



DFTB Manual

Amsterdam Modeling Suite 2019.3

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CONTENTS

1	General	1
1.1	Introduction	1
1.2	What's new in DFTB2019?	1
1.2.1	New in DFTB2019.3	1
1.2.2	New in DFTB2019.1	1
1.3	What's new in DFTB2018?	2
1.3.1	New features	2
1.3.2	AMS: a new driver program	2
2	Exploring the PES with AMS	5
2.1	Input geometry	5
2.2	Single point calculations	5
2.3	Geometry optimization	5
2.4	Transition state search	5
2.5	Linear transit and other PES scan	5
2.6	Molecular dynamics	6
2.7	Nuclear gradients and stress tensor	6
3	Model Hamiltonians	7
3.1	Slater-Koster based DFTB	7
3.2	Extended tight-binding (xTB)	7
3.3	Model Hamiltonian	8
3.4	Dispersion correction	8
3.5	Solvation (GBSA)	9
3.6	SCC details and spin-polarization	10
3.7	k-space integration	13
3.8	xTB specific keywords	14
3.9	Technical options	15
4	Spectroscopy and properties	19
4.1	Electronic structure of periodic systems	19
4.2	Excited states with time-dependent DFTB	22
4.3	Frequencies, phonons and elastic tensor	27
4.4	Other properties	27
5	Electronic transport (NEGF)	29
5.1	Transport with NEGF in a nutshell	29
5.2	Simulations work flow	30
5.3	Conductance input options	31
5.4	Miscellaneous remarks on DFTB-NEGF	33

6	Examples	35
6.1	Example: Normal modes (frequencies) for aspirin	35
6.2	Example: Molecular dynamics	36
6.3	Example: Linear transit	37
6.4	Example: PES scan and transition state search for H2 on graphene	41
6.5	Example: Vibrational circular dichroism	44
6.6	Example: Electronic transport with NEGF	45
6.7	Example: Diamond under pressure	48
6.8	Example: Elastic tensor	49
6.9	Example: Excited states frequencies	52
6.10	Example: Geometry optimization for an excited state	53
6.11	Example: Geometry optimization following a specific excited state	54
6.12	Example: Fullerene excitations	56
6.13	Example: Band structure with user-defined BZ path	59
6.14	Example: Restarting a geometry optimization	60
7	Parameterizations	67
7.1	Parameter meta-info	67
7.2	Slater-Koster based DFTB	68
7.2.1	Available parameter sets	68
	DFTB.org	68
	QUASINANO	69
	Dresden	69
7.2.2	Files in the resources directory	69
	Slater-Koster files	70
	Additional .yaml files	70
	Basis function information in .rkf files	71
7.3	Extended tight-binding (xTB)	71
8	Required citations	73
8.1	General references	73
8.2	Parameter references	73
9	References	75
9.1	Slater-Koster based DFTB	75
9.1.1	General Description	75
9.1.2	Parameter sets	76
	QUASINANO2013.1	76
9.1.3	QUASINANO2015	76
9.1.4	Dresden	76
9.1.5	DFTB.org	76
9.2	Extended tight-binding (xTB)	77
9.3	External programs and Libraries	77
10	Keywords	79
10.1	Links to manual entries	79
10.2	Summary of all keywords	79
	Index	95

1.1 Introduction

The DFTB engine implements density functional based tight-binding methods, which can be viewed as computationally very efficient approximations to density functional theory (DFT). As such it is a good engine for cheap calculations that still include quantum effects. DFTB is a computational engine that runs through the AMS driver. It can be used directly from the command line, from Python, and through our graphical interface.

1.2 What's new in DFTB2019?

1.2.1 New in DFTB2019.3

- The internals of the DFTB engine have been restructured, making it faster, more scalable and more accurate for periodic systems, while at the same time enabling previously locked combinations of features:
 - The default for the accuracy of *k-space integration* (page 13) has been changed: DFTB used to sample only the Γ -point by default. As of this release the default k-points depend on the system size, using the same logic as in BAND. See the page on k-space integration in the BAND manual.
 - Calculations with *k-space integration* (page 13) are generally faster and scale much better on parallel machines.
 - The *GFN1-xTB model* (page 7) can now be used together with *k-space integration* (page 13).
 - *Unrestricted calculations* (page 10) can now also be performed in conjunction with *k-space integration* (page 13).
 - The orbital dependent (l-dependent) *SCC cycle* (page 10) is now compatible with *k-space integration* (page 13).
 - The stress tensor is now calculated analytically, making its calculation faster and the result more accurate.
- An *implicit solvation model* (page 9) (GBSA: Generalized Born (GB) model augmented with the solvent accessible surface area (SA) term) has been added to DFTB, allowing simulations of molecules in solution.
- Various new applications in the AMS driver.

1.2.2 New in DFTB2019.1

- Grimme's GFN1-xTB has been added as a new *model Hamiltonian* (page 7). It supports molecular as well as periodic calculations for systems including elements up to Radon. Visualization of the results (e.g. molecular orbitals) in ADFView is also supported.

- Various new applications in the AMS driver.
- More robust and easier to set up *k-space integration* (page 13).
- More robust SCC convergence:
 - *Adaptive mixing* (page 10): The charge mixing parameter is automatically decreased if the energy increases during the SCC cycle.
 - The default electronic temperature has been increased to 300K, making SCC convergence more robust for systems with small HOMO-LUMO gaps.

1.3 What's new in DFTB2018?

1.3.1 New features

- Elastic tensor and related properties (e.g. Bulk modulus) (via AMS driver)
- Linear transit and PES scan (via AMS driver)
- Geometry optimization under pressure (via AMS driver)
- ...

1.3.2 AMS: a new driver program

Important: In the 2018 release of the Amsterdam Modeling Suite we introduced a new driver program call **AMS**. We recommend you to first read the General section of the AMS Manual

If you use DFTB exclusively via the Graphical User Interface (GUI), this change should not create any issues. If, on the other hand, you create input files *by hand* (or you use DFTB via PLAMS), then you should be aware that **shell scripts for DFTB2017 and previous versions are not compatible with DFTB2019 and have to be adjusted to the new setup.**

The example below shows how a shell script for DFTB2017 is converted to DFTB2019.

DFTB2017 shell script (obsolete):

```
#!/bin/sh

# This is a shell script for DFTB2017 which will not work for DFTB2019

$ADFBIN/dftb << EOF

Task
  RunType GO
End

System
  Atoms
    H 0.0 0.0 0.0
    H 0.9 0.0 0.0
  End
End

DFTB
```

```
ResourcesDir Dresden
End

Geometry
  iterations 100
End

EOF
```

DFTB2019 shell script:

```
#!/bin/sh

# This is a shell script for DFTB2019

# The executable '$ADFBIN/dftb' is no longer present.
# You should use '$ADFBIN/ams' instead.

$ADFBIN/ams << EOF
  # Input options for the AMS driver:

  System
    Atoms
      H 0.0 0.0 0.0
      H 0.9 0.0 0.0
    End
  End

  Task GeometryOptimization

  GeometryOptimization
    MaxIterations 100
  End

  # The input options for DFTB, which are described in this manual,
  # should be specified in the 'Engine DFTB' block:

  Engine DFTB
    ResourcesDir Dresden
  EndEngine

EOF
```


EXPLORING THE PES WITH AMS

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 energy and forces calculated by DFTB.

The input options for these tasks (including the definition of the input geometry) are described in the AMS User Manual.

Important: We recommend you to read the General section of the AMS Manual

2.1 Input geometry

The atom-types, atomic coordinates, lattice vectors and total charge are defined in the AMS part of the input. See the System definition section of the AMS manual

2.2 Single point calculations

See the Tasks section of the AMS manual

2.3 Geometry optimization

See the Geometry optimization section of the AMS manual

2.4 Transition state search

See the Transition state search section of the AMS manual

2.5 Linear transit and other PES scan

See the Linear transit and other PES scan section of the AMS manual

2.6 Molecular dynamics

See the Molecular dynamics section of the AMS manual

2.7 Nuclear gradients and stress tensor

See the nuclear gradients and stress tensor section of the AMS manual

MODEL HAMILTONIANS

As of the 2019 release, the DFTB engine supports two different classes of model Hamiltonians, Grimme's extended tight-binding, and the classic Slater-Koster based DFTB. All of these model Hamiltonians are obtained by applying tight-binding approximations to the DFT total energy expression.

3.1 Slater-Koster based DFTB

The efficiency of Slater-Koster based DFTB stems from its use of an optimized minimum valence orbital basis that reduces the linear algebra operations, and a two center-approximation for the Kohn-Sham potential that allows pre-calculation and storage of integrals using the Slater-Koster technique. This makes DFTB orders of magnitude faster than DFT, but requires parameter files (containing the integrals) for all pair-wise combinations of atoms in a molecule. Many elements can be handled with the parameter sets included in the distribution. Alternatively, sets of parameters in the SKF format can be downloaded and used from third party sources.

There are three flavors of Slater-Koster based DFTB available in our implementation:

- The "plain" DFTB Hamiltonian as introduced by Porezag and Seifert without a self-consistency cycle.
- The second order self-consistent charge extension SCC-DFTB (recently also called DFTB2), which accounts for density fluctuations and improves results on polar bonds. Note that the self-consistent calculations is about an order of magnitude slower than calculations with the "plain" DFTB Hamiltonian.
- The third order extension known as DFTB3, which improve the description of hydrogen-bonded complexes and proton affinities. Note that DFTB3 calculations are only marginally slower than SCC-DFTB based calculations.

Note that since these methods have been respectively parametrized, it is important to specify a matching parameter set when applying one of these models.

3.2 Extended tight-binding (xTB)

The extended tight-binding (xTB) model Hamiltonian as recently been introduced by Grimme and coworkers. It makes similar approximations as Slater-Koster based DFTB, but instead of using precalculated integrals, xTB employs a (small) basis of Slater-type orbitals and uses an extended Hückel-like approximation for the Hamiltonian.

The DFTB Engine in AMS2019 supports the GFN1-xTB parameterization of xTB, which is optimized for geometries, frequencies and non-covalent interactions and covers all elements of the periodic table up to radon.

3.3 Model Hamiltonian

The following keys allow you to select a model Hamiltonian and control different aspects of how the stationary Schroedinger equation is solved.

```
Model [DFTB | SCC-DFTB | DFTB3 | GFN1-xTB | NonSCC-GFN1-xTB]
```

Model

Type Multiple Choice

Default value SCC-DFTB

Options [DFTB, SCC-DFTB, DFTB3, GFN1-xTB, NonSCC-GFN1-xTB]

Description Selects the Hamiltonian used in the DFTB calculation: - DFTB/DFTB0/DFTB1 for classic DFTB without a self-consistent charge cycle - SCC-DFTB/DFTB2 with a self-consistency loop for the Mulliken charges - DFTB3 for additional third-order contributions. - GFN1-xTB for Grimme's extended tight-binding model in the GFN1 version. - NonSCC-GFN1-xTB for a less accurate but faster version of GFN1-xTB without a self-consistency cycle. The choice has to be supported by the selected parameter set.

Different parameters may be suitable for different model Hamiltonians. It is important to choose the appropriate parameter set for the type of calculation and molecular system under study, see [parameter sets](#) (page 68).

```
ResourcesDir string
```

ResourcesDir

Type String

Description The directory containing the parameter files. Absolute starting with / or relative to \$ADFRESOURCES/DFTB otherwise. This key is required for the Slater-Koster based DFTB models, but optional for xTB.

Examples:

ResourcesDir Dresden Uses the resource directory \$ADFRESOURCES/DFTB/Dresden.

ResourcesDir /home/myusername/myparamsdir Uses the specified path /home/myusername/myparamsdir as the resource directory.

NOTE: Each resource directory must contain a file called *metainfo.yaml*, which specifies the capabilities of the parameter set. For details see [metainfo.yaml](#) (page 67).

3.4 Dispersion correction

The selected model Hamiltonian can be extended with dispersion correction:

```
DispersionCorrection [None | Auto | UFF | ULG | D2 | D3-BJ]
```

DispersionCorrection

Type Multiple Choice

Default value None

Options [None, Auto, UFF, ULG, D2, D3-BJ]

GUI name Dispersion

Description This key is used to specify a empirical dispersion model. Please refer to the DFTB documentation for details on the different methods. By default no dispersion correction will be applied. Setting this to auto applies the dispersion correction recommended in the DFTB parameter set's metainfo file. Note that the D3-BJ dispersion correction is always enabled when using the GFN1-xTB model Hamiltonian.

3.5 Solvation (GBSA)

Solvation effects can be included via the implicit GBSA solvation model. We gratefully acknowledge the Grimme's group in Bonn for their contribution of the GBSA solvation method code.

To enable the GBSA method, specify the desired solvent:

```
Solvation
  Solvent [...]
End
```

Solvation

Type Block

Description Generalized Born solvation model with Solvent Accessible Surface Area (GBSA).

Solvent

Type Multiple Choice

Default value None

Options [None, Acetone, Acetonitrile, CHCl₃, CS₂, DMSO, Ether, H₂O, Methanol, THF, Toluene]

Description Solvent used in the GBSA implicit solvation model.

More options can be specified in the `Solvation` block:

```
Solvation
  UseGSASA [True | False]
  GSolvState [Gas1BarSolvent | Gas1MSolvent1M | Gas1BarSolvent1M]
  Temperature float
  SurfaceGrid [230 | 974 | 2030 | 5810]
End
```

Solvation

UseGSASA

Type Bool

Default value True

GUI name Solvation Free Energy

Description Include shift term and G(SASA) terms in the energy and gradient.

GSolvState

Type Multiple Choice

Default value Gas1MSolvent1M

Options [Gas1BarSolvent, Gas1MSolvent1M, Gas1BarSolvent1M]

Description Reference state for solvation free energy shift.

Temperature

Type Float

Default value 298.15

Unit Kelvin

Description The temperature used when calculating the solvation free energy shift. Only used for 'Gas1BarSolvent' and 'Gas1BarSolvent1M' GSolvState options.

SurfaceGrid

Type Multiple Choice

Default value 230

Options [230, 974, 2030, 5810]

Description Number of angular grid points for the construction of the solvent accessible surface area. Usually the default number of grid point suffices, but in case of suspicious behaviors you can increase the number of points.

3.6 SCC details and spin-polarization

```

SCC
  AdaptiveMixing [True | False]
  Converge
    Charge float
  End
  HXDamping [True | False]
  Iterations integer
  Mixing float
  OrbitalDependent [True | False]
  Unrestricted [True | False]
  nDIIS integer
End

```

SCC

Type Block

Description This optional section configures various details of the self-consistent charge cycle. If the model Hamiltonian does not need a self-consistent solution (e.g. plain DFTB0), none of this information is used and the entire section will be ignored.

AdaptiveMixing

Type Bool

Default value True

Description Change the mixing parameter based on the monitored energy. A significant increase of energy will strongly reduce the mixing. Then it will slowly grow back to the SCC%Mixing value.

Converge

Type Block

Description Controls the convergence criteria of the SCC cycle.

Charge**Type** Float**Default value** 1e-08**GUI name** Charge convergence**Description** The maximum change in atomic charges between subsequent SCC iterations. If the charges change less, the SCC cycle is considered converged.**HXDamping****Type** Bool**Description** This option activates the DFTB3 style damping for H-X bonds. Note that this is always enabled if the DFTB%Model key is set to DFTB3. Not used with xTB.**Iterations****Type** Integer**Default value** 500**Description** Allows to specify the maximum number of SCC iterations. The default should suffice for most standard calculations. Convergence issues may arise due to the use of the Aufbau occupations for systems with small HOMO-LUMO gaps. In this case the use of a Fermi broadening strategy may improve convergence. Choosing a smaller mixing parameter (see DFTB%SCC%Mixing) may also help with convergence issues: it often provides a more stable but slower way to converge the SCC cycle.**Mixing****Type** Float**Default value** 0.15**Description** The parameter used to mix the DIIS linear combination of previously sampled atomic charge vectors with an analogous linear combination of charge vectors resulting from population analysis combination. It can assume real values between 0 and 1.**OrbitalDependent****Type** Bool**Description** Activates or disables orbital resolved calculations. If this key is absent the recommended settings from the parameter file's metainfo.**Unrestricted****Type** Bool**Default value** False**Description** Enables spin unrestricted calculations. Only collinear spin polarization is supported, see Theor Chem Acc (2016) 135: 232, for details. Must be supported by the chosen parameter set. Not yet compatible with DFTB3, k-space sampling periodic calculations or the xTB models.**nDIIS****Type** Integer**Default value** 20

Description Specifies the maximum number of samples considered during the direct inversion of iteration of subspace (DIIS) extrapolation of the atomic charges during the SCC iterations. A smaller number of samples potentially leads to a more aggressive convergence acceleration, while a larger number often guarantees a more stable iteration. Due to often occurring linear dependencies within the set of sample vectors, the maximum number of samples is reached only in very rare cases.

```
Occupation
  Strategy [Auto | Aufbau | Fermi]
  Temperature float
End
```

Occupation

Type Block

Description Configures the details of how the molecular orbitals are occupied with electrons.

