
# BAND Manual

## *ADF Modeling Suite 2016*

**www.scm.com**

November 18, 2016

CHAPTER

ONE

# GENERAL

## 1.1 Introduction

Amsterdam Density Functional Band-structure program (BAND) can be used for calculations on periodic systems, i.e. polymers, slabs and crystals, and is supplemental to the molecular ADF program for non-periodic systems. It employs density functional theory in the Kohn-Sham approach. BAND is very similar to ADF in the chosen algorithms, although important differences remain. Like ADF, BAND makes use of atomic orbitals, it can handle elements throughout the periodic table, and has several analysis options available. Unlike ADF, BAND can use numerical atomic orbitals, so that the core is described very accurately. Because of the numerical orbitals BAND can calculate accurate total energies. Furthermore it can handle basis functions for arbitrary l-values.

The installation of BAND is explained in the Installation manual. There you can also find information about the license file that you need to run the program.

This User's Guide describes how to use the program, how input is structured, what files are produced, and so on. The Examples section explains the most popular features in detail, by commenting on the input and output files in the $ADFHOME/examples/band directory.

Where references are made to the operating system (OS) and to the file system on your computer the terminology of UNIX type OSs is used.

This guide and other documentation is available at http://www.scm.com. As mentioned in the license agreement, it is mandatory, for publications in which BAND has been used, to cite the lead references.

## 1.2 Characterization of BAND

**Functionality**

- Automatic geometry optimization
- Formation energy with respect to isolated atoms that are computed with a fully numerical Herman-Skillman type subprogram
- A choice of density functionals, including LDA (Local Density Approximation), GGA (Generalized Gradient Approximation), meta GGA (with kinetic energy density dependence), and Hybrid (including exact exchange) functionals
- Time-dependent DFT for calculation of frequency-dependent dielectric functions of systems periodic in one or three dimensions.
- The ZORA method for scalar relativistic effects is available (also for the TDDFT option). Spin-orbit coupling can be taken into account, including non-collinear magnetization.
- Phonon spectrum.

- Electric field perpendicular to the periodic direction(s)

**Analysis**

- Mulliken populations for basis functions, overlap populations between atoms or between basis functions.
- Hirshfeld charge analysis
- Densities-of-States: DOS, PDOS and OPWDOS/COOP
- Local Densities-of-States: LDOS (STM images)
- Form factors (X-ray structures)
- Charge analysis using Voronoi cells (yielding Voronoi Deformation Charges)
- Orbital plots
- Deformation density plots
- Band structure plots along the edges of the Brillouin zone
- One-electron energies and orbitals at the Brillouin Zone sample points
- Fragment orbitals and a Mulliken type population analysis in terms of the fragment orbitals
- Quantum Theory of Atoms In Molecules (QT-AIM). Atomic charges and critical points.
- Electron Localization Function (ELF).
- Fragment based Periodic Energy Decomposition Analysis (PEDA).
- PEDA combined with Natural Orbitals for Chemical Valency (NOCV) to decompose the orbital relaxation (PEDA-NOCV).

**Technical**

- Linear scaling techniques are used to speed up calculations on large unit cells
- SCF convergence based on a Direct Inversion of Iterative Subspace (DIIS) method. For problematic systems also LIST is available.
- The implementation is built upon a highly optimized numerical integration scheme for the evaluation of matrix elements of the Hamiltonian, property integrals involving the charge density, etc. This is the same numerical integration scheme as used in ADF.
- Basis functions are Slater-Type Orbitals (STOs) and/or Numerical Orbitals (NOs).
- The ZlmFit is used to fit the deformation density, which is the difference between the final density and the startup density. The deformation density has zero charge and will in general be small. The fitted deformation density is used for the calculation of the Coulomb potential and the derivatives of the total density (needed for the gradient corrections in the exchange-correlation functionals). In both cases the main part, due to the startup density, is calculated accurately by a numerical procedure, and only the small part from the deformation density is obtained via the fit.
- A frozen core facility is provided to allow efficient treatment of the inner atomic shells.
- Space group symmetry is used to reduce the computational effort in the integrals over the Brillouin zone.

## 1.3 Release 2016

In comparison to BAND 2014, the BAND 2016 release offers the following new functionality:

- Geometry Optimization

  - *Analytical Lattice Gradients* (page 43)
- Model Hamiltonians
  - *Hybrids for non-periodic systems* (page 19)
  - *Short Range-Separated Hybrids for periodic systems* (page 20)
- TDDFT
  - *Parameter-free Polarization Kernel for Bulk Systems* (page 50)
- Tweaking Excited States
  - *User-defined Spinpolarization* (page 72)
  - *Defining Electron Holes* (page 72)
- Analysis
  - *Periodic Energy Decomposition Analysis (PEDA)* (page 61)
  - *PEDA Combined with Natural Orbitals for Chemical Valency (PEDA-NOCV)* (page 61)
- Default settings changed
  - *COSMO surface changed to Delley instead of Esurf* (page 22)

Apart from this new functionality and performance improvements, certain bugs have been fixed.

CHAPTER

TWO

# INPUT AND OUTPUT

When the program has been installed properly on your machine, you should be able to run it by supplying appropriate input.

In the Examples section you can find sample input files covering most basic options.

**Delimiters**

An input record may contain several items. The general rule is that each sequence of characters that does not contain a delimiter is an entity. Delimiters in this context are:

1. the blank or space character ' '
2. the comma ',' and
3. the equal sign '='.

It is assumed throughout that only characters of the Fortran character set are used.

> **Warning:** Do not use tabs in the input file! The program may *not* see them as delimiters and the effects are hard to predict.

**Uppercase and lowercase**

Virtually all input items are case-insensitive, but take notice of the obvious exceptions: names of files and directories are case-sensitive.

## 2.1 Keywords

Input is structured by keywords, or keys. A key is a string of letters, dollar signs ($), and digits. It must not start with a digit. It must not contain any other character, in particular not any blank.

Key-controlled input occurs in two forms: either one record (which contains both the key and/or associated data) or a sequence of records, collectively denoted as a key *block*. The first record of the block specifies the key (and may supply additional information); the block is closed by the 'end-key' code: a record containing only the word 'End'. The other records in the block provide data associated with the key.

The form to be used for a key is not optional: each admissible key corresponds to a particular form. The block form is used for keys which relate to 'lists' of data, such as atomic coordinates or basis functions.

As is the case in the molecular code, the 'title' must be specified explicitly with the key 'Title' and may be put on any record of the input file. The input file should end with a record 'End Input', that is, the program reads input until such a record is encountered or until the Fortran end-of-file condition becomes true, whichever comes first.

'End Input' is not a key.

Summarizing, the input file must have the following format:

## 2.2 Format of the Input file

```
TITLE jobname
   key-controlled data
   key-controlled data
   (et cetera...)
End Input
```

The ordering of keys in input is free and has no consequences.

All numerical information is 'free format': the absolute positions of numbers and the format of reals is irrelevant.

In most cases lowercase characters and capitals can both be used and the program will not discriminate between them, except in filenames.

## 2.3 Setting up an Input File

We now give a brief guide how to set up input.

You first specify the minimally required information: the definition of the geometry and the basis sets.

- Define the geometry with the key `Atoms` and the key `Lattice`.
- Specify the `BasisDefaults` key. With this you can set the quality of the basis set to be used, and the size of the frozen core.
- Terminate the input file by typing 'End Input'

```
Atoms
   Atomnames and natural/cartesian coordinates
End

Lattice
   Lattice vectors of the unit cell
End

BasisDefaults
   BasisType ...
   Core      ...
End
```

Then you add keys for all aspects for which you don't want to use the defaults.

- Specify a title using the key `Title`.
- Other keys: `Unrestricted` (if you want to do a spin-unrestricted calculation), `Accuracy` (general precision parameter), `KSpace` (parameter for numerical integration over the Brillouin Zone), `DOS` (generation of the density-of-states), and so on.
- Comments: everything behind a exclamation mark "!" is treated as comment. If you put it behind a key, leave some space between it, otherwise it will be seen as part of the key.

Consult the sample runs and description below, to see how you may use the various keys (`Lattice`, `Atoms`, `BasisDefaults`).

## 2.4 General Input Features

The program supports the following features to enhance user-friendliness of input:

- Arithmetic expressions can be used (wherever numbers are required) involving the standard arithmetic operands in Fortran (`+ - * / **`), together with parentheses where necessary or convenient. Blanks are allowed in expressions and ignored, but they are interpreted as separators, i.e. as denoting the end of an expression, whenever the part before the blank can be evaluated as a correct expression. For instance `3*  4` will be interpreted as 12, but `3  *4` will be interpreted as 3, followed by a character `*`, followed in turn by the number 4. All numbers and results are interpreted and handled as being of type real, but whenever the result is a whole number (allowing for small round-off deviations), it will be recognized as possibly denoting an integer.
- (Single) quotes can be used to designate strings, i.e. (parts of) records which are not to be parsed for expressions, but which are to be taken as they are. The quotes themselves are ignored. Double quotes inside a string are understood to denote the single quote character (as part of the string).
- Empty records and starting blanks in records are allowed, and can be used to enhance clarity and readability of the input file for human readers by structuring its layout.
- A double colon `::` is interpreted as an end of line character, hence the double colon and anything after it is ignored

## 2.5 Title, Comments and Ignore

**`Title`** Specifies the title of this run. The title is used for identification of the result files.

**`Comment (block-type), and line oriented`** The content of this key is a text that will be copied to the output header, where general program information is also printed. The exclamation mark can also be used to add comments to you input that should not interpreted by BAND. Example:

```
Comment ! here are my comments
   Description of the calculation
   Some more description
End

Lattice ! FCC lattice
   0 a a
   a 0 a
   0 a a
End

! Here are my defines
Define...

End
```

Finally it is possible to let BAND ignore parts of the input

**`Ignore (block-type)`** Suppress reading of input until the next end-key code (END).

## 2.6 Defining variables and functions

The user may define *variables* and *functions* in the input file, and apply them subsequently in expressions. The input file is read sequentially and variables and functions must be defined before they can be used. Note carefully that

replacement of a variable (or function) by its value will occur wherever possible (textually), even if it leads to non-sense input. A frequently occurring mistake is that the user defines a variable 'C' in the input and then gets it corrupted because of subsequent isolated C characters being replaced by the defined numerical value. *Therefore: avoid single-character variables and function names.* Always check carefully that the identifier you introduce is not 'used' already in the input file. A few variables and functions are pre-defined:

- variables: pi = 3.1415....
- functions: sin, cos, tan, asin, acos, atan, exp, log, sqrt, nint.

The argument list of a function must be enclosed in parentheses, and the arguments (in case of more than one) must be separated by commas. Defining variables and/or functions is done with the block-type key `define`.

**`Define (block-type)`** Definition of user-supplied functions and variables that can subsequently be used in the input file. (see the note on auxiliary input features)

Example (part of input):

```
DEFINE
   ab = sin(pi/3)
   s13 = 14*sqrt(2)
   func(x,y,z) = x*ab+y**2-y*z
End
AKEY = FUNC (S13/5, S13/7, SIN(PI/6))
```

Here a function func and variables ab and s13 are defined, using the pre-defined functions sin and sqrt, as well as the pre-defined variable pi. These are then applied to assign a value to the (hypothetical) key `AKEY`.

