type string_fixed_length

Description Atom-wise info possibly used by the engine.

`ChemicalSystem(#)%fromAtoms`

Type int_array

Description Index of the first atom in a bond. See the bondOrders array

`ChemicalSystem(#)%latticeDisplacements`

Type int_array

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

`ChemicalSystem(#)%LatticeVectors`

Type float_array

Description Lattice vectors

Unit bohr

Shape [3, nLatticeVectors]

`ChemicalSystem(#)%nAtoms`

Type int

Description The number of atoms in the system

`ChemicalSystem(#)%nAtomsTypes`

Type int

Description The number different of atoms types

`ChemicalSystem(#)%nLatticeVectors`

Type int

Description Number of lattice vectors (i.e. number of periodic boundary conditions)

Possible values [0, 1, 2, 3]

`ChemicalSystem(#)%toAtoms`

Type int_array

Description Index of the second atom in a bond. See the bondOrders array

CrestMTDHistory **Section content:** Data related to Crest MD.

CVHDBiasHistory **Section content:** ?

`CVHDBiasHistory%blockSize`

Type int

Description Explain the block-system… ?

`CVHDBiasHistory%currentEntryOpen`

Type bool

Description ?

`CVHDBiasHistory%CVValue(#)`

Type float_array

Description ?

`CVHDBiasHistory%Height(#)`

Type float_array

Description ?

`CVHDBiasHistory%ItemName(#)`

Type string

Description ?

`CVHDBiasHistory%nBlocks`

Type int

Description Explain the block-system… ?

`CVHDBiasHistory%nEntries`

Type int

Description Number of MD history entries.

`CVHDBiasHistory%Step(#)`

Type int_array

Description The step number of the MD calculation. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

EnergyLandscape **Section content:** Information on PES exploration.

`EnergyLandscape%counts`

Type int_array

Description Number of times that the exploration job found each state.

Shape [nStates]

`EnergyLandscape%Edge(#)`

Type subsection

Description From acerxn ?

`EnergyLandscape%Edge(#)%brokenAtomsFrom`

Type int_array

Description From acerxn ?

`EnergyLandscape%Edge(#)%brokenAtomsTo`

Type int_array

Description From acerxn ?

`EnergyLandscape%Edge(#)%formedAtomsFrom`

Type int_array

Description From acerxn ?

`EnergyLandscape%Edge(#)%formedAtomsTo`

Type int_array

Description From acerxn ?

`EnergyLandscape%edgesBegin`

Type int_array

Description From acerxn ?

`EnergyLandscape%edgesEnd`

Type int_array

Description From acerxn ?

`EnergyLandscape%energies`

Type float_array

Description Energies of the stationary states.

Unit hartree

Shape [nStates]

`EnergyLandscape%energyReferenceLabels`

Type string

Description ?

`EnergyLandscape%energyReferenceValues`

Type float_array

Description ?

`EnergyLandscape%fileNames`

Type ftl_string_array

Description Filenames for the stationary state calculations.

Shape [nStates]

`EnergyLandscape%fragmentsEnergies`

Type float_array

Description ?

`EnergyLandscape%fragmentsFileNames`

Type string

Description ?

`EnergyLandscape%fragmentsRegions`

Type string

Description ?

`EnergyLandscape%fStatesAdsorptionPrefactors(#)`

Type float_array

Description ?

`EnergyLandscape%fStatesComposition(#)`

Type int_array

Description ?

`EnergyLandscape%fStatesConnections(#)`

Type int_array

Description ?

`EnergyLandscape%fStatesDesorptionPrefactors(#)`

Type float_array

Description ?

`EnergyLandscape%fStatesEnergy(#)`

Type float

Description ?

`EnergyLandscape%fStatesNConnections(#)`

Type int

Description ?

`EnergyLandscape%fStatesNFragments(#)`

Type int

Description ?

`EnergyLandscape%historyIndices`

Type int_array

Description Indices of the corresponding entries in the History section.

Shape [nStates]

`EnergyLandscape%isTS`

Type bool_array

Description Whether a state is a transition state or a minimum.

Shape [nStates]

`EnergyLandscape%names`

Type string

Description From acerxn ?

`EnergyLandscape%nEdges`

Type int

Description From acerxn ?

`EnergyLandscape%nFragments`

Type int

Description ?

`EnergyLandscape%nFStates`

Type int

Description ?

`EnergyLandscape%nStates`

Type int

Description The number of stationary states (points with vanishing gradient).

`EnergyLandscape%prefactorsFromProduct`

Type float_array

Description ?

`EnergyLandscape%prefactorsFromReactant`

Type float_array

Description ?

`EnergyLandscape%prefactorsTemperature`

Type float

Description ?

`EnergyLandscape%products`

Type int_array

Description For stationary states that are a TS state this is the connected product.

Shape [nStates]

`EnergyLandscape%reactants`

Type int_array

Description For stationary states that are a TS state this is the connected reactant.

Shape [nStates]

`EnergyLandscape%referenceRegionLabel`

Type string

Description ?

EngineResults **Section content:** Description and names of engine result files.

`EngineResults%Description(#)`

Type string

Description Description of the results.

`EngineResults%Files(#)`

Type string

Description Filenames of the result files from the engine

`EngineResults%nEntries`

Type int

Description Number of engine results files.

`EngineResults%Title(#)`

Type string

Description Title of engine calculations.

GCMC **Section content:** Data related to the Gran Canonical Monte Carlo procedure

`GCMC%AccessibleVolume`

Type float

Description input accessible volume

`GCMC%AtomicNumbers`

Type int_array

Description Atomic number 'Z' of the atoms in the system

Shape [nAtoms]

`GCMC%AtomMasses`

Type float_array

Description Masses of the atoms

Unit a.u.

Values range [0, '\infinity']

Shape [nAtoms]

GCMC%AtomSymbols

Type string

Description The atom's symbols (e.g. 'C' for carbon)

Shape [nAtoms]

GCMC%bondOrders

Type float_array

Description The bond orders for the bonds in the system. The indices of the two atoms participating in the bond are defined in the arrays 'fromAtoms' and 'toAtoms'. e.g. bondOrders[1]=2, fromAtoms[1]=4 and toAtoms[1]=7 means that there is a double bond between atom number 4 and atom number 7

GCMC%Box

Type float_array

Description Range of cell coordinates where atoms are allowed to be added (x,y,z min,max?)

Unit bohr

Shape [3, 2]

GCMC%ChangeVolume

Type bool

Description Allow volume changes

GCMC%Charge

Type float

Description Net charge of the system

Unit e

GCMC%Coords

Type float_array

Description Coordinates of the nuclei (x,y,z)

Unit bohr

Shape [3, nAtoms]

GCMC%eeAttachTo

Type int_array

Description A multipole may be attached to an atom. This influences the energy gradient.

GCMC%eeChargeWidth

Type float

Description If charge broadening was used for external charges, this represents the width of the charge distribution.

GCMC%eeEField

Type float_array

Description The external homogeneous electric field.

Unit hartree/(e*bohr)

Shape [3]

GCMC%eeLatticeVectors

Type float_array

Description The lattice vectors used for the external point- or multipole- charges.

Unit bohr

Shape [3, eeNLatticeVectors]

GCMC%eeMulti

Type float_array

Description The values of the external point- or multipole- charges.

Unit a.u.

Shape [eeNZlm, eeNMulti]

GCMC%eeNLatticeVectors

Type int

Description The number of lattice vectors for the external point- or multipole- charges.

GCMC%eeNMulti

Type int

Description The number of external point- or multipole- charges.

GCMC%eeNZlm

Type int

Description When external point- or multipole- charges are used, this represents the number of spherical harmonic components. E.g. if only point charges were used, eeNZlm=1 (s-component only). If point charges and dipole moments were used, eeNZlm=4 (s, px, py and pz).

GCMC%eeUseChargeBroadening

Type bool

Description Whether or not the external charges are point-like or broadened.

GCMC%eeXYZ

Type float_array

Description The position of the external point- or multipole- charges.

Unit bohr

Shape [3, eeNMulti]

GCMC%EngineAtomicInfo

Type string_fixed_length

Description Atom-wise info possibly used by the engine.

GCMC%fromAtoms

Type int_array

Description Index of the first atom in a bond. See the bondOrders array

`GCMC%HistoryAccepted`

Type int_array

Description result (1-accepted, 0-rejected)

Shape [NIterMCtried]

`GCMC%HistoryAMSEnergy`

Type float_array

Description energy (AMSEnergy)

Shape [NIterMCtried]

`GCMC%HistoryMCEnergy`

Type float_array

Description corrected MC energy (AMSEnergy - sum(ChemicalPotential))

Shape [NIterMCtried]

`GCMC%HistoryMoleculeIndex`

Type int_array

Description molecule index of the type

Shape [NIterMCtried]

`GCMC%HistoryMoleculeType`

Type int_array

Description molecule type

Shape [NIterMCtried]

`GCMC%HistoryMoveType`

Type int_array

Description action type

Shape [NIterMCtried]

`GCMC%HistoryVolume`

Type float_array

Description ?

