DFTB Manual

Amsterdam Modeling Suite 2019

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Apr 18, 2019

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GENERAL

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?

- Grimme's GFN1-xTB has been added as a new *model Hamiltonian* (page 7). It supports molecular as well es 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 11).

- More robust SCC convergence:

  - *Adaptive mixing* (page 9): 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

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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 Input keywords

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 64).

```
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 63).

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

DispersionCorrection

>**Type** Multiple Choice
>
>**Default value** None
>
>**Options** [None, Auto, UFF, ULG, D2, D3-BJ]
>
>**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.

3.3.1 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
>   >
>   >   **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]
>
> **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
>
> **Description** The Fermi temperature used for the Fermi-Dirac distribution. Ignored in case of aufbau occupations.

```
UnpairedElectrons integer
```

UnpairedElectrons

> **Type** Integer
>
> **Default value** 0
>
> **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.

3.3.2 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. See the page on k-space integration in the BAND manual for details and recommendations. Note however, that the default for DFTB is to **only sample the Gamma-point**, i.e. k-space sampling must be explicitly enabled if desired.

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)
>
> **Quality**
>
> > **Type** Multiple Choice
> >
> > **Default value** GammaOnly

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

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

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]

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).

3.3.3 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.

3.3.4 Technical options

```
Purify
   Enabled [True | False]
   Iterations integer
   Tolerance float
End
```

Purify

>> **Type** Block

>> **Description** By default (when the DFTB%Purify section is not present), the next step's density matrix is calculated from molecular orbitals obtained as eigenvectors of the charge-dependent Hamiltonian. An alternative way to obtain the density matrix is using an iterative purification procedure enabled by this keyword. Note also that molecular orbitals are not calculated when using the density matrix purification method, meaning that any subsequent calculations using molecular orbitals (e.g. TD-DFTB or Mayer bond order analysis) are incompatible with this keyword. Density matrix purification can be considerably faster than diagonalization for molecular of gamma-only periodic systems with large HOMO-LUMO gaps. Note that density matrix purification is faster for systems where the density matrix is sparse. The fill-in of the density matrix is printed to the standard output during the calculation. If it is too large (e.g. >50%), it is probably faster to use normal diagonalization.

Enabled

>> **Type** Bool

>> **Default value** False

>> **Description** By default (when purification is not used), the next step's density matrix is calculated from molecular orbitals obtained as eigenvectors of the charge-dependent Hamiltonian. An alternative way to obtain the density matrix is using an iterative purification procedure. Note that molecular orbitals are not calculated when using the density matrix purification method, meaning that any subsequent calculations using molecular orbitals (e.g. TD-DFTB

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or Mayer bond order analysis) are incompatible with this keyword. Density matrix purification can be considerably faster than diagonalization for molecular of gamma-only periodic systems with large HOMO-LUMO gaps. Density matrix purification is faster for systems where the density matrix is sparse. The fill-in of the density matrix is printed to the standard output during the calculation. If it is too large (e.g. >50%), it is probably faster to use normal diagonalization.

Iterations

> **Type** Integer
>
> **Default value** 50
>
> **Description** Set the maximum number of steps in the purification cycle. If the desired tolerance is not reached by then, the calculation is aborted.

Tolerance

> **Type** Float
>
> **Default value** 1e-08
>
> **Description** Set the purification convergence threshold. Purification is considered converged when the trace of the density matrix becomes equal to the total number of electrons within the specified tolerance.

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

StoreMatrices

> **Type** Bool
>
> **Default value** False
>
> **Description** Determines whether the Hamiltonian and overlap matrices are stored in the binary result file.

ADDITIONAL PERIODICITY DATA

```
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
      NSteps integer
   End
   Screening
      dMadel float
      rMadel float
   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

> **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
>
> **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
>
> **Description** Whether or not to calculate the band structure.

FatBands

> **Type** Bool
>
> **Default value** True
>
> **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.