**Note 1**: the variable ab is also used in the definition of func! This is allowed because ab is defined before func.

**Note 2**: variable- and function *names* must have the same form as keywords, i.e. only certain characters are allowed.

**Note 3**: in the definition of variables and functions blanks are ignored altogether (in the value part) and will not be interpreted as possible separators of the expression that defines the variable or function.

## 2.7 Execution flow

There are a few ways to alter the standard execution flow, which may be useful to developers or expert users.

**`StopAfter`** Specifies that the program is stopped after execution of a specified program-part (subroutine). The specified name should be one of a pre-defined list. The most relevant ones are **gemtry** (all geometrical aspects are checked, symmetry analysis is carried out, and numbers of (symmetry-unique) integration points in real space and in k-space are determined; this part takes only little cpu-time) and **atomic** (in addition to the geometry-part all radial parts of basis- and fit functions are generated, and the spherically symmetric atoms are computed and inserted in the crystal; the initial charge density is defined and integrated (check on integration-precision), and the electrostatic interaction is computed between the unrelaxed free atoms).

**`SKIP`** followed by any number of strings (separated by blanks or commas) tells the program to skip certain parts. Should only be used by those who know what they're doing. Recognized are certain pre-defined strings. Useful argument may be **DOS** when that part of the program takes a long time (usually not), or **eigenvalues** (to suppress printing the eigenvalues at the (first and last) SCF cycles).

**`ALLOW`** debugging feature to let the program continue even when intermediate results seem to be wrong or very inaccurate. Currently there are only few places in the program where this key is used. Argument to the key is what should be allowed. Possible arguments: **BadIntegration**, **OCC**, **CHARGEERROR**, **DEPENDBASIS**.

## 2.8 Printed Output

The amount of output in different stages of the program is controlled by print keys, that can be toggled with the key Print followed by a key (see description of Print key).

**Print** One or more strings (separated by blanks or comma's) from a pre-defined set may be typed after the key. This induces printing of various kinds of information, usually only used for debugging and checking. The set of recognized strings frequently changes (mainly expands) in the course of software-developments. Useful arguments may be symmetry, and fit. A list of all important arguments to this key follows:

**Eigens** Prints the (complex) coefficients in the form (norm, phase factor) of the eigenvectors with respect to the valence basis. Coefficients with a norm smaller than eigthreshold will be skipped. This threshold can be set with the option eigthreshold x, default x=.01.

**MullikenOverlapPopulations** Prints overlap population of all basis functions.

**OrbitalLabels** Prints the labels of the orbitals. If you are interested in the labels of an old calculation and you don't want to repeat it completely, you can add the option StopAfter gemtry to your input file.

**OrbPop** Prints the Mulliken population per orbital, for all eigenstates. This is the most detailed population analysis that you can get, one for all k-points and for each band. Populations below a certain threshold are ignored. This threshold can be set with the option popthreshold $x$. By default $x$ =.01.

**BLCKAT** Print the information about the distance effects used in the numerical integrals.

**Fit** Print more details about the fitting procedure, such as the fit coefficients at each SCF cycle.

**Symmetry** Print the symmetry operators.

### 2.8.1 Thresholds

**POPTHRESHOLD** Threshold for printing Mulliken population terms. Default 1e-2. Works with print orbpop.

**EIGTHRESHOLD** Components smaller (absolute value) than this parameter (default 1e-2) are not printed in the output of the DOS section, where the breakdown of crystal orbitals in the primitive basis is printed. Works with print eigens.

### 2.8.2 More options

The following print options only make sense when debugging the code.

**Print** One or more strings (separated by blanks or comma's) from a pre-defined set may be typed after the key. The following names replace the IRPNT[IPRSE] keys of the previous versions of BAND:

- `PrepNone, PrepMore, PrepDetail replace IPRNTP 0, 2, 5`
- `IntNone, IntMore, IntDetail replace IPRNTI 0, 2, 5`
- `FrmNone, FrmMore, FrmDetail replace IPRNTR 0, 2, 5`
- `SCFNone, SCFMore, SCFDetail replace IPRNTS 0, 2, 5`
- `EigNone, EigMore, EigDetail replace IPRNTE 0, 2, 5`

### 2.8.3 Debug key

(programmers only)

**DEBUG** The argument is usually a (list of) subroutine names that you want to debug. (The programmer can check for this in the same way as PRINT or ALLOW keys.)

CHAPTER

THREE

# GEOMETRY

Let us start with are few examples showing how to define the geometry of your system in BAND.

Sodium chloride crystal:

```
Units
  length Angstrom
End

Lattice
  0.00 2.82 2.82
  2.82 0.00 2.82
  2.82 2.82 0.00
End

Atoms
  Na  0.00 0.00 0.00
  Cl  2.82 2.82 2.82
End
```

Graphene (2D slab):

```
Units
  length Angstrom
End

Lattice
  2.46 0.0     0.0
  1.23 2.13042 0.0
End

Atoms
  C  0.0  0.0     0.0
  C  1.23 0.71014 0.0
End
```

Water molecule:

```
! Notes:
! - If you leave out the Lattice key, BAND will not use periodic boundary condition
! - the default unit of length is Bohr

Atoms
  O  0.0  0.0   0.0
  H  0.0  1.446 1.137
  H  0.0 -1.446 1.137
End
```

## 3.1 Units

Geometric data (atomic positions and lattice vectors) are by **default** understood to be in atomic units (**Bohr**). Alternatively, one may supply data in Angstroms via the `Units` block key (Each of the subkeys is optional, as is the key `Units` itself):

```
Units
  {Length [Bohr|Angstrom]}
  {Angle [Degree|Radian]}
End
```

**`Length`** (**Default: Bohr**) Units of length.

**`Angle`** (**Default: Degree**) Units of angle.

## 3.2 Lattice vectors

**`Lattice (block-type)`** Vectors (Cartesian coordinates x,y,z) defining the Bravais lattice, one vector per line. The number of lines defines the periodicity of the system: 1: polymer, 2: slab, 3: bulk crystal. If the `Lattice` block is omitted, no periodic boundary conditions will be used.

For 1D periodic systems (polymers) the lattice vector must be aligned with the x-axis

```
! This is OK (lattice vector aligned with the x-axis):

Lattice
  2.0 0.0 0.0
End
```

```
! This is WRONG (lattice vector not aligned with the x-axis):

Lattice
  1.0 1.0 0.0
End
```

For 2D periodic systems (slabs) the lattice vectors must be on the xy-plane:

```
! This is OK (lattice vectors in the xy-plane):

Lattice
  2.0 0.0 0.0
  1.0 1.0 0.0
End
```

```
! This is WRONG (lattice vector not in the xy-plane):

Lattice
  2.0 0.0 0.0
  0.0 0.0 2.0
End
```

## 3.3 Coordinates of atoms in the unit cell

`Atoms (block-type)`

There exist two different styles which allow a compact or a type-specific formulation of the atom positions.

### 3.3.1 The compact format (ADF-like)

```
Atoms
  H  x1 y1 z1
  O  x2 y2 z2
  H  x3 y3 z3
End
```

The chemical symbol, preceding the Cartesian or natural coordinates, defines the atom type. Choosing the ADF-like style allows only one Atoms block in the input. One has to be aware that BAND will automatically reorder the atoms, so that atoms of the same type are in a block.

### 3.3.2 In case of Regions and Types

```
Atoms H
   x1 y1 z1
End
Atoms O
   x2 y2 z2
End
Atom H
   x3 y3 z3
End
```

The chemical symbol must be given on the keyword-line. The data-records contain the Cartesian or natural coordinates, one atom per line. The atoms key is allowed to appear more than once for an atom type. These multiple occurrences are then treated as different types. This is useful to define different basis sets for different types (example *BasisDefaults* (page 99)), manipulate the spin (example *BetaIron* (page 89)) or the potential (e.g. *NiO Hubbard* (page 97)) of a certain type.

You can add the following subkeys which override the behavior of the BasisDefaults key

`BasisType` This overrides the setting of the BasisDefaults%AtomType key for this atom type.

`Core` This overrides the setting of the BasisDefaults%Core key.

`File` Specify an absolute path to a basis set file.

## 3.4 Natural coordinates

**`Coordinates`** The only sensible value for this key is `natural`, which specifies that nuclear coordinates (key atoms) are given as expansions in the Bravais lattice vectors, rather than in a Cartesian representation. See the *NaCl example* (page 107).

## 3.5 Selected atoms

**`SelectedAtoms`** With this key you can select atoms. This has an effect on a couple of options, like for instance the Gradients, Hessian (FREQUENCIES), NMR, and EFG options. In these cases, the properties will only be calculated for the selected atoms, which can make the job faster.

```
    SelectedAtoms n1, n2, n...
```

The numbers of the atoms are as on input. If the selection breaks the symmetry the program will stop. Leaving out this key in general selects *all* atoms.

CHAPTER

FOUR

# MODEL HAMILTONIANS

The program calculates by default the non relativistic self-consistent field solution from the potential in the spin-restricted local density approximation (LDA) to the exchange-correlation (XC) potential. The post-SCF generalized gradient (GGA) corrections for the exchange and the correlation energies (each for a few different functionals) are calculated and printed on output. The program can be instructed to use the GGA corrections in the potential during the SCF as well. This will in general have little effect on the formation energy, but it may affect the Density of States (DOS).

## 4.1 Density Functional

The starting point for the xc functional is usually the result for the homogeneous electron gas, after which so called nonlocal or generalized gradient corrections (GGA: Generalized Gradient Approximation) are added.

### 4.1.1 XC functionals

The density functional approximation is controlled by the XC key. `XC (block-type)`

Three classes of exchange-correlation functionals are supported: LDA, GGA, and meta-GGA. There is also the option to add an empirical dispersion correction. The only ingredient of the LDA energy density is the (local) density, the GGA depends additionally on the gradient of the density, and the meta GGA has an extra dependency on the kinetic energy density.

In principle you may specify different functionals to be used for the *potential,* which determines the self-consistent charge density, and for the *energy* expression that is used to evaluate the (XC part of the) energy of the charge density. This is not so important for a single point calculation as BAND prints the bonding energies of a set of common functionals, but the *energy* functional is used for the nuclear gradients (geometry optimization). To be consistent, one should generally apply the same functional to evaluate the potential and energy respectively. Two reasons, however, may lead one to do otherwise:

1. The evaluation of the GGA part (especially for Meta GGAs) in the *potential* is rather time-consuming. The effect of the GGA term in the potential on the self-consistent charge density is often not very large. From the point of view of computational efficiency it may, therefore, be attractive to solve the SCF equations at the LDA level (i.e. not including GGA terms in the potential), and to apply the full expression, including GGA terms, to the energy evaluation *a posteriori*: post-SCF.
2. A particular XC functional may have only an implementation for the potential, but not for the energy (or vice versa). This is a rather special case, intended primarily for fundamental research of Density Functional Theory, rather than for run-of-the-mill production runs.