Shape [NIterMCtried]

`GCMC%InitialEnergy`

Type float

Description ?

Unit hartree

`GCMC%Iterations`

Type int

Description Number of MC iterations before stopping

`GCMC%latticeDisplacements`

Type int_array

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

`GCMC%LatticeVectors`

Type float_array

Description Lattice vectors

Unit bohr

Shape [3, nLatticeVectors]

`GCMC%MapToOriginalCell`

Type bool

Description map atoms back to the original cell?

`GCMC%MaxDistance`

Type float

Description Max radius for atom placement

Unit bohr

`GCMC%MinDistance`

Type float

Description Min radius for atom placement

Unit bohr

`GCMC%Mol#`

Type subsection

Description ?

`GCMC%Mol#%addedAtoms`

Type archived_int_array

Description Atom species indices

`GCMC%Mol#%AtomicInfo`

Type archived_string_array

Description

`GCMC%Mol#%BondOrders`

Type archived_float_array

Description The bond orders for the bonds in the system. The indices of the two atoms participating in the bond are defined in the arrays 'fromAtoms' and 'toAtoms'. e.g. bondOrders[1]=2, fromAtoms[1]=4 and toAtoms[1]=7 means that there is a double bond between atom number 4 and atom number 7

`GCMC%Mol#%Charge`

Type float

Description Net charge of the system

Unit e

`GCMC%Mol#%chemPot`

Type float

Description ?

`GCMC%Mol#%eeAttachTo`

Type archived_int_array

Description A multipole may be attached to an atom. This influences the energy gradient.

`GCMC%Mol#%eeChargeWidth`

Type float

Description If charge broadening was used for external charges, this represents the width of the charge distribution

`GCMC%Mol#%eeEField`

Type float_array

Description The external homogeneous electric field

Unit hartree/(e*bohr)

Shape [3]

`GCMC%Mol#%eeLatticeVectors`

Type archived_float_array

Description The lattice vectors used for the external point- or multipole- charges

Unit bohr

`GCMC%Mol#%eeMultipoles`

Type archived_float_array

Description The multiple charges.

Unit bohr

`GCMC%Mol#%eenMulti`

Type int

Description The number of multipoles.

`GCMC%Mol#%eeUseChargeBroadening`

Type bool

Description Whether or not the external charges are point-like or broadened

`GCMC%Mol#%eeXYZ`

Type archived_float_array

Description The position of the external point- or multipole- charges

Unit bohr

`GCMC%Mol#%FromAtoms`

Type archived_int_array

Description Index of the first atom in a bond. See the bondOrders array

GCMC%Mol#%hasLatticeDisplacements

Type bool

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

GCMC%Mol#%inserted

Type int_array

Description ?

GCMC%Mol#%kVectors

Type float_array

Description Reciprocal lattice vectors (corresponding to the strained lattice vectors)

Unit 1/bohr

Shape [3, 3]

GCMC%Mol#%LatticeDisplacements

Type archived_int_array

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

GCMC%Mol#%name

Type string

Description ?

GCMC%Mol#%nAtoms

Type int

Description The number of atoms in the system

GCMC%Mol#%nInsert

Type int

Description ?

GCMC%Mol#%noAR

Type bool

Description ?

GCMC%Mol#%nSpecies

Type int

Description The number different of atoms types

GCMC%Mol#%nVectors

Type int

Description Number of lattice vectors (0:molecule, 1:chain, 2:slab, 3:bulk).

GCMC%Mol#%removedAtoms

Type archived_int_array

Description Atom species indices

GCMC%Mol#%sp#inputSymbol

Type string

Description Symbol as specifined in the input

GCMC%Mol#%sp#mass

Type float

Description mass

GCMC%Mol#%sp#regions

Type archived_string_array

Description regions

GCMC%Mol#%sp#symbol

Type string

Description Element symbol

GCMC%Mol#%sp#Z

Type int

Description Atomic number

GCMC%Mol#%SpIndices

Type archived_int_array

Description Atom species indices

GCMC%Mol#%SPlen

Type int

Description Number of species

GCMC%Mol#%strain

Type float_array

Description The strain matrix.

Shape [3, 3]

GCMC%Mol#%strainedVectors

Type float_array

Description Strained real space lattice vectors

Unit bohr

Shape [3, 3]

GCMC%Mol#%ToAtoms

Type archived_int_array

Description Index of the second atom in a bond. See the bondOrders array

GCMC%Mol#%unstrainedVectors

Type float_array

Description Real space lattice vectors (unstrained).

Unit bohr

Shape [3, 3]

`GCMC%Mol#%version`

Type int

Description

`GCMC%Mol#%xyzAtoms`

Type archived_float_array

Description Coordinates of the nuclei (x,y,z)

Unit bohr

`GCMC%MoleculeName(#)`

Type string

Description ?

`GCMC%MoveType(#)`

Type string

Description ?

`GCMC%nAtoms`

Type int

Description The number of atoms in the system

`GCMC%nAtomsTypes`

Type int

Description The number different of atoms types

`GCMC%NIterMCaccept`

Type int

Description Number of moves accepted

`GCMC%NIterMCreject`

Type int

Description Number of moves rejected

`GCMC%NIterMCtried`

Type int

Description Number of moves tried, aka iteration number

`GCMC%nLatticeVectors`

Type int

Description Number of lattice vectors (i.e. number of periodic boundary conditions)

Possible values [0, 1, 2, 3]

`GCMC%NMCacceptAdd`

Type int

Description statistics about success rates of MC

`GCMC%NMCacceptMove`

Type int

Description ?

`GCMC%NMCacceptRemove`

Type int

Description ?

`GCMC%NMCacceptVolume`

Type int

Description ?

`GCMC%NMCrejectAdd`

Type int

Description ?

`GCMC%NMCrejectMove`

Type int

Description ?

`GCMC%NMCrejectRemove`

Type int

Description ?

`GCMC%NMCrejectVolume`

Type int

Description ?

`GCMC%NMols`

Type int

Description ?

`GCMC%NonAccessibleVolume`

Type float

Description input non-accessible (vacuum) volume

`GCMC%NumAttempts`

Type int

Description Maximum number of trial steps when inserting/moving a molecule

`GCMC%Pressure`

Type float

Description NPT pressure

Unit a.u.

`GCMC%Temperature`

Type float

Description system temperature

Unit kelvin

`GCMC%toAtoms`

Type int_array

Description Index of the second atom in a bond. See the bondOrders array

`GCMC%UseGCPreFactor`

Type bool

Description include GCE factors in probability?

`GCMC%VolumeChangeMax`

Type float

Description input max volume change factor for NPT MC

`GCMC%VolumeOption`

Type int

Description input accessible volume? 0=no (use total cell volume) 1=yes 2=bulk

General **Section content:** General information about the AMS driver calculation.

`General%account`

Type string

Description Name of the account from the license

`General%CPUTime`

Type float

Description CPU time of the AMS calculation.

Unit second

`General%ElapsedTime`

Type float

Description Elapsed time of the AMS calculation.

Unit second

`General%engine`

Type string

Description The main engine of the calculation.

`General%engine messages`

Type string

Description Message from the engine. In case the engine fails to solves, this may contains extra information on why.

`General%file-ident`

Type string

Description The file type identifier, e.g. RKF, RUNKF, TAPE21…

`General%jobid`

Type int

Description Unique identifier for the job.

`General%program`

Type string

Description The name of the program/engine that generated this kf file.

`General%release`

Type string

Description The version of the program that generated this kf file (including svn revision number and date).

`General%SysTime`

Type float

Description System time of the AMS calculation.

Unit second

`General%task`

Type string

Description The Task of the AMS driver (e.g. singlepoint, geometryoptimization, moleculardynamics…).

`General%termination status`

Type string

Description The termination status. Possible values: 'NORMAL TERMINATION', 'NORMAL TERMINATION with warnings', 'NORMAL TERMINATION with errors', 'ERROR', 'IN PROGRESS'.

`General%title`

Type string

Description Title of the calculation.

`General%uid`

Type string

Description SCM User ID

`General%user input`

Type string

Description The text input of the AMS calculation.

`General%version`

Type int

Description Version number?

History Section content: History of the system during the AMS calculation. What is stored here depends on the task of the AMS calculation. For example, for a GeometryOptimization this will contain the intermediate steps of the GO, while for a MoleculeDynamics calculation it will contain the MD frames.

`History%Angle(#)`

Type float

Description IRC (Intrinsic Reaction Coordinate) angle((pivot->start),(pivot->coords)), indication of the path curvature.

Unit degrees

`History%ArcLength(#)`

Type float

Description IRC (Intrinsic Reaction Coordinate): length of arc(start->pivot->coords).

Unit angstrom

`History%Bonds`

Type subsection

Description ?

`History%Bonds%Atoms(#)`

Type int_array

Description ?

`History%Bonds%CellShifts(#)`

Type int_array

Description ?

`History%Bonds%Index(#)`

Type int_array

Description ?

`History%Bonds%Orders(#)`

Type float_array

Description ?

`History%Converged(#)`

Type bool

Description Whether the entry corresponds to a converged structure. The meaning of 'converged' depends on the Task.