Strategy

Type Multiple Choice

Default value Auto

Options [Auto, Aufbau, Fermi]

GUI name Occupation

Description This optional key allows to specify the fill strategy to use for the molecular orbitals. Can either be 'Aufbau' for simply filling the energetically lowest orbitals, or 'Fermi' for a smeared out Fermi-Dirac occupation. By default the occupation strategy is determined automatically, based on the other settings (such as the number of unpaired electrons).

Temperature

Type Float

Default value 300.0

Unit Kelvin

GUI name Fermi temperature

Description The Fermi temperature used for the Fermi-Dirac distribution. Ignored in case of aufbau occupations.

```
UnpairedElectrons integer
```

UnpairedElectrons

Type Integer

Default value 0

GUI name Spin polarization

Description This specifies the number of unpaired electrons (not the multiplicity!). This number will then be used in the orbital-filling strategy. Has to be compatible with the total number of electrons, meaning it must be an even number if the total number of electrons is even and odd if the total number is odd. Must be an integer value. Note that this does not activate spin polarization, it only affects the filling of the orbitals.

3.7 k-space integration

As of the 2019 release, the k-space integration is unified between BAND and DFTB and uses the same keys as input, and the same defaults. See the page on k-space integration in the BAND manual for details and recommendations.

Note: k-space integration is currently not supported together with the extended tight-binding (xTB) model Hamiltonians, i.e. periodic calculations with xTB are restricted to sample only the gamma-point.

```
KSpace
  Quality [GammaOnly | Basic | Normal | Good | VeryGood | Excellent]
  Regular
    NumberOfPoints integer_list
  End
  Symmetric
    KInteg integer
  End
  Type [Regular | Symmetric]
End
```

KSpace

Type Block

Description Options for the k-space integration (i.e. the grid used to sample the Brillouin zone). Note that k-space sampling calculations are currently not supported with the xTB model Hamiltonians.

Quality

Type Multiple Choice

Default value Normal

Options [GammaOnly, Basic, Normal, Good, VeryGood, Excellent]

GUI name K-space

Description Select the quality of the K-space grid used to sample the Brillouin Zone. If ‘GammaOnly’, only one point (the gamma point) will be used. For the other options, the actual number of K points generated depends on the size of the unit cell. The larger the real space cell, the fewer K points will be generated. The CPU-time and accuracy strongly depend on this option.

Regular

Type Block

Description Options for the regular k-space integration grid.

NumberOfPoints

Type Integer List

Description Use a regular grid with the specified number of k-points along each reciprocal lattice vector. For 1D periodic systems you should specify only one number, for 2D systems two numbers, and for 3D systems three numbers.

Symmetric

Type Block

Description Options for the symmetric k-space integration grid.

KInteg

Type Integer

GUI name Accuracy

Description Specify the accuracy for the Symmetric method. 1: absolutely minimal (only the G-point is used) 2: linear tetrahedron method, coarsest spacing 3: quadratic tetrahedron method, coarsest spacing 4,6,... (even): linear tetrahedron method 5,7,... (odd): quadratic method The tetrahedron method is usually by far inferior.

Type

Type Multiple Choice

Default value Regular

Options [Regular, Symmetric]

GUI name K-space grid type

Description The type of k-space integration grid used to sample the Brillouin zone (BZ) used. ‘Regular’: simple regular grid. ‘Symmetric’: symmetric grid for the irreducible wedge of the first BZ (useful when high-symmetry points in the BZ are needed to capture the correct physics of the system, graphene being a notable example).

3.8 xTB specific keywords

A few keywords only apply to the xTB model Hamiltonian.

```
XTBConfig
  SlaterRadialThreshold float
  useXBTerm [True | False]
End
```

XTBConfig

Type Block

Description This block allows for minor tweaking.

SlaterRadialThreshold

Type Float

Default value 1e-05

Description Threshold determining the range of the basis functions. Using a larger threshold will speed up the calculation, but will also make the results less accurate.

useXBTerm

Type Bool

Default value False

Description Whether to use the Halogen bonding (XB) term. This is not advised as it has a non-continuous PES.

Note: The GFN1-xTB implementation in AMS currently does not implement the electronic entropy term from the article by Grimme et al. It therefore gives slightly different energies (but not gradients!) for systems with partially occupied molecular orbitals.

3.9 Technical options

```

Technical
  AnalyticalStressTensor [True | False]
  EwaldSummation
    CellRangeFactor float
    Enabled [True | False]
    Tolerance float
  End
  Parallel
    nCoresPerGroup integer
    nGroups integer
    nNodesPerGroup integer
  End
  ReuseKSpaceConfig [True | False]
  Screening
    dMadel float
    rMadel float
  End
  UseGeneralizedDiagonalization [True | False]
End

```

Technical

Type Block

Description This optional section is about technical aspects of the program that should not concern the normal user.

AnalyticalStressTensor

Type Bool

Default value True

Description Whether to compute the stress tensor analytically. Note: This can only be used together with Ewald summation as it will give (slightly) wrong results with Madelung screening.

EwaldSummation

Type Block

Description Configures the details of the Ewald summation of the Coulomb interaction.

CellRangeFactor

Type Float

Default value 2.0

Description Smaller values will make the Ewald summation less accurate but faster.

Enabled

Type Bool

Default value True

Description Whether to use Ewald summation for the long-range part of the Coulomb interaction. Otherwise screening is used.

Tolerance

Type Float

Default value 1e-10

Description Larger values will make the Ewald summation less accurate but faster.

Parallel

Type Block

Description Calculation of the orbitals in several k-points is trivially 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.

ReuseKSpaceConfig

Type Bool

Default value True

Description Keep the number of k-points constant during a lattice optimization. Otherwise the PES might display jumps, because the number of points depends on the lattice vector sizes. If this option is on it will always use the number of k-points that was used from a previous result.

Screening

Type Block

Description For SCC-DFTB in periodic systems the Coulomb interaction can (instead of using Ewald summation) be screened with a Fermi-Dirac like function defined as $S(r)=1/(\exp((r-r_{\text{madel}})/d_{\text{madel}})+1)$. This section allows to change some details of the screening procedure. Note that Coulomb screening is only used if the Ewald summation is disabled.

dMadel

Type Float

Unit Bohr

Description Sets the smoothness of the screening function. The default is 1/10 of [rMadel].

rMadel

Type Float

Unit Bohr

Description Sets the range of the screening function. The default is 2x the norm of the longest lattice vector.

UseGeneralizedDiagonalization

Type Bool

Default value True

Description Whether or not to use generalized diagonalization. Does not affect the results, but might be faster or slower.

```
StoreMatrices [True | False]
```

StoreMatrices

Type Bool

Default value False

Description Determines whether the Hamiltonian and overlap matrices are stored in the binary result file.

SPECTROSCOPY AND PROPERTIES

4.1 Electronic structure of periodic systems

```
Periodic
  EffectiveMass
    Enabled [True | False]
    KPointCoord float_list
    NumAbove integer
    NumBelow integer
    StepSize float
  End
  BandStructure
    Automatic [True | False]
    DeltaK float
    Enabled [True | False]
    FatBands [True | False]
    UseSymmetry [True | False]
  End
  BZPath
    Path # Non-standard block. See details.
    ...
  End
End
DOS
  EMax float
  EMin float
  Enabled [True | False]
  NSteps integer
End
End
```

Periodic

Type Block

Description Block that sets various details of the calculation only relevant for periodic systems.

EffectiveMass

Type Block

Description In a semi-conductor, the mobility of electrons and holes is related to the curvature of the bands at the top of the valence band and the bottom of the conduction band. With the effective mass option, this curvature is obtained by numerical differentiation. The estimation is done with the specified step size, and twice the specified step size, and both results are

printed to give a hint on the accuracy. By far the most convenient way to use this key is without specifying any options.

Enabled

Type Bool

Default value False

Description In a semi-conductor, the mobility of electrons and holes is related to the curvature of the bands at the top of the valence band and the bottom of the conduction band. With the effective mass option, this curvature is obtained by numerical differentiation. The estimation is done with the specified step size, and twice the specified step size, and both results are printed to give a hint on the accuracy. By far the most convenient way to use this key is without specifying any options.

KPointCoord

Type Float List

Unit 1/Bohr

Recurring True

Description Coordinate of the k-points for which you would like to compute the effective mass.

NumAbove

Type Integer

Default value 1

Description Number of bands to take into account above the Fermi level.

NumBelow

Type Integer

Default value 1

Description Number of bands to take into account below the Fermi level.

StepSize

Type Float

Default value 0.001

Description Size of the step taken in reciprocal space to perform the numerical differentiation

BandStructure

Type Block

Description Options for band structure plotting. This has no effect on the calculated energy. [Warning: The band structure is only computed in case of k-space sampling, i.e. it is not computed for Gamma-only calculations (see: Periodic%KSpace).]

Automatic

Type Bool

Default value True

GUI name Automatic generate path

Description Generate and use the standard path through the Brillouin zone. If not, use the user defined path (set via Custom path in the GUI, or with the Periodic%BZPath keyword in the run script).

DeltaK

Type Float

Default value 0.1

Unit 1/Bohr

GUI name Interpolation delta-K

Description Step size in reciprocal space for band structure interpolation. Using a smaller number will produce smoother band curves at an increased computational time.

Enabled

Type Bool

Default value True

GUI name Calculate band structure

Description Whether or not to calculate the band structure.

FatBands

Type Bool

Default value True

GUI name Calculate fatbands

Description Control the computation of the fat bands (only when the bandstructure is calculated). The fat bands are the periodic equivalent of the Mulliken population analysis. The definition of the fat bands can be found in the Band Documentation.

UseSymmetry

Type Bool

Default value True

Description If set, only the irreducible wedge of the Wigner-Seitz cell is sampled. If not, the whole (inversion-unique) Wigner-Seitz cell is sampled.

BZPath

Type Block

Description If [BandStructure%Automatic] is disabled, DFTB will compute the band structure 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, you need to specify a new [Path] sub-block.

Path

Type Non-standard block

Recurring True

Description A section of a k space path.

DOS

Type Block

Description The subkeys of [DOS] allow to customize the calculation of the density of states.

EMax

Type Float

Default value 0.75

Unit Hartree

Description Upper end of the energy interval in which the density of states is calculated.

EMin

Type Float

Default value -0.75

Unit Hartree

Description Lower end of the energy interval in which the density of states is calculated.

Enabled

Type Bool

Default value True

GUI name Calculate DOS

Description Whether or not to calculate the DOS. Note that the DOS will always be calculated when also the band structure is calculated.

NSteps

Type Integer

Default value 300

Description The number of energy intervals between [EMin] and [EMax] for which the density of states is calculated.

4.2 Excited states with time-dependent DFTB

DFTB allows for excited state calculations on molecular systems by means of single orbital transitions as well as time-dependent DFTB as published by Niehaus et al. in *Phys. Rev. B* **63**, 085108 (2001). Singlet-singlet as well as singlet-triplet excitations can be calculated. DFTB also supports the calculation of excited state gradients, which allows geometry optimizations and vibrational frequency calculations for excited states.

The TD-DFTB implementation uses the PRIMME library (PREconditioned Iterative MultiMethod Eigensolver) by Andreas Stathopoulos and James R. McCombs, PRIMME: PREconditioned Iterative MultiMethod Eigensolver (<http://www.cs.wm.edu/~andreas/publications/primmeTOMS.pdf>): *Methods and software description ACM Transaction on Mathematical Software* Vol. 37, No. 2, (2010), 21:1–21:30 (<https://doi.org/10.1145/1731022.1731031>).

DFTB excited state calculations are controlled by the following keywords:

```
Properties
  Excitations
    SingleOrbTrans
      Enabled [True | False]
    Filter
      OSMin float
      dEMax float
```

```

    dEMin float
  End
  PrintLowest integer
End
TDDFTB
  Calc [None | Singlet | Triplet]
  DavidsonConfig
    ATCharges [Precalc | OnTheFly]
    SafetyMargin integer
    Tolerance float
  End
  Diagonalization [Auto | Davidson | Exact]
  Lowest integer
  Print string
  ScaleKernel float
  UpTo float
End
TDDFTBGradients
  Eigenfollow [True | False]
  Excitation integer_list
End
End
End

```

Properties

Type Block

Description DFTB can calculate various properties of the simulated system. This block configures which properties will be calculated.

Excitations

Type Block

Description Contains all options related to the calculation of excited states, either as simple single orbitals transitions or from a TD-DFTB calculation.

SingleOrbTrans

Type Block

Description The simplest approximation to the true excitations are the single orbital transitions (sometimes called Kohn-Sham transitions), that is transitions where a single electron is excited from an occupied Kohn-Sham orbital into a virtual orbital. The calculation of these transitions is configured in this section. Note that the SingleOrbTrans section is optional even though the single orbital transitions are also needed for TD-DFTB calculations. If the section is not present all single orbital transitions will still be calculated and used in a subsequent TD-DFTB calculation, but no output will be produced.

Enabled

Type Bool

Default value False

GUI name Single orbital transistions: Calculate

Description Calculate the single orbital transitions.

Filter

Type Block

Description This section allows to remove single orbital transitions based on certain criteria. All filters are disabled by default.

OSMin

Type Float

GUI name Minimum oscillator strength

Description Removes single orbital transitions with an oscillator strength smaller than this threshold. A typical value to start (if used at all) would be 1.0e-3.

dEMax

Type Float

Unit Hartree

Description Removes single orbital transitions with an orbital energy difference larger than this threshold.

dEMin

Type Float

Unit Hartree

Description Removes single orbital transitions with an orbital energy difference smaller than this threshold.

PrintLowest

Type Integer

Default value 10

Description The number of single orbital transitions that are printed to the screen and written to disk. If not a TD-DFTB calculation, the default is to print the 10 lowest single orbital transitions. In case of a TD-DFTB calculation it is assumed that the single orbital transitions are only used as an input for TD-DFTB and nothing will be printed unless PrintLowest is specified explicitly.

TDDFTB

Type Block

Description Calculations with time-dependent DFTB can be configured in the TDDFTB section and should in general give better results than the raw single orbital transitions. TD-DFTB calculates the excitations in the basis of the single orbital transitions, whose calculation is configured in the SingleOrbTrans section. Using a filter in SingleOrbTrans can therefore be used to reduce the size of the basis for TD-DFTB. One possible application of this is to accelerate the calculation of electronic absorption spectra by removing single orbital transitions with small oscillator strengths from the basis. Note that the entire TDDFTB section is optional. If no TDDFTB section is found, the behavior depends on the existence of the SingleOrbTrans section: If no SingleOrbTrans section is found (the Excitations section is completely empty then) a TD-DFTB calculation with default parameters will be performed. If only the SingleOrbTrans section is present no TD-DFTB calculation will be done.

Calc

Type Multiple Choice

Default value None

Options [None, Singlet, Triplet]

GUI name Type of excitations

Description Specifies the multiplicity of the excitations to be calculated.

DavidsonConfig

Type Block

Description This section contains a number of keywords that can be used to override various internals of the Davidson eigensolver. The default values should generally be fine.

ATCharges

Type Multiple Choice

Default value Precalc

Options [Precalc, OnTheFly]

GUI name Transition charges

Description Select whether the atomic transition charges are precalculated in advance or reevaluated during the iterations of the Davidson solver. Precalculating the charges will improve the performance, but requires additional storage. The default is to precalculate the atomic transition charges, but the precalculation may be disabled if not enough memory is available.

SafetyMargin

Type Integer

Default value 4

Description The number of eigenvectors the Davidson method will calculate in addition to the ones requested by the user. With the Davidson eigensolver it is generally a good idea to calculate a few more eigenvectors than needed, as depending on the initial guess for the eigenvectors it can happen that the found ones are not exactly the lowest ones. This problem is especially prominent if one wants to calculate only a small number of excitations for a symmetric molecule, where the initial guesses for the eigenvectors might have the wrong symmetry. Note that the additionally calculated excitations will neither be written to the result file nor be visible in the output.

Tolerance

Type Float

Default value 1e-09

Description Convergence criterion for the norm of the residual.