All subkeys of `XC` are optional and may occur twice in the data block: if one wants to specify different functionals for potential and energy evaluations respectively, see above.

```
XC
   {LDA  {Apply}   LDA {Stoll}}
   {GGA  {Apply}   GGA}
   {DiracGGA  GGA}
   {MetaGGA  {Apply}   GGA}
   {Dispersion {s6scaling} {RSCALE=r0scaling} {Grimme3} {BJDAMP} {PAR1=par1} {PAR2=par2} {PAR3=par3}
   {Model [LB94|TB-mBJ|KTB-mBJ|JTS-MTB-MBJ|GLLB-SC]}
   {SpinOrbitMagnetization [None|NonCollinear|CollinearX|CollinearY|CollinearZ]}
   {LibXC {Functional}}
End
```

The common use is to specify either an LDA or a (meta)GGA line. (Technically it is possible to have an LDA line *and* a GGA line, in which case the LDA part of the GGA functional (if applicable) is replaced by what is specified by the LDA line.)

**Apply** States whether the functional defined on the pertaining line will be used self-consistently (in the SCF-potential), or only post-SCF, i.e. to evaluate the XC energy corresponding to the charge density. The value of apply must be **SCF** or **POSTSCF**. (**default=SCF**)

### LDA/GGA/metaGGA

**LDA** Defines the LDA part of the XC functional and can be any of the following:

**Xonly**: The pure-exchange electron gas formula. Technically this is identical to the Xalpha form with a value 2/3 for the X-alpha parameter.

**Xalpha**: the scaled (parameterized) exchange-only formula. When this option is used you may (optionally) specify the X-alpha *parameter* by typing a numerical value after the string Xalpha (**Default: 0.7**).

**VWN**: the parameterization of electron gas data given by Vosko, Wilk and Nusair (ref [*1* (page 163)], formula version V). Among the available LDA options this is the more advanced one, including correlation effects to a fair extent.

**Stoll**: For the VWN or GL variety of the LDA form you may include Stoll's correction [*2* (page 163)] by typing Stoll on the same line, after the main LDA specification. You must not use Stoll's correction in combination with the Xonly or the Xalpha form for the Local Density functional.

**GGA** Specifies the GGA part of the XC Functional, in earlier times often called the 'non-local' correction to the LDA part of the density functional. It uses derivatives (gradients) of the charge density. Separate choices can be made for the GGA exchange correction and the GGA correlation correction respectively. Both specifications must be typed (if at all) on the same line, after the GGA subkey.

For the exchange part the options are:

- **Becke**: the gradient correction proposed in 1988 by Becke [*3* (page 163)]
- **PW86x**: the correction advocated in 1986 by Perdew-Wang [*4* (page 163)]
- **PW91x**: the exchange correction proposed in 1991 by Perdew-Wang [*5* (page 163)]
- **mPWx**: the modified PW91 exchange correction proposed in 1998 by Adamo-Barone [*27* (page 164)]
- **PBEx**: the exchange correction proposed in 1996 by Perdew-Burke-Ernzerhof [*12* (page 163)]
- **HTBSx**: the HTBS exchange functional [*43* (page 165)]
- **RPBEx**: the revised PBE exchange correction proposed in 1999 by Hammer-Hansen-Norskov [*13* (page 163)]
- **revPBEx**: the revised PBE exchange correction proposed in 1998 by Zhang-Wang [*28* (page 164)]
- **mPBEx**: the modified PBE exchange correction proposed in 2002 by Adamo-Barone [*29* (page 164)]

- **OPTX**: the OPTX exchange correction proposed in 2001 by Handy-Cohen [*30* (page 164)]

For the correlation part the options are:

- **Perdew**: the correlation term presented in 1986 by Perdew [*6* (page 163)]
- **PBEc**: the correlation term presented in 1996 by Perdew-Burke-Ernzerhof [*12* (page 163)]
- **PW91c**: the correlation correction of Perdew-Wang (1991), see [*5* (page 163)], [*8* (page 163)], [*9* (page 163)]
- **LYP**: the Lee-Yang-Parr 1988 correlation correction [*7* (page 163)]

Some GGA options define the exchange and correlation parts in one stroke. These are:

- **BP86**: this is equivalent to **Becke** + **Perdew** together
- **PW91**: this is equivalent to **pw91x** + **pw91c** together
- **mPW**: this is equivalent to **mPWx** + **pw91c** together
- **PBE**: this is equivalent to **PBEx** + **PBEc** together
- **HTBS**: this is equivalent to **HTBSx** + **PBEc** together
- **RPBE**: this is equivalent to **RPBEx** + **PBEc** together
- **revPBE**: this is equivalent to **revPBEx** + **PBEc** together
- **mPBE**: this is equivalent to **mPBEx** + **PBEc** together
- **BLYP**: this is equivalent to **Becke** (exchange) + **LYP** (correlation)
- **OLYP**: this is equivalent to **OPTX** (exchange) + **LYP** (correlation)
- **OPBE**: this is equivalent to **OPTX** (exchange) + **PBEc** (correlation) [*31* (page 164)]

**`DiracGGA`** (Expert option!) This key handles which XC functional is used during the Dirac calculations of the reference atoms. A string is expected which is not restricted to names of GGAs but can be LDA-like functionals, too.

**Note**: In some cases using a GGA functional leads to slow convergence of matrix elements of the kinetic energy operator w. r. t. the `Accuracy` parameter. Then one can use the LDA potential for the calculation of the reference atom instead.

**`MetaGGA`** Key to select the evaluation of a meta GGA. A byproduct of this option is that the bonding energies of all known functionals are printed (using the same density). Meta GGA calculations can be quite a bit more time consuming, especially when active during the SCF.

Self consistency of the meta GGA is implemented as suggested by Neuman, Nobes, and Handy.[*11* (page 163)]

The available functionals of this type are:

- **TPSS**: The 2003 Meta GGA [*15* (page 163)]
- **M06L**: The Meta GGA as developed by the Minesota group [*16* (page 164)]
- **revTPSS**: The 2009 revised Meta GGA [*26* (page 164)]

### Dispersion Correction

In BAND parameters for Grimme3 and Grimme3 BJDAMP can be used according to version 3.1 (Rev. 1) of the coefficients, published on the Bonn .

**DISPERSION Grimme3 BJDAMP {PAR1=par1 PAR2=par2 PAR3=par3 PAR4=par4}** If this key is present a dispersion correction (DFT-D3-BJ) by Grimme [42 (page 165)] will be added to the total bonding energy, gradient and second derivatives, where applicable. Parametrizations are implemented e.g. for B3LYP, TPSS, BP86, BLYP, PBE, PBEsol [14 (page 163)] , and RPBE. It has four parameters. One can override these using *PAR1=.. PAR2=..*, etc. In the table the relation is shown between the parameters and the real parameters in the dispersion correction.

| variable | variable on Bonn |
|---|---|
| PAR1 | s6 |
| PAR2 | a1 |
| PAR3 | s8 |
| PAR4 | a2 |

**DISPERSION Grimme3 {PAR1=par1 PAR2=par2 PAR3=par3}** If this key is present a dispersion correction (DFT-D3) by Grimme [41 (page 165)] will be added to the total bonding energy, gradient and second derivatives, where applicable. Parametrizations are available e.g. for B3LYP, TPSS, BP86, BLYP, revPBE, PBE, PBEsol [14 (page 163)], and RPBE, and will be automatically set if one of these functionals is used. For all other functionals, PBE-D3 parameters are used as default. You can explicitly specify the three parameters.

| variable | variable on Bonn |
|---|---|
| PAR1 | s6 |
| PAR2 | sr,6 |
| PAR3 | s8 |

**Dispersion {s6scaling RSCALE=r0scaling}** If the DISPERSION keyword is present a dispersion correction will be added to the total bonding energy, where applicable. By default the correction of Grimme.[32 (page 165)] The term is added to the bonding energies of all printed functionals, standard the LDA and a couple of GGAs. The global scaling factor with which the correction is added depends on the exchange-correlation functional used at SCF but it can be modified using the *s6scaling* parameter. The following scaling factors are used (with the XC functional in parantheses): 1.20 (BLYP), 1.05 (BP), 0.75 (PBE), 1.05 (B3LYP). In all other cases a factor 1.0 is used unless modified via the s6scaling parameter. The van der Waals radii used in this implementation are hard-coded. However, it is possible to modify the global scaling parameter for them using the *RSCALE=r0scaling* argument. The default value is 1.1 as proposed by Grimme.[32 (page 165)] With the extra option Grimme3 the latest dispersion correction, known as D3, will be used.[41 (page 165)]

### Model Potentials

**Model** Some functionals give only a potential and have no energy expression. We call such functionals model potentials. In BAND there are three available:

**LB94** With this model the asymptotically correct potential of van Leeuwen and Baerends is invoked.[10 (page 163)]

**TB-mBJ** This model can be used to fix the band gap in bulk systems.[44 (page 165)] This potential depends on a c-factor for which there is a density dependent automatic expression. However you can override the automatic value by specifying XC%TB_mBJCFactor cfac. In principle: the bigger the value the larger the gap. **KTB-mBJ/JTS-mTB-mBJ** are variations of **TB-mBJ**. The formula for C contains three parameters: A,B, and E. The logic is as follows

| potential | A | B | E |
|---|---|---|---|
| TB-mBJ[44 (page 165)] | -0.012 | 1.023 | 0.5 |
| KTB-mBJ[54 (page 166)] | 0.267 | 0.656 | 1.0 |
| JTS-mTB-mBJ[55 (page 166)] | 0.4 | 1.0 | 0.5 |

All the three parameters (A,B, and E) can be user-defined set as follows:

```
XC
   Model TB_mBJ
   TB_mBJAFactor valA
   TB_mBJBFactor valB
   TB_mBJEFactor valE
End
```

**GLLB-SC** This parameter-free functional models the derivative discontinuity.[*49* (page 166)]

### Non-Collinear Approach

**`SpinOrbitMagnetization`** (**Default=CollinearZ**) Most XC functionals have as one ingredient the spin polarization. Normally the direction of the spin quantization axis is arbitrary and conveniently chosen to be the $z$-axis. However, in a *spin-orbit* (page 22) calculation the direction matters, and it is arbitrary to put the z-component of the magnetization vector into the XC functional. It is also possible to plug the size of the magnetization vector into the XC functional. This is called the non-collinear approach. There is also the exotic option to choose the quantization axis along the $x$ or $y$ axis. To summarize, the value **NonCollinear** invokes the non-collinear method. The other three option **CollinearX**, **CollinearY** and **CollinearZ** causes either the x, y, or z component to be used as spin polarization for the XC functional.

### LibXC Library Integration

**`LibXC functional`** LibXC is a library of approximate exchange-correlation functionals, see Ref. [*63* (page 166)]. The development version 3 of LibXC is used. See the LibXC website for the complete list of functionals: http://www.tddft.org/programs/Libxc.