`History%Coords(#)`

Type float_array

Description Coordinates of the systems of a given entry.

Shape [3, :]

`History%currentEntryOpen`

Type bool

Description Currently open entry?

`History%Energy(#)`

Type float

Description Energy of the system of a given entry.

Unit hartree

`History%EnergySubtype`

Type string

Description ?

`History%EngineEnergy(#)`

Type float

Description The energy as computed by the engine of a given entry.

Unit hartree

`History%EngineEnergyU(#)`

Type float

Description The uncertainty of the energy as computed by the engine of a givn entry.

Unit hartree

`History%EngineGradients(#)`

Type float_array

Description The gradients as computed by the engine of a given entry.

Unit hartree/bohr

Shape [3, :]

`History%EngineGradientsNormU(#)`

Type float_array

Description The uncertainty of the norm of the gradients (using the variance formula) as computed by the engine of a given entry.

Unit hartree/bohr

Shape [3, :]

`History%EngineGradientsU(#)`

Type float_array

Description The uncertainty of the gradients as computed by the engine of a given entry.

Unit hartree/bohr

Shape [3, :]

`History%ExitConditionMsg`

Type string

Description Message from the exit condition on what condition was met.

`History%Gradients(#)`

Type float_array

Description Nuclear gradients of a given entry

Unit hartree/bohr

Shape [3, :]

`History%IRCDirection(#)`

Type int

Description IRC (Intrinsic Reaction Coordinate) direction of a given entry (1=forward, 2=backwards).

`History%IRCGradMax(#)`

Type float

Description IRC (Intrinsic Reaction Coordinate) Max of the gradient determining the step in the inner loop.

Unit hartree/bohr

`History%IRCGradRms(#)`

Type float

Description IRC (Intrinsic Reaction Coordinate) Root mean square of the gradient determining the step in the inner loop.

Unit hartree/bohr

`History%IRCIteration(#)`

Type int

Description IRC (Intrinsic Reaction Coordinate) outer loop iteration number.

`History%ItemName(#)`

Type string

Description Name of generic item on this section?

`History%LatticeVectors(#)`

Type float_array

Description The lattice vectors of a given entry.

Unit bohr

Shape [3, :]

`History%maxGrad(#)`

Type float

Description Maximum Cartesian component of the nuclear gradients of a given entry. This is generally used as a convergence criterion in geometry optimizations and similar tasks.

Unit hartree/bohr

`History%maxStep(#)`

Type float

Description Maximum difference in the Cartesian nuclear coordinates from the previous step. This is generally used as a convergence criterion in geometry optimizations and similar tasks.

Unit bohr

`History%MaxStressEnergyPerAtom(#)`

Type float

Description Maximum value of stress_tensor * cell_volume / number_of_atoms (for 2D and 1D systems, the cell_volume is replaced by the cell_area and cell_length respectively). This is the quantity used for determining whether a lattice optimization has converged.

`History%MCMolecule(#)`

Type int

Description Index of the randomly selected molecule/atom type to MCMove?

`History%MCMove(#)`

Type int

Description Index of monte carlo move of a given entry.

`History%MCMoveType(#)`

Type string

Description The type of monte carlo move. Can be one of the following: 'Insert', 'Delete', 'Displace', 'ChangeVolume'

`History%Mols`

Type subsection

Description Molecule detection info at various steps.

`History%Mols%Atoms(#)`

Type int_array

Description atoms(index(i):index(i+1)-1) = atom indices of molecule i

`History%Mols%Index(#)`

Type int_array

Description Size: Molecules%Num molecules. index(i) = index of the first atom of molecule i in array atoms(:)

`History%Mols%Type(#)`

Type int_array

Description Index indicating the type of the molecule ('Molecules%Molecule name #")

`History%nEntries`

Type int

Description Number of history entries.

`History%nLatticeVectors(#)`

Type int

Description The number of lattice vectors (i.e. the number of periodic boundary conditions) of a given entry.

`History%OptIteration(#)`

Type int

Description IRC (Intrinsic Reaction Coordinate) inner loop iteration number.

`History%OrigStep(#)`

Type int

Description Index of the original step for the Replay task.

`History%PathLength(#)`

Type float

Description IRC (Intrinsic Reaction Coordinate): sum of the arc lengths up to the latest point.

Unit angstrom

`History%rmsGrad(#)`

Type float

Description Root mean square of the nuclear gradients of a given entry. This is generally used as a convergence criterion in geometry optimizations and similar tasks.

Unit hartree/bohr

`History%rmsStep(#)`

Type float

Description Root mean square of the difference between the nuclear coordinates at this step and at the previous step. This is generally used as a convergence criterion in geometry optimizations and similar tasks.

`History%Step(#)`

Type int

Description The step number in a Molecular Dynamics calculation.

`History%StressTensor(#)`

Type float_array

Description The stress tensor of a given entry.

Unit hartree/bohr^nLatticeVectors

Shape [:, :]

`History%SystemVersion(#)`

Type int

Description Index of the versioned-chemical system of a given frame.

IMDHORaman **Section content:** Resonance raman spectra using IMDHO

`IMDHORaman%nspectrum`

Type int

Description ?

`IMDHORaman%overtones`

Type int_array

Description ?

`IMDHORaman%ramanorder`

Type int

Description Maximum order of raman final state

`IMDHORaman%spectrum`

Type float_array

Description ?

InputMolecule **Section content:** The main input molecule of the calculation.

`InputMolecule%AtomicNumbers`

Type int_array

Description Atomic number 'Z' of the atoms in the system

Shape [nAtoms]

`InputMolecule%AtomMasses`

Type float_array

Description Masses of the atoms

Unit a.u.

Values range [0, '\infinity']

Shape [nAtoms]

`InputMolecule%AtomSymbols`

Type string

Description The atom's symbols (e.g. 'C' for carbon)

Shape [nAtoms]

`InputMolecule%bondOrders`

Type float_array

Description The bond orders for the bonds in the system. The indices of the two atoms participating in the bond are defined in the arrays 'fromAtoms' and 'toAtoms'. e.g. bondOrders[1]=2, fromAtoms[1]=4 and toAtoms[1]=7 means that there is a double bond between atom number 4 and atom number 7

`InputMolecule%Charge`

Type float

Description Net charge of the system

Unit e

`InputMolecule%Coords`

Type float_array

Description Coordinates of the nuclei (x,y,z)

Unit bohr

Shape [3, nAtoms]

`InputMolecule%eeAttachTo`

Type int_array

Description A multipole may be attached to an atom. This influences the energy gradient.

`InputMolecule%eeChargeWidth`

Type float

Description If charge broadening was used for external charges, this represents the width of the charge distribution.

`InputMolecule%eeEField`

Type float_array

Description The external homogeneous electric field.

Unit hartree/(e*bohr)

Shape [3]

`InputMolecule%eeLatticeVectors`

Type float_array

Description The lattice vectors used for the external point- or multipole- charges.

Unit bohr

Shape [3, eeNLatticeVectors]

`InputMolecule%eeMulti`

Type float_array

Description The values of the external point- or multipole- charges.

Unit a.u.

Shape [eeNZlm, eeNMulti]

`InputMolecule%eeNLatticeVectors`

Type int

Description The number of lattice vectors for the external point- or multipole- charges.

`InputMolecule%eeNMulti`

Type int

Description The number of external point- or multipole- charges.

`InputMolecule%eeNZlm`

Type int

Description When external point- or multipole- charges are used, this represents the number of spherical harmonic components. E.g. if only point charges were used, eeNZlm=1 (s-component only). If point charges and dipole moments were used, eeNZlm=4 (s, px, py and pz).

`InputMolecule%eeUseChargeBroadening`

Type bool

Description Whether or not the external charges are point-like or broadened.

`InputMolecule%eeXYZ`

Type float_array

Description The position of the external point- or multipole- charges.

Unit bohr

Shape [3, eeNMulti]

`InputMolecule%EngineAtomicInfo`

Type string_fixed_length

Description Atom-wise info possibly used by the engine.

`InputMolecule%fromAtoms`

Type int_array

Description Index of the first atom in a bond. See the bondOrders array

`InputMolecule%latticeDisplacements`

Type int_array

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

`InputMolecule%LatticeVectors`

Type float_array

Description Lattice vectors

Unit bohr

Shape [3, nLatticeVectors]

`InputMolecule%nAtoms`

Type int

Description The number of atoms in the system

`InputMolecule%nAtomsTypes`

Type int

Description The number different of atoms types

`InputMolecule%nLatticeVectors`

Type int

Description Number of lattice vectors (i.e. number of periodic boundary conditions)

Possible values [0, 1, 2, 3]

`InputMolecule%toAtoms`

Type int_array

Description Index of the second atom in a bond. See the bondOrders array

InputMolecule(#) **Section content:** Any auxilliary, named input molecules of the calculation.

`InputMolecule(#)%AtomicNumbers`

Type int_array

Description Atomic number ‘Z’ of the atoms in the system

Shape [nAtoms]

`InputMolecule(#)%AtomMasses`

Type float_array

Description Masses of the atoms

Unit a.u.