NSteps

Type Integer

Default value 300

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

Screening

Type Block

Description For SCC-DFTB in periodic systems the Coulomb interaction is screened with a Fermi-Dirac like function defined as TODO S(r)=1/(exp((r-r_madel)/d_madel)+1). Screening is always enable, even if this section is absent. This section allows to change some details of the screening procedure.

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.

SPECTROSCOPY AND PROPERTIES

5.1 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
      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
>
> **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
>
> **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]
>
> **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]
>
> **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 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]
>
> **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
>
> **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
>
> **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. Vibrationally resolved UV/Vis spectroscopy (Franck-Condon Factors) can be calculated in combination with the FCF program. See the ADF documentation on Vibrationally resolved electronic spectra.

Eigenfollow

> **Type** Bool
>
> **Default value** False
>
> **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
>
> **Description** Select which excited state 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.

5.2 System properties

DFTB can calculate various properties of the simulated system.

```
Properties
   DipoleMoment [True | False]
   BondOrders [True | False]
   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.

DipoleMoment

Type Bool

Default value True

Description Whether of not the electric dipole moment is calculated from the calculated Mulliken charges. While it is technically possible to calculate the dipole moment with the DFTB0 model, it is not recommended and the SCC-DFTB or DFTB3 model should be used instead. For periodic systems the dipole moment is ill-defined and should not be interpreted.

BondOrders

Type Bool

Default value False

Description Whether or not Mayer bond orders are calculated based on the final molecular orbitals.

NBOInput

Type Bool

Default value False

Description Whether or not an input file for the NBO program is written to disk as nboInput.FILE74. 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

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

5.3 Frequencies, phonons and elastic tensor

Frequencies and phonons and 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.
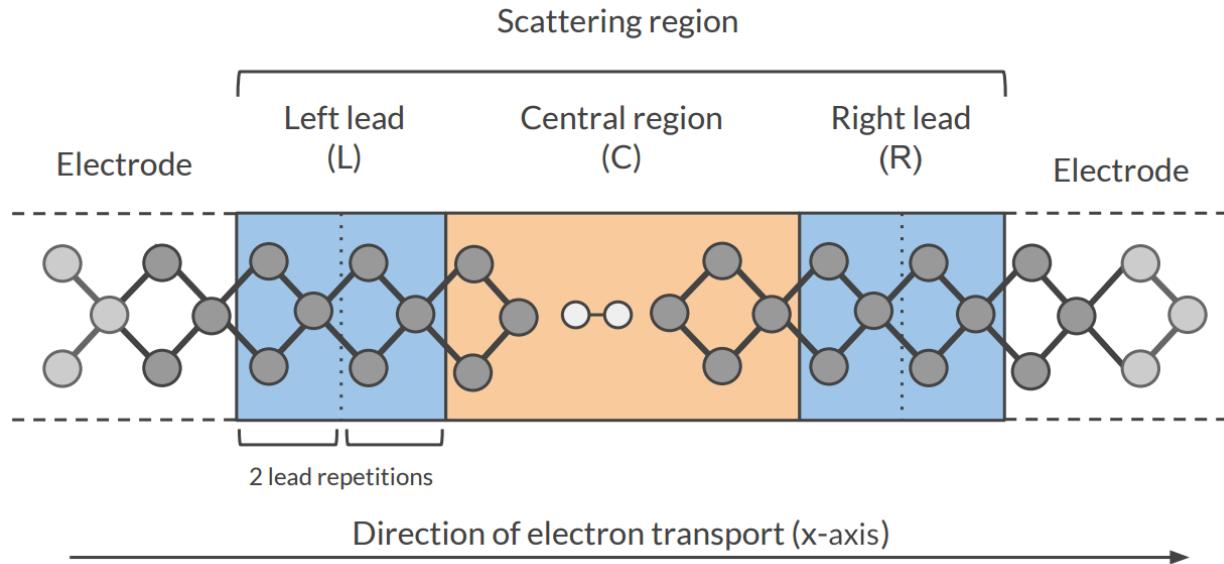
ELECTRONIC TRANSPORT (NEGF)

See also:

- DFTB-NEGF GUI tutorial

- *Example: Electronic transport with NEGF* (page 41)

6.1 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:

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

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) of Mahdi Ghorbani-Asl (DFTB-NEGF developer)

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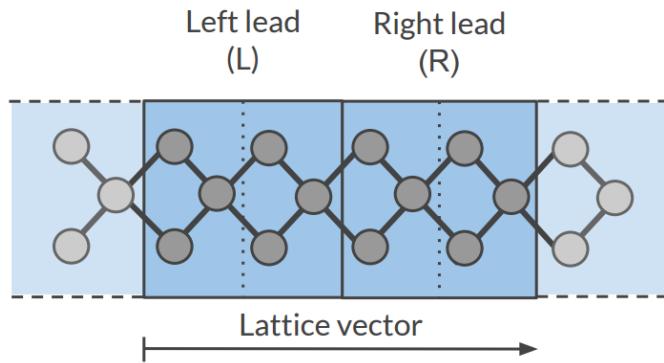
The computation of the transmission function $T(E)$ within the DFTB-NEGF formalisms requires three individual simulations.

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

---
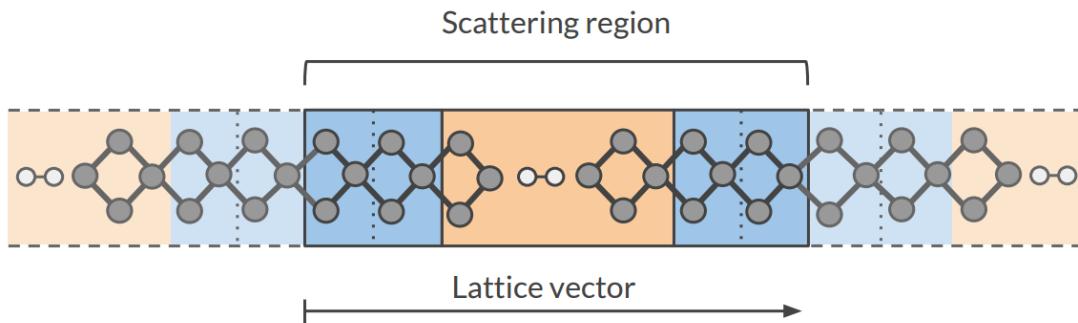
1): DFTB leads calculation A 1D-periodic DFTB calculation of the leads (*StoreMatrices* (page 14): yes, *KSpace* (page 11) sampling 13):

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 a 1D-periodic DFTB calculation of the scattering region (*StoreMatrices* (page 14): yes, gamma-only, *i.e.*, no *KSpace* (page 11) 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.

6.3 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

6.4 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.

7.1 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
```