The following functionals can be evaluated with LibXC (incomplete list):

- **LDA:** LDA, PW92, TETER93
- **GGA:** AM05, BGCP, B97-GGA1, B97-K, BLYP, BP86, EDF1, GAM, HCTH-93, HCTH-120, HCTH-147, HCTH-407, HCTH-407P, HCTH-P14, PBEINT, HTBS, KT2, MOHLYP, MOHLYP2, MPBE, MPW, N12, OLYP, PBE, PBEINT, PBESOL, PW91, Q2D, SOGGA, SOGGA11, TH-FL, TH-FC, TH-FCFO, TH-FCO, TH1, TH2, TH3, TH4, VV10, XLYP, XPBE
- **MetaGGA:** B97M-V, M06-L, M11-L, MN12-L, MS0, MS1, MS2, MVS, PKZB, TPSS
- **Hybrids** (**only for non-periodic systems**): B1LYP, B1PW91, B1WC, B3LYP, B3LYP*, B3LYP5, B3LYP5, B3P86, B3PW91, B97, B97-1 B97-2, B97-3, BHANDH, BHANDHLYP, EDF2, MB3LYP-RC04, MPW1K, MPW1PW, MPW3LYP, MPW3PW, MPWLYP1M, O3LYP, OPBE, PBE0, PBE0-13, REVB3LYP, REVPBE, RPBE, SB98-1A, SB98-1B, SB98-1C, SB98-2A, SB98-2B, SB98-2C, SOGGA11-X, SSB, SSB-D, X3LYP
- **MetaHybrids** (**only for non-periodic systems**): B86B95, B88B95, BB1K, M05, M05-2X, M06, M06-2X, M06-HF, M08-HX, M08-SO, MPW1B95, MPWB1K, MS2H, MVSH, PW6B95, PW86B95, PWB6K, REVTPSSH, TPSSH, X1B95, XB1K
- **Range-separated** (**for periodic systems, only short range-separated functionals can be used**, see *Range-separated hybrid functionals* (page 20)): CAM-B3LYP, CAMY-B3LYP, HJS-PBE, HJS-PBESOL, HJS-B97X, HSE03, HSE06, LRC_WPBE, LRC_WPBEH, LC-VV10, LCY-BLYP, LCY-PBE, M11, MN12-SX, N12-SX, TUNED-CAM-B3LYP, WB97, WB97X, WB97X-V

Example usage for the MVS functional:

```
XC
  LibXC MVS
End
```

**Notes:** * **All electron basis sets should be used** (see `CORE NONE` in section *Basis set* (page 27)). * For periodic systems only short range-separated functionals can be used (see *Range-separated hybrid functionals* (page 20)) * In case of LibXC the output of the BAND calculation will give the reference for the used functional, see also the LibXC website http://www.tddft.org/programs/Libxc.

- Do not use any of the subkeys LDA, GGA, METAGGA, MODEL in combination with the subkey LIBXC.
- One can use the DISPERSION key icw LIBXC. For a selected number of functionals the optimized dispersion parameters will be used automatically, please check the output in that case.

### Range-separated hybrid functionals

Short range-separated hybrid functionals, like the **HSE03** functional [*62* (page 166)], can be useful for prediction of band gap. These must be specified via the *LibXC* (page 19) key

```
XC
   LibXC functional {omega=value}
End
```

**`functional`** The functional to be used. (Incomplete) list of available functionals: **HSE06**, **HSE03**, **HJS-B97X**, **HJS-PBE** and **HJS-PBESOL** (See the LibXC website (http://www.tddft.org/programs/octopus/wiki/index.php/Libxc_functionals) for a complete list of available functionals).

**`omega`** *Optional*. You can optionally specify the switching parameter omega of the range-separated hybrid. Only possible for the **HSE03** and **HSE06** functionals (See [*62* (page 166)]).

**Notes:**

- Hybrid functionals can only be used in combination with all-electron basis sets (see `CORE NONE` in section *Basis set* (page 27)).
- The Hartree-Fock exchange matrix is calculated through a procedure known as Resolution of the Identity (RI). See *RIHartreeFock* (page 38) key.
- Regular hybrids (such as B3LYP) and long range-separated hybrids (such as CAM-B3LYP) **cannot** be used in periodic boundary conditions calculations (they can only be used for non-perdioc systems).
- There is some confusion in the scientific literature about the value of the switching parameter $\omega$ for the HSE functionals. In LibXC, and therefore in BAND, the HSE03 functional uses $\omega = 0.106066$ while the HSE06 functional uses $\omega = 0.11$.

**Usage example**:

```
XC
   LibXC HSE06 omega=0.1
End
```

### Defaults and special cases

- If the XC key is not used, the program will apply only the Local Density Approximation (no GGA terms). The chosen LDA form is then VWN.
- If only a GGA part is specified, omitting the *LDA* subkey, the LDA part defaults to VWN, except when the LYP correlation correction is used: in that case the LDA default is Xonly: pure exchange.
- The reason for this is that the LYP formulas assume the pure-exchange LDA form, while for instance the Perdew-86 correlation correction is a correction to a *correlated* LDA form. The precise form of this correlated LDA form assumed in the Perdew-86 correlation correction is not available as an option in ADF but the VWN formulas are fairly close to it.

- Be aware that typing only the subkey *LDA*, without an argument, will activate the VWN form (also if LYP is specified in the GGA part).

### 4.1.2 GGA+U

A special way to treat correlation is with so-called LDA+U, or GGA+U calculations. It is intended to solve the band gap problem of traditional DFT, the problem being an underestimation of band gaps for transition-metal complexes. A Hubbard like term is added to the normal Hamiltonian, to model on-site interactions. In its very simplest form it depends on only one parameter, U, and this is the way it has been implemented in BAND. The energy expression is equation (11) in the work of Cococcioni.[*47* (page 165)] See also the review article [*46* (page 165)].

**`HubbardU (block-type)`** Key to control the GGA+U calculation:

```
HubbardU
   Enabled          [false | true]
   UValue           u1 u2 ...
   lValue           l1 l2 ...
   {PrintOccupations [true | false]}
End
```

**`Enabled`** (**Default: false**) Whether or not to apply the Hubbard Hamiltonian

**`UValue`** For each atom type specify the U value [atomic units]. A value of 0.0 is interpreted as no U.

**`lValue`** For each atom type specify the l value (0 - s orbitals, 1 - p orbitals, 2 - d orbitals). A negative value is interpreted as no l-value.

**`PrintOccupations`** (**Default: true**) Whether or not to print the occupations during the SCF.

An example to apply LDA+U to the d-orbitals of NiO looks like

```
HubbardU
   printOccupations true
   Enabled          true
   uvalue           0.3 0.0
   lvalue           2   -1
End

ATOMS Ni
   0.000  0.000  0.000
END

ATOMS O
   2.085  2.085  2.085
END
```

### 4.1.3 Spin polarization

By default BAND calculations are spin-restricted. To perform a spin-unrestricted calculation you should include the Unrestricted key:

```
UNRESTRICTED
```

Be aware that spin-unrestricted calculations are computationally roughly twice as expensive as spin-restricted.

## 4.2 Relativistic Effects

Relativistic effects are treated with the accurate and efficient ZORA approach [*17* (page 164), *18* (page 164)], controlled by the `Relativistic` keyword. Relativistic effects are negligible for light atoms, but grow to dramatic changes for heavy elements. A rule of thumb is: Relativistic effects are quite small at row 4, but very large at row 6 (and later).

```
Relativistic [None|ZORA|ZORA Spin]
```

This key instructs BAND to take relativistic effects into account. (**Default: none**)

**`None`** No relativistic effects

**`ZORA`** Scalar relativistic ZORA. This option comes at very little cost.

**`ZORA Spin`** Spin-orbit coupled ZORA. This is the best level of theory, but it is more (4-8 times) expensive than a normal calculations. Spin-orbit effects are generally quite small, unless there are very heavy atoms in your system, especially with p valence electrons (like Pb). See also the *SpinOrbitMagnetization* (page 19) key.

## 4.3 Solvation

### 4.3.1 COSMO: Conductor like Screening Model and the Solvation-key

You can study chemistry in solution, as contrasted to the gas phase, with the implementation in BAND of the Conductor like Screening Model (COSMO) of solvation.[*36* (page 165)]

In the COSMO model all solvents are roughly the same, and approximated by an enveloping metal sheet. One explicit dependency on the solvent is that the solvation energy is scaled by

$$f(\epsilon) = \frac{\epsilon - 1}{\epsilon + \chi}$$

and this depends on the dielectric constant of the solvent, and an empirical factor $\chi$. The other is that the shape of the surface is influenced by the *Rad* parameter, see below. `SOLVATION (block type)`

```
SOLVATION
   {Surf [Delley|Wsurf|Asurf|Esurf|Klamt]}
   {Solv {Name=solvent} {Eps=78.4} {Rad=1.4} {Del=1.4} {Emp=0.0}}
   {Div {Ndiv=3} {NFdiv=1} {Min=0.5} {OFAC=0.8} {leb1=23} {leb2=29} {rleb=1.5}}
   {RADII
     name1=value1
     name2=value2
   subend}
   {Charge {Method=meth} {Conv=1e-10} {Iter=1000} {NoCorr}}
   {Cvec [Exact|FitPot]}
   {SCF [Var|Pert]}
End
```

Presence of the `SOLVATION` key block triggers the solvent calculation and does not require additional data. With subkeys you can customize various aspects of the model, for instance to specify the type of solute. None of the subkeys is obligatory

See also the subkey *StaticCosmoSurface* (page 44) in the `GEOOPT` block and the subkey *StaticCosmoSurface* (page 45) in the `FREQUENCIES` block.

Follows a description of the subkeys

**Surf [Delley|Wsurf|Asurf|Esurf|Klamt]** (**Default: Delley**) Five different cavity types are available. The Wsurf, Asurf, and Esurf surfaces are constructed with the GEPOL93 algorithm.[*38* (page 165)]

**Wsurf** Wsurf triggers the Van der Waals surface (VdW), which consists of the union of all atomic spheres.

**Asurf** Asurf gives the Solvent-Accessible-Surface (SAS). This is similar to VdW but consists of the path traced by the center of a spherical solvent molecule rolling about the VdW surface or, equivalently, a VdW surface created by atomic spheres to which the solvent radius has been added. These two surface types contain cusps at the intersection of spheres.

**Esurf** Esurf gives the Solvent-Excluding-Surface (SES), which consists of the path traced by the *surface* of a spherical solvent molecule rolling about the VdW surface. Primarily, this consists of the VdW surface but in the regions where the spheres would intersect, the concave part of the solvent sphere replaces the cusp. This SES surface is the default.