Values range [0, '\infinity']

Shape [nAtoms]

`InputMolecule(#)%AtomSymbols`

Type string

Description The atom's symbols (e.g. 'C' for carbon)

Shape [nAtoms]

`InputMolecule(#)%bondOrders`

Type float_array

Description The bond orders for the bonds in the system. The indices of the two atoms participating in the bond are defined in the arrays 'fromAtoms' and 'toAtoms'. e.g. bondOrders[1]=2, fromAtoms[1]=4 and toAtoms[1]=7 means that there is a double bond between atom number 4 and atom number 7

`InputMolecule(#)%Charge`

Type float

Description Net charge of the system

Unit e

`InputMolecule(#)%Coords`

Type float_array

Description Coordinates of the nuclei (x,y,z)

Unit bohr

Shape [3, nAtoms]

`InputMolecule(#)%eeAttachTo`

Type int_array

Description A multipole may be attached to an atom. This influences the energy gradient.

`InputMolecule(#)%eeChargeWidth`

Type float

Description If charge broadening was used for external charges, this represents the width of the charge distribution.

`InputMolecule(#)%eeEField`

Type float_array

Description The external homogeneous electric field.

Unit hartree/(e*bohr)

Shape [3]

`InputMolecule(#)%eeLatticeVectors`

Type float_array

Description The lattice vectors used for the external point- or multipole- charges.

Unit bohr

Shape [3, eeNLatticeVectors]

`InputMolecule(#)%eeMulti`

Type float_array

Description The values of the external point- or multipole- charges.

Unit a.u.

Shape [eeNZlm, eeNMulti]

`InputMolecule(#)%eeNLatticeVectors`

Type int

Description The number of lattice vectors for the external point- or multipole- charges.

`InputMolecule(#)%eeNMulti`

Type int

Description The number of external point- or multipole- charges.

`InputMolecule(#)%eeNZlm`

Type int

Description When external point- or multipole- charges are used, this represents the number of spherical harmonic components. E.g. if only point charges were used, eeNZlm=1 (s-component only). If point charges and dipole moments were used, eeNZlm=4 (s, px, py and pz).

`InputMolecule(#)%eeUseChargeBroadening`

Type bool

Description Whether or not the external charges are point-like or broadened.

`InputMolecule(#)%eeXYZ`

Type float_array

Description The position of the external point- or multipole- charges.

Unit bohr

Shape [3, eeNMulti]

`InputMolecule(#)%EngineAtomicInfo`

Type string_fixed_length

Description Atom-wise info possibly used by the engine.

`InputMolecule(#)%fromAtoms`

Type int_array

Description Index of the first atom in a bond. See the bondOrders array

`InputMolecule(#)%latticeDisplacements`

Type int_array

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

`InputMolecule(#)%LatticeVectors`

Type float_array

Description Lattice vectors

Unit bohr

Shape [3, nLatticeVectors]

`InputMolecule(#)%nAtoms`

Type int

Description The number of atoms in the system

`InputMolecule(#)%nAtomsTypes`

Type int

Description The number different of atoms types

`InputMolecule(#)%nLatticeVectors`

Type int

Description Number of lattice vectors (i.e. number of periodic boundary conditions)

Possible values [0, 1, 2, 3]

`InputMolecule(#)%toAtoms`

Type int_array

Description Index of the second atom in a bond. See the bondOrders array

InputMolecules **Section content:** Section to store additional information about the auxilliary, named input molecules.

`InputMolecules%Name(#)`

Type string

Description The name that was given to the molecule stored in the corresponding InputMolecule(*) section. The name comes from the System block header in the AMS input file.

`InputMolecules%numNamedMolecules`

Type int

Description The number of auxilliary, named input molecules.

IRC **Section content:** Data regarding the IRC caluclation.

`IRC%AtomicNumbers`

Type int_array

Description Atomic number ‘Z’ of the atoms in the system

Shape [nAtoms]

`IRC%AtomMasses`

Type float_array

Description Masses of the atoms

Unit a.u.

Values range [0, '\infinity']

Shape [nAtoms]

IRC%AtomSymbols

Type string

Description The atom's symbols (e.g. 'C' for carbon)

Shape [nAtoms]

IRC%barriers

Type float_array

Description TS barrier energies (forward and backward?)

Unit hartree

Shape [2]

IRC%bondOrders

Type float_array

Description The bond orders for the bonds in the system. The indices of the two atoms participating in the bond are defined in the arrays 'fromAtoms' and 'toAtoms'. e.g. bondOrders[1]=2, fromAtoms[1]=4 and toAtoms[1]=7 means that there is a double bond between atom number 4 and atom number 7

IRC%cen

Type subsection

Description ?

IRC%cen%addedAtoms

Type archived_int_array

Description Atom species indices

IRC%cen%AtomicInfo

Type archived_string_array

Description

IRC%cen%BondOrders

Type archived_float_array

Description The bond orders for the bonds in the system. The indices of the two atoms participating in the bond are defined in the arrays 'fromAtoms' and 'toAtoms'. e.g. bondOrders[1]=2, fromAtoms[1]=4 and toAtoms[1]=7 means that there is a double bond between atom number 4 and atom number 7

IRC%cen%Charge

Type float

Description Net charge of the system

Unit e

IRC%cen%eeAttachTo

Type archived_int_array

Description A multipole may be attached to an atom. This influences the energy gradient.

`IRC%cen%eeChargeWidth`

Type float

Description If charge broadening was used for external charges, this represents the width of the charge distribution

`IRC%cen%eeEField`

Type float_array

Description The external homogeneous electric field

Unit hartree/(e*bohr)

Shape [3]

`IRC%cen%eeLatticeVectors`

Type archived_float_array

Description The lattice vectors used for the external point- or multipole- charges

Unit bohr

`IRC%cen%eeMultipoles`

Type archived_float_array

Description The multiple charges.

Unit bohr

`IRC%cen%eenMulti`

Type int

Description The number of multipoles.

`IRC%cen%eeUseChargeBroadening`

Type bool

Description Whether or not the external charges are point-like or broadened

`IRC%cen%eeXYZ`

Type archived_float_array

Description The position of the external point- or multipole- charges

Unit bohr

`IRC%cen%FromAtoms`

Type archived_int_array

Description Index of the first atom in a bond. See the bondOrders array

`IRC%cen%hasLatticeDisplacements`

Type bool

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

`IRC%cen%kVectors`

Type float_array

Description Reciprocal lattice vectors (corresponding to the strained lattice vectors)

Unit 1/bohr

Shape [3, 3]

`IRC%cen%LatticeDisplacements`

Type archived_int_array

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

`IRC%cen%nAtoms`

Type int

Description The number of atoms in the system

`IRC%cen%nSpecies`

Type int

Description The number different of atoms types

`IRC%cen%nVectors`

Type int

Description Number of lattice vectors (0:molecule, 1:chain, 2:slab, 3:bulk).

`IRC%cen%removedAtoms`

Type archived_int_array

Description Atom species indices

`IRC%cen%sp#inputSymbol`

Type string

Description Symbol as specifined in the input

`IRC%cen%sp#mass`

Type float

Description mass

`IRC%cen%sp#regions`

Type archived_string_array

Description regions

`IRC%cen%sp#symbol`

Type string

Description Element symbol

`IRC%cen%sp#Z`

Type int

Description Atomic number

`IRC%cen%SpIndices`

Type archived_int_array

Description Atom species indices

`IRC%cen%SPlen`

Type int

Description Number of species

`IRC%cen%strain`

Type float_array

Description The strain matrix.

Shape [3, 3]

`IRC%cen%strainedVectors`

Type float_array

Description Strained real space lattice vectors

Unit bohr

Shape [3, 3]

`IRC%cen%ToAtoms`

Type archived_int_array

Description Index of the second atom in a bond. See the bondOrders array

`IRC%cen%unstrainedVectors`

Type float_array

Description Real space lattice vectors (unstrained).

Unit bohr

Shape [3, 3]

`IRC%cen%version`

Type int

Description

`IRC%cen%xyzAtoms`

Type archived_float_array

Description Coordinates of the nuclei (x,y,z)

Unit bohr

`IRC%Charge`

Type float

Description Net charge of the system

Unit e

`IRC%conf`

Type subsection

Description Configuration data for the IRC procedure.

`IRC%conf%ConvGrad`

Type float

Description Convergence criterion for gradient

Unit hartree/bohr

IRC%conf%ConvStep

Type float

Description Convergence criterion for step in optim coords

Unit bohr

IRC%conf%CoordType

Type int

Description 0, 1 or 2, see IRC_OPTIM_COORDS

IRC%conf%Directions

Type int

Description one of IRC_DIRECTION_* constants

IRC%conf%HessFile

Type string

Description File to get the Hessian from if hessianType==’fromfile’

IRC%conf%HessType

Type string

Description The hessian type used in the IRC calculation: ‘calculate’, ‘fromfile’ or ‘restart’

IRC%conf%IrcStep

Type float

Description Step size

Unit bohr

IRC%conf%keepResult

Type bool

Description Keep rkf files from single point calculations for each converged path point

IRC%conf%MaxIRCStps

Type int

Description Max number of IRC points before switching to energy minimization

IRC%conf%MaxIter

Type int

Description Max num steps in each geometry optimization (inner IRC loop)

IRC%conf%MaxPoints

Type int

Description Max number of IRC points before switching to the next direction

IRC%conf%MinEnProf

Type bool

Description ! Minimum energy profile (i.e. no mass-weighting) instead of IRC?