Diagonalization

Type Multiple Choice

Default value Auto

Options [Auto, Davidson, Exact]

GUI name Method

Description Select the method used to solve the TD-DFTB eigenvalue equation. The most straightforward procedure is a direct diagonalization of the matrix from which the excitation energies and oscillator strengths are obtained. Since the matrix grows quickly with system size (number of used single orbital transitions squared), this option is possible only

for small molecules. The alternative is the iterative Davidson method, which finds a few of the lowest excitations within an error tolerance without ever storing the full matrix. The default is to make this decision automatically based on the system size and the requested number of excitations.

Lowest

Type Integer

Default value 10

GUI name Number of excitations

Description Specifies the number of excitations that are calculated. Note that in case of the exact diagonalization all excitations are calculated, but only the lowest ones are printed to screen and written to the output file. Also note that if limited both by number and by energy, (lowest and upto), DFTB will always use whatever results in the smaller number of calculated excitations.

Print

Type String

Description Specifies whether to print details on the contribution of the individual single orbital transitions to the calculated excitations.

ScaleKernel

Type Float

Default value 1.0

Unit None

Description Set the scaling parameter of the response kernel. A scaling approach can be used to identify plasmons in molecules. While single-particle excitations are only slightly affected by scaling of the response kernel, plasmonic excitations are sensitive to variations in the scaling parameter. Default no scaling is used (scaling parameter = 1.0)

UpTo

Type Float

Unit Hartree

GUI name Excitations up to

Description Set the maximum excitation energy. Attempts to calculate all excitations up to a given energy by calculating a number of excitations equal to the number of single orbital transitions in this window. This is only approximately correct, so one should always add some safety margin. Note that if limited both by number and by energy, (lowest and upto), DFTB will always use whatever results in the smaller number of calculated excitations.

TDDFTBGradients

Type Block

Description This block configures the calculation of analytical gradients for the TD-DFTB excitation energies, which allows the optimization of excited state geometries and the calculation of vibrational frequencies in excited states (see J. Comput. Chem., 28: 2589-2601). If the gradients are calculated, they will automatically be used for geometry optimizations or vibrational frequency calculations, if the corresponding Task is selected and only 1 excitation is selected. Vibrationally resolved UV/Vis spectroscopy (Franck-Condon Factors) can be calculated in combination with the FCF program or using the Vibrational

Analysis Tools in AMS. See the ADF documentation on Vibrationally resolved electronic spectra or the AMS documentation for the Vibrational Analysis Tools.

Eigenfollow

Type Bool

Default value False

GUI name Follow initial excitation

Description If this option is set, DFTB uses the transition density in atomic orbital basis to follow the initially selected excited state during a geometry optimization. This is useful if excited state potential energy surfaces cross each other and you want to follow the surface you started on.

Excitation

Type Integer List

GUI name Excitation number

Description Select which excited states to calculate the gradients for. Gradients can only be calculated for an excited states that has been calculated using TD-DFTB. Make sure that enough excitations are calculated.

4.3 Frequencies, phonons and elastic tensor

Frequencies and phonons can be computed via numerical differentiation by the AMS driver. See the Normal Modes section or the Phonon section of the AMS manual.

Several thermodynamic properties, such as zero-point energy, internal energy, entropy, free energy and specific heat are computed by default when calculating phonons.

The elastic tensor (and related elastic properties such as bulk modulus, shear modulus and young modulus) can be computed via numerical differentiation by AMS. See the Elastic Tensor section of the AMS manual.

4.4 Other properties

DFTB can calculate various properties of the simulated system.

```
Properties
  NBOInput [True | False]
  VCD [True | False]
End
```

Properties

Type Block

Description DFTB can calculate various properties of the simulated system. This block configures which properties will be calculated.

NBOInput

Type Bool

Default value False

Description Whether or not an input file for the NBO program is written to disk as nboInput.FILE47. The input file follows the FILE47 format as described in the NBO6 manual available on nbo6.chem.wisc.edu. By default, only the calculation of the natural bond orbitals and the natural localized molecular orbitals is enabled, but the nboInput.FILE47 file can be edited by hand to enable other analysis models. Please refer to the NBO6 manual for details.

VCD

Type Bool

Default value False

GUI name Calculate VCD intensities

Description Calculate the VCD spectrum after calculating the IR spectrum. Note: symmetry must be set to NOSYM.

The calculation of Mayer bond orders can be requested in the AMS Properties block.

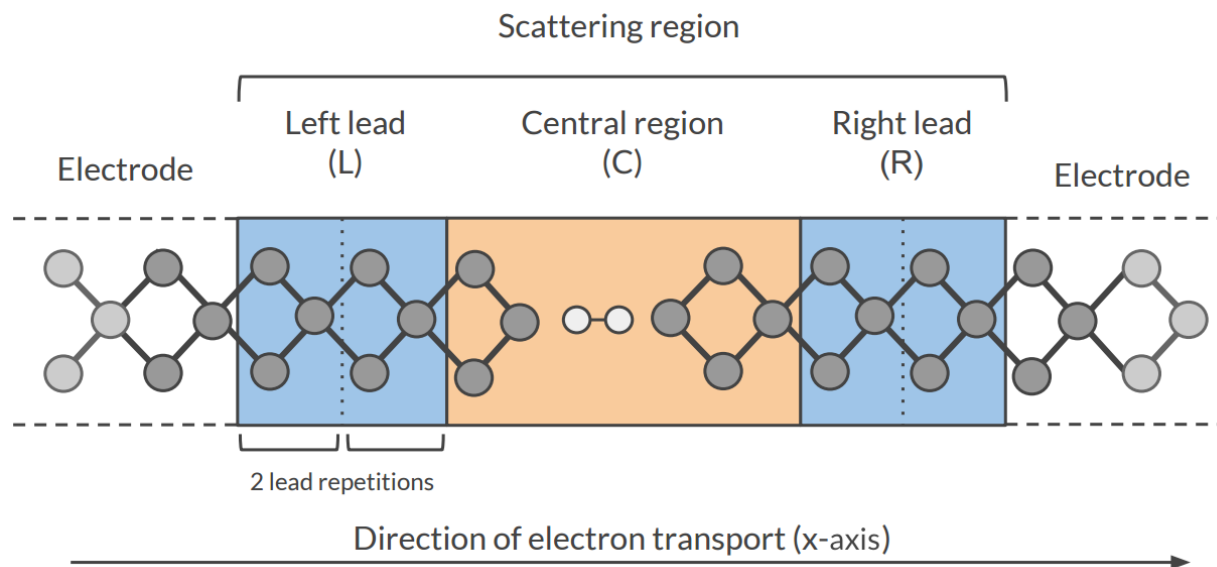
ELECTRONIC TRANSPORT (NEGF)

See also:

- DFTB-NEGF GUI tutorial
- *Example: Electronic transport with NEGF* (page 45)

5.1 Transport with NEGF in a nutshell

The **Non-Equilibrium Green's Functions** formalism (**NEGF**) is a theoretical framework for modeling electron transport through nano-scale devices. Electron transport is treated as a one-dimensional coherent scattering process in the “scattering region” for electrons coming in from the electrodes:



Our goal is to compute the **transmission function** $T(E)$, which describes the rate at which electrons of energy E are transferred from the left electrode to the right electrode by propagating through the scattering region. From the transmission function we can calculate the electric current for given **Bias Voltage** V applied between the electrodes:

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} T(E) (f(E - \mu_L) - f(E - \mu_R)) dE$$

where $f(E)$ is the Fermi-Dirac distribution function for a given temperature, and μ_L (μ_R) is $\epsilon_F + eV/2$ ($\epsilon_F - eV/2$), ϵ_F being the Fermi energy of the electrodes.

The transmission function $T(E)$ can be computed from the **Green's function** of our system.

The Green's function $G(E)$ of the scattering region is obtained solving the following equation:

$$(ES - H)G(E) = I$$

where S is the overlap matrix, H is the Hamiltonian and I is the identity matrix. The Hamiltonian is composed as follows (**L**, **C** and **R** denote the **left lead**, the **central region** and the **right lead** respectively):

$$H = \begin{pmatrix} H_L + \Sigma_L & H_{LC} & 0 \\ H_{LC} & H_C & H_{RC} \\ 0 & H_{RC} & H_R + \Sigma_R \end{pmatrix}$$

The two *self-energies* Σ_L and Σ_R model the two semi-infinite electrodes.

The transmission function $T(E)$ can be calculated from the Green's function $G(E)$ and the so-called *coupling matrices* $\Gamma_L(E)$ and $\Gamma_R(E)$ (which are related to Σ_L and Σ_R):

$$T(E) = Tr[G(E)\Gamma_R(E)G(E)\Gamma_L(E)]$$

See also:

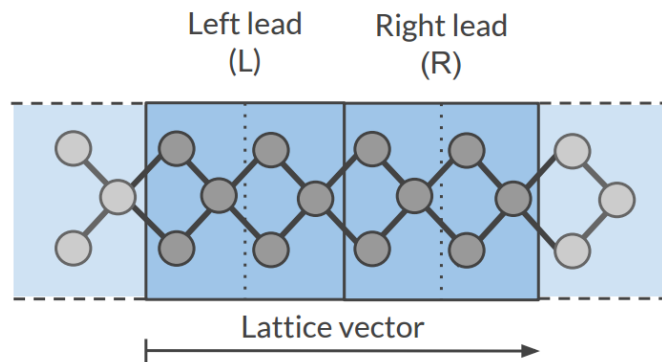
[PhD Thesis](https://opus.jacobs-university.de/frontdoor/index/index/docId/478) (<https://opus.jacobs-university.de/frontdoor/index/index/docId/478>) of Mahdi Ghorbani-Asl (DFTB-NEGF developer)

5.2 Simulations work flow

The computation of the transmission function $T(E)$ within the DFTB-NEGF formalisms requires three individual simulations.

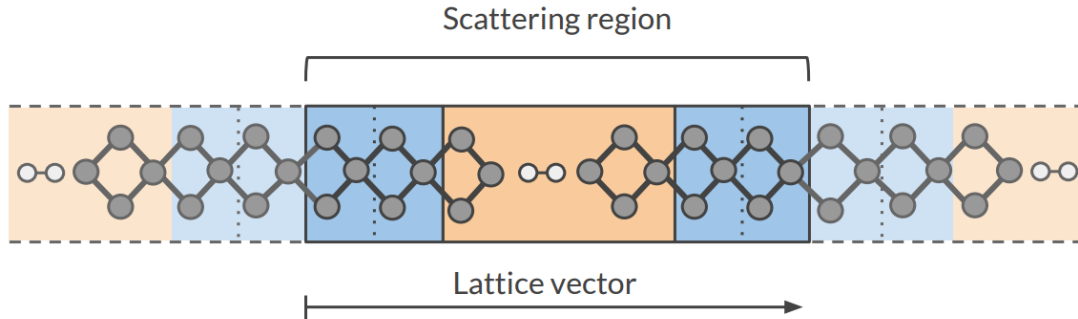
Tip: Use ADFInput (GUI) to set up your DFTB-NEGF calculation (see the DFTB-NEGF GUI tutorial)

1): DFTB leads calculation A 1D-periodic DFTB calculation of the leads (*StoreMatrices* (page 17): yes, *KSpace* (page 13) sampling 13):



The Hamiltonian matrices H_L and H_R and the Fermi energy of the electrode ϵ_F are computed in this calculation (H_L , H_R and H_{LR} are also used to compute the surface Green's functions g_L and g_R of the semi-infinite electrodes).

2): DFTB scattering-region calculation A 1D-periodic DFTB calculation of the scattering region (*StoreMatrices* (page 17): yes, gamma-only, *i.e.*, no *KSpace* (page 13) sampling):



The Hamiltonian matrices H_{LC} and H_{RC} and H_C are computed in this calculation.

3): Conductance calculation The **Conductance program** computes the NEGF transmission function $T(E)$ using the Hamiltonians and Overlap matrices from the previous two DFTB calculations.

5.3 Conductance input options

The **Conductance** program computes the transmission function using the NEGF approach. This is the input structure of the **conductance** program:

```
$ADFBIN/conductance <<EOF > conductance.out

EnergyGrid
  Min value
  Max value
  Num value

Files
  Leads      /path/DFTB_lead_filename.rkf
  Scattering /path/DFTB_scattering_filename.rkf
End

Technical
  Eta          value
  OverwriteLeads [True|False]
  SetOffDiagonalToZero [True|False]
End

end input
EOF
```

EnergyGrid

Type Block

Description Energy grid for Transmission Function

Max

Type Float

Default value 5.0

Unit eV

Description Max Energy (relative to Fermi energy)

Min

Type Float

Default value -5.0

Unit eV

Description Min energy (relative to Fermi energy)

Num

Type Integer

Default value 200

Description Number of energy values in which the interval Min-Max is subdivided

Technical

Type Block

Description options describing technical parts of the calculation

Eta

Type Float

Default value 1e-05

Description To avoid poles of the Green's function, a small imaginary number is added to the energy

overwriteLeads

Type Bool

Default value True

Description If true, Hamiltonians H_L and H_R are taken from the DFTB-leads calculation. If False, they are taken from the DFTB scattering-region calculation

setOffDiagonalToZero

Type Bool

Default value True

Description If true, H_LR and S_LR are explicitly set to zero. If False, they are taken from the DFTB scattering-region calculation.

Files

Type Block

Description path of files

Leads

Type String

Default value

Description Path (either absolute or relative) of the lead results file

Scattering

Type String

Default value

Description Path (either absolute or relative) of the scattering region results

5.4 Miscellaneous remarks on DFTB-NEGF

- You should make sure that your results are converged with respect to the number of lead repetitions; the results should not change significantly if you increase the number of lead repetitions.
- It's good practice to include at least one lead repetition in the central region.
- The transmission function is computed at zero bias voltage. The zero-bias transmission function is then used for computing the electric current for non-zero bias voltage.

EXAMPLES

The `$ADFHOME/examples/dftb` directory contains many different example files, covering various DFTB options. This is a selection of relevant examples.

6.1 Example: Normal modes (frequencies) for aspirin

Download `FREQ_aspirin_SCC.run`

```
#!/bin/sh
$ADFBIN/ams << eor

Task SinglePoint

Properties
  NormalModes True
End

System
  Atoms [Bohr]
    C    0.10101850    0.08267677    0.12682447
    C    2.73114989    0.06204296    0.11077263
    C    4.06439820    2.33164310   -0.06363346
    C    2.75114112    4.60824084   -0.20693134
    C    0.10560321    4.61925499   -0.15860918
    C   -1.28409307    2.34805008   -0.03252711
    O   -1.20792113    7.03183985   -0.40850190
    C   -4.13965656    2.14765157    0.02233364
    O   -5.54836431    4.25852921   -0.97228229
    C   -1.20247915    8.69980548    1.91027321
    C   -0.35706426    7.45382767    4.35689712
    H   -0.93489190   -1.72586813    0.25196453
    H    3.75849578   -1.74924086    0.22698872
    H    6.15018038    2.32888238   -0.09570448
    H    3.79180159    6.41027432   -0.34559245
    O   -5.25833423    0.30011724    0.82528893
    H   -4.29660486    5.51580277   -1.46089257
    O   -1.91824073   10.83838092    1.66234642
    H   -0.92159688    8.64229425    5.99197100
    H    1.73372033    7.23956114    4.42010264
    H   -1.20899026    5.55080173    4.61014609
  End
End
```

```

Engine DFTB
  ResourcesDir Dresden
  Repulsion
    forcePolynomial true
  End
  DispersionCorrection Auto
EndEngine

eor

```

6.2 Example: Molecular dynamics

Download MD_aspirin.run

```

#!/bin/sh

$ADFBIN/ams << eor

Task MolecularDynamics

MolecularDynamics
  nSteps 3
  TimeStep 0.2
  InitialVelocities Type=zero
  Thermostat Type=berendsen BerendsenApply=local Tau=20 Temperature=1200
  Trajectory SamplingFreq=1
  Preserve CenterOfMass=true
  Print System=true
End

System
  Atoms [Bohr]
    C    1.05960877221036    -4.29661605444804    -0.634037783371545
    C    3.70944109230336    -4.29661605444804    -0.634037783371545
    C    5.01105409669631    -1.99043606903162    -0.634037783371545
    C    3.65522107511068    0.286575996219979    -0.625747555592921
    C    0.994311181450713    0.336536571102876    -0.603233360526924
    C   -0.284455036107599    -2.00337880211933    -0.623649959779319
    O   -0.281193369103746    2.57767407876400    -0.596339640231410
    C   -2.98801415491818    -2.09305007828785    -0.642322341972295
    O   -4.09533876437070    -0.211143806102700    -1.93967968350738
    C   -0.320197312880997    4.26468724370209    1.32592550924302
    C    0.933554602168619    3.32259649258268    3.72681289050655
    H    5.555390692156803E-002  -6.12434199368563    -0.648191830798464
    H    4.76167074144455    -6.09597720705304    -0.642072898145812
    H    7.09553143269668    -1.96900279721371    -0.645115356938515
    H    4.71261912474754    2.08377152287689    -0.639226970852763
    O   -4.22220929602639    -3.71173831148125    0.403176103305787
    H   -3.05020881565447    1.05602705297610    -2.76001350141399
    O   -1.32857587116215    6.31113951397156    1.15028115060619
    H    0.422139955826862    4.57364609951207    5.33966942939295
    H    3.02803425766575    3.36265301371865    3.55019154354933
    H    0.292508534546246    1.38261705197608    4.22808915708257

  End
End