**Klamt** The fourth surface option is Klamt as described in [*36* (page 165)]. It excludes the cusp regions also.

**Delley** The fifth surface is the so called Delley surface.[*39* (page 165)]

**Solv** Solvent details.

**Del** Del is the value of Klamt's delta_sol parameter, only relevant in case of Klamt surface.

**Emp** Emp addresses the empirical scaling factor $x$ for the energy scaling.

**Name, Eps, Rad** Eps specifies the dielectric constant (the default relates to water). An infinite value for Eps is chosen if Eps is specified to be lower than 1.0. Rad specifies the radius of the (rigid sphere) solvent molecules, in angstrom. Instead of specifying Eps and Rad one can specify a solvent name or formula after 'name='. The following table lists names and formulas that are recognized with the corresponding values for Eps and Rad. The names and formulas are case-insensitive.

| Name | Formula | Eps | Rad |
|---|---|---|---|
| AceticAcid | CH3COOH | 6.19 | 2.83 |
| Acetone | CH3COCH3 | 20.7 | 3.08 |
| Acetonitrile | CH3CN | 37.5 | 2.76 |
| Ammonia | NH3 | 16.9 | 2.24 |
| Aniline | C6H5NH2 | 6.8 | 3.31 |
| Benzene | C6H6 | 2.3 | 3.28 |
| BenzylAlcohol | C6H5CH2OH | 13.1 | 3.45 |
| Bromoform | CHBr3 | 4.3 | 3.26 |
| Butanol | C4H9OH | 17.5 | 3.31 |
| isoButanol | (CH3)2CHCH2OH | 17.9 | 3.33 |
| tertButanol | (CH3)3COH | 12.4 | 3.35 |
| CarbonDisulfide | CS2 | 2.6 | 2.88 |
| CarbonTetrachloride | CCl4 | 2.2 | 3.37 |
| Chloroform | CHCl3 | 4.8 | 3.17 |
| Cyclohexane | C6H12 | 2 | 3.5 |
| Cyclohexanone | C6H10O | 15 | 3.46 |
| Dichlorobenzene | C6H4Cl2 | 9.8 | 3.54 |
| DiethylEther | (CH3CH2)2O | 4.34 | 3.46 |
| Dioxane | C4H8O2 | 2.2 | 3.24 |
| DMFA | (CH3)2NCHO | 37 | 3.13 |
| DMSO | (CH3)2SO | 46.7 | 3.04 |
| Ethanol | CH3CH2OH | 24.55 | 2.85 |
| EthylAcetate | CH3COOCH2CH3 | 6.02 | 3.39 |
| Dichloroethane | ClCH2CH2Cl | 10.66 | 3.15 |

Continued on next page

Table 4.1 – continued from previous page

| | | | |
|---|---|---|---|
| EthyleneGlycol | HOCH2CH2OH | 37.7 | 2.81 |
| Formamide | HCONH2 | 109.5 | 2.51 |
| FormicAcid | HCOOH | 58.5 | 2.47 |
| Glycerol | C3H8O3 | 42.5 | 3.07 |
| HexamethylPhosphoramide | C6H18N3OP | 43.3 | 4.1 |
| Hexane | C6H14 | 1.88 | 3.74 |
| Hydrazine | N2H4 | 51.7 | 2.33 |
| Methanol | CH3OH | 32.6 | 2.53 |
| MethylEthylKetone | CH3CH2COCH3 | 18.5 | 3.3 |
| Dichloromethane | CH2Cl2 | 8.9 | 2.94 |
| Methylformamide | HCONHCH3 | 182.4 | 2.86 |
| Methypyrrolidinone | C5H9NO | 33 | 3.36 |
| Nitrobenzene | C6H5NO2 | 34.8 | 3.44 |
| Nitrogen | N2 | 1.45 | 2.36 |
| Nitromethane | CH3NO2 | 35.87 | 2.77 |
| PhosphorylChloride | POCl3 | 13.9 | 3.33 |
| IsoPropanol | (CH3)2CHOH | 19.9 | 3.12 |
| Pyridine | C5H5N | 12.4 | 3.18 |
| Sulfolane | C4H8SO2 | 43.3 | 3.35 |
| Tetrahydrofuran | C4H8O | 7.58 | 3.18 |
| Toluene | C6H5CH3 | 2.38 | 3.48 |
| Triethylamine | (CH3CH2)3N | 2.44 | 3.81 |
| TrifluoroaceticAcid | CF3COOH | 42.1 | 3.12 |
| Water | H2O | 78.39 | 1.93 |

**DIV**

**Ndiv, NFdiv** Ndiv controls how fine the spheres that in fact describe the surface are partitioned in small surface triangles, each containing one point charge to represent the polarization of the cavity surface. Default division level for triangles Ndiv=3. Default final division level for triangles NFdiv=1 (NFdiv $\leq$ Ndiv).

**Min** (**Default: 0.5**) Min specifies the size, in angstrom, of the smallest sphere that may be constructed by the SES surface. For VdW and SAS surfaces it has no meaning.

**Ofac** (**Default: 0.8**) Ofac is a maximum allowed overlap of new created spheres, in the construction procedure.

**leb1, leb2, rleb** For the Delley type of construction one needs to set the variables leb1 (**Default: 23**), leb2 (**Default: 29**), and rleb (**Default: 1.5**) to set the number of surface points. If the cavity radius of an atom is lower than rleb use leb1, otherwise use leb2. These values can be changed: using a higher value for leb1 and leb2 gives more surface points (maximal value leb1, leb2 is 29). A value of 23 means 194 surface points in case of a single atom, and 29 means 302 surface points in case of a single atom Typically one could use leb1 for the surface point of H, and leb2 for the surface points of other elements.

**Radii** In the Radii data block you give a list of atom types and values:

```
SOLVATION
  . . .
  Radii
     H 0.7
     C 1.3
     . . .
  Subend
  . . .
End
```

The values are the radii of the atomic spheres, in the default unit of length (angstrom or bohr). If not specified the default values are those by Allinger.[*40* (page 165)]

**Charge** This addresses the determination of the (point) charges that model the cavity surface polarization. In COSMO calculations you compute the surface point charges $q$ by solving the equation A*q*=-$f$, where $f$ is the molecular potential at the location of the surface charges $q$ and A is the self-interaction matrix of the charges. The number of charges can be substantial and the matrix A hence very large. A direct method, i.e. inversion of A, may be very cumbersome or even impossible due to memory limitations, in which case you have to resort to an iterative method. *Meth* (**Default: INVER**) specifies the equation-solving algorithm. The option *INVER* requests direct inversion. The option *CONJ* uses the preconditioned biconjugate gradient method. This is guaranteed to converge and does not require huge amounts of memory. CONV and ITER are the convergence criterion and the maximum number of iterations for the iterative method. In periodic calculations the unit cell needs to be neutral. Therefore, by default the COSMO charges are forced to sum to zero. When NOCORR is present, this constraint is not applied.

**CVec** (**Default: Exact**) There are two ways to calculate the molecule- (COSMO)surface interaction. EXACT: Consider the interactions between the electron density and the potential due to the COSMO points. FITPOT: Use the COSMO point charges in the potential of the molecule (obtained by density fitting).

The EXACT option is exact on paper, but in reality numerical integration is used to get the energy. The standard grid is formally not suitable to handle the cusps at the COSMO points. Still this option works well because the singularity is softened by the smallness of the electronic density at the COSMO points. The EXACT option is much faster when doing a geometry optimization.

**SCF** (**Default: VAR**) The option VAR is to apply the external potential of the COSMO surface during the SCF. To apply COSMO only post SCF you can use the PERT option.

### 4.3.2 Additional keys for periodic systems

**PeriodicSolvation (block-type)** For the simulation of periodic structures additional information might be necessary. Therefore, the `PeriodicSolvation` block can be used.

```
PeriodicSolvation
   {RemovePointsWithNegativeZ [True|False]}
   {Nstar integer}
End
```

**RemovePointsWithNegativeZ** (**Default: false**) This option, expecting a boolean value (true or false), handles whether a COSMO surface is constructed on both sides of a surface. If one is only interested in the solvation effect on the upper side of a surface then this option should be set to true.

**Nstar** (**Default: 4**) This option, expecting an integer number (>2), handles the accuracy for the construction of the COMSO surface. The larger the given number the more accurate the construction.

**General remarks:** The accuracy of the result and the calculation time is influenced by the screening radius `SCREENING%RMADEL` (see *Screening* (page 40)). If the calculation does take too long, defining a smaller radius does help. **But:** too small radii, especially smaller than the lattice constants, will give unphysical results.

## 4.4 Static Electric Field

For systems without 3D periodic symmetry it is possible to specify an external electric field in the z-direction.

**EField** Include a homogeneous static electric field in the z-direction:

```
EField
   Ez rval
   {Unit [Volt/Angstrom | a.u. | Volt/bohr | Volt/Meter]}
End
```

`Ez` This option expects a real value which is the strength of the electric field.

`Unit` (**Default: Volt/Angstrom**) This options specifies the unit of the electric field.

The static field is explicitly handled in the determination of the orbital coefficients, energy, and gradients. If you apply it to any other property, such as the NMR shielding tensor, dielectric function, solvation energy, etc., the result is probably not entirely correct. In case of doubt contact the SCM staff.

## 4.5 Nuclear model

Normally the nucleus is modeled as a point charge.

**`NuclearModel`** (**Default: PointCharge**) Specify what model to use for the nucleus:

```
NuclearModel [PointCharge | Gaussian | Uniform]
```

One can choose between the standard point charge model and a Gaussian model. For the Gaussian model the nuclear radius is calculated according to the work of Visscher and Dyall.[*50* (page 166)]

The static field is explicitly handled in the determination of the orbital coefficients, energy, and gradients. If you apply it to any other property, such as the NMR shielding tensor, dielectric function, solvation energy, etc., the result is probably not entirely correct. In case of doubt contact the SCM staff.

CHAPTER

FIVE

# ACCURACY AND EFFICIENCY

Given a chosen model Hamiltonian (discussed elsewhere), the three main issues that influence the accuracy of a calculation are: *integration in real space* (page 32), *integration in reciprocal space* (page 34), and the quality of the *basis set* (page 27).

**General Numerical Quality**

The key `NumericalQuality` sets the quality of several important technical aspects of a BAND calculation (with the notable exception of the *basis set* (page 27))

```
NumericalQuality [Basic | Normal | Good | VeryGood | Excellent]
```

**`NumericalQuality`** (**Default: Normal**) This key sets the default Quality of the *Becke grid* (page 32), *ZlmFit* (page 35), *k-space integration* (page 34), and *SoftConfinement* (page 31). Possible values are Basic, Normal, Good, VeryGood, and Excellent. For the user this is the most convenient way to influence the precision, and estimate the error. It is always possible to tweak things more, as is explained below.

**Defaults Convention**

There has been a big change in many default settings with the 2014 release. To switch between the two styles

```
DefaultsConvention [Pre2014 | 2014]
```

With the *pre2014* settings, you will get STO fitting, the Voronoi grid, the old, symmetric *k*-point sampling, and no confinement, resembling the behavior of the 2013 version.

## 5.1 Basis set

With the key `BasisDefaults` you can control the quality of the basis set, and the level of frozen core approximation. Given your preferences the basis and fit sets are retrieved from the database. The output starts with a copy of your input, but with the basis and fit sets inserted from the database: at this point you can exactly see which values are used. You can always override the defaults by specifying the AtomType keyword. There is no need for special basis sets for relativistic calculations.

### 5.1.1 Automatic mode: BasisDefaults

The simplest way of specifying a basis set is via the `BasisDefaults` block key. For example:

```
BasisDefaults
   BasisType TZP
   Core None
End
```

instructs BAND to use an all-electron (`Core None`) TZP basis set.

