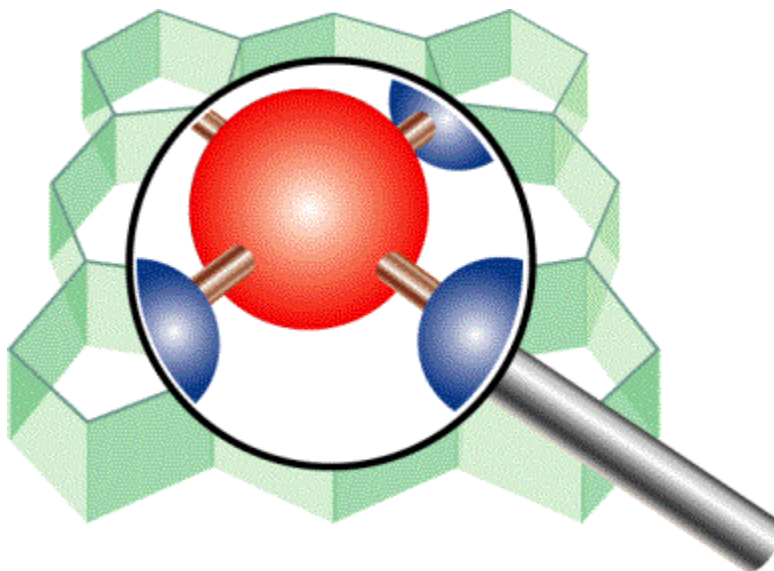Scientific Computing & Modelling

DFTB Manual

ADF Program System
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Manual for the Density Functional Tight Binding (DFTB) program.
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Introduction

The DFTB program is orders of magnitude faster than DFT, but requires parameter files to be installed for all pair-wise combinations of atoms in a molecule. Unfortunately, parameters are not available for some elements, but calculations for many common molecules should be possible.

The ADF package contains an implementation of the DFTB method. It can be used to perform single point calculations, geometry optimizations, transition state searches, and frequency calculations. It can be used as a stand-alone program, or as a pre-optimizer with the ADF-GUI.

To use DFTB you need parameter files. Only one set of parameter files is available within the ADF package. To use other sets of parameter files you will need to download them yourself.

Input

The input for DFTB is similar to ADF, but not exactly the same. At this point, it is possible to perform single point, geometry optimization, transition state search, and frequency calculations. Results are written to standard output and to a keyed-file DFTB.kf.

Parameter files

The set of DFTB parameter files available in the ADF 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. These parameter files are kept in the directory $ADFHOME/atomicdata/DFTB/Dresden.

You can also use a different set of parameter files. Note that different sets of parameter files are often not compatible. Note also that often parameter files were designed for a specific purpose, which may be different than your application, and therefore may give not the desired accuracy. An important place to find parameter files is the DFTB.org web site, where you can request parameter files. After downloading you should put these files in the directory $ADFHOME/atomicdata/DFTB/resourcesDir. The name of the directory resourcesDir can be specified with the key RESOURCESDIR.

```
RESOURCESDIR DirName
```

`DirName`

> The name of the directory where the DFTB parameter files are kept. This directory should be a directory within the directory $ADFHOME/atomicdata/DFTB. The default directory name is Dresden. Thus by default the DFTB parameter files in $ADFHOME/atomicdata/DFTB/Dresden will be used.

The DFTB naming scheme for parameter files should be the same as the scheme used in the DFTB+ code. That is, the (mixed-case) name of each atom, separated by a hyphen, and including the extension 'skf' (Eg. C-Co.skf)

Atomic coordinates

The input of (initial) atomic positions as Cartesian coordinates can be given with the key ATOMS.

```
ATOMS
 Atom Coords
 ...
End
```

`Atom`

> The name of an *atom type*. It must be the standard one- or two-character symbol for the chemical element: H, He, Li, and so on.

`Coords`

> This specifies the coordinates of the atom. The x, y, z values of the Cartesian coordinates must be given in Angstrom.

Net Charge

The net charge of the molecule can be controlled with the key CHARGE.

```
CHARGE NetQ
```

NetQ

The net total charge of the molecule. If the key CHARGE is omitted the net total charge of the molecule is zero.

SCF

The SCF procedure is regulated with a key that sets the convergence criterion.

```
SCF
 Converge SCFcnv
End
```

SCFcnv

The criterion to stop the SCF updates. The default is 1e-10.