`IRC%Coords`

Type float_array

Description Coordinates of the nuclei (x,y,z)

Unit bohr

Shape [3, nAtoms]

`IRC%curIRCStep`

Type float

Description ircConfig%ircStep, possibly reduced for a curved path

`IRC%direction`

Type int

Description Current direction: 1 - forward, 2 - backward

`IRC%directionDone`

Type bool_array

Description Flag to see which direction has been already done (for restart)

Shape [2]

`IRC%eeAttachTo`

Type int_array

Description A multipole may be attached to an atom. This influences the energy gradient.

`IRC%eeChargeWidth`

Type float

Description If charge broadening was used for external charges, this represents the width of the charge distribution.

`IRC%eeEField`

Type float_array

Description The external homogeneous electric field.

Unit hartree/(e*bohr)

Shape [3]

`IRC%eeLatticeVectors`

Type float_array

Description The lattice vectors used for the external point- or multipole- charges.

Unit bohr

Shape [3, eeNLatticeVectors]

`IRC%eeMulti`

Type float_array

Description The values of the external point- or multipole- charges.

Unit a.u.

Shape [eeNZlm, eeNMulti]

`IRC%eeNLatticeVectors`

Type int

Description The number of lattice vectors for the external point- or multipole- charges.

`IRC%eeNMulti`

Type int

Description The number of external point- or multipole- charges.

`IRC%eeNZlm`

Type int

Description When external point- or multipole- charges are used, this represents the number of spherical harmonic components. E.g. if only point charges were used, eeNZlm=1 (s-component only). If point charges and dipole moments were used, eeNZlm=4 (s, px, py and pz).

`IRC%eeUseChargeBroadening`

Type bool

Description Whether or not the external charges are point-like or broadened.

`IRC%eeXYZ`

Type float_array

Description The position of the external point- or multipole- charges.

Unit bohr

Shape [3, eeNMulti]

`IRC%EngineAtomicInfo`

Type string_fixed_length

Description Atom-wise info possibly used by the engine.

`IRC%fromAtoms`

Type int_array

Description Index of the first atom in a bond. See the bondOrders array

`IRC%gradCart`

Type archived_float_array

Description Cartesian gradients

Unit hartree/bohr

`IRC%hessCart`

Type archived_float_array

Description Current Hessian in Cartesian coords

Unit hartree/bohr^2

`IRC%hessInit`

Type archived_float_array

Description Initial Hessian in Cartesian coords

Unit hartree/bohr^2

`IRC%histEnergy`

Type archived_float_array

Description Energy history

Unit hartree

`IRC%histGradRms`

Type archived_float_array

Description Gradients RMS history

Unit hartree/bohr

`IRC%histPathLength`

Type archived_float_array

Description Path length history

`IRC%histStatus`

Type archived_int_array

Description Status history

`IRC%histXYZ`

Type archived_float_array

Description XYZ history

`IRC%initialEnergy`

Type float

Description TS energy

Unit hartree

`IRC%initialGradRms`

Type float

Description TS RMS gradient

Unit hartree/bohr

`IRC%ircIteration`

Type int

Description outer loop iteration number

`IRC%latticeDisplacements`

Type int_array

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

`IRC%LatticeVectors`

Type float_array

Description Lattice vectors

Unit bohr

Shape [3, nLatticeVectors]

`IRC%nAtoms`

Type int

Description The number of atoms in the system

`IRC%nAtomsTypes`

Type int

Description The number different of atoms types

`IRC%nLatticeVectors`

Type int

Description Number of lattice vectors (i.e. number of periodic boundary conditions)

Possible values [0, 1, 2, 3]

`IRC%optIteration`

Type int

Description inner loop iteration number

`IRC%pathLength`

Type float

Description Sum of the arc lengths up to the latest point

`IRC%sys`

Type subsection

Description ?

`IRC%sys%addedAtoms`

Type archived_int_array

Description Atom species indices

`IRC%sys%AtomicInfo`

Type archived_string_array

Description

`IRC%sys%BondOrders`

Type archived_float_array

Description The bond orders for the bonds in the system. The indices of the two atoms participating in the bond are defined in the arrays 'fromAtoms' and 'toAtoms'. e.g. bondOrders[1]=2, fromAtoms[1]=4 and toAtoms[1]=7 means that there is a double bond between atom number 4 and atom number 7

`IRC%sys%Charge`

Type float

Description Net charge of the system

Unit e

IRC%sys%eeAttachTo

Type archived_int_array

Description A multipole may be attached to an atom. This influences the energy gradient.

IRC%sys%eeChargeWidth

Type float

Description If charge broadening was used for external charges, this represents the width of the charge distribution

IRC%sys%eeEField

Type float_array

Description The external homogeneous electric field

Unit hartree/(e*bohr)

Shape [3]

IRC%sys%eeLatticeVectors

Type archived_float_array

Description The lattice vectors used for the external point- or multipole- charges

Unit bohr

IRC%sys%eeMultipoles

Type archived_float_array

Description The multiple charges.

Unit bohr

IRC%sys%eenMulti

Type int

Description The number of multipoles.

IRC%sys%eeUseChargeBroadening

Type bool

Description Whether or not the external charges are point-like or broadened

IRC%sys%eeXYZ

Type archived_float_array

Description The position of the external point- or multipole- charges

Unit bohr

IRC%sys%FromAtoms

Type archived_int_array

Description Index of the first atom in a bond. See the bondOrders array

IRC%sys%hasLatticeDisplacements

Type bool

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

IRC%sys%kVectors

Type float_array

Description Reciprocal lattice vectors (corresponding to the strained lattice vectors)

Unit 1/bohr

Shape [3, 3]

IRC%sys%LatticeDisplacements

Type archived_int_array

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

IRC%sys%nAtoms

Type int

Description The number of atoms in the system

IRC%sys%nSpecies

Type int

Description The number different of atoms types

IRC%sys%nVectors

Type int

Description Number of lattice vectors (0:molecule, 1:chain, 2:slab, 3:bulk).

IRC%sys%removedAtoms

Type archived_int_array

Description Atom species indices

IRC%sys%sp#inputSymbol

Type string

Description Symbol as specifined in the input

IRC%sys%sp#mass

Type float

Description mass

IRC%sys%sp#regions

Type archived_string_array

Description regions

IRC%sys%sp#symbol

Type string

Description Element symbol

IRC%sys%sp#Z

Type int

Description Atomic number

`IRC%sys%SpIndices`

Type archived_int_array

Description Atom species indices

`IRC%sys%SPlen`

Type int

Description Number of species

`IRC%sys%strain`

Type float_array

Description The strain matrix.

Shape [3, 3]

`IRC%sys%strainedVectors`

Type float_array

Description Strained real space lattice vectors

Unit bohr

Shape [3, 3]

`IRC%sys%ToAtoms`

Type archived_int_array

Description Index of the second atom in a bond. See the bondOrders array

`IRC%sys%unstrainedVectors`

Type float_array

Description Real space lattice vectors (unstrained).

Unit bohr

Shape [3, 3]

`IRC%sys%version`

Type int

Description

`IRC%sys%xyzAtoms`

Type archived_float_array

Description Coordinates of the nuclei (x,y,z)

Unit bohr

`IRC%toAtoms`

Type int_array

Description Index of the second atom in a bond. See the bondOrders array

KFDefinitions **Section content:** The definitions of the data on this file

KFDefinitions%json

Type string

Description The definitions of the data on this file in json.

MDHistory **Section content:** History of a Molecular dynamics simulation.

MDHistory%Area(#)

Type float_array

Description The area of the cell (only for 2D PBC). This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit bohr^2

MDHistory%BerBstatEnergy(#)

Type float_array

Description ?

Unit hartree

MDHistory%BerTstat#Energy(#)

Type float_array

Description ?

Unit hartree

MDHistory%BerTstat#Temperature(#)

Type float_array

Description Local temperature of the thermostat region

Unit kelvin

MDHistory%BiasEnergy(#)

Type float_array

Description ? This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

MDHistory%blockSize

Type int

Description Explain the block-system… ?

MDHistory%BondBoostEnergy(#)

Type float_array

Description BondBoost energy, part of the potential energy

Unit hartree

MDHistory%BoostFactor(#)

Type float_array

Description The boost factor for hyper-dynamics. Expand? This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

`MDHistory%Charges(#)`

Type float_array

Description Net atomic charges as computed by the engine (for example, the Charges for a water molecule might be [-0.6, 0.3, 0.3]).

Unit e

`MDHistory%ConservedEnergy(#)`

Type float_array

Description The conserved energy…? Some MD person, please fix. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

`MDHistory%CosineShearVelocity(#)`

Type float_array

Description ?

`MDHistory%currentEntryOpen`

Type bool

Description ?