```



```

Engine DFTB
  ResourcesDir Dresden
  SCC
    Iterations 200
    Converge charge=1e-7
  End
  Repulsion
    ForcePolynomial true
  End
  DispersionCorrection Auto
EndEngine

eor

```

6.3 Example: Linear transit

Download `LinearTransit.run`

```

#!/bin/sh

echo "====="
echo "HCN isomerization"
echo "====="
echo

AMS_JOBNAME=HCN_isomerization $ADFBIN/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

AMS_JOBNAME=water_angle $ADFBIN/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 $ADFBIN/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
    End
  End

```

```

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
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 $ADFBIN/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
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
```

6.4 Example: PES scan and transition state 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 $ADFBIN/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

Constraints
  # Fix the entire graphene slab.
  Atom 3
  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 ADFMovie 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
H   -0.05533871972549955   -0.06805093626643093    1.500000013242627
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 $ADFBIN/ams << EOF

Task SinglePoint

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.
SelectedAtomsForHessian 1 2

```

```

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 adfreport:"
$ADFBIN/adfreport 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 $ADFBIN/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.
    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
  SelectedAtomsForHessian 1 2
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 adfreport:"
$ADFBIN/adfreport TS.results/dftb.rkf -r "AMSResults%Energy"

```

6.5 Example: Vibrational circular dichroism

Download `FREQ_HNDT_VCD.run`

```

#!/bin/sh

$ADFBIN/ams << eor

Task SinglePoint

Properties
  NormalModes true
End

System
  Atoms
    N 0 0 0
    H 0 0 1.02445577e+00
    H.2 -8.95690087e-01 4.13994999e-01 -2.75059085e-01
    H.3 -5.58123764e-02 -9.84657022e-01 -2.74917481e-01
  End

  AtomMasses
    H.3 3.01604927
    H.2 2.01410178
  End
End

Engine DFTB
  ResourcesDir DFTB.org/3ob-3-1
  Properties
    VCD true
  End
EndEngine

```



```
eor
```

6.6 Example: Electronic transport with NEGF

Download `conductance.run`

```
#!/bin/sh

# =====
# First test: Aluminum chain (DFTB0)
# =====

# Lead:
# =====

AMS_JOBNAME=Al_lead $ADFBIN/ams <<EOF
Task SinglePoint
System
  Atoms
    Al 0.0 0.0 0.0
    Al 2.83 0.0 0.0
    Al 5.66 0.0 0.0
    Al 8.49 0.0 0.0
  End

  Charge 0

  Lattice
    11.32 0.0 0.0
  End
End

Engine DFTB
  ResourcesDir QUASINANO2013.1
  StoreMatrices yes
  Model DFTB0
  Occupation Strategy=Fermi Temperature=5
  KSpace
    Type Symmetric
    Symmetric KInteg=13
  End
EndEngine
EOF

# Scattering region:
# =====

AMS_JOBNAME=Al_scattering $ADFBIN/ams <<EOF
Task SinglePoint
System
  Atoms
    Al -14.15 0.0 0.0
    Al -11.32 0.0 0.0
    Al -8.49 0.0 0.0
    Al -5.66 0.0 0.0
```

```

        Al -2.83 0 0
        Al 0 0 0
        Al 2.83 0 0
        Al 5.66 0.0 0.0
        Al 8.49 0.0 0.0
        Al 11.32 0.0 0.0
        Al 14.15 0.0 0.0
    End

    Charge 0
End

Engine DFTB
    ResourcesDir QUASINANO2013.1
    StoreMatrices yes
    Model DFTB0
    Occupation Strategy=Fermi Temperature=5
EndEngine
EOF

# Conductance:
# =====

$ADFBIN/conductance <<EOF
    EnergyGrid min=-5 max=5 num=500

    Files
        Leads      Al_lead.results/dftb.rkf
        Scattering Al_scattering.results/dftb.rkf
    End
EOF

mv ConductanceResults.kf Al_ConductanceResults.kf

echo "Extract DOS from the kf file Al_ConductanceResults.kf:"
$ADFBIN/adfreport Al_ConductanceResults.kf -r "results%dos#12.5f##1"

echo "Extract transmission from the kf file Al_ConductanceResults.kf:"
$ADFBIN/adfreport Al_ConductanceResults.kf -r "results%transmission#12.5f##1"

# =====
#   Second test: CO on gold chain (SCC-DFTB)
#   =====

# Lead:
# =====

AMS_JOBNAME=Au_lead $ADFBIN/ams <<EOF
    Task SinglePoint
    System
        Atoms
            Au 0.0 0.0 0.0
            Au 2.884996 0.0 0.0
            Au 5.769992 0.0 0.0
        End

        Charge 0

```

```

    Lattice
      8.654988 0.0 0.0
    End
  End
  Engine DFTB
    ResourcesDir QUASINANO2013.1
    Occupation Strategy=Fermi Temperature=5
    StoreMatrices yes
    KSpace
      Type Symmetric
      Symmetric KInteg=13
    End
  EndEngine
EOF

# Scattering region:
# =====

AMS_JOBNAME=Au_scattering $ADFBIN/ams <<EOF
  Task SinglePoint
  System
    Atoms
      Au -20.194972 0.0 0.0
      Au -17.309976 0.0 0.0
      Au -14.42498 0.0 0.0
      Au -11.539984 0.0 0.0
      Au -8.654988 0.0 0.0
      Au -5.769992 0.0 0.0
      Au -2.884996 0.0 0.0
      Au 0.0 0.0 0.20
      Au 2.884996 0.0 0.0
      Au 5.769992 0.0 0.0
      Au 8.654988 0.0 0.0
      Au 11.539984 0.0 0.0
      O 0.0 0.0 3.12
      C 0.0 0.0 1.96
      Au 14.42498 0.0 0.0
      Au 17.309976 0.0 0.0
      Au 20.194972 0.0 0.0
    End

    Charge 0

    Lattice
      43.27494 0.0 0.0
    End
  End

  Engine DFTB
    ResourcesDir QUASINANO2013.1
    Occupation Strategy=Fermi Temperature=5
    StoreMatrices yes
  EndEngine
EOF

# Conductance:
# =====

```

```

$ADFBIN/conductance <<EOF
  EnergyGrid min=-3.5 max=3 num=200

  Files
    Leads      Au_lead.results/dftb.rkf
    Scattering Au_scattering.results/dftb.rkf
  End
EOF

mv ConductanceResults.kf Au_ConductanceResults.kf

echo "Extract DOS from the kf file Au_ConductanceResults.kf:"
$ADFBIN/adfreport Au_ConductanceResults.kf -r "results%dos#12.5f##1"

echo "Extract transmission from the kf file Au_ConductanceResults.kf:"
$ADFBIN/adfreport Au_ConductanceResults.kf -r "results%transmission#12.5f##1"

```

6.7 Example: Diamond 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 $ADFBIN/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
  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
  ResourcesDir DFTB.org/mio-1-1
  KSpace
    Type Symmetric
    Symmetric KInteg=5
  End
  Technical AnalyticalStressTensor=False
EndEngine

EOF
done

```

6.8 Example: Elastic tensor

Download ElasticTensor.run

```

#!/bin/sh

# === Diamond ===

AMS_JOBNAME=Diamond $ADFBIN/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
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 Gradients=1.0e-5 StressEnergyPerAtom=1.0e-4
  Method Quasi-Newton
End

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, no k-space sampling

AMS_JOBNAME=BN_sheet $ADFBIN/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
    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 Gradients=1.0e-4
  Method Quasi-Newton
End

Engine DFTB
  ResourcesDir DFTB.org/matsci-0-3
  KSpace Quality=GammaOnly
EndEngine

EOF

# === Polyoxyethylene ===
# primitive cell with k-space sampling
AMS_JOBNAME=Polyoxyethylene $ADFBIN/ams << EOF

  Task GeometryOptimization

  Properties
    ElasticTensor Yes
  End

  ElasticTensor
    StrainStepSize 0.002
    MaxGradientForGeoOpt 2.0e-4
  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 Gradients=1.0e-4
  End
End

```

```

Engine 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:"
$ADFBIN/adfreport Diamond.results/dftb.rkf -r "AMSResults%ElasticTensor#12.4f##6"

echo ""
echo "Extract the elastic tensor of Boron-Nitride from the rkf file:"
$ADFBIN/adfreport BN_sheet.results/dftb.rkf -r "AMSResults%ElasticTensor#12.4f##3"

echo ""
echo "Extract the elastic tensor of Polyoxyethylene from the rkf file:"
$ADFBIN/adfreport Polyoxyethylene.results/dftb.rkf -r "AMSResults%ElasticTensor#12.4f#
↪#1"

```

6.9 Example: Excited states frequencies

Download `FREQ_LR-TDDFTB_benzene.run`

```

#!/bin/sh

# This test calculates frequencies of the lowest singlet excitation
# of benzene. This was also done in Niehaus paper on excited state
# gradients, see:
#   D. Heringer et al. J. Comput. Chem. 28:2589-2601, 2007

$ADFBIN/ams << eor

Task SinglePoint

Properties
  NormalModes true
End

System
  Atoms
    H      0.00000000    2.52578099    0.00000000
    H      0.00000000   -2.52578099    0.00000000
    H      2.18739047    1.26289148    0.00000000
    H     -2.18739047   -1.26289148    0.00000000
    H     -2.18739047    1.26289148    0.00000000
    H      2.18739047   -1.26289148    0.00000000

```



```

C      0.00000000    1.42809579    0.00000000
C      0.00000000   -1.42809579    0.00000000
C      1.23676731    0.71404770    0.00000000
C     -1.23676731   -0.71404770    0.00000000
C     -1.23676731    0.71404770    0.00000000
C      1.23676731   -0.71404770    0.00000000
End
End
Engine DFTB
  ResourcesDir DFTB.org/mio-1-1
  Properties
    Excitations
      TDDFTB
        Calc singlet
        Lowest 1
        Diagonalization exact
      End
      TDDFTBGradients
        Excitation 1
      End
    End
  End
End
EndEngine
eor

```

6.10 Example: Geometry optimization for an excited state

Download GO_LR-TDDFTB_benzene.run

```

#!/bin/sh

# This test optimizes the geometry of the lowest singlet excitation
# of benzene. This was an example from Niehaus' original paper on
# TD-DFTB gradients. See
#   D. Heringer et al. J. Comput. Chem. 28:2589-2601, 2007
# for his results and the C-C and C-H bond distances this test
# should produce.

$ADFBIN/ams << eor

Task GeometryOptimization

System
  Atoms
    H      0.000000    2.484212    0.000000
    H      0.000000   -2.484212    0.000000
    H      2.151390    1.242106    0.000000
    H     -2.151390   -1.242106    0.000000
    H     -2.151390    1.242106    0.000000
    H      2.151390   -1.242106    0.000000
    C      0.000000    1.396792    0.000000
    C      0.000000   -1.396792    0.000000
    C      1.209657    0.698396    0.000000
    C     -1.209657   -0.698396    0.000000

```

```

      C  -1.209657      0.698396      0.000000
      C   1.209657     -0.698396      0.000000
    End
  End
End

Engine DFTB
  ResourcesDir DFTB.org/mio-1-1
  Properties
    Excitations
      TDDFTB
        Calc singlet
        Lowest 1
        Diagonalization exact
      End
      TDDFTBGradients
        Excitation 1
      End
    End
  End
EndEngine

eor

```

6.11 Example: Geometry optimization following a specific excited state

Download GO_LR-TDDFTB_CO_eigenfollow.run

```

#!/bin/sh

# This test optimizes the 1st and 3rd triplet excitation of
# carbon monoxide. The difficult thing about these two is
# that they change character during the optimization. What
# is the lowest triplet at the ground state equilibrium will
# become the third triplet during the optimization and vice
# versa. We are using the eigenfollow keyword to follow the
# excitations during the geometry optimization.

AMS_JOBNAME=followT1 $ADFBIN/ams << eor

Task GeometryOptimization

System
  Atoms
    C  0.0000  0.0000  0.0000
    O  1.1000  0.0000  0.0000
  End
End

Engine DFTB

  ResourcesDir DFTB.org/mio-1-1

  Properties

```

```

    Excitations
      TDDFTB
        Calc triplet
        Lowest 10
        Print EVContribs
      End
      TDDFTBGradients
        Excitation 1
        Eigenfollow true
      End
    End
  End
End

EndEngine

Log
  Info TDDFTBExcitationFollowerModule
End

eor

AMS_JOBNAME=followT3 $ADFBIN/ams << eor

Task GeometryOptimization

System
  Atoms
    C   0.0000   0.0000   0.0000
    O   1.1000   0.0000   0.0000
  End
End

Engine DFTB

  ResourcesDir DFTB.org/mio-1-1

  Properties
    Excitations
      TDDFTB
        Calc triplet
        Lowest 10
        Print EVContribs
      End
      TDDFTBGradients
        Excitation 3
        Eigenfollow true
      End
    End
  End
End

EndEngine

Log
  Info TDDFTBExcitationFollowerModule
End

eor

```

6.12 Example: Fullerene excitations

Download SP_LR-TDDFTB_fullerene.run

```
#!/bin/sh
AMS_JOBNAME=SOOnly $ADFBIN/ams << eor

Task SinglePoint

System
  Atoms
    C   -0.72604297   0.99931275   3.33713795
    C   -1.17476257  -0.38170316   3.33713793
    C   -1.42973769   1.96786514   2.59722371
    C   -2.31336391  -0.75165747   2.59722338
    C   -2.31336503  -1.98687660   1.83381747
    C    0.00000000  -1.23521836   3.33713791
    C    0.00000000  -2.43241456   2.59722318
    C   -1.17476306  -2.81412029   1.83381769
    C    0.70369481   2.96717937   1.83381781
    C    1.42973769   1.96786514   2.59722371
    C   -0.70369481   2.96717937   1.83381781
    C    0.72604297   0.99931275   3.33713795
    C    1.17476257  -0.38170316   3.33713793
    C    2.60450100   1.58616203   1.83381755
    C    3.03940953   0.24765522   1.83381790
    C    2.31336391  -0.75165747   2.59722338
    C   -0.72604313   3.43172901  -0.59859929
    C    0.72604313   3.43172901  -0.59859929
    C   -1.42973797   3.20308436   0.59859932
    C    1.42973797   3.20308436   0.59859932
    C    2.60450023   2.34956878   0.59859923
    C    1.17476306   2.81412029  -1.83381769
    C    2.31336503   1.98687660  -1.83381747
    C    3.03940785   1.75097015  -0.59859921
    C   -3.03940785   1.75097015  -0.59859921
    C   -2.31336503   1.98687660  -1.83381747
    C   -2.60450023   2.34956878   0.59859923
    C   -1.17476306   2.81412029  -1.83381769
    C    0.00000000   2.43241456  -2.59722318
    C   -2.31336391   0.75165747  -2.59722338
    C   -1.17476257   0.38170316  -3.33713793
    C    0.00000000   1.23521836  -3.33713791
    C   -3.03940953   0.24765522   1.83381790
    C   -3.48812825  -0.36995429   0.59859935
    C   -2.60450100   1.58616203   1.83381755
    C   -3.48812825   0.36995429  -0.59859935
    C   -3.03940953  -0.24765522  -1.83381790
    C   -3.03940785  -1.75097015   0.59859921
    C   -2.60450023  -2.34956878  -0.59859923
    C   -2.60450100  -1.58616203  -1.83381755
    C    0.72604297  -0.99931275  -3.33713795
    C   -0.72604297  -0.99931275  -3.33713795
    C   -1.42973769  -1.96786514  -2.59722371
    C    1.42973769  -1.96786514  -2.59722371
    C    3.03940953  -0.24765522  -1.83381790
    C    2.31336391   0.75165747  -2.59722338
```

```

C      1.17476257      0.38170316     -3.33713793
C      2.60450100     -1.58616203     -1.83381755
C      3.03940785     -1.75097015      0.59859921
C      3.48812825     -0.36995429      0.59859935
C      3.48812825      0.36995429     -0.59859935
C      2.60450023     -2.34956878     -0.59859923
C      0.72604313     -3.43172901      0.59859929
C      1.17476306     -2.81412029      1.83381769
C      2.31336503     -1.98687660      1.83381747
C      1.42973797     -3.20308436     -0.59859932
C      -0.70369481     -2.96717937     -1.83381781
C      -1.42973797     -3.20308436     -0.59859932
C      -0.72604313     -3.43172901      0.59859929
C      0.70369481     -2.96717937     -1.83381781
End
End
Engine DFTB
  ResourcesDir DFTB.org/mio-1-1
  Properties
    Excitations
      SingleOrbTrans
        printlowest 166
      End
    End
  End
EndEngine
eor

AMS_JOBNAME=fullTDDFTB $ADFBIN/ams << eor

Task SinglePoint

System
  Atoms
    C      -0.72604297      0.99931275      3.33713795
    C      -1.17476257     -0.38170316      3.33713793
    C      -1.42973769      1.96786514      2.59722371
    C      -2.31336391     -0.75165747      2.59722338
    C      -2.31336503     -1.98687660      1.83381747
    C      0.00000000     -1.23521836      3.33713791
    C      0.00000000     -2.43241456      2.59722318
    C      -1.17476306     -2.81412029      1.83381769
    C      0.70369481      2.96717937      1.83381781
    C      1.42973769      1.96786514      2.59722371
    C      -0.70369481      2.96717937      1.83381781
    C      0.72604297      0.99931275      3.33713795
    C      1.17476257     -0.38170316      3.33713793
    C      2.60450100      1.58616203      1.83381755
    C      3.03940953      0.24765522      1.83381790
    C      2.31336391     -0.75165747      2.59722338
    C      -0.72604313      3.43172901     -0.59859929
    C      0.72604313      3.43172901     -0.59859929
    C      -1.42973797      3.20308436      0.59859932
    C      1.42973797      3.20308436      0.59859932
    C      2.60450023      2.34956878      0.59859923