7.2 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
```

7.3 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
```

```
          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
```

7.4 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"
```

7.5 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
```

7.6 Example: Electronic transport with NEGF

Download conductance.run

```sh
#!/bin/sh

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

# Lead:
# =====

AMS_JOBNAME=Al_lead NSCM=1 $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 NSCM=1 $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"
```

7.7 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
      Pressure $P
      Convergence Gradients=1.0e-5
   End

   NumericalDifferentiation
      # Parallelize the calculation of the strain displacements, necessary for
      # numerically calculating the stress tensor during the lattice optimization.
      Parallel nGroups=2
   End
```

```
    Properties
        # Request the calculation of phonons at the optimized geometry.
        Phonons Yes
    End

    NumericalPhonons
        Parallel nGroups=2
        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
    EndEngine

EOF
done
```

7.8 Example: Elastic tensor

Download ElasticTensor.run

```
#! /bin/sh


# === Diamond ===

AMS_JOBNAME=Diamond $ADFBIN/ams << EOF

    Task GeometryOptimization

    Properties
        ElasticTensor Yes
    End

    # Maximum possible parallelism at the driver level
    NumericalDifferentiation
        Parallel nCoresPerGroup=1
    End
    ElasticTensor
        Parallel nCoresPerGroup=1
    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-4
      End