`MDHistory%Density(#)`

Type float_array

Description The density of the system (mass/simulation_cell_volume). Only for 3D PBC. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit dalton/bohr^3

`MDHistory%Eng*FrcRgn*(#)`

Type float_array

Description ?

`MDHistory%Engine*ForceRegion*(#)`

Type float_array

Description ?

`MDHistory%Hypertime(#)`

Type float_array

Description Hyper time for hyper-dynamics. Expand? This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit femtosecond

`MDHistory%ItemName(#)`

Type string

Description ?

`MDHistory%KineticEnergy(#)`

Type float_array

Description The kinetic energy of the system. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

MDHistory%Length(#)

Type float_array

Description The length of the cell (only for 1D PBC). This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit bohr

MDHistory%MaxBiasEnergy(#)

Type float_array

Description ? This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

MDHistory%MaxBoostFactor(#)

Type float_array

Description The maximum boost factor for hyper-dynamics. Expand? This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

MDHistory%MeanCosineShearVelocity(#)

Type float_array

Description ?

MDHistory%MeanEng*FrcRgn*(#)

Type float_array

Description ?

MDHistory%MeanEngine*ForceRegion*(#)

Type float_array

Description ?

MDHistory%MovingRestr*Energy(#)

Type float_array

Description Moving restraints energy, part of the potential energy

Unit hartree

MDHistory%nBlocks

Type int

Description Explain the block-system… ?

MDHistory%nEntries

Type int

Description Number of MD history entries.

MDHistory%NHCTstat#Energy(#)

Type float_array

Description ?

Unit hartree

`MDHistory%NHCTstat#Temperature(#)`

Type float_array

Description Local temperature of the thermostat region

Unit kelvin

`MDHistory%NHTBstat#Energy(#)`

Type float_array

Description ?

Unit hartree

`MDHistory%NHTBstat#Temperature(#)`

Type float_array

Description Local temperature of the thermostat region

Unit kelvin

`MDHistory%Number of molecules(#)`

Type int_array

Description Number of molecules. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

`MDHistory%PotentialEnergy(#)`

Type float_array

Description The potential energy, i.e. the energy as computed by the engine. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

`MDHistory%Pressure(#)`

Type float_array

Description The pressure of the system (only for 3D PBC). This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree/bohr^3

`MDHistory%PressureTensor(#)`

Type float_array

Description Pressure tensor in Voigt notation.

Unit hartree/bohr^3

`MDHistory%ReactionBoostEnergy(#)`

Type float_array

Description ReactionBoost energy, part of the potential energy

Unit hartree

`MDHistory%ReactorEnergy(#)`

Type float_array

Description Reactor energy, part of the potential energy

Unit hartree

`MDHistory%StdevCosineShearVelocity(#)`

Type float_array

Description ?

`MDHistory%StdevEng*FrcRgn*(#)`

Type float_array

Description ?

`MDHistory%StdevEngine*ForceRegion*(#)`

Type float_array

Description ?

`MDHistory%Step(#)`

Type int_array

Description The step number of the MD calculation. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

`MDHistory%Temperature(#)`

Type float_array

Description The temperature of the system, computed from the kinetic energy?. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit kelvin

`MDHistory%TempProfile_a(#)`

Type float_array

Description The temperature profile…? Some MD person, please fix.

Unit kelvin

`MDHistory%TempProfile_b(#)`

Type float_array

Description The temperature profile…? Some MD person, please fix.

Unit kelvin

`MDHistory%TempProfile_c(#)`

Type float_array

Description The temperature profile…? Some MD person, please fix.

Unit kelvin

`MDHistory%Time(#)`

Type float_array

Description The MD simulation time. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit femtosecond

`MDHistory%TotalEnergy(#)`

Type float_array

Description The total energy of the system: potential energy (as computed by the engine) + kinetic energy. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit hartree

`MDHistory%Velocities(#)`

Type float_array

Description The velocity of the atoms.

Unit bohr/femtosecond

Shape [3, :]

`MDHistory%Volume(#)`

Type float_array

Description The volume of the cell (only for 3D PBC). This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

Unit bohr^3

MDHookState **Section content:** Data related to MD hooks

MDResults **Section content:** Results of an MD calculation.

`MDResults%EndStep`

Type int

Description Step number of the last step.

`MDResults%EndTime[fs]`

Type float

Description The time at the end of the MD simulation.

Unit femtosecond

`MDResults%EndVelocities`

Type float_array

Description The atomic velocities at the last step of the MD simulation.

Unit a.u.

Shape [3, :]

`MDResults%MaxConservedEnergy`

Type float

Description Maximum value of the conserved energy during the MD simulation.

Unit hartree

`MDResults%MaxKineticEnergy`

Type float

Description Maximum value of the kinetic energy during the MD simulation.

Unit hartree

`MDResults%MaxPotentialEnergy`

Type float

Description Maximum value of the potential energy during the MD simulation.

Unit hartree

`MDResults%MaxTemperature`

Type float

Description Maximum value of the temperature during the MD simulation.

Unit kelvin

`MDResults%MaxTotalEnergy`

Type float

Description Maximum value of the total energy during the MD simulation.

Unit hartree

`MDResults%MeanConservedEnergy`

Type float

Description Mean conserved energy during the MD simulation.

Unit hartree

`MDResults%MeanKineticEnergy`

Type float

Description Mean kinetic energy during the MD simulation.

Unit hartree

`MDResults%MeanPotentialEnergy`

Type float

Description Mean potential energy during the MD simulation. The potential energy is the energy computed by the engine.

Unit hartree

`MDResults%MeanTemperature`

Type float

Description Mean temperature during the MD simulation.

Unit kelvin

`MDResults%MeanTotalEnergy`

Type float

Description Mean total energy during the MD simulation (total energy = potential energy from engine + kinetic energy).

Unit hartree

`MDResults%MinConservedEnergy`

Type float

Description Minimum value of the conserved energy during the MD simulation.

Unit hartree

`MDResults%MinKineticEnergy`

Type float

Description Minimum value of the kinetic energy during the MD simulation.

Unit hartree

`MDResults%MinPotentialEnergy`

Type float

Description Minimum value of the potential energy during the MD simulation.

Unit hartree

`MDResults%MinTemperature`

Type float

Description Minimum value of the temperature during the MD simulation.

Unit kelvin

`MDResults%MinTotalEnergy`

Type float

Description Minimum value of the total energy during the MD simulation.

Unit hartree

`MDResults%StartStep`

Type int

Description Step number of the first step.

`MDResults%StartTime[fs]`

Type float

Description The time at the beginning of the MD simulation.

Unit femtosecond

`MDResults%StdDevConservedEnergy`

Type float

Description Standard deviation of the conserved energy during the MD simulation.

Unit hartree

`MDResults%StdDevKineticEnergy`

Type float

Description Standard deviation of the kinetic energy during the MD simulation.

Unit hartree

`MDResults%StdDevPotentialEnergy`

Type float

Description Standard deviation of the potential energy during the MD simulation.

Unit hartree

`MDResults%StdDevTemperature`

Type float

Description Standard deviation of the temperature during the MD simulation.

Unit kelvin

`MDResults%StdDevTotalEnergy`

Type float

Description Standard deviation of the total energy during the MD simulation.

Unit hartree

Molecule **Section content:** The final molecule in the calculation. What is stored here depends on the task of the AMS calculation. For example, for a GeometryOptimization this will contain the optimized molecule, while for a TransitionStateSearch this will contain the molecule at the TS geometry.

`Molecule%AtomicNumbers`

Type int_array

Description Atomic number 'Z' of the atoms in the system

Shape [nAtoms]

`Molecule%AtomMasses`

Type float_array

Description Masses of the atoms

Unit a.u.

Values range [0, '\infinity']

Shape [nAtoms]

`Molecule%AtomSymbols`

Type string

Description The atom's symbols (e.g. 'C' for carbon)

Shape [nAtoms]

`Molecule%bondOrders`

Type float_array

Description The bond orders for the bonds in the system. The indices of the two atoms participating in the bond are defined in the arrays 'fromAtoms' and 'toAtoms'. e.g. bondOrders[1]=2, fromAtoms[1]=4 and toAtoms[1]=7 means that there is a double bond between atom number 4 and atom number 7

`Molecule%Charge`

Type float

Description Net charge of the system

Unit e

`Molecule%Coords`

Type float_array

Description Coordinates of the nuclei (x,y,z)

Unit bohr

Shape [3, nAtoms]

`Molecule%eeAttachTo`

Type int_array

Description A multipole may be attached to an atom. This influences the energy gradient.

`Molecule%eeChargeWidth`

Type float

Description If charge broadening was used for external charges, this represents the width of the charge distribution.

`Molecule%eeEField`

Type float_array

Description The external homogeneous electric field.

Unit hartree/(e*bohr)

Shape [3]

`Molecule%eeLatticeVectors`

Type float_array

Description The lattice vectors used for the external point- or multipole- charges.

Unit bohr

Shape [3, eeNLatticeVectors]

`Molecule%eeMulti`

Type float_array

Description The values of the external point- or multipole- charges.