```

```
C 1.17476306 2.81412029 -1.83381769
C 2.31336503 1.98687660 -1.83381747
C 3.03940785 1.75097015 -0.59859921
C -3.03940785 1.75097015 -0.59859921
C -2.31336503 1.98687660 -1.83381747
C -2.60450023 2.34956878 0.59859923
C -1.17476306 2.81412029 -1.83381769
C 0.00000000 2.43241456 -2.59722318
C -2.31336391 0.75165747 -2.59722338
C -1.17476257 0.38170316 -3.33713793
C 0.00000000 1.23521836 -3.33713791
C -3.03940953 0.24765522 1.83381790
C -3.48812825 -0.36995429 0.59859935
C -2.60450100 1.58616203 1.83381755
C -3.48812825 0.36995429 -0.59859935
C -3.03940953 -0.24765522 -1.83381790
C -3.03940785 -1.75097015 0.59859921
C -2.60450023 -2.34956878 -0.59859923
C -2.60450100 -1.58616203 -1.83381755
C 0.72604297 -0.99931275 -3.33713795
C -0.72604297 -0.99931275 -3.33713795
C -1.42973769 -1.96786514 -2.59722371
C 1.42973769 -1.96786514 -2.59722371
C 3.03940953 -0.24765522 -1.83381790
C 2.31336391 0.75165747 -2.59722338
C 1.17476257 0.38170316 -3.33713793
C 2.60450100 -1.58616203 -1.83381755
C 3.03940785 -1.75097015 0.59859921
C 3.48812825 -0.36995429 0.59859935
C 3.48812825 0.36995429 -0.59859935
C 2.60450023 -2.34956878 -0.59859923
C 0.72604313 -3.43172901 0.59859929
C 1.17476306 -2.81412029 1.83381769
C 2.31336503 -1.98687660 1.83381747
C 1.42973797 -3.20308436 -0.59859932
C -0.70369481 -2.96717937 -1.83381781
C -1.42973797 -3.20308436 -0.59859932
C -0.72604313 -3.43172901 0.59859929
C 0.70369481 -2.96717937 -1.83381781
End
End
Engine DFTB
  ResourcesDir DFTB.org/mio-1-1
  Properties
    Excitations
      TDDFTB
        calc singlet
        lowest 166
        print evcontriBs
    End
  End
End
EndEngine
eor
```

6.13 Example: Band structure with user-defined BZ path

Download `Li_BZPlot.run`

```
#!/bin/sh

# both the following runs follow the same path through the BZ

# first: automatic plot
AMS_JOBNAME=Li_auto $ADFBIN/ams << eor

Task SinglePoint

System
  Atoms
    Li 0.0 0.0 0.0
  End
  Lattice
    -1.745 1.745 1.745
    1.745 -1.745 1.745
    1.745 1.745 -1.745
  End
End

Engine DFTB
  ResourcesDir Demo
  Model DFTB0
  KSpace
    Type Symmetric
    Symmetric KInteg=5
  End
  Periodic
    BandStructure enabled=yes automatic=yes fatbands=no
  End
EndEngine

eor

# second: user defined path
AMS_JOBNAME=Li_user $ADFBIN/ams << eor

Task SinglePoint

System
  Atoms
    Li 0.0 0.0 0.0
  End
  Lattice
    -1.745 1.745 1.745
    1.745 -1.745 1.745
    1.745 1.745 -1.745
  End
End

Engine DFTB
  ResourcesDir Demo
```

```

Model DFTB0
KSpace
  Type Symmetric
  Symmetric KInteg=5
End
Periodic
  BandStructure enabled=yes automatic=no fatbands=no
  BZPath
    Path
      0.0  0.0  0.0
      0.5 -0.5  0.5
      0.0  0.0  0.5
      0.0  0.0  0.0
      0.25 0.25 0.25
      0.5 -0.5  0.5
    End
    Path
      0.25 0.25 0.25
      0.0  0.0  0.5
    End
  End
End
EndEngine

eor

# The band structure is best visualized using the BandStructure GUI module.

echo 'Extract the band_curves section from the rkf files:'
$ADFBIN/dmpkf Li_auto.results/dftb.rkf 'band_curves'
$ADFBIN/dmpkf Li_user.results/dftb.rkf 'band_curves'
echo "Done"

```

6.14 Example: Restarting a geometry optimization

Download `GO_restart.run`

```

#!/bin/sh

# Step 1: Run the entire optimization in one go to get the reference result.

AMS_JOBNAME=reference $ADFBIN/ams 2>&1 << EOF

Task GeometryOptimization

System
  Atoms
    Mg      0.00000000      0.00000000      0.00000000
    H      -1.27917000      4.11016000      4.72389000
    O       2.16655000     -0.38813000     -7.10271000
    H      -1.42939000      1.48933000     -2.39439000
    H       1.09521000      1.50513000    -11.11199000
    C      -1.73924000     -3.56815000     -7.25491000
    O       1.13468000      2.30574000     -6.31297000
    H      -1.00635000     -3.89600000      0.57440000
    C       2.39949000      1.96079000     -8.76280000

```


H	-0.50312000	-2.26723000	5.55260000
H	0.50312000	2.26723000	-5.55260000
C	-1.58070000	0.43033000	8.37317000
C	1.68553000	0.69328000	-9.20655000
H	3.10514000	2.27128000	-9.54815000
C	-2.12273000	1.75783000	3.90134000
C	-1.41195000	-3.08564000	8.52014000
C	-0.80701000	1.55547000	8.71125000
H	2.96787000	1.75892000	-7.84715000
H	-3.10514000	-2.27128000	9.54815000
H	1.41484000	-2.74396000	-7.00335000
H	1.12426000	-3.20203000	2.78552000
C	-0.17468000	1.56294000	9.95926000
C	-0.72719000	-2.63659000	-6.99325000
C	-1.09765000	-3.99973000	9.52904000
H	-0.25814000	-8.23193000	-3.30969000
C	1.14520000	-2.61556000	-3.22986000
O	0.72583000	-0.95806000	-1.56717000
H	-2.36816000	-5.34341000	-4.50996000
H	-2.96787000	-1.75892000	7.84715000
H	-2.25336000	0.75053000	3.46787000
N	2.80755000	-2.14965000	-4.91471000
C	-0.30154000	0.48014000	10.82965000
C	0.54101000	-2.17341000	-2.01004000
C	2.39908000	0.51189000	4.29012000
H	-1.63623000	-3.94265000	10.47839000
H	0.19490000	0.50042000	11.80153000
N	0.47889000	1.91215000	-0.81627000
C	-0.66060000	-2.05093000	2.26021000
H	-0.20633000	-7.24015000	-5.59602000
H	1.49008000	0.40226000	3.68367000
H	-0.39995000	4.15871000	-4.93170000
H	-1.12426000	3.20203000	-2.78552000
C	-1.03828000	-0.64018000	10.44800000
H	1.56169000	4.33269000	8.01583000
C	-0.11223000	-4.97150000	9.34588000
C	-0.03554000	7.26375000	2.87602000
H	-1.09521000	-1.50513000	11.11199000
H	3.22983000	0.79151000	3.62424000
C	3.45382000	-1.03521000	-6.98441000
O	-0.72583000	0.95806000	1.56717000
H	2.36816000	5.34341000	4.50996000
C	-1.68553000	-0.69328000	9.20655000
H	4.21952000	-0.40168000	-7.46345000
H	-1.28611000	-2.92413000	2.51305000
C	1.07673000	-4.19100000	5.79908000
C	0.46002000	6.10723000	3.76764000
H	0.19942000	5.47949000	5.84797000
H	-0.11989000	5.68080000	-10.14146000
N	-2.80755000	2.14965000	4.91471000
H	1.23144000	-6.29513000	-5.15638000
C	3.74078000	-1.20712000	-5.50076000
N	-0.47889000	-1.91215000	0.81627000
C	-0.57607000	5.02038000	-8.13428000
H	1.60192000	-5.15615000	5.75895000
H	-1.13094000	-1.13799000	2.64965000
C	-0.23845000	-3.15299000	-1.28978000
C	-0.05550000	-4.76579000	-3.14405000

H	-1.35753000	5.76910000	-7.98196000
H	3.72395000	-0.21480000	-5.00525000
H	-1.13142000	7.24453000	2.78458000
H	-4.76310000	1.61527000	5.41439000
H	4.76310000	-1.61527000	-5.41439000
C	2.12273000	-1.75783000	-3.90134000
C	-0.28104000	4.13616000	-7.08959000
C	0.73514000	3.17615000	-7.28394000
C	0.81335000	-3.86199000	-3.77035000
C	-2.39908000	-0.51189000	-4.29012000
H	2.25336000	-0.75053000	-3.46787000
C	1.41195000	3.08564000	-8.52014000
C	-0.52384000	-4.40125000	-1.88411000
C	-1.84973000	1.90289000	-4.97333000
H	0.20633000	7.24015000	5.59602000
C	1.09765000	3.99973000	-9.52904000
H	0.11989000	-5.68080000	10.14146000
H	0.25814000	8.23193000	3.30969000
H	-1.49008000	-0.40226000	-3.68367000
H	1.63623000	3.94265000	-10.47839000
C	-2.10065000	3.07251000	-5.70877000
C	0.57607000	-5.02038000	8.13428000
H	-1.56169000	-4.33269000	-8.01583000
C	0.11223000	4.97150000	-9.34588000
H	-1.13449000	-5.10187000	-1.30711000
H	0.39995000	-4.15871000	4.93170000
H	1.35753000	-5.76910000	7.98196000
C	-3.29750000	3.15241000	-6.42939000
C	0.23845000	3.15299000	1.28978000
H	-3.22983000	-0.79151000	-3.62424000
C	-0.59486000	2.70197000	7.73655000
C	0.28104000	-4.13616000	7.08959000
C	0.52384000	4.40125000	1.88411000
H	0.43755000	2.42353000	10.23864000
H	-3.50575000	4.04950000	-7.01656000
H	0.38971000	7.20647000	1.86361000
H	1.13449000	5.10187000	1.30711000
C	1.84973000	-1.90289000	4.97333000
C	-1.07673000	4.19100000	-5.79908000
H	0.62192000	-3.64814000	-8.29677000
C	-4.20635000	2.09524000	-6.41695000
C	2.10065000	-3.07251000	5.70877000
O	-0.62968000	1.82005000	-4.28278000
C	0.03554000	-7.26375000	-2.87602000
C	1.99778000	6.16492000	3.88117000
C	3.29750000	-3.15241000	6.42939000
H	-1.41484000	2.74396000	7.00335000
O	-0.07653000	-0.68618000	-5.67912000
H	-5.13801000	2.17027000	-6.98038000
H	3.50575000	-4.04950000	7.01656000
C	-3.45382000	1.03521000	6.98441000
C	-1.14520000	2.61556000	3.22986000
H	-2.30900000	-7.11968000	-4.33255000
C	4.20635000	-2.09524000	6.41695000
H	0.78141000	-0.75072000	-6.17605000
H	1.13142000	-7.24453000	-2.78458000
C	-0.54101000	2.17341000	2.01004000
H	5.13801000	-2.17027000	6.98038000

C	-3.91320000	0.93142000	-5.70744000
H	-1.60192000	5.15615000	-5.75895000
H	-0.43755000	-2.42353000	-10.23864000
C	3.91320000	-0.93142000	5.70744000
C	0.72575000	-2.17732000	2.89574000
H	-4.21952000	0.40168000	7.46345000
H	-4.60197000	0.08443000	-5.74068000
H	4.60197000	-0.08443000	5.74068000
H	-0.62192000	3.64814000	8.29677000
H	2.30900000	7.11968000	4.33255000
H	1.27917000	-4.11016000	-4.72389000
C	2.72586000	-0.80591000	4.97465000
C	-2.72586000	0.80591000	-4.97465000
H	-0.19942000	-5.47949000	-5.84797000
H	1.42939000	-1.48933000	2.39439000
C	0.96682000	1.65125000	6.01252000
C	-1.99778000	-6.16492000	-3.88117000
C	0.59486000	-2.70197000	-7.73655000
C	-0.96682000	-1.65125000	-6.01252000
C	2.18562000	1.61836000	5.30149000
C	0.05550000	4.76579000	3.14405000
H	3.43079000	-2.01409000	-7.48984000
C	1.58070000	-0.43033000	-8.37317000
C	3.16089000	2.57613000	5.58075000
C	-3.74078000	1.20712000	5.50076000
C	-0.81335000	3.86199000	3.77035000
H	-3.43079000	2.01409000	7.48984000
H	4.09911000	2.55793000	5.02051000
C	-2.18562000	-1.61836000	-5.30149000
C	0.80701000	-1.55547000	-8.71125000
H	-2.47896000	-6.08599000	-2.89560000
C	2.94890000	3.55128000	6.55908000
C	-0.13167000	6.28247000	5.17426000
C	0.13167000	-6.28247000	-5.17426000
C	0.17468000	-1.56294000	-9.95926000
H	3.71667000	4.29632000	6.77231000
C	-3.16089000	-2.57613000	-5.58075000
C	-0.46002000	-6.10723000	-3.76764000
C	-0.61444000	-2.98553000	0.08587000
C	1.73924000	3.56815000	7.25491000
O	0.62968000	-1.82005000	4.28278000
H	-0.38971000	-7.20647000	-1.86361000
H	2.47896000	6.08599000	2.89560000
H	-4.09911000	-2.55793000	-5.02051000
C	-0.72575000	2.17732000	-2.89574000
O	0.07653000	0.68618000	5.67912000
C	0.61444000	2.98553000	-0.08587000
O	-2.16655000	0.38813000	7.10271000
C	0.30154000	-0.48014000	-10.82965000
H	-3.72395000	0.21480000	5.00525000
H	1.00635000	3.89600000	-0.57440000
H	-0.78141000	0.75072000	6.17605000
C	-2.94890000	-3.55128000	-6.55908000
C	0.72719000	2.63659000	6.99325000
C	0.66060000	2.05093000	-2.26021000
H	-1.23144000	6.29513000	5.15638000
H	-0.19490000	-0.50042000	-11.80153000
C	-2.39949000	-1.96079000	8.76280000

```
H      1.28611000      2.92413000     -2.51305000
O     -1.13468000     -2.30574000      6.31297000
H     -3.71667000     -4.29632000     -6.77231000
C      1.03828000      0.64018000    -10.44800000
H      1.13094000      1.13799000     -2.64965000
C     -0.73514000     -3.17615000      7.28394000
End
End

GeometryOptimization
  CoordinateType Cartesian
End

Engine DFTB
  ResourcesDir DFTB.org/3ob-3-1
  Model DFTB3
  DispersionCorrection D3-BJ
EndEngine

EOF

# Step 2: Start the optimization but abort after 5 steps.
AMS_JOBNAME=aborted $ADFBIN/ams 2>&1 << EOF

Task GeometryOptimization

GeometryOptimization
  MaxIterations 5
  CoordinateType Cartesian
End

LoadSystem
  File reference.results/ams.rkf
  Section InputMolecule
End

LoadEngine reference.results/dftb.rkf

EOF

# Step 3: Restart the aborted optimization and finish it.
AMS_JOBNAME=resume $ADFBIN/ams 2>&1 << EOF

Task GeometryOptimization

GeometryOptimization
  CoordinateType Cartesian
End

LoadSystem
  File aborted.results/ams.rkf
End

LoadEngine aborted.results/dftb.rkf
```

```
EngineRestart aborted.results/dftb.rkf
```

```
EOF
```


PARAMETERIZATIONS

7.1 Parameter meta-info

There is a file named `metainfo.yaml` in each resources directory (see *ResourcesDir* (page 8)), for example `DFTB.org/3ob-3-1/metainfo.yaml`, which contains information about the capabilities of a parameter set. The file is in accordance with the **YAML** (<http://www.yaml.org>) syntax convention. In older versions of AMS this file was optional and its format was slightly different. Starting with the 2017 release of ADF/AMS, the `metainfo.yaml` file is required to use a parameter set.