      Engine DFTB
           Model DFTB
           ResourcesDir DFTB.org/mio-1-1
           KSpace
                Type Symmetric
                Symmetric KInteg=3
           End
      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

   # Maximum possible parallelism at the driver level
   NumericalDifferentiation
        Parallel nCoresPerGroup=1
   End
   ElasticTensor
        Parallel nCoresPerGroup=1
   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
   End

   Engine DFTB
      ResourcesDir DFTB.org/matsci-0-3
   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
      Parallel nCoresPerGroup=1
   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

   Engine DFTB
      ResourcesDir DFTB.org/3ob-3-1
      KSpace
          Type Symmetric
          Symmetric KInteg=5
      End
   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"
```

7.9 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
EndEngine

eor
```

7.10 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


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
```

7.11 Example: Geometry optimization following a specific excited state

Download GO_LR-TDDFTB_CO_eigenfollow.run

```sh
#!/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

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

EndEngine

Log
   Info TDDFTBExcitationFollowerModule
End

eor
```

7.12 Example: Fullerene excitations

Download SP_LR-TDDFTB_fullerene.run

```
#!/bin/sh

AMS_JOBNAME=SOTonly $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
```

7.13 Example: Band structure with user-defined BZ path

Download Li_BZPlot.run

```
#! /bin/sh

export NSCM=1

# 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
        NStar 5
        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
      NStar 5
      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"
```

7.14 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

8.1 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 QUASI-NANO 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. Howver, 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. Philipsen, 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.

8.2 Slater-Koster based DFTB

The most popular parameter sets for Slater-Koster based DFTB are *distributed with the AMS package* (page 64). Other parameter sets can easily be *added* (page 65).

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.

8.2.1 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 chrisotyle nanotubes

- miomod-hh: contains a modified parameter set for H2

- miomod-nh: contains a modified parameter set fo 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) 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 72) 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 72) 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 72). These parameter files are kept in the directory $ADFHOME/atomicdata/DFTB/Dresden.

8.2.2 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 64) 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 66), the *metainfo.yaml file* (page 63) and the optionally some *additional .yaml files* (page 66) as well as *binary .rkf files containing the basis functions* (page 67).

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 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) of the Slater-Koster file format can be found at DFTB.org (http://www.dftb.org).

Additional .yaml files

The Slater-Koster file format (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 is 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.

8.3 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.

9.1 General references

For calculations with the Density Functional Tight Binding (DFTB) engine: AMS DFTB 2019, 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. Philipsen, S. Borini, P. Melix, A. F. Oliveira, M. Franchini, 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)

9.2 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. 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)

QUASINANO2013.1 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)

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).

REFERENCES

10.1 Slater-Koster based DFTB

10.1.1 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)

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)

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)

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)

10.1.2 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)

10.1.3 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)

10.1.4 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 fr 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)

10.1.5 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.

10.2 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)

10.3 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

11.1 Links to manual entries

11.2 Summary of all keywords

DispersionCorrection

> **Type** Multiple Choice
>
> **Default value** None
>
> **Options** [None, Auto, UFF, ULG, D2, D3-BJ]
>
> **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.

KSpace

> **Type** Block
>
> **Description** Options for the k-space integration (i.e. the grid used to sample the Brillouin zone)

> **Quality**
>
> > **Type** Multiple Choice

Default value GammaOnly

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

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

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]

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]
>>
>> **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
>>
>> **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

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
>
> **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
>
> **Description** Whether or not to calculate the band structure.

FatBands

> **Type** Bool
>
> **Default value** True
>
> **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.