**`BasisDefaults (block-type)`** This key allows you to generate automatically the required AtomType blocks (i.e. basis and fit sets) from the database. The basis sets database is located in "$ADFHOME/atomicdata/band". You can always see what has been generated at the beginning of the output file, where your input is echoed with the AtomType blocks expanded. It shows as a comment from which file each AtomType has been copied.

```
! --- basis from file /path/to/TZ2P/C.1s---

AtomType C
...
End

! --- basis from file /path/to/DZ/H---

AtomType H
...
End
```

The `BasisDefaults` block has the following subkeys.

**`BasisType`** The following basis sets are available.

- **DZ**: Double zeta. Adapted from the ADF basis set of the same name. The smallest basis set. The results are most likely not so accurate
- **DZP**: Double zeta plus polarization function. Is only available for *main group elements* up to Krypton. For other elements a TZP basis set will be used automatically!
- **TZP**: Triple zeta plus polarization. Adapted from the ADF basis set of the same name.
- **TZ2P**: Triple zeta plus double polarization. Adapted from the ADF basis set of the same name. This is a good basis set.
- **QZ4P**: Quadruple zeta plus quadrupole polarization. The biggest basis set. For benchmark purposes only.

If you have a large unit cell, you could start with the DZ basis, to see if it will be feasible at all. For more reliable results, use a triple zeta basis set. You can override the defaults per type by specifying Atoms%Core and Atoms%BasisType, or Atoms%Path (sub)keys.

**`Core`** (**Default: Large**) This influences the size of the frozen core used. Possible values are *None*, *Small*, *Medium*, *Large*. You should be aware that a change of this parameter does not necessarily mean that a different frozen core is used. You can again check in the output what file was really used. You can see it from the extension in the comment line preceding the AtomType key

```
! --- basis from file /path/to/TZ2P/C.1s---
```

or from the Dirac block in the AtomType key.

**Note**: For all elements up to Au the *Medium* and *Large* frozen core are identical. And starting with Thallium there are three different frozen core definitions available.

**`FitType`** The STO fit set is by default determined via the BasisType. With this key one can choose the fit set independently from the BasisType key. (See *obsolete density fitting* (page 35))

### 5.1.2 Available standard basis sets

The next table gives an idication which all electron (ae) and frozen core (fc) standard basis sets are available for the different elements in BAND.

Table 5.1: Available standard basis sets for non-relativistic and ZORA calculations H-Uuo (Z=1-118)

| Element | ae | fc | SZ, DZ | DZP | TZP, TZ2P, QZ4P |
|---|---|---|---|---|---|
| H-He (Z=1-2) | ae | | Yes | Yes | Yes |
| Li-Ne (Z=3-10) | ae | .1s | Yes | Yes | Yes |
| Na-Mg (Z=11-12) | ae | .1s .2p | Yes | Yes | Yes |
| Al-Ar (Z=13-18) | ae | .2p | Yes | Yes | Yes |
| K-Ca (Z=19-20) | ae | .2p .3p | Yes | Yes | Yes |
| Sc-Zn (Z=21-30) | ae | .2p .3p | Yes | | Yes |
| Ga-Kr (Z=31-36) | ae | .3p .3d | Yes | Yes | Yes |
| Rb-Sr (Z=37-38) | ae | .3p .3d .4p | Yes | | Yes |
| Y-Cd (Z=39-48) | ae | .3d .4p | Yes | | Yes |
| In-Ba (Z=49-56) | ae | .4p .4d | Yes | | Yes |
| La-Lu (Z=57-71) | ae | .4d .5p | Yes | | Yes |
| Hf-Hg (Z=72-80) | ae | .4d .4f | Yes | | Yes |
| Tl (Z=81) | ae | .4d .4f .5p | Yes | | Yes |
| Pb-Rn (Z=82-86) | ae | .4d .4f .5p .5d | Yes | | Yes |
| Fr-Ra (Z=87-88) | ae | .5p .5d | Yes | | Yes |
| Ac-Lr (Z=89-103) | ae | .5d .6p | Yes | | Yes |
| Rf-Uuo(Z=104-118) | ae | .5d .5f | Yes | | Yes |

- element name (without suffix): all electron (ae)
- .1s frozen: 1s
- .2p frozen: 1s 2s 2p
- .3p frozen: 1s 2s 2p 3s 3p
- .3d frozen: 1s 2s 2p 3s 3p 3d
- .4p frozen: 1s 2s 2p 3s 3p 3d 4s 4p
- .4d frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d
- .4f frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f
- .5p frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 5s 5p (La-Lu)
- .5p frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p (other)
- .5d frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p 5d
- .6p frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p 5d 6s 6p (Ac-Lr)
- .5f frozen: 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p 5d 5f 6s 6p

### 5.1.3 Manually specifying AtomTypes

**`AtomType (block-type)`** (*Expert Option*) Description of the atom type. Contains the block keys `Dirac`, `BasisFunctions` and `FitFunctions`. The key corresponds to one atom type. The ordering of the `AtomType` keys (in case of more than one atom type) is **NOT** arbitrary. It is interpreted as corresponding to the ordering of the `Atoms` keys. The n-th `AtomType` key supplies information for the numerical atom of the $n^{th}$ type, which in turn has atoms at positions defined by the $n^{th}$ `Atoms` key.

```
AtomType ElementSymbol
   Dirac ChemSym
      {option}
```

```
      ...
      shells cores
      shell_specification {occupation_number}
      ...
   SubEnd
   {BasisFunctions
      shell_specification STO_exponent
      ...
   SubEnd}
   FitFunctions
      shell_specification STO_exponent
      ...
   SubEnd
END
```

The argument *ElementSymbol* to `AtomType` is the symbol of the element that is referred to in the `Atoms` key block.

**`Dirac (block-type)`** Specification of the numerical ('Herman-Skillman') free atom, which defines the initial guess for the SCF density, and which also (optionally) supplies Numerical Atomic Orbitals (NOs) as basis functions, and/or as STO fit functions for the crystal calculation. The argument *ChemSym* of this option is the symbol of the element of the atom type. The data records of the `Dirac` key are:

1. the number of atomic shells (1s,2s,2p,etc.) and the nr. of core-shells (two integers on one line).
2. specification of the shell and its electronic occupation.

This specification can be done via quantum numbers or using the standard designation (e.g. '1 0' is equivalent to '1s'). Optionally one may insert anywhere in the Dirac block a record *Valence*, which signifies that all numerical valence orbitals will be used as basis functions (NOs) in the crystal calculation. You can also insert *NumericalFit* followed by a number (max. $l$-value) in the key block, which causes the program to use numerical STO fit functions. For example NumericalFit 2 means that the squares of all s,p, and d NOs will be used as STO fit functions with $l = 0$, since the NOs are spherically symmetric. If you insert *Spinor*, a spin-orbit relativistic calculation for the single-atom will be carried out.

The Herman-Skillman program generates all its functions (atomic potential, charge density, one-electron states) as tables of values in a logarithmic radial grid. The number of points in the grid, and the min. and max. r-value are defaulted at 3000, 0.000001, and 100.0 (a.u.) respectively. These defaults can be overwritten by specifying anywhere in the Dirac block the (sub)keys *radial*, *rmin* and *rmax*.

The program will do a spin-unrestricted calculation for the atoms in addition to the restricted one. The occupation of the spin-orbitals will be of maximum spin-multiplicity and cannot be controlled in the Dirac key-block.

**`BasisFunctions (block-type)`** Slater-type orbitals, specified by quantum numbers $n$,:math:$l$ or by the letter designation (e.g. 2p) and one real (alpha) per STO. One STO per record. Use of this key is optional in the sense that Slater-type functions are not needed if other basis functions have been specified (i.e. the numerical atomic orbitals, see key Dirac).

**`FitFunctions (block-type)`** Slater-type fit functions, described in the same way as in `BasisFunctions`. Each `FitFunctions` key corresponds to one atom type, the type being the one of the preceding `Dirac` key. The selection choice of a 'good' fit set is a matter of experience. Fair quality sets are included in the database of the molecular program ADF.

Example:

```
   AtomType C :: Carbon atom
      Dirac C
         3 1
      VALENCE
```

```
            1s
            2s
            2p 2.0
         SubEnd
         BasisFunctions
            1s 1.7
            ...
         SubEnd
         FitFunctions
            1s 13.5
            2s 11.0
            ...
         SubEndEnd
```

**TestFunctions (block-type)** An optional subkey of the AtomType key block is TestFunctions which has the same format as the BasisFunctions and FitFunctions blocks. The TestFunctions block specifies STOs to be used as test functions in the numerical integration package. For the time being the $l$ value is ignored. A possible application is to include a very tight function, to increase the accuracy near a nucleus.

### 5.1.4 Confinement of basis functions

It is possible to alter the radial part of the basis functions in order to make them more compact.

**SOFTCONFINEMENT (block-type)** With soft confinement the radial part of the basis functions is multiplied with a Fermi-Dirac (FD) function. A FD function goes from one to zero, controlled by two parameters. It has a value 0.5 at Radius, and the decay width is Delta.

```
SoftConfinement
  Quality [Basic|Normal|Good|VeryGood|Excellent]
  Radius r
  Delta  d
End
```

This will set the confinement for all atoms. The most convenient way is to specify the Quality subkey. The resulting confinement parameters are

| Quality | Radius | Delta |
|---|---|---|
| Basic | 7.0 | 0.7 |
| Normal | 10.0 | 1.0 |
| Good | 20.0 | 2.0 |
| VeryGood | / | / |

Specifying the Radius or Delta subkey will override the defaults. A negative value means no confinement.

**CONFINEMENT (block-type): subkey of atomtype** You can also control the soft confinement at the atom type level. In a slab calculation this allows one to use different settings for surface atoms than for those in inner layers. You can specify the range and the decay speed of the FD function like:

```
Confinement
   Radius 7
   Delta 0.7
SubEnd
```

If the decay Delta is not specified it defaults to 0.1*'Radius'. Relativistic effects are treated correctly. If the confinement option is used in combination with the TAILS option, the calculation may run significantly faster. The Confinement option can also be useful without the tails option in cases where near linear dependency reduces the numerical reliability of the results (cf. Dependency keyword). This typically occurs for highly

coordinated systems with large basis sets containing diffuse functions. For such cases, the confinement option (possibly in combination with the `Dependency` keyword) reduces the numerical problems.

**NB:** does not work with the `BasisDefaults` key (because it is a subkey of `AtomType`).

## 5.2 Real Space Numerical Integration

Many of the integrals are obtained by numerical integration. Two grids are available: the old Voronoi scheme (deprecated) and the Becke grid (**default**). One can switch between the two using:

```
IntegrationMethod [Becke | Voronoi]
```

### 5.2.1 Becke Grid

This numerical integration grid is a refined version of the fuzzy cells integration scheme developed by Becke.[*51* (page 166)] The implementation in BAND is described in Ref. [*52* (page 166)].

The quality of the Becke integration grid can be changed within the `BECKEGRID` block key

```
BECKEGRID
   Quality [basic|normal|good|verygood|excellent]
End
```

**`Quality`** (**Default: Normal**) For a description of the various "qualities" and the associated numerical accuracy see reference *52* (page 166). The integration grid quality defined in the `BECKEGRID` block key overrules the *NumericalQuality* (page 27).