The following entries `metainfo.yaml` specify the capabilities of the parameter set:

supports: `[dftb0, scc-dftb, dftb3, gfn-xtb]` A comma-separated list of model Hamiltonians for which the parameter set can be used. If the parameter set only supports a single model Hamiltonian, the enclosing `[]` can be dropped. This entry is mandatory. Without it, DFTB will refuse to use the parameter set.

format: `txt|txtq` Specifies which format is used for the Slater-Koster files of the parameter set. Use `txt` for normal text files with extension `.skf`. `txtq` is used for the encrypted Slater-Koster files from the QUASINANO parameter sets. Encrypted Slater-Koster files have the extension `.ske`. If the `format` entry is not there, normal (unencrypted) text files are assumed. Note that this entry is only relevant for Slater-Koster based DFTB and not used by the extended tight-binding model Hamiltonians.

repulsion: `no|partial|yes` Specifies whether the parameter set has repulsive potentials for all pairs of elements. Parameter sets that do not have repulsive potentials (e.g. QUASINANO2013.1) can not be used in geometry optimizations, molecular dynamics or frequency calculations. However, they can still be used in single point calculations, e.g. for UV/Vis absorption spectra of molecules or band structures of solids. Some parameter sets (e.g. `DFTB.org/halorg-0-1`) have most, *but not quite all* repulsive potentials. If `repulsion` is set to `partial`, DFTB will allow calculations with run-types normally requiring repulsive potentials and will only print a warning about which pairs are missing. It is then the user's responsibility to ensure that element pairs for which the repulsion is missing do not get too close during the calculation. If the `repulsion` entry is not found, DFTB will assume that there are repulsive potentials for all element pairs.

spin_polarization: `no|yes` Whether the parameter set supports unrestricted calculations. The default value is `no`.

orbital_dependence: `[noldep, ldep]` Whether the parameter set supports an atomic and/or shell-resolved SCC cycle. If only one of the two is supported, the enclosing `[]` can be dropped and the `default_orbital_dependence` entry (see below) does not need to be specified. If the `orbital_dependence` key is not found, DFTB assumes that the parameter set only supports atomic SCC cycles.

default_orbital_dependence: `noldep|ldep` The default mode for the SCC cycle.

dispersion: `[uff, ulg, d2, d3-bj]` A comma-separated list of London dispersion corrections supported by the parameter set. If only one method is supported, the enclosing `[]` can be dropped and the

`default_dispersion` entry (see below) does not need to be specified.

default_dispersion: `uff|ulg|d2|d3-bj` The default dispersion method to be used if the user enables dispersion but does not specify a method explicitly. If the `default_dispersion` entry is not found and more than one method is supported according to `dispersion` entry, **no** dispersion correction will be used by default. The user then has to select a dispersion method explicitly in the input file.

In addition to specifying the parameter set's capabilities, the `metainfo.yaml` file should also contain references to the scientific publication describing the parameter set:

```
url: http://www.scm.com

reference: |
  M. Wahiduzzaman, A. F. Oliveira, P. Philippsen, L. Zhechkov, E. van Lenthe, H. Witek,
  ↪ T. Heine
  "DFTB Parameters for the Periodic Table: Part 1, Electronic Structure",
  J. Chem. Theory Comput., 9, 2013, 4006-4017, DOI: 10.1021/ct4004959

short_reference: J. Chem. Theory Comput., 9, 2013, 4006-4017
```

All these entries are optional and at the moment only the `reference` entry is read by DFTB (and reproduced verbatim in its output). Note that the pipe symbol `|` is necessary to start a multiline entry (with preserved line breaks) and that the following lines have to be indented by at least one space.

7.2 Slater-Koster based DFTB

The most popular parameter sets for Slater-Koster based DFTB are *distributed with the AMS package* (page 68). Other parameter sets can easily be *added* (page 69).

Often parameter files are designed for a specific purpose, which may be different from your application, and therefore may give not the desired accuracy. Note that parameter files coming from different parameter sets are in general not compatible with each other and should not be mixed.

Additional licenses may be required to use some of the distributed parameter sets. Please contact us at license@scm.com for details.

7.2.1 Available parameter sets

DFTB.org

The DFTB implementation shipped by SCM provides the most up-to-date parameter sets available on the DFTB.org website. The following sets are currently shipped:

- 3ob-3-1 (Br, C, Ca, Cl, F, H, I, K, Mg, N, Na, O, P, S, Zn): general purpose set for the DFTB3 method
- mio-1-1 (H, C, N, O, S, P): for bio and organic molecules with SCC-DFTB
- pbc-0-3 (Si, F, O, N, C, H, Fe): for solid and surfaces
- matsci-0-3 (Al, Si, Cu, Na, Ti, Ba): for various compounds in material science

In addition, we ship the following specific purpose parameter sets:

- 3ob-freq: modified 3ob parameters for a better description of vibrational frequencies
- 3ob-hhmod: modified H-H for 3ob (for a better description of H2)
- 3ob-nhmod: modified N-H for 3ob (improves sp³-N proton affinities)

- 3ob-ophyd: modified O-P for 3ob (improves description of pentavalent phosphorus species)
- auorg (Au + mio): for gold-thiolate compounds
- borg (B, H): boron systems (solids and molecules)
- chalc-0-1 (As + mio): for chalcogenide glasses
- halorg (F, Cl, Br, I + mio): for halogens
- hyb-0-1 (Ag, Ga, As, Si + mio): for organic and inorganic hybrid systems
- magsil (Mg, Si, O, H, Mg): for chrysotile nanotubes
- miomod-hh: contains a modified parameter set for H₂
- miomod-nh: contains a modified parameter set for N-H to improve N-H binding energies
- siband (Si, O, H): electronic parameters for accurate silicon and silicon dioxide band structures
- tiorg-0-1 (Ti + mio): for Ti bulk, TiO₂ bulk, TiO₂ surfaces, and TiO₂ with organic molecules
- trans3d-0-1 (Sc, Ti, Fe, Co, Ni + mio): transition metal elements for biological systems
- znorg-0-1 (Zn + mio): for Zn bulk, ZnO bulk, ZnO surfaces, and ZnO with organic molecules

We recommend to visit the [DFTB.org](http://www.dftb.org) (<http://www.dftb.org>) web site for more detailed information about each set. We are committed to shipping all DFTB.org parameter sets in their latest version. If you miss one of the DFTB.org parameter sets in our distribution, please contact us at support@scm.com. Please note that our implementation of DFTB currently does not support parameter sets containing f-functions, such as the “rare” set.

QUASINANO

The *QUASINANO2013.1* (page 76) set of DFTB parameter files available in the AMS package is designed by Mohammad Wahiduzzaman et al. contains parameters for a large part of the periodic table (no f-elements). Note that the *QUASINANO2013.1* set only contains the electronic part of the interaction, so that only the spectrum for a given geometry can be calculated, but no total energy, and thus also no forces. These parameters can be used in TD-DFTB calculations, for example.

The *QUASINANO2015* (page 76) parameter set extends the *QUASINANO2013.1* parameter set, and includes terms that are needed to compute the total energy and its gradient.

Dresden

The so called Dresden set of DFTB parameter files available in the AMS package were designed by J. Frenzel, A.F. Oliveira, N. Jardillier, T. Heine, and G. Seifert, mainly at the Technische Universität in Dresden, Germany, see also some *additional information about the generation of these parameter files* (page 76). These parameter files are kept in the directory \$ADFHOME/atomicdata/DFTB/Dresden.

7.2.2 Files in the resources directory

This section contains a technical description of all the files and their formats which together constitute a DFTB parameter set. The parameter sets *distributed with the AMS package* (page 68) are ready to be used out-of-the box, and no knowledge about their format should be necessary to run DFTB calculations. However, users who want to use their own DFTB parameters with our implementation, will need to package them in a way that is understood by it.

DFTB parameter sets in the AMS package have up to four components: The *Slater-Koster files* (page 70), the *metainfo.yaml file* (page 67) and the optionally some *additional .yaml files* (page 70) as well as *binary .rkf files containing the basis functions* (page 71).

Slater-Koster files

Most of the data constituting a DFTB parameter set is contained in the so called Slater-Koster files. These are typically text files with the file extension `.skf`. For legal reasons, some parameter sets that are shipped with AMS the Slater-Koster files are encrypted though, in which case their file extension is `.ske`.

There is generally a Slater-Koster file per **pair of elements** supported by the parameter set, e.g. for a set supporting the four elements C,H,O,N there will be 16 Slater-Koster files in total. The Slater-Koster file names contain the symbols of the elements, e.g. `C-H.skf`, `H-O.skf` and `C-C.skf`. Note that files for both element orders, e.g. `C-H.skf` and `H-C.skf`, are needed and differ in general. The Slater-Koster files contain the matrix elements of the Hamiltonian operator and the overlap between basis functions centered on two atoms, tabulated for different distances. They also contain a description of a repulsive potential between the two atoms. Furthermore the one element Slater-Koster files (like `H-H.skf` and `C-C.skf`) contain some information about the individual atom, e.g. orbital energies of the atomic orbitals. A [detailed description](http://www.dftb.org/fileadmin/DFTB/public/misc/slakoformat.pdf) (<http://www.dftb.org/fileadmin/DFTB/public/misc/slakoformat.pdf>) of the Slater-Koster file format can be found at [DFTB.org](http://www.dftb.org) (<http://www.dftb.org>).

Additional .yaml files

The [Slater-Koster file format](http://www.dftb.org/fileadmin/DFTB/public/misc/slakoformat.pdf) (<http://www.dftb.org/fileadmin/DFTB/public/misc/slakoformat.pdf>) is relatively old and very inflexible. Over the years extensions of the DFTB method (e.g. spin-polarization, DFTB3, dispersion corrections) have been developed that require parameters which do not have a place in the Slater-Koster files. In the AMS implementation of DFTB, these parameters are stored in additional `.yaml` files in the resources directory of the parameter set: The `additional_parameters.yaml` file as well as per element `.yaml` files, e.g. `H.yaml` and `C.yaml`.

The `additional_parameters.yaml` file contains anything that applies to the entire parameter set and does not depend on the individual elements. At the moment this is:

grimme_d3bj_params: `s6 s8 a1 a2` The fitting parameters for Grimme's D3-BJ dispersion correction. This entry is mandatory if the `metainfo.yaml` file lists D3-BJ as a supported dispersion correction methods.

zeta_Hcorr: `zeta` A single number `zeta` used in the HX-damping usually applied in DFTB3 calculations.

The per element `.yaml` files may contain the following entries:

hubbard: `U_atom` The atomic Hubbard parameter used in a normal, atomic SCC cycle is specified in the element's `.yaml` file as the `hubbard` entry. It is quite surprising that such a commonly used parameter does not have its place in the Slater-Koster files, which only hold the shell-dependent Hubbard parameters. For atomic SCC cycles it is common practice to use the Hubbard parameter of the s-shell as the atomic Hubbard parameter, even though the two values are not strictly related. For consistency with other DFTB implementations, AMS DFTB will do the same if the atomic Hubbard parameter is not found in the element's `.yaml` file. However, it will also notify the user about this potentially questionable behavior.

hubbard_derivative: `dUdq` The derivative of the the atomic hubbard parameter with respect to the atomic charge. This information is required to perform DFTB3 calculations.

magnetic_hubbard and magnetic_hubbard_ldep The magnetic Hubbard parameters (often abbreviated `W` in the literature). These are required for unrestricted calculations and TD-DFTB singlet-triplet excitations. Depending on whether the parameter set allows atomic and/or shell resolved SCC cycles, the magnetic Hubbard parameter is given as a single number and/or a small matrix:

```
magnetic_hubbard: W_atom

magnetic_hubbard_ldep: >
  W_ss  W_sp
  W_ps  W_pp
```

The size of the matrix is determined by the number of basis functions on the element. Note that the `>` is essential to start a multiline entry (in which line breaks are ignored).

Basis function information in .rkf files

The QUASINANO parameter sets additionally have per element `.rkf` files in the resources directory, e.g. `H.rkf` and `C.rkf`. These binary files, which can be opened in the GUI with KFBrowser, contain information about the basis functions used to calculate the matrix elements in the Slater-Koster files. While this information is not needed to perform the DFTB calculation itself, it is used by the GUI in order to visualize properties like molecular orbitals or densities.

7.3 Extended tight-binding (xTB)

The AMS package comes with the GFN1-xTB parameterization of the extended tight-binding Hamiltonian. This is the parameterization published in the original article on GFN1-xTB, which is optimized for accurate geometries, frequencies and non-covalent interactions.

In contrast to Slater-Koster based DFTB, the extended tight-binding (xTB) method does not store precalculated matrix elements in Slater-Koster files. Instead there is a parameter file which contains information about the basis functions themselves, which is used to calculate matrix elements at run-time. The entire parameterization of GFN1-xTB is stored in simple text files found in `$ADFHOME/atomicdata/DFTB/GFN1-xTB`. Expert users can copy this directory, modify the parameterization to their needs, and use the *ResourcesDir* (page 8) keyword to load their modified parameterization.

elements.xtbpar Contains most the element specific parameters, e.g. the Hubbard parameters and their derivative, as well as the parameters used for the repulsive potential.

basis.xtbpar Contains the definition of the used basis functions. Note that one can add or remove basis functions for an element by adding or deleting lines in this file, as long as there is at most one set of basis functions per angular momentum for each element. For example one can not have two sets of p-functions with a different main quantum number on an atom. (The only exception here is hydrogen, which has both a `1s` and `2s` function. Hydrogen is treated in a special way in the GFN1-xTB implementation in AMS, which allows this. However, one should not change the hydrogen basis by editing the `basis.xtbpar` file. DFTB will refuse to run if this is done.)

atomic_configurations.xtbpar Contains the electron configurations of the isolated atoms.

electronegativity.xtbpar Contains the Pauling electronegativities for all elements.

globals.xtbpar Contains the global parameters of the method, see Table 2 of the GFN1-xTB article.

metals.xtbpar This file defines which elements are considered metals. (The coordination induced scaling of the atomic energy levels is only used for nonmetals.)

REQUIRED CITATIONS

When you publish results in the scientific literature that were obtained with programs of the package, you are required to include references to the program package with the appropriate release number, and a few key publications.

In addition to these general references, references to special features are mandatory, in case you have used them.

8.1 General references

For calculations with the Density Functional Tight Binding (DFTB) engine: AMS DFTB 2019.3, 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, A. Yakovlev, P. Philippsen, S. Borini, P. Melix, A. F. Oliveira, M. Franchini, T. van Vuren, T. Soini, M. de Reus, M. Ghorbani Asl, T. Q. Teodoro, D. McCormack, S. Patchkovskii, T. Heine.

For TD-DFTB, cite: R. Rüger, E. van Lenthe, Y. Lu, J. Frenzel, T. Heine, and L. Visscher, *Efficient Calculation of Electronic Absorption Spectra by Means of Intensity-Selected Time-Dependent Density Functional Tight Binding*, *J. Chem. Theory Comp.*, 2015, 11 (1), pp 157-167 (<https://doi.org/10.1021/ct500838h>).

For DFTB-NEGF, cite: Mahdi Ghorbani-Asl *Electronic transport through two-dimensional transition-metal chalcogenides*, PhD Thesis (2014) (<https://opus.jacobs-university.de/frontdoor/index/index/docId/478>)

8.2 Parameter references

If you use one of the included parameter sets you must also add the proper reference for it.