Unit a.u.

Shape [eeNZlm, eeNMulti]

`Molecule%eeNLatticeVectors`

Type int

Description The number of lattice vectors for the external point- or multipole- charges.

`Molecule%eeNMulti`

Type int

Description The number of external point- or multipole- charges.

`Molecule%eeNZlm`

Type int

Description When external point- or multipole- charges are used, this represents the number of spherical harmonic components. E.g. if only point charges were used, eeNZlm=1 (s-component only). If point charges and dipole moments were used, eeNZlm=4 (s, px, py and pz).

`Molecule%eeUseChargeBroadening`

Type bool

Description Whether or not the external charges are point-like or broadened.

`Molecule%eeXYZ`

Type float_array

Description The position of the external point- or multipole- charges.

Unit bohr

Shape [3, eeNMulti]

`Molecule%EngineAtomicInfo`

Type string_fixed_length

Description Atom-wise info possibly used by the engine.

`Molecule%fromAtoms`

Type int_array

Description Index of the first atom in a bond. See the bondOrders array

`Molecule%latticeDisplacements`

Type int_array

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

`Molecule%LatticeVectors`

Type float_array

Description Lattice vectors

Unit bohr

Shape [3, nLatticeVectors]

`Molecule%nAtoms`

Type int

Description The number of atoms in the system

`Molecule%nAtomsTypes`

Type int

Description The number different of atoms types

`Molecule%nLatticeVectors`

Type int

Description Number of lattice vectors (i.e. number of periodic boundary conditions)

Possible values [0, 1, 2, 3]

`Molecule%toAtoms`

Type int_array

Description Index of the second atom in a bond. See the bondOrders array

Molecules **Section content:** Results of the molecules detection algorithms. Note: molecules with the same formula are considered to be the same molecule.

`Molecules%Molecule name #`

Type string

Description The name of the molecules, i.e. their molecular formula.

`Molecules%Num molecules`

Type int

Description Number distinct (i.e. with different molecular formula) molecules found.

NEB **Section content:** Data related to the Nudge Elastic Band procedure.

`NEB%climbing`

Type bool

Description Climb the highest image to the TS

`NEB%climbingThresh`

Type float

Description Threshold on the max perpendicular force component for the climbing image

`NEB%doubleNudge`

Type string

Description Henkelman: smoothly turns off the double nudging as the NEB converges; Trygubenko: JCP 120, 2082 (2005)

`NEB%energy`

Type float_array

Description energy per image, including ends

Unit hartree

`NEB%fixed`

Type bool_array

Description Flag fixed atoms

`NEB%forces`

Type float_array

Description forces per image, including stress forces (1st nVectors ‘atoms’ of each image)

Unit hartree/bohr

`NEB%highestIndex`

Type int

Description Index of the highest (or climbing) image

`NEB%historyIndex`

Type int_array

Description (i,j) element contains history index of image i on iteration j

NEB%im#

Type subsection

Description The molecule info of image #

NEB%im#%addedAtoms

Type archived_int_array

Description Atom species indices

NEB%im#%AtomicInfo

Type archived_string_array

Description

NEB%im#%BondOrders

Type archived_float_array

Description The bond orders for the bonds in the system. The indices of the two atoms participating in the bond are defined in the arrays 'fromAtoms' and 'toAtoms'. e.g. bondOrders[1]=2, fromAtoms[1]=4 and toAtoms[1]=7 means that there is a double bond between atom number 4 and atom number 7

NEB%im#%Charge

Type float

Description Net charge of the system

Unit e

NEB%im#%eeAttachTo

Type archived_int_array

Description A multipole may be attached to an atom. This influences the energy gradient.

NEB%im#%eeChargeWidth

Type float

Description If charge broadening was used for external charges, this represents the width of the charge distribution

NEB%im#%eeEField

Type float_array

Description The external homogeneous electric field

Unit hartree/(e*bohr)

Shape [3]

NEB%im#%eeLatticeVectors

Type archived_float_array

Description The lattice vectors used for the external point- or multipole- charges

Unit bohr

NEB%im#%eeMultipoles

Type archived_float_array

Description The multiple charges.

Unit bohr

`NEB%im#%eenMulti`

Type int

Description The number of multipoles.

`NEB%im#%eeUseChargeBroadening`

Type bool

Description Whether or not the external charges are point-like or broadened

`NEB%im#%eeXYZ`

Type archived_float_array

Description The position of the external point- or multipole- charges

Unit bohr

`NEB%im#%FromAtoms`

Type archived_int_array

Description Index of the first atom in a bond. See the bondOrders array

`NEB%im#%hasLatticeDisplacements`

Type bool

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

`NEB%im#%kVectors`

Type float_array

Description Reciprocal lattice vectors (corresponding to the strained lattice vectors)

Unit 1/bohr

Shape [3, 3]

`NEB%im#%LatticeDisplacements`

Type archived_int_array

Description The integer lattice translations for the bonds defined in the variables bondOrders, fromAtoms and toAtoms.

`NEB%im#%nAtoms`

Type int

Description The number of atoms in the system

`NEB%im#%nSpecies`

Type int

Description The number different of atoms types

`NEB%im#%nVectors`

Type int

Description Number of lattice vectors (0:molecule, 1:chain, 2:slab, 3:bulk).

NEB%im#%removedAtoms

Type archived_int_array

Description Atom species indices

NEB%im#%sp#inputSymbol

Type string

Description Symbol as specifined in the input

NEB%im#%sp#mass

Type float

Description mass

NEB%im#%sp#regions

Type archived_string_array

Description regions

NEB%im#%sp#symbol

Type string

Description Element symbol

NEB%im#%sp#Z

Type int

Description Atomic number

NEB%im#%SpIndices

Type archived_int_array

Description Atom species indices

NEB%im#%SPlen

Type int

Description Number of species

NEB%im#%strain

Type float_array

Description The strain matrix.

Shape [3, 3]

NEB%im#%strainedVectors

Type float_array

Description Strained real space lattice vectors

Unit bohr

Shape [3, 3]

NEB%im#%ToAtoms

Type archived_int_array

Description Index of the second atom in a bond. See the bondOrders array

`NEB%im#%unstrainedVectors`

Type float_array

Description Real space lattice vectors (unstrained).

Unit bohr

Shape [3, 3]

`NEB%im#%version`

Type int

Description

`NEB%im#%xyzAtoms`

Type archived_float_array

Description Coordinates of the nuclei (x,y,z)

Unit bohr

`NEB%interIntCoords`

Type bool

Description Interpolate in the internal coords instead of Cartesian

`NEB%interpolateOption`

Type int

Description 1=only dist, 2=1+linear angles, 3=1+val. angles, 4=1+dihedrals, 99=all coordinates

`NEB%interShortest`

Type bool

Description Interpolate across cell boundary if necessary

`NEB%jacobian`

Type float

Description Scaling factor used to convert the lattice strain to a NEB coordinate value

`NEB%LeftBarrier`

Type float

Description Left barrier energy

Unit hartree

`NEB%mapToOriginalCell`

Type bool

Description Map atoms to the [-0.5,0.5] cell

`NEB%nebImages`

Type int

Description number of intermediate NEB images, without ends. With them, there will be nebImages+2 images

NEB%nebIterations

Type int

Description Max number of iterations

NEB%nParallel

Type int

Description Number of images to do in parallel

NEB%oldTangent

Type bool

Description use old tangent

NEB%optimizeEnds

Type bool

Description Start NEB with optimization of the products/reactants

NEB%optimizeLattice

Type bool

Description Optimize lattice vectors

NEB%ReactionEnergy

Type float

Description Reaction energy

Unit hartree

NEB%RightBarrier

Type float

Description Left barrier energy

Unit hartree

NEB%spring

Type float

Description spring force constant

Unit a.u.

NEB%stressTensors

Type float_array

Description stress tensor per image

NEB%success

Type int_array

Description Single-point success flag (0 or 1)

PESScan **Section content:** Data related to the Potential Energy Surface (PES) Scan procedure.

PESScan%GOConverged

Type bool_array

Description Whether the (constrained) optimization at the various PES scan points converged.

Shape [nPoints]

`PESScan%HistoryIndices`

Type int_array

Description The indices of the frames in the History section corresponding to the PES point values.

Shape [nPoints]

`PESScan%HistoryPESPoints`

Type int_array

Description ?

`PESScan%nPoints`

Type int

Description The total number of scanned PES points. This is the product of all nPoints(#) values.

`PESScan%nPoints(#)`

Type int

Description Number of points along the corresponding scan coordinate.

`PESScan%nScanCoord`

Type int

Description Number of (independent) coordinates along which the PES scan is performed.

`PESScan%PES`

Type float_array

Description The total energy at each particular PES point.

Unit hartree

Shape [nPoints]

`PESScan%PESCoords`

Type float_array

Description The values of all coordinates for each particular PES point.

Shape [:, nPoints]

`PESScan%RangeEnd(#)`

Type float_array

Description The final value(s) for the corresponding scan coordinate.

`PESScan%RangeStart(#)`

Type float_array

Description The starting value(s) for the corresponding scan coordinate.