**Advanced options:**

```
BECKEGRID
  {AtomDepQuality
     Ia1 [basic|normal|good|verygood|excellent]
     Ia2 [basic|normal|good|verygood|excellent]
     ...
  SubEnd}
  {RadialGridBoost boost}
End
```

**`AtomDepQuality`** One can define a different grid quality for each atom, with input numbers *Ia1*, *Ia2*, etc. If an atom is not present in the `AtomDepQuality` section, the quality defined in the `Quality` key will be used. *Example: Multiresolution* (page 101) illustrates how to use this option.

**`RadialGridBoost`** (**Default: 1.0** (or 3.0 if a numerically sensitive functional is used)) The number of radial integration points will be boosted by this factor. Some XC functionals require very accurate radial integration grids, so BAND will automatically *boost* the radial grid for the following numerically sensitive functionals: `LibXC M05`, `LibXC M05-2X`, `LibXC M06-2X`, `LibXC M06-HF`, `LibXC M06-L`, `LibXC M08-HX`, `LibXC M08-SO`, `LibXC M11-L`, `LibXC MS0`, `LibXC MS1`, `LibXC MS2`, `LibXC MS2H`, `LibXC MVS`, `LibXC MVSH`, `LibXC N12`, `LibXC N12-SX`, `LibXC SOGGA11`, `LibXC SOGGA11-X`, `LibXC TH1`, `LibXC TH2`, `LibXC WB97`, `LibXC WB97X`, `MetaGGA M06L`, `MetaHybrid M06-2X`, `MetaHybrid M06-HF`, `MetaGGA MVS`

**Notes:**

- The space-partition function used in BAND differs from the one described in Ref. [*52* (page 166)]. The unnormalized partition function used in the program is defined as ($\Omega_I$ is an element-dependent parameter: 0.1 Bohr for H, 0.3 Bohr for He-Xe and 0.6 Bohr for Cs-Uuo):

$$\mathcal{P}_{i,U} = \begin{cases} 1 & \text{if } r_{i,U} < \Omega_I \\ 0 & \text{if } \exists j : r_{j,U} < \Omega_J \\ \eta_i \frac{e^{-2(r_{i,U}-\Omega_I)/a_0}}{(r_{i,U}-\Omega_I)^2} & \text{elsewhere} \end{cases}$$

- A Becke grid of normal quality is roughly equivalent (in both absolute accuracy and computation time) to INTEGRATION 4 (Voronoi scheme), and a Becke grid of good quality is roughly equivalent to INTEGRATION 6 (Voronoi scheme).
- The Becke grid is not very well suited to calculate Voronoi deformation density (VDD) charges. For accurate calculation of VDD charges the Voronoi integration scheme is recommended.

### 5.2.2 Radial grid

With this keyword the radial grid can be controlled.

```
RadialDefaults
  NR nr
  RMin rmin
  RMax rmax
End
```

**NR** (**Default: 3000**) This key hanldes the number of radial points. With very high values like 30.000 the Dirac subprogram may not converge.

**RMin, RMax** These keys define the lower (**Default: 1e-6**) and upper (**Default: 100**) bound of the logarithmic grid.

### 5.2.3 Elliptic integrals

(*Expert Option*) The integration of the electrostatic interaction between spherical atoms is done very precisely in an elliptic grid, which depends on NUELSTAT and NVELSTAT

**NUELSTAT** (**Default: 50**) Electrostatic interaction integrals between spherical atomic densities are computed by numerical integration over an elliptic grid. *Nuelstat* is the outward (parabolic) coordinate number of integration points.

**NVELSTAT** (**Default: 80**) Electrostatic interaction integrals between spherical atomic densities are computed by numerical integration over an elliptic grid. *Nvelstat* is the angular (elliptic) coordinate number of integration points.

### 5.2.4 Voronoi grid (deprecated)

**INTEGRATION (block-type)** Parameter-specifications for the generation of numerical integration points and weights. Most data records must be of the form 'parameter value'. The most important parameter is accint, which is defaulted to the value of key ACCURACY. Unless one is very familiar with the details of the numerical integration package, we strongly recommend not to use the INTEGRATION key, and to specify only ACCURACY. More information can be found in the literature.

**ACCURACY** This key expects a real value, normally between 3 and 7, and will automatically set all necessary options for the numerical integration with the Voronoi grid. A value of 3 would be basic quality and a value of 7 would be good quality

## 5.3 Reciprocal Space Numerical Integration (KSpace)

The k-space integration can be controlled via the `KSpace` block key. Two different k-space integration methods are available: the *Regular Grid* (**default**) and the *Tetrahedron Method*.

### 5.3.1 Regular K-Space grid

By default BAND uses a regular grid to sample the Brillouin zone (BZ).

#### Automatic mode

The simplest way to adjust the quality of the k-space integration is via the `Quality` key:

```
KSpace
  Quality [Basic|Normal|Good|VeryGood|Excellent]
End
```

**`Quality`** (**Default: Normal**) With the automatic grid, the program will look at the size of a lattice vector. A big vector in real space, means a small one in reciprocal space. Thinking in real space lattice vectors the following intervals will be distinguished: 0-5 bohr, 5-10 bohr, 10-20 bohr, 20-50 bohr, and beyond. Here is the table explaining how many points will be used along a lattice vector.

| range | Basic | Normal | Good | VeryGood | Excellent |
|---|---|---|---|---|---|
| 0-5 | 5 | 9 | 13 | 17 | 21 |
| 5-10 | 3 | 5 | 9 | 13 | 17 |
| 10-20 | 1 | 3 | 5 | 9 | 13 |
| 20-50 | 1 | 1 | 3 | 5 | 9 |
| 50-... | 1 | 1 | 1 | 3 | 5 |

By preferring odd-numbered values we can use a quadratic interpolation method, and have the $\Gamma$ point in the grid. It is then reasonable to assume a decaying error when going to a better quality setting.

#### User-defined regular grid

It is possible to manually define the number of k-space points along each reciprocal lattice vector:

```
KSpace
  Grid n1 {n2} {n3}
End
```

For 1D periodic systems you should specify only `n1`, for 2D systems `n1` and `n2`, and for 3D systems `n1`, `n2` and `n3`.

### 5.3.2 Tetrahedron Method

The tetrahedron method can be useful when especially high symmetry points in the BZ are needed to capture the correct physics of the system, graphene being a notable example.

```
KSpace integer &
   Grid Symmetric
End
```

The parameter for numerical integration over the BZ is an integer value.

- 1: absolutely minimal (only the $\Gamma$ point is used)

- 2/4/...: linear tetrahedron method
- 3/5/...: quadratic tetrahedron method

The linear tetrahedron method is usually inferior to the quadratic tetrahedron method. Try 3 for a reasonable result, or 5 for higher precision.

**General Remark**: The tetrahedron method samples the irreducible wedge of the first BZ, whereas the regular grid samples the whole, first BZ. As a rule of thumb you need to choose roughly twice the value for the regular grid. For example kspace 2 compares to grid 4 4 4, kspace 3 to grid 5 5 5, etc.. Sticking to this rule the number of unique k-points will be roughly similar.

## 5.4 Density fitting

The default density fitting scheme in BAND is the so-called **Zlm Fit**, described in reference *53* (page 166). We do **not** recommend to use the STO Fit anymore.

### 5.4.1 Zlm Fit

The basic idea behind Zlm Fit can be described as follows: the total electron-density is split into atomic densities (in a similar way as the volume is partitioned for the Becke grid). These atomic densities are then approximated by a combination of radial spline functions and real spherical harmonics (Zlm).

`ZlmFit (block-type)`

```
ZlmFit
  Quality [Basic|Normal|Good|VeryGood|Excellent]
End
```

**`Quality`** (**Default: Normal**) controls the accuracy and quality of fitted properties.

**Advanced options:**

```
ZlmFit
  {AtomDepQuality
     Ia1 [basic|normal|good|verygood|excellent]
     Ia2 [basic|normal|good|verygood|excellent]
     ...
  SubEnd}
End
```

**`AtomDepQuality`** One can define a different fit quality for each atom, with input numbers *Ia1*, *Ia2*, etc. If an atom is not present in the `AtomDepQuality` section, the quality defined in the `Quality` key will be used. *Example: Multiresolution* (page 101) illustrates how to use this option.

### 5.4.2 Obsolete Method - STO Fit

In previous version of BAND this was the default option, which is now replaced by Zlm Fit. It is still used in the context of NMR and Response calculations.

## 5.5 Self-consistency

The SCF procedure searches for a self-consistent density. The self-consistent error is the square root of the integral of the squared difference between the input and output density of the cycle operator. When the SCF error is below a

certain criterion, controlled by subkey `Criterion` of block key `Convergence`, convergence is reached. In case of bad convergence the SCF look at the subkeys `Mixing`, and `Degenerate`, and the subkeys of block key `DIIS`.

### 5.5.1 SCF key

The SCF key block controls technical SCF parameters

```
SCF
  {Mixing value}
  {Iterations n}
  {Eigenstates}
  {Pmatrix}
  {Rate value}
  {VSplit value}
End
```

**`Mixing`** (**Default: 0.075**) Initial 'damping' parameter in the SCF procedure, for the iterative update of the potential: new potential = old potential + mix (computed potential-old potential). Note: the program automatically adapts Mixing during the SCF iterations, in an attempt to find the optimal mixing value.

**`Iterations`** (**Default: 0**) The maximum number of SCF iterations to be performed. If zero, termination of the SCF procedure will depend on other aspects (convergence, time-out, insufficient progress towards convergence, ...).

**`EigenStates`** The program knows two alternative ways to evaluate the charge density iteratively in the SCF procedure: from the P-matrix, and directly from the squared occupied eigenstates. By default the program actually uses both at least one time and tries to take the most efficient. If present, `Eigenstates` turns off this comparison and lets the program stick to one method (from the eigenstates).

**`Pmatrix`** If present, evaluate the charge density from the P-matrix. See also the subkey Eigenstates.

**`Rate`** (**Default: 0.99**) Minimum rate of convergence for the SCF procedure. If progress is too slow the program will take measures (such as smearing out occupations around the Fermi level, see subkey `Degenerate` of block key `Convergence`) or, if everything seems to fail, it will stop.

**`VSplit`** (**Default: 5E-2**) To disturb degeneracy of alpha and beta spin MOs the value of this key is added to the beta spin potential at the startup.

### 5.5.2 Convergence key

All options and parameters related to the convergence behavior of the SCF procedure are defined in the `Convergence` block key. Also the finite temperature distribution is part of this

```
Convergence
  {Criterion value}
  {ElectronicTemperature value}
  {Degenerate value}
  {SpinFlip list}
  {StartWithMaxSpin [True|False]}
  {InitialDensity [RHO|PSI]}
  {Boltzmann n}
  {LessDegenerate [False|True]}
  {NoDegenerate}
End
```

**`Criterion`** Criterion for termination of the SCF procedure. The default depends on *NumericalQuality* (page 27). For Normal numerical quality it is 1E-6.