Runtype

With the block key GEOMETRY you define the runtype and strategy parameters.

```
GEOMETRY
 {RunType      RunTypeData}
 {Optim        Cartesian|Delocal}
 {Iterations   Niter}
 {Converge     {E=TolE} {Grad=TolG} {Rad=TolR}}
 {Step         {TrustRadius=MaxRadius}}
End
```

RunType

RunTypeData

Can be:
- SinglePoint or SP
- GeometryOptimization or GO
- TransitionState or TS
- Frequencies or F
If omitted the run type is GeometryOptimization.
If the key GEOMETRY is not used at all the run type is SinglePoint.

Optim

Cartesian|Delocal

Optimization in delocalized coordinates (Delocal) can only be used in geometry optimizations or transition state searches.

```
Iterations

    Niter
```

The maximum number of geometry iterations allowed to locate the desired structure. The default is 50.
This is a fairly large number. If the geometry has not converged (at least to a reasonable extent) within that many iterations you should sit down and consider the underlying cause rather than simply increase the allowed number of cycles and try again.

```
Converge
```

Convergence is monitored for two items: the energy and the Cartesian gradients. Convergence criteria can be specified separately for each of these items:

```
    TolE
```

The criterion for changes in the energy, in Hartrees. Default: 1e-5.

```
    TolG
```

Applies to gradients, in Hartree/angstrom. Default: 1e-3.

```
    TolR
```

The maximum Cartesian step allowed for a converged geometry. Default: 0.001 Angstrom.

```
Step
```

Controls that changes in geometry from one cycle to another are not too large:

```
    MaxRadius
```

By default, the trust radius is set to 0.2. Using the key, the user can override this, setting a constant value. A conservative value is 0.2. A large system (eg 100 atoms) typically needs a larger trust radius (eg 0.8).

Examples

Examples of DFTB calculations can be found in the $ADFHOME/examples/dftb directory. Here is a run script for one such example:

```
$ADFBIN/dftb << eor

ResourcesDir Dresden

Geometry
  RunType GO
  Optim Delocal
  Converge Grad=0.0001
End

Atoms
    C        0.000000  0.000000  0.000000
    C        1.402231  0.000000  0.000000
    C        2.091015  1.220378  0.000000
    C        1.373539  2.425321  0.004387
    C       -0.034554  2.451759  0.016301
    C       -0.711248  1.213529  0.005497
    O       -0.709522  3.637718  0.019949
    C       -2.141910  1.166077 -0.004384
    O       -2.727881  2.161939 -0.690916
    C       -0.730162  4.530447  1.037168
    C       -0.066705  4.031914  2.307663
    H       -0.531323 -0.967191 -0.007490
    H        1.959047 -0.952181 -0.004252
    H        3.194073  1.231720 -0.005862
    H        1.933090  3.376356 -0.002746
    O       -2.795018  0.309504  0.548870
    H       -2.174822  2.832497 -1.125018
    O       -1.263773  5.613383  0.944221
    H       -0.337334  4.693941  3.161150
    H        1.041646  4.053111  2.214199
    H       -0.405932  3.005321  2.572927
End

eor
```

References

DFTB: general description

M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai, G. Seifert, *Self-consistent charge density functional tight-binding method for simulation of complex material properties.* Physical Review B **58**, 7260 (1998)

Th. Frauenheim, G. Seifert, M. Elstner, Z. Hajnal, G. Jungnickel, D. Porezag, S. Suhai, 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)

M. Elstner, Th. Frauenheim, E. Kaxiras, G. Seifert, S. Suhai, *A self-consistent charge density-functional based tight-binding scheme for large biomolecules.* Physica Status Solidi (b) **217**, 357 (2000)

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)

T. Frauenheim, G. Seifert, M. Elstner, T. Niehaus, C. Kohler, M. Armkreutz, M. Sternberg, Z. Hajnal, A. di Carlo, S. Suhai, *Atomistic Simulations of complex materials: ground and excited state properties.* Journal of Physics: Condensed Matter **14**, 3015 (2002)

DFTB: elements

Dresden

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

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

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

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

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)

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)

DFTB.org

The parameter files that can be requested at the DFTB.org web site, are not part of the ADF distribution. Some references are given below, but for more detailed information see the DFTB.org web site.

For construction of integral tables for O, N, C, H:
M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai, G. Seifert, *Self-consistent charge density functional tight-binding method for simulation of complex material properties.* Physical Review B **58**, 7260 (1998)

T. Niehaus, M. Elstner, T. Frauenheim, S. Suhai, *Application of an approximate density functional method to sulfur containing compounds.* Journal of Molecular Structure (THEOCHEM) **541**, 185 (2001)

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Keywords

ATOMS 4

GEOMETRY 5

SCF 5

CHARGE 5

RESOURCESDIR 4