QUASINANO2015 A.F. Oliveira, P. Philippsen, T. Heine. *DFTB Parameters for the Periodic Table, Part 2: Energies and Energy Gradients from Hydrogen to Calcium*, *Journal of Chemical Theory and Computation* 11 (11), pp 5209–5218 (2015) (<https://doi.org/10.1021/acs.jctc.5b00702>)

QUASINANO2013.1 M. Wahiduzzaman, A.F. Oliveira, P.H.T. Philippsen, L. Zhechkov, E. van Lenthe, H.A. Witek, T. Heine, *DFTB Parameters for the Periodic Table: Part 1, Electronic Structure*, *Journal of Chemical Theory and Computation* 9, 4006 (2013) (<https://doi.org/10.1021/ct4004959>)

Dresden (same origin as matsci-0-3 parameters in DFTB.org) J. Frenzel, A. F. Oliveira, N. Jardillier, T. Heine, G. Seifert, *Semi-relativistic, self-consistent charge Slater-Koster tables for density-functional based tight-binding (DFTB) for materials science simulations*, TU-Dresden 2004-2009**

J. Frenzel, A. F. Oliveira, H. A. Duarte, T. Heine, G. Seifert, *Structural and electronic properties of bulk gibbsite and gibbsite surfaces*, *Z. Anorg. Allg. Chem.* 631, 1267-1271 (2005) (<https://doi.org/10.1002/chin.200529002>)

L. Guimaraes, A. N. Enyashin, J. Frenzel, T. Heine, H. A. Duarte, G. Seifert, *Imogolite Nanotubes: Stability, electronic and mechanical properties*, *Nano* 1, 362-368 (2007) (<https://doi.org/10.1021/nn700184k>)

R. Luschtinetz, A. F. Oliveira, J. Frenzel, J. Joswig, G. Seifert, H. A. Duarte, *Adsorption of phosphonic and ethylphosphonic acid on aluminum oxide surfaces*, *Surf. Sci.* 602, 1347-1359 (2008) (<https://doi.org/10.1016/j.susc.2008.01.035>)

R. Luschtinetz, J. Frenzel, T. Milek, G. Seifert *Adsorption of phosphonic acid at the TiO₂ anatase (101) and rutile (110) surface*, *J. Phys. Chem. C* 113, 5730-5740 (2009) (<https://doi.org/10.1021/jp8110343>)

DFTB.org Required citations for the various DFTB.org parameter sets can be found on the official DFTB webpage: [DFTB.org](http://www.dftb.org) (<http://www.dftb.org>).

REFERENCES

9.1 Slater-Koster based DFTB

9.1.1 General Description

D. Porezag, T. Frauenheim, T. Köhler, G. Seifert, R. Kaschner, *Construction of tight-binding-like potentials on the basis of density-functional theory: Application to carbon*, *Phys. Rev. B* **51**, 12947-12957 (1995) (<https://doi.org/10.1103/PhysRevB.51.12947>)

G. Seifert, D. Porezag, T. Frauenheim, *Calculations of molecules, clusters, and solids with a simplified LCAO-DFT-LDA scheme*, *Int. J. Quantum Chem.* **58**, 185-192 (1996) ([https://doi.org/10.1002/\(SICI\)1097-461X\(1996\)58:2%3C185::AID-QUA7%3E3.0.CO;2-U](https://doi.org/10.1002/(SICI)1097-461X(1996)58:2%3C185::AID-QUA7%3E3.0.CO;2-U))

M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai, and G. Seifert, *Self-consistent charge density functional tight-binding method for simulation of complex material properties*, *Physical Review B* **58**, 7260 (1998) (<http://link.aps.org/doi/10.1103/PhysRevB.58.7260>)

T. Frauenheim, G. Seifert, M. Elstner, Z. Hajnal, G. Jungnickel, D. Porezag, S. Suhai, and R. Scholz, *A self-consistent charge density-functional based tight-binding method for predictive materials simulations in physics, chemistry and biology*, *Physica Status Solidi (b)* **217**, 41 (2000) ([http://onlinelibrary.wiley.com/doi/10.1002/\(SICI\)1521-3951\(200001\)217:1%3C41::AID-PSSB41%3E3.0.CO;2-V/abstract](http://onlinelibrary.wiley.com/doi/10.1002/(SICI)1521-3951(200001)217:1%3C41::AID-PSSB41%3E3.0.CO;2-V/abstract))

M. Elstner, T. Frauenheim, E. Kaxiras, G. Seifert, and S. Suhai, *A self-consistent charge density-functional based tight-binding scheme for large biomolecules*, *Physica Status Solidi (b)* **217**, 357 (2000) ([http://onlinelibrary.wiley.com/doi/10.1002/\(SICI\)1521-3951\(200001\)217:1%3C357::AID-PSSB357%3E3.0.CO;2-J/abstract](http://onlinelibrary.wiley.com/doi/10.1002/(SICI)1521-3951(200001)217:1%3C357::AID-PSSB357%3E3.0.CO;2-J/abstract))

C. Koehler, G. Seifert, U. Gerstmann, M. Elstner, H. Overhof, and T. Frauenheim, *Approximate density-functional calculations of spin densities in large molecular systems and complex solids*, *Physical Chemistry Chemical Physics* **3**, 5109 (2001) (<http://www.rsc.org/publishing/journals/CP/article.asp?doi=b105782k>)

T. Frauenheim, G. Seifert, M. Elstner, T. Niehaus, C. Kohler, M. Armkreutz, M. Sternberg, Z. Hajnal, A. di Carlo, and S. Suhai, *Atomistic Simulations of complex materials: ground and excited state properties*, *Journal of Physics: Condensed Matter* **14**, 3015 (2002) (<http://www.iop.org/EJ/abstract/0953-8984/14/11/313>)

M. Gaus, Q. Cui, and M. Elstner, *DFTB3: Extension of the Self-Consistent-Charge Density-Functional Tight-Binding Method (SCC-DFTB)*, *Journal of Chemical Theory and Computation* **7**, 931 (2011) (<http://pubs.acs.org/doi/abs/10.1021/ct100684s>)

T. A. Niehaus, S. Suhai, F. Della Sala, P. Lugli, M. Elstner, G. Seifert, and Th. Frauenheim, *Tight-binding approach to time-dependent density-functional response theory*, *Phys. Rev. B* **63**, 085108 (2001) (<https://doi.org/10.1103/PhysRevB.63.085108>)

D. Heringer, T. A. Niehaus, M. Wanko, Th. Frauenheim *Analytical excited state forces for the time-dependent density-functional tight-binding method*, *J. Comput. Chem.*, **28**: 2589-2601 (<https://doi.org/10.1002/jcc.20697>)

9.1.2 Parameter sets

QUASINANO2013.1

The DFTB parameter files in \$ADFHOME/atomicdata/DFTB/QUASINANO2013.1 are distributed with the AMS package. These are parameters only for the electronic part of the DFTB method that covers almost the complete periodic table (no f-elements). No forces can be calculated. These parameters can be used in TDDFTB calculations, for example.

M. Wahiduzzaman, A.F. Oliveira, P.H.T. Philipsen, L. Zhechkov, E. van Lenthe, H.A. Witek, T. Heine, *DFTB Parameters for the Periodic Table: Part 1, Electronic Structure*, *Journal of Chemical Theory and Computation* 9, 4006 (2013) (<https://doi.org/10.1021/ct4004959>)

9.1.3 QUASINANO2015

The DFTB parameter files in \$ADFHOME/atomicdata/DFTB/QUASINANO2015 are distributed with the AMS package. The QUASINANO2015 parameter set extends the QUASINANO2013.1 parameter set, and includes terms that are needed to compute the total energy and its gradient.

A. F. Oliveira, P. Philipsen, T. Heine. *DFTB Parameters for the Periodic Table, Part 2: Energies and Energy Gradients from Hydrogen to Calcium*, *Journal of Chemical Theory and Computation* 11 (11), pp 5209–5218 (2015) (<https://doi.org/10.1021/acs.jctc.5b00702>)

9.1.4 Dresden

The DFTB parameter files in \$ADFHOME/atomicdata/DFTB/Dresden are distributed with the AMS package. For more detailed information, see also the README file in the directory \$ADFHOME/atomicdata/DFTB/Dresden.

General reference for the construction of all integral tables in \$ADFHOME/atomicdata/DFTB/Dresden: J. Frenzel, A. F. Oliveira, N. Jardillier, T. Heine, and G. Seifert, *Semi-relativistic, self-consistent charge Slater-Koster tables for density-functional based tight-binding (DFTB) for materials science simulations*, TU-Dresden 2004-2009.

For construction and application of integral tables for Al-O-H: J. Frenzel, A. F. Oliveira, H. A. Duarte, T. Heine, and G. Seifert, *Structural and electronic properties of bulk gibbsite and gibbsite, surfaces*, *Zeitschrift für Anorganische und Allgemeine Chemie* 631, 1267 (2005) (<https://doi.org/10.1002/zaac.200500051>)

For construction and application of integral tables for Al-Si-O-H: L. Guimares, A. N. Enyashin, J. Frenzel, T. Heine, H. A. Duarte, and G. Seifert, *Imogolite Nanotubes: Stability, electronic and mechanical properties*, *Nano* 1, 362 (2007) (<https://doi.org/10.1021/nn700184k>)

For construction and application of integral tables for Al-O-P-C-H: R. Luschtinetz, A. F. Oliveira, J. Frenzel, J. Joswig, G. Seifert, and H. A. Duarte, *Adsorption of phosphonic and ethylphosphonic acid on aluminum oxide surfaces*, *Surface Science* 602, 1347 (2008) (<https://doi.org/10.1016/j.susc.2008.01.035>)

For construction and application of integral tables for Ti-O-P-C-H: R. Luschtinetz, J. Frenzel, T. Milek, and G. Seifert, *Adsorption of phosphonic acid at the TiO₂ anatase (101) and rutile (110) surface*, *Journal of Physical Chemistry C* 113, 5730 (2009) (<https://doi.org/10.1021/jp8110343>)

9.1.5 DFTB.org

For detailed information please visit the official DFTB webpage: www.dftb.org (<http://www.dftb.org/parameters/>). Detailed references of each specific parameter set are available in the corresponding *metainfo.yaml* file.

9.2 Extended tight-binding (xTB)

S. Grimme, C. Bannwarth, P. Shushkov, *A Robust and Accurate Tight-Binding Quantum Chemical Method for Structures, Vibrational Frequencies, and Noncovalent Interactions of Large Molecular Systems Parametrized for All spd-Block Elements (Z = 1-86)*, *J. Chem. Theory Comput.*, 2017, 13 (5), pp 1989–2009 (<https://doi.org/10.1021/acs.jctc.7b00118>)

9.3 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.

KEYWORDS

10.1 Links to manual entries

- *DispersionCorrection* (page 8)
- *EnergyGrid* (page 31)
- *Files* (page 32)
- *KSpace* (page 13)
- *Model* (page 8)
- *Occupation* (page 12)
- *Periodic* (page 19)
- *Properties* (page 22)
- *ResourcesDir* (page 8)
- *SCC* (page 10)
- *Solvation* (page 9)
- *StoreMatrices* (page 17)
- *Technical* (page 15)
- *UnpairedElectrons* (page 12)
- *XTBConfig* (page 14)

10.2 Summary of all keywords

DispersionCorrection

Type Multiple Choice

Default value None

Options [None, Auto, UFF, ULG, D2, D3-BJ]

GUI name Dispersion

Description This key is used to specify an empirical dispersion model. Please refer to the DFTB documentation for details on the different methods. By default no dispersion correction will be applied. Setting this to auto applies the dispersion correction recommended in the DFTB parameter set's meta-info file. Note that the D3-BJ dispersion correction is always enabled when using the GFN1-xTB model Hamiltonian.

KSpace

Type Block

Description Options for the k-space integration (i.e. the grid used to sample the Brillouin zone). Note that k-space sampling calculations are currently not supported with the xTB model Hamiltonians.

Quality

Type Multiple Choice

Default value Normal

Options [GammaOnly, Basic, Normal, Good, VeryGood, Excellent]

GUI name K-space

Description Select the quality of the K-space grid used to sample the Brillouin Zone. If ‘GammaOnly’, only one point (the gamma point) will be used. For the other options, the actual number of K points generated depends on the size of the unit cell. The larger the real space cell, the fewer K points will be generated. The CPU-time and accuracy strongly depend on this option.

Regular

Type Block

Description Options for the regular k-space integration grid.

NumberOfPoints

Type Integer List

Description Use a regular grid with the specified number of k-points along each reciprocal lattice vector. For 1D periodic systems you should specify only one number, for 2D systems two numbers, and for 3D systems three numbers.

Symmetric

Type Block

Description Options for the symmetric k-space integration grid.

KInteg

Type Integer

GUI name Accuracy

Description Specify the accuracy for the Symmetric method. 1: absolutely minimal (only the G-point is used) 2: linear tetrahedron method, coarsest spacing 3: quadratic tetrahedron method, coarsest spacing 4,6,... (even): linear tetrahedron method 5,7,... (odd): quadratic method The tetrahedron method is usually by far inferior.

Type

Type Multiple Choice

Default value Regular

Options [Regular, Symmetric]

GUI name K-space grid type

Description The type of k-space integration grid used to sample the Brillouin zone (BZ) used. ‘Regular’: simple regular grid. ‘Symmetric’: symmetric grid for the irreducible wedge of the first BZ (useful when high-symmetry points in the BZ are needed to capture the correct physics of the system, graphene being a notable example).

Model

Type Multiple Choice

Default value SCC-DFTB

Options [DFTB, SCC-DFTB, DFTB3, GFN1-xTB, NonSCC-GFN1-xTB]

Description Selects the Hamiltonian used in the DFTB calculation: - DFTB/DFTB0/DFTB1 for classic DFTB without a self-consistent charge cycle - SCC-DFTB/DFTB2 with a self-consistency loop for the Mulliken charges - DFTB3 for additional third-order contributions. - GFN1-xTB for Grimme's extended tight-binding model in the GFN1 version. - NonSCC-GFN1-xTB for a less accurate but faster version of GFN1-xTB without a self-consistency cycle
The choice has to be supported by the selected parameter set.

Occupation

Type Block

Description Configures the details of how the molecular orbitals are occupied with electrons.

Strategy

Type Multiple Choice

Default value Auto

Options [Auto, Aufbau, Fermi]

GUI name Occupation

Description This optional key allows to specify the fill strategy to use for the molecular orbitals. Can either be 'Aufbau' for simply filling the energetically lowest orbitals, or 'Fermi' for a smeared out Fermi-Dirac occupation. By default the occupation strategy is determined automatically, based on the other settings (such as the number of unpaired electrons).

Temperature

Type Float

Default value 300.0

Unit Kelvin

GUI name Fermi temperature

Description The Fermi temperature used for the Fermi-Dirac distribution. Ignored in case of aufbau occupations.

Periodic

Type Block

Description Block that sets various details of the calculation only relevant for periodic systems.

BZPath

Type Block

Description If [BandStructure%Automatic] is disabled, DFTB will compute the band structure 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, you need to specify a new [Path] sub-block.

Path

Type Non-standard block

Recurring True

Description A section of a k space path.

BandStructure

Type Block

Description Options for band structure plotting. This has no effect on the calculated energy. [Warning: The band structure is only computed in case of k-space sampling, i.e. it is not computed for Gamma-only calculations (see: `Periodic%KSpace`).]

Automatic

Type Bool

Default value True

GUI name Automatic generate path

Description Generate and use the standard path through the Brillouin zone. If not, use the user defined path (set via Custom path in the GUI, or with the `Periodic%BZPath` keyword in the run script).

DeltaK

Type Float

Default value 0.1

Unit 1/Bohr

GUI name Interpolation delta-K

Description Step size in reciprocal space for band structure interpolation. Using a smaller number will produce smoother band curves at an increased computational time.

Enabled

Type Bool

Default value True

GUI name Calculate band structure

Description Whether or not to calculate the band structure.

FatBands

Type Bool

Default value True

GUI name Calculate fatbands

Description Control the computation of the fat bands (only when the bandstructure is calculated). The fat bands are the periodic equivalent of the Mulliken population analysis. The definition of the fat bands can be found in the Band Documentation.

UseSymmetry

Type Bool

Default value True

Description If set, only the irreducible wedge of the Wigner-Seitz cell is sampled. If not, the whole (inversion-unique) Wigner-Seitz cell is sampled.

DOS

Type Block

Description The subkeys of [DOS] allow to customize the calculation of the density of states.

EMax

Type Float

Default value 0.75

Unit Hartree

Description Upper end of the energy interval in which the density of states is calculated.