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

Screening

>   **Type** Block
>
>   **Description** For SCC-DFTB in periodic systems the Coulomb interaction is screened with a Fermi-Dirac like function defined as TODO S(r)=1/(exp((r-r_madel)/d_madel)+1). Screening is always enable, even if this section is absent. This section allows to change some details of the screening procedure.

>   **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.

Properties

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

>   **BondOrders**
>
>>   **Type** Bool
>>
>>   **Default value** False
>>
>>   **Description** Whether or not Mayer bond orders are calculated based on the final molecular orbitals.

>   **DipoleMoment**
>
>>   **Type** Bool
>>
>>   **Default value** True
>>
>>   **Description** Whether of not the electric dipole moment is calculated from the calculated Mulliken charges. While it is technically possible to calculate the dipole moment with the DFTB0 model, it is not recommended and the SCC-DFTB or DFTB3 model should be used instead. For periodic systems the dipole moment is ill-defined and should not be interpreted.

>   **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
>
> **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
> >
> > **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]
>
> **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]
>
> **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 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]

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

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

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 cal-
culation 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 op-
timizations or vibrational frequency calculations, if the corresponding Task is selected.
Vibrationally resolved UV/Vis spectroscopy (Franck-Condon Factors) can be calculated in
combination with the FCF program. See the ADF documentation on Vibrationally resolved
electronic spectra.

Eigenfollow

> **Type** Bool

> **Default value** False

> **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

> **Description** Select which excited state 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 nboIn-
> put.FILE74. 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 or-
> bitals 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

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

Purify

> **Type** Block

> **Description** By default (when the DFTB%Purify section is not present), the next step's density
> matrix is calculated from molecular orbitals obtained as eigenvectors of the charge-dependent
> Hamiltonian. An alternative way to obtain the density matrix is using an iterative purification
> procedure enabled by this keyword. Note also that molecular orbitals are not calculated when
> using the density matrix purification method, meaning that any subsequent calculations using
> molecular orbitals (e.g. TD-DFTB or Mayer bond order analysis) are incompatible with this
> keyword. Density matrix purification can be considerably faster than diagonalization for molec-
> ular of gamma-only periodic systems with large HOMO-LUMO gaps. Note that density matrix
> purification is faster for systems where the density matrix is sparse. The fill-in of the density

matrix is printed to the standard output during the calculation. If it is too large (e.g. >50%), it is probably faster to use normal diagonalization.

Enabled

> **Type** Bool
>
> **Default value** False
>
> **Description** By default (when purification is not used), the next step's density matrix is calculated from molecular orbitals obtained as eigenvectors of the charge-dependent Hamiltonian. An alternative way to obtain the density matrix is using an iterative purification procedure. Note that molecular orbitals are not calculated when using the density matrix purification method, meaning that any subsequent calculations using molecular orbitals (e.g. TD-DFTB or Mayer bond order analysis) are incompatible with this keyword. Density matrix purification can be considerably faster than diagonalization for molecular of gamma-only periodic systems with large HOMO-LUMO gaps. Density matrix purification is faster for systems where the density matrix is sparse. The fill-in of the density matrix is printed to the standard output during the calculation. If it is too large (e.g. >50%), it is probably faster to use normal diagonalization.

Iterations

> **Type** Integer
>
> **Default value** 50
>
> **Description** Set the maximum number of steps in the purification cycle. If the desired tolerance is not reached by then, the calculation is aborted.

Tolerance

> **Type** Float
>
> **Default value** 1e-08
>
> **Description** Set the purification convergence threshold. Purification is considered converged when the trace of the density matrix becomes equal to the total number of electrons within the specified tolerance.

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 False

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

AdaptiveMixingStrategy

Type Integer

Default value 1

Description Currently there are three flavors, 1, 2, and 3. The first is the most conservative. The difference between 2 and 3 is that number 3 decreases the mixing when the energy seems to go up.

Converge

Type Block

Description Controls the convergence criteria of the SCC cycle.

Charge

Type Float

Default value 1e-08

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.

StoreMatrices

    Type Bool

    Default value False

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

UnpairedElectrons

    Type Integer

    Default value 0

    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 accurate.

useXBTerm

    Type Bool

    Default value False

Description Whether to use the Halogen bonding (XB) term. This is not advised at it has a non-continuous PES. Only useful for comparing against the article.