`PESScan%ScanCoord(#)`

Type string_fixed_length

Description A human readable description of the scan coordinate.

Replay Section content: Output of the Replay task of the AMS driver.

`Replay%File`

Type string

Description The path to the file from which the trajectory was replayed.

`Replay%Frames`

Type int_array

Description The indices of the frames in the history section that were replayed.

`Replay%Type`

Type string

Description The type if job that was replayed, e.g. PESScan, NEB, IRC or Generic.

ReplicaExchangeHistory Section content: ?

`ReplicaExchangeHistory%AvgSwapProbability #-#(#)`

Type float_array

Description ?

`ReplicaExchangeHistory%blockSize`

Type int

Description Explain the block-system… ?

`ReplicaExchangeHistory%currentEntryOpen`

Type bool

Description ?

`ReplicaExchangeHistory%EnsembleOfSystem #(#)`

Type int_array

Description ?

`ReplicaExchangeHistory%ItemName(#)`

Type string

Description ?

`ReplicaExchangeHistory%MaxPotentialEnergy #(#)`

Type float_array

Description ?

`ReplicaExchangeHistory%MDHistoryFrame(#)`

Type int_array

Description ?

`ReplicaExchangeHistory%MeanPotentialEnergy #(#)`

Type float_array

Description ?

`ReplicaExchangeHistory%MinPotentialEnergy #(#)`

Type float_array

Description ?

`ReplicaExchangeHistory%nBlocks`

Type int

Description Explain the block-system… ?

`ReplicaExchangeHistory%nEntries`

Type int

Description Number of MD history entries.

`ReplicaExchangeHistory%StdDevPotentialEnergy #(#)`

Type float_array

Description ?

`ReplicaExchangeHistory%Step(#)`

Type int_array

Description The step number of the MD calculation. This is a 'blocked' property. See the 'blockSize' and 'nBlocks' variables for more details.

`ReplicaExchangeHistory%SystemInEnsemble #(#)`

Type int_array

Description ?

`ReplicaExchangeHistory%TemperatureOfSystem #(#)`

Type float_array

Description ?

SystemVersionHistory **Section content:** ?

`SystemVersionHistory%AddedAtoms(#)`

Type int_array

Description ?

`SystemVersionHistory%currentEntryOpen`

Type bool

Description ?

`SystemVersionHistory%ItemName(#)`

Type string

Description ?

`SystemVersionHistory%nEntries`

Type int

Description ?

`SystemVersionHistory%RemovedAtoms(#)`

Type int_array

Description ?

`SystemVersionHistory%SectionNum(#)`

Type int

Description ?

Vibrations **Section content:** Data concerting the vibrational modes/spectra of the system.

`Vibrations%ExcitedStateLifetime`

Type float

Description Raman excited state lifetime.

Unit hartree

`Vibrations%ForceConstants`

Type float_array

Description The force constants of the vibrations.

Unit hartree/bohr^2

Shape [nNormalModes]

`Vibrations%FreqBeforeScan[cm-1]`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%Frequencies[cm-1]`

Type float_array

Description The vibrational frequencies of the normal modes.

Unit cm^-1

Shape [nNormalModes]

`Vibrations%Intensities[km/mol]`

Type float_array

Description The intensity of the normal modes.

Unit km/mol

Shape [nNormalModes]

`Vibrations%IRBeforeScan[km/mol]`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%IrReps`

Type lchar_string_array

Description Symmetry symbol of the normal mode.

Shape [nNormalModes]

Vibrations%IrRepsBeforeScan

Type lchar_string_array

Description ?

Shape [nNormalModes]

Vibrations%ModesNorm2

Type float_array

Description Norms of the rigid motions.

Shape [nNormalModes+nRigidModes]

Vibrations%ModesNorm2*

Type float_array

Description Norms of the rigid motions (for a given irrep…?).

Shape [nNormalModes+nRigidModes]

Vibrations%nNormalModes

Type int

Description Number of normal modes.

Vibrations%NoWeightNormalMode(#)

Type float_array

Description ?.

Shape [3, Molecule%nAtoms]

Vibrations%NoWeightRigidMode(#)

Type float_array

Description ?

Shape [3, Molecule%nAtoms]

Vibrations%nRigidModes

Type int

Description Number of rigid modes.

Vibrations%nSemiRigidModes

Type int

Description Number of semi-rigid modes.

Vibrations%PVDOS

Type float_array

Description Partial vibrational density of states.

Values range [0.0, 1.0]

Shape [nNormalModes, Molecule%nAtoms]

Vibrations%RamanDepolRatioLin

Type float_array

Description Raman depol ratio (lin).

Shape [nNormalModes]

`Vibrations%RamanDepolRatioLinBeforeScan`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%RamanDepolRatioNat`

Type float_array

Description Raman depol ratio (nat).

Shape [nNormalModes]

`Vibrations%RamanDepolRatioNatBeforeScan`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%RamanIncidentFreq`

Type float

Description Raman incident light frequency.

Unit hartree

`Vibrations%RamanIntens[A^4/amu]`

Type float_array

Description Raman intensities

Unit A^4/amu

Shape [nNormalModes]

`Vibrations%RamanIntensBeforeScan[A^4/amu]`

Type float_array

Description Raman intensities

Unit A^4/amu

Shape [nNormalModes]

`Vibrations%ReducedMasses`

Type float_array

Description The reduced masses of the normal modes.

Unit a.u.

Values range [0, '\infinity']

Shape [nNormalModes]

`Vibrations%RotationalStrength`

Type float_array

Description The rotational strength of the normal modes.

Shape [nNormalModes]

`Vibrations%ScannedModes`

Type int_array

Description ?

Shape [nNormalModes]

`Vibrations%TransformationMatrix`

Type float_array

Description ?

Shape [3, Molecule%nAtoms, nNormalModes]

`Vibrations%VROACIDBackward`

Type float_array

Description VROA Circular Intensity Differential: Backward scattering.

Unit 10¯3

Shape [nNormalModes]

`Vibrations%VROACIDBackwardBeforeScan`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%VROACIDDePolarized`

Type float_array

Description VROA Circular Intensity Differential: Depolarized scattering.

Unit 10¯3

Shape [nNormalModes]

`Vibrations%VROACIDDePolarizedBeforeScan`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%VROACIDForward`

Type float_array

Description VROA Circular Intensity Differential: Forward scattering.

Unit 10¯3

Shape [nNormalModes]

`Vibrations%VROACIDForwardBeforeScan`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%VROACIDPolarized`

Type float_array

Description VROA Circular Intensity Differential: Polarized scattering.

Unit 10¯3

Shape [nNormalModes]

`Vibrations%VROACIDPolarizedBeforeScan`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%VROADeltaBackward`

Type float_array

Description VROA Intensity: Backward scattering.

Unit 10¯3 A^4/amu

Shape [nNormalModes]

`Vibrations%VROADeltaBackwardBeforeScan`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%VROADeltaDePolarized`

Type float_array

Description VROA Intensity: Depolarized scattering.

Unit 10¯3 A^4/amu

Shape [nNormalModes]

`Vibrations%VROADeltaDePolarizedBeforeScan`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%VROADeltaForward`

Type float_array

Description VROA Intensity: Forward scattering.

Unit 10¯3 A^4/amu

Shape [nNormalModes]

`Vibrations%VROADeltaForwardBeforeScan`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%VROADeltaPolarized`

Type float_array

Description VROA Intensity: Polarized scattering.

Unit 10¯3 A^4/amu

Shape [nNormalModes]

`Vibrations%VROADeltaPolarizedBeforeScan`

Type float_array

Description ?

Shape [nNormalModes]

`Vibrations%ZeroPointEnergy`

Type float

Description Vibrational zero-point energy.

Unit hartree

VibronicStructure **Section content:** Data related to the Vibronic Structure Tracking procedure.

`VibronicStructure%nspectrum`

Type int

Description ?

`VibronicStructure%spectrum`

Type float_array

Description ?

CHAPTER

SEVENTEEN

FAQ

17.1 What is the difference between AMS and the AMS driver?

Amsterdam Modeling Suite (AMS) refers to the whole suite which includes the AMS driver for complex potential energy surface tasks with any underlying engine. The AMS bundle further includes the integrated GUI and the compute engines ADF, BAND, DFTB, MOPAC, ReaxFF, UFF, COSMO-RS.

17.2 What is the AMS driver?

It's a driver for running molecular dynamics or exploring the potential energy surface (finding transition states etc.)

It can be used with different modules: ADF, BAND, DFTB, MOPAC, ReaxFF and external engines. And as such you can switch easily between them, e.g. to transfer a Hessian from a low-lying method.

17.3 What will AMS do when one point fails to converge?

With AMS2018.103 it will exit with an error.

Starting with r69000, AMS geometry optimizations try to continue even if engine fails to solve for a geometry.

This can happen if there are for example SCF convergence problems in the engine. The energy/gradients might then not be quite correct, but it is probably safe to continue the optimization and hope that things are fine again for the next step. Note that this fix also applies to PES scans, transition state searches, and any other applications that use geometry optimizations internally (e.g. elastic property calculations).

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