EMin

Type Float

Default value -0.75

Unit Hartree

Description Lower end of the energy interval in which the density of states is calculated.

Enabled

Type Bool

Default value True

GUI name Calculate DOS

Description Whether or not to calculate the DOS. Note that the DOS will always be calculated when also the band structure is calculated.

NSteps

Type Integer

Default value 300

Description The number of energy intervals between [EMin] and [EMax] for which the density of states is calculated.

EffectiveMass

Type Block

Description In a semi-conductor, the mobility of electrons and holes is related to the curvature of the bands at the top of the valence band and the bottom of the conduction band. With the effective mass option, this curvature is obtained by numerical differentiation. The estimation is done with the specified step size, and twice the specified step size, and both results are printed to give a hint on the accuracy. By far the most convenient way to use this key is without specifying any options.

Enabled

Type Bool

Default value False

Description In a semi-conductor, the mobility of electrons and holes is related to the curvature of the bands at the top of the valence band and the bottom of the conduction band. With the effective mass option, this curvature is obtained by numerical differentiation. The estimation is done with the specified step size, and twice the specified step size, and both results are printed to give a hint on the accuracy. By far the most convenient way to use this key is without specifying any options.

KPointCoord

Type Float List

Unit 1/Bohr

Recurring True

Description Coordinate of the k-points for which you would like to compute the effective mass.

NumAbove

Type Integer

Default value 1

Description Number of bands to take into account above the Fermi level.

NumBelow

Type Integer

Default value 1

Description Number of bands to take into account below the Fermi level.

StepSize

Type Float

Default value 0.001

Description Size of the step taken in reciprocal space to perform the numerical differentiation

Properties

Type Block

Description DFTB can calculate various properties of the simulated system. This block configures which properties will be calculated.

Excitations

Type Block

Description Contains all options related to the calculation of excited states, either as simple single orbital transitions or from a TD-DFTB calculation.

SingleOrbTrans

Type Block

Description The simplest approximation to the true excitations are the single orbital transitions (sometimes called Kohn-Sham transitions), that is transitions where a single electron is excited from an occupied Kohn-Sham orbital into a virtual orbital. The calculation of these transitions is configured in this section. Note that the SingleOrbTrans section is optional even though the single orbital transitions are also needed for TD-DFTB calculations. If the section is not present all single orbital transitions will still be calculated and used in a subsequent TD-DFTB calculation, but no output will be produced.

Enabled

Type Bool

Default value False

GUI name Single orbital transitions: Calculate

Description Calculate the single orbital transitions.

Filter

Type Block

Description This section allows to remove single orbital transitions based on certain criteria. All filters are disabled by default.

OSMin

Type Float

GUI name Minimum oscillator strength

Description Removes single orbital transitions with an oscillator strength smaller than this threshold. A typical value to start (if used at all) would be 1.0e-3.

dEMax

Type Float

Unit Hartree

Description Removes single orbital transitions with an orbital energy difference larger than this threshold.

dEMin

Type Float

Unit Hartree

Description Removes single orbital transitions with an orbital energy difference smaller than this threshold.

PrintLowest

Type Integer

Default value 10

Description The number of single orbital transitions that are printed to the screen and written to disk. If not a TD-DFTB calculation, the default is to print the 10 lowest single orbital transitions. In case of a TD-DFTB calculation it is assumed that the single orbital transitions are only used as an input for TD-DFTB and nothing will be printed unless PrintLowest is specified explicitly.

TDDFTB

Type Block

Description Calculations with time-dependent DFTB can be configured in the TDDFTB section and should in general give better results than the raw single orbital transitions. TD-DFTB calculates the excitations in the basis of the single orbital transitions, whose calculation is configured in the SingleOrbTrans section. Using a filter in SingleOrbTrans can therefore be used to reduce the size of the basis for TD-DFTB. One possible application of this is to accelerate the calculation of electronic absorption spectra by removing single orbital transitions with small oscillator strengths from the basis. Note that the entire TDDFTB section is optional. If no TDDFTB section is found, the behavior depends on the existence of the SingleOrbTrans section: If no SingleOrbTrans section is found (the Excitations section is completely empty then) a TD-DFTB calculation with default parameters will be performed. If only the SingleOrbTrans section is present no TD-DFTB calculation will be done.

Calc**Type** Multiple Choice**Default value** None**Options** [None, Singlet, Triplet]**GUI name** Type of excitations**Description** Specifies the multiplicity of the excitations to be calculated.**DavidsonConfig****Type** Block**Description** This section contains a number of keywords that can be used to override various internals of the Davidson eigensolver. The default values should generally be fine.**ATCharges****Type** Multiple Choice**Default value** Precalc**Options** [Precalc, OnTheFly]**GUI name** Transition charges**Description** Select whether the atomic transition charges are precalculated in advance or reevaluated during the iterations of the Davidson solver. Precalculating the charges will improve the performance, but requires additional storage. The default is to precalculate the atomic transition charges, but the precalculation may be disabled if not enough memory is available.**SafetyMargin****Type** Integer**Default value** 4**Description** The number of eigenvectors the Davidson method will calculate in addition to the ones requested by the user. With the Davidson eigensolver it is generally a good idea to calculate a few more eigenvectors than needed, as depending on the initial guess for the eigenvectors it can happen that the found ones are not exactly the lowest ones. This problem is especially prominent if one wants to calculate only a small number of excitations for a symmetric molecule, where the initial guesses for the eigenvectors might have the wrong symmetry. Note that the additionally calculated excitations will neither be written to the result file nor be visible in the output.**Tolerance****Type** Float**Default value** 1e-09**Description** Convergence criterion for the norm of the residual.**Diagonalization****Type** Multiple Choice**Default value** Auto**Options** [Auto, Davidson, Exact]**GUI name** Method

Description Select the method used to solve the TD-DFTB eigenvalue equation. The most straightforward procedure is a direct diagonalization of the matrix from which the excitation energies and oscillator strengths are obtained. Since the matrix grows quickly with system size (number of used single orbital transitions squared), this option is possible only for small molecules. The alternative is the iterative Davidson method, which finds a few of the lowest excitations within an error tolerance without ever storing the full matrix. The default is to make this decision automatically based on the system size and the requested number of excitations.

Lowest

Type Integer

Default value 10

GUI name Number of excitations

Description Specifies the number of excitations that are calculated. Note that in case of the exact diagonalization all excitations are calculated, but only the lowest ones are printed to screen and written to the output file. Also note that if limited both by number and by energy, (lowest and upto), DFTB will always use whatever results in the smaller number of calculated excitations.

Print

Type String

Description Specifies whether to print details on the contribution of the individual single orbital transitions to the calculated excitations.

ScaleKernel

Type Float

Default value 1.0

Unit None

Description Set the scaling parameter of the response kernel. A scaling approach can be used to identify plasmons in molecules. While single-particle excitations are only slightly affected by scaling of the response kernel, plasmonic excitations are sensitive to variations in the scaling parameter. Default no scaling is used (scaling parameter = 1.0)

UpTo

Type Float

Unit Hartree

GUI name Excitations up to

Description Set the maximum excitation energy. Attempts to calculate all excitations up to a given energy by calculating a number of excitations equal to the number of single orbital transitions in this window. This is only approximately correct, so one should always add some safety margin. Note that if limited both by number and by energy, (lowest and upto), DFTB will always use whatever results in the smaller number of calculated excitations.

TDDFTBGradients

Type Block

Description This block configures the calculation of analytical gradients for the TD-DFTB excitation energies, which allows the optimization of excited state geometries and the calculation of vibrational frequencies in excited states (see J. Comput. Chem., 28: 2589-

2601). If the gradients are calculated, they will automatically be used for geometry optimizations or vibrational frequency calculations, if the corresponding Task is selected and only 1 excitation is selected. Vibrationally resolved UV/Vis spectroscopy (Franck-Condon Factors) can be calculated in combination with the FCF program or using the Vibrational Analysis Tools in AMS. See the ADF documentation on Vibrationally resolved electronic spectra or the AMS documentation for the Vibrational Analysis Tools.

Eigenfollow

Type Bool

Default value False

GUI name Follow initial excitation

Description If this option is set, DFTB uses the transition density in atomic orbital basis to follow the initially selected excited state during a geometry optimization. This is useful if excited state potential energy surfaces cross each other and you want to follow the surface you started on.

Excitation

Type Integer List

GUI name Excitation number

Description Select which excited states to calculate the gradients for. Gradients can only be calculated for an excited states that has been calculated using TD-DFTB. Make sure that enough excitations are calculated.

NBOInput

Type Bool

Default value False

Description Whether or not an input file for the NBO program is written to disk as nboInput.FILE47. The input file follows the FILE47 format as described in the NBO6 manual available on nbo6.chem.wisc.edu. By default, only the calculation of the natural bond orbitals and the natural localized molecular orbitals is enabled, but the nboInput.FILE47 file can be edited by hand to enable other analysis models. Please refer to the NBO6 manual for details.

VCD

Type Bool

Default value False

GUI name Calculate VCD intensities

Description Calculate the VCD spectrum after calculating the IR spectrum. Note: symmetry must be set to NOSYM.

Repulsion

Type Block

Description Configures various details of the repulsive potential.

ResourcesDir

Type String

Description The directory containing the parameter files. Absolute starting with / or relative to \$ADFRESOURCES/DFTB otherwise. This key is required for the Slater-Koster based DFTB models, but optional for xTB.

SCC

Type Block

Description This optional section configures various details of the self-consistent charge cycle. If the model Hamiltonian does not need a self-consistent solution (e.g. plain DFTB0), none of this information is used and the entire section will be ignored.

AdaptiveMixing

Type Bool

Default value True

Description Change the mixing parameter based on the monitored energy. A significant increase of energy will strongly reduce the mixing. Then it will slowly grow back to the SCC%Mixing value.

Converge

Type Block

Description Controls the convergence criteria of the SCC cycle.

Charge

Type Float

Default value 1e-08

GUI name Charge convergence

Description The maximum change in atomic charges between subsequent SCC iterations. If the charges change less, the SCC cycle is considered converged.

HXDamping

Type Bool

Description This option activates the DFTB3 style damping for H-X bonds. Note that this is always enabled if the DFTB%Model key is set to DFTB3. Not used with xTB.

Iterations

Type Integer

Default value 500

Description Allows to specify the maximum number of SCC iterations. The default should suffice for most standard calculations. Convergence issues may arise due to the use of the Aufbau occupations for systems with small HOMO-LUMO gaps. In this case the use of a Fermi broadening strategy may improve convergence. Choosing a smaller mixing parameter (see DFTB%SCC%Mixing) may also help with convergence issues: it often provides a more stable but slower way to converge the SCC cycle.

Mixing

Type Float

Default value 0.15

Description The parameter used to mix the DIIS linear combination of previously sampled atomic charge vectors with an analogous linear combination of charge vectors resulting from population analysis combination. It can assume real values between 0 and 1.

OrbitalDependent

Type Bool

Description Activates or disables orbital resolved calculations. If this key is absent the recommended settings from the parameter file's metainfo.

Unrestricted

Type Bool

Default value False

Description Enables spin unrestricted calculations. Only collinear spin polarization is supported, see Theor Chem Acc (2016) 135: 232, for details. Must be supported by the chosen parameter set. Not yet compatible with DFTB3, k-space sampling periodic calculations or the xTB models.

nDIIS

Type Integer

Default value 20

Description Specifies the maximum number of samples considered during the direct inversion of iteration of subspace (DIIS) extrapolation of the atomic charges during the SCC iterations. A smaller number of samples potentially leads to a more aggressive convergence acceleration, while a larger number often guarantees a more stable iteration. Due to often occurring linear dependencies within the set of sample vectors, the maximum number of samples is reached only in very rare cases.

Solvation

Type Block

Description Generalized Born solvation model with Solvent Accessible Surface Area (GBSA).

GSolvState

Type Multiple Choice

Default value Gas1MSolvent1M

Options [Gas1BarSolvent, Gas1MSolvent1M, Gas1BarSolvent1M]

Description Reference state for solvation free energy shift.

Solvent

Type Multiple Choice

Default value None

Options [None, Acetone, Acetonitrile, CHCl₃, CS₂, DMSO, Ether, H₂O, Methanol, THF, Toluene]

Description Solvent used in the GBSA implicit solvation model.

SurfaceGrid

Type Multiple Choice

Default value 230

Options [230, 974, 2030, 5810]

Description Number of angular grid points for the construction of the solvent accessible surface area. Usually the default number of grid point suffices, but in case of suspicious behaviors you can increase the number of points.

Temperature

Type Float

Default value 298.15

Unit Kelvin

Description The temperature used when calculating the solvation free energy shift. Only used for 'Gas1BarSolvent' and 'Gas1BarSolvent1M' GSolvState options.

UseGSASA

Type Bool

Default value True

GUI name Solvation Free Energy

Description Include shift term and G(SASA) terms in the energy and gradient.

StoreMatrices

Type Bool

Default value False

Description Determines whether the Hamiltonian and overlap matrices are stored in the binary result file.

Technical

Type Block

Description This optional section is about technical aspects of the program that should not concern the normal user.

AnalyticalStressTensor

Type Bool

Default value True

Description Whether to compute the stress tensor analytically. Note: This can only be used together with Ewald summation as it will give (slightly) wrong results with Madelung screening.

EwaldSummation

Type Block

Description Configures the details of the Ewald summation of the Coulomb interaction.

CellRangeFactor

Type Float

Default value 2.0

Description Smaller values will make the Ewald summation less accurate but faster.

Enabled

Type Bool

Default value True

Description Whether to use Ewald summation for the long-range part of the Coulomb interaction. Otherwise screening is used.

Tolerance

Type Float

Default value 1e-10

Description Larger values will make the Ewald summation less accurate but faster.

Parallel

Type Block

Description Calculation of the orbitals in several k-points is trivially 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.

ReuseKSpaceConfig

Type Bool

Default value True

Description Keep the number of k-points constant during a lattice optimization. Otherwise the PES might display jumps, because the number of points depends on the lattice vector sizes. If this option is on it will always use the number of k-points that was used from a previous result.

Screening

Type Block

Description For SCC-DFTB in periodic systems the Coulomb interaction can (instead of using Ewald summation) be screened with a Fermi-Dirac like function defined as $S(r)=1/(\exp((r-r_{\text{madel}})/d_{\text{madel}})+1)$. This section allows to change some details of the screening procedure. Note that Coulomb screening is only used if the Ewald summation is disabled.

dMadel

Type Float

Unit Bohr

Description Sets the smoothness of the screening function. The default is 1/10 of [rMadel].

rMadel

Type Float

Unit Bohr

Description Sets the range of the screening function. The default is 2x the norm of the longest lattice vector.

UseGeneralizedDiagonalization

Type Bool

Default value True

Description Whether or not to use generalized diagonalization. Does not affect the results, but might be faster or slower.

UnpairedElectrons

Type Integer

Default value 0

GUI name Spin polarization

Description This specifies the number of unpaired electrons (not the multiplicity!). This number will then be used in the orbital-filling strategy. Has to be compatible with the total number of electrons, meaning it must be an even number if the total number of electrons is even and odd if the total number is odd. Must be an integer value. Note that this does not activate spin polarization, it only affects the filling of the orbitals.

XTBConfig

Type Block

Description This block allows for minor tweaking.

SlaterRadialThreshold

Type Float

Default value 1e-05

Description Threshold determining the range of the basis functions. Using a larger threshold will speed up the calculation, but will also make the results less accurate.

useXBTerm

Type Bool

Default value False

Description Whether to use the Halogen bonding (XB) term. This is not advised as it has a non-continuous PES.

A

AMS, 3
Atoms, 5

B

Band structure, 19
Bulk modulus, 27

C

Charge, 5
Coordinates, 5

D

Dispersion correction, 8

E

Elastic tensor, 27
Electronic transport, 28
Entropy, 27

F

Fat bands, 19
Free energy, 27
Frequencies, 27

G

GBSA, 9
Geometry, 5
Geometry optimization, 5
Geometry relaxation, 5
GFN-xTB, 7

H

Hessian, 27

I

Internal energy, 27

K

k-space integration, 13

L

Lattice vectors, 5
Linear transit, 5

M

Molecular dynamics, 5

N

NEGF, 28
Normal modes, 27
Nuclear gradients, 6

P

PES, 3
PES scan, 5
Phonons, 27
Potential energy surface, 3

S

Shear modulus, 27
Single point calculation, 5
Slater-Koster based DFTB, 7
Solvation model, 9
Specific heat, 27
Stress tensor, 6
Structure relaxation, 5

T

Task, 3
Thermodynamic properties, 27
Transition state search, 5

X

xTB, 7

Y

Young modulus, 27

Z

Zero-point energy, 27