**ElectronicTemperature** (**Default: 0**) Requires a numerical argument, which is an energy width (in a.u.). It simulates a finite-temperature electronic distribution. The key may be used to achieve convergence in an otherwise problematically converging system. The energy of a finite-T distribution is different from the T=0 value, but for small T a fair approximation of the zero-T energy is obtained by extrapolation. The extrapolation energy correction term is printed with the survey of the bonding energy in the output file. Check that this value is not too large. Build experience yourself how different settings may affect the outcomes. **Note**: this key is meant to help you overcome convergence problems, not to do finite-temperature research! Only the electronic distribution is computed T-dependent, other aspects are not accounted for!

**Degenerate** (**Default: default**) Smooths (slightly) occupation numbers around the Fermi level, so as to insure that nearly-degenerate states get (nearly-) identical occupations. **Be aware**: In case of problematic SCF convergence the program will turn this key on automatically, unless the key `Nodegenerate` is set in input. The smoothing depends on the argument to this key, which can be considered a 'degeneration width'. When the argument reads **default**, the program will use the value **1e-4 a.u.** for the energy width.

**SpinFlip** List here the atoms for which you want the initial spin polarization to be flipped. This way you can distinguish between ferromagnetic and anti ferromagnetic states. Currently, it is not allowed to give symmetry equivalent atoms a different spin orientation. To achieve that you have to break the symmetry.

**StartWithMaxSpin** (**Default: True**) To break the initial perfect symmetry of up and down densities there are two strategies. One is to occupy the numerical orbitals in a maximum spin configuration. The alternative is to add a constant to the potential. See also *Vsplit* (page 36) key.

**InitialDensity** (**Default: RHO**) The SCF is started with a guess of the density. There are the following choices **RHO**: the sum of atomic density. **PSI**: construct an initial eigensystem by occupying the atomic orbitals. The guessed eigensystem is orthonormalized, and from this the density is calculated.

**LESSDEGENERATE** If smoothing of occupations over nearly degenerate orbitals is applied (see *Degenerate* (page 37) key)), then, if this key is set in the input file, the program will limit the smoothing energy range to 1e-4 a.u. as soon as the SCF has converged 'halfway', i.e. when the SCF error has decreased to the square root of its convergence criterion.

**NODEGENERATE** This key prevents any internal automatic setting of the key *DEGENERATE* (page 37).

### 5.5.3 DIIS key

The DIIS procedure to obtain the SCF solution depends on several parameters. Default values can be overruled with this key-block.

```
DIIS
  {dimix rval}
  {adaptable lval}
  {ncycledamp ival}
  {nvctrx ival}
  {clarge rval}
  {chuge rval}
  {condition rval}
  {variant sval}
END
```

**dimix** (**Default: 0.2**) mixing parameter for the DIIS procedure.

**adaptable** (**Default: true**) change automatically the value of `dimix` during the SCF.

**ncycledamp** (**Default: 5**) number of initial iterations where damping is applied, before any DIIS is considered.

**nvctrx** (**Default: 20**) maximum number of DIIS expansion vectors.

**clarge** (**Default: 20**) when the largest DIIS coefficient exceeds this value, the oldest DIIS vector is removed and the procedure re-applied.

**chuge** (**Default: 50**) when the largest coefficient in the DIIS expansion exceeds this value, damping is applied.

**condition** (**Default: 1e+6**) the condition number of the DIIS matrix, the largest eigenvalue divided by the smallest, must not exceed this value. If this value is exceeded, this vector will be removed.

**variant** if specified, you can invoke one of the LIST methods, possible values are **LISTi**, **LISTb**, and **LISTd**. It appears that among these LISTi is the advised method. This can be tried if SCF convergence turns out to be problematic. As it requires an extra fitting step, it is more expensive per SCF iteration.

### 5.5.4 DIRIS key

**DIRIS (block-type)** Same options as `DIIS` key, except that this one applies to the DIIS procedure used in the Dirac subprogram, for numerical single atom calculations, which constructs the radial tables for the NAOs.

## 5.6 Hartree–Fock RI scheme

The Hartree-Fock exchange matrix is calculated through a procedure known as Resolution of the Identity (RI). The implementation of the RI scheme in BAND is loosely based on work by Ren *et al.* [*57* (page 166)]. For more information on hybrid functionals in BAND, see the *XC section* (page 15).

Technical aspects of the RI scheme can be tweaked in the `RIHartreeFock` key block:

```
RIHartreeFock
  Quality [basic|normal|good|verygood]
  FitSetType [Mirko|ET6|ET7|ET8]
  DependencyThreshold 1.0E-3
End
```

**Quality** (**Default: Normal**) Set the numerical quality of some internal technical procedures, including numerical integration and linear scaling parameters.

**FitSetType** (**Default: Mirko**) The auxiliary fit set employed in the RI scheme. ET8 is a fairly large fit set, and can be used for assessing the accuracy of the RI procedure.

**DependencyThreshold** (**Default: 1.0E-3**) To improve numerical stability, almost linearly-dependent combination of basis functions are removed from the Hartree-Fock exchange matrix. If you obtain unphysically large bond energy in an Hybrid calculation, you might try setting the DependencyThreshold to a larger value (*e.g.* 3.0E-3).

For efficiency and numerical stability reasons, it is advisable to include:

```
SoftConfinement
  Quality Basic
End
```

See the *Confinement of basis functions* (page 31) section for more info.

Notes:

- For periodic systems it is only possible to use short-range hybrid functionals (*e.g.* HSE06)

## 5.7 Technical Settings

There are of course many other settings influencing the precision and performance. Usually the user does not need to care about them.

### 5.7.1 Linear Scaling

**Tails** Ignore function tails. By default no tails are ignored. Both CPU time and disk space can be saved by using the TAILS option. This option is most effective when combined with the Confine suboption.

```
TAILS {bas crbas} {core crcore} {fit crfit}
```

One real argument for keys bas and core, which should be a small value (**Default: crbas = 1e-6**). The core criterion defaults to the bas criterion (if set). The tail criterion specifies that tails of exponentially decaying (basis) functions are ignored, in the construction of Bloch functions, beyond the point where the remaining part of the function tail (radially) integrates to less than the criterion, relative to the integral of the function from zero to infinity. Also for the fit one can specify a cutoff, but this is turned off by default (**Default: crfit = 1e-15**). Here we advise to use a more strict criterion than for crbas (because the fit is usually much more dependent than the basis). This option has some refinements. For example

```
Tails confine=1e-2 bas=1e-5 Rosa
```

As you see there are two new elements (**confine** and **Rosa**). The first (**confine**) specifies that all basis functions are optimized for the tails option, by multiplying the tail of the function with a rapidly decaying function. This step affects the shape of all functions outside the radius where the relative norm of the function is smaller than 1e-2. The effects on the shape of the functions are typically very small. The second entry (**Rosa**) has the effect that the criterion becomes more strict for tight functions. For safer (but slower) calculations, specify smaller values for **confine** and **bas**, such as confine=1e-3 bas=1e-6.

The **Rosa** key works as follows. Determine the radius R where according to the normal criterion the function is negligible. Next substitute R - R + 3*exp(-R/3). This means that for tight functions the tails radius is replaced by 3, and for diffuse functions this modifier has no effect.

Tentatively, based on the work by *Rosa Bulo*, we suggest to use

```
Tails bas=1e-3 Rosa
```

The TAILS keyword works most effectively when combined with the confinement keyword.

**Note**: The confine key described here should not be confused with the confinement option for each atom type. The confine option here affects functions in the region where they become very small, independent of the distance to the nucleus. The confinement option introduces a soft cut-off for all functions of a particular atom type, at a specific distance from the nucleus.

### 5.7.2 Dependency

**DEPENDENCY** Criterion for dependency of the basis and fit set:

```
DEPENDENCY {basis tolbas} {core tolcor} {fit tolfit} {corevalence tolovl}
```

**basis** (**Default: 1e-8**) Smallest eigenvalue of the overlap matrix of normalized Bloch functions. See also the discussion in *Recommendations* (page 75) about basis set dependency.

**core** (**Default: 0.98**) The program verifies that the frozen core approximation is reasonable, by checking the smallest value of the overlap matrix of the core (Bloch) orbitals against this criterion.

**fit** (**Default: 1e-6**) Criterion for dependency of the total set of fit functions. The value monitored is the smallest eigenvalue of the overlap matrix of normalized Bloch sums of symmetrized fit functions.

**corevalence** (**Default: 1e-5**) Criterion for dependency of the core functions on the valence basis. The maximum overlap between any two normalized functions in the two respective function spaces should not exceed 1.0-coreval(...).

### 5.7.3 Screening

The program BAND performs many lattice summations which are in practice truncated. The two prime examples are the construction of the Bloch basis and of the fit basis (*obsolete option*) and the construction of the Coulomb potential of the STO fit functions. The precision of the lattice summations is controlled by the `SCREENING` key

**`SCREENING (block)`** Parameters that influence the screening and tails of basis functions. Recognized options are

**`CUTOFF`** Criterion for negligibility of tails in the construction of Bloch sums. Default depends on Accuracy.

**`DMADEL`** One of the parameters that define the screening of Coulomb-potentials in lattice sums. Depends by default on Accuracy, rmadel, and rcelx. One should consult the literature for more information.

**`RCELX`** Max. distance of lattice site from which tails of atomic functions will be taken into account for the Bloch sums. Default depends on Accuracy.

**`RMADEL`** One of the parameters that define screening of the Coulomb potentials in lattice summations. Depends by default on Accuracy, dmadel, rcelx. One should consult the literature for more information.

**`NODIRECTIONALSCREENING`** Real space lattice sums of slowly (or non-) convergent terms, such as the Coulomb potential, are computed by a screening technique. In previous releases, the screening was applied to all (long-range) Coulomb expressions. Starting from BAND98 screening is only applied in the periodicity directions. This key restores the original situation: screening in all directions.

### 5.7.4 Direct (on the fly) calculation of basis and fit

BAND normally calculates basis functions and theirs derivatives on the fly. However, for small bulk systems it can be faster to write the information to disk. Then one can set the `DirectBas` key to false. (**Default = true**)

```
Programmer
   {DirectBas [true | false]}
End
```

### 5.7.5 Fermi energy search

**`Fermi (block type)`** This key sets technical parameter used in the search for the Fermi energy, which is carried out at each cycle of the SCF procedure.

**`MaxTry`** (**Default: 50**) Maximum number of attempts to locate the Fermi energy accurately. The procedure is iterative in nature, narrowing the energy band in which the Fermi energy must lie, between an upper and a lower bound. If the procedure has not sufficiently converged within `MaxTry` iterations, the program takes a reasonable value and constructs the charge density by interpolation between the functions corresponding to the last used upper and lower bounds for the Fermi energy

**`Delta`** (**Default: 1e-4**) Converge criterion: upper and lower bounds for the Fermi energy and the corresponding integrated charge volumes must be equal within delta.

**`Eps`** (**Default: 1e-10**) After convergence of the Fermi energy search procedure, a final estimate is defined by interpolation and the corresponding integrated charge volume is tested. It should be exact, to machine precision. Tested is that it deviates not more than eps.

### 5.7.6 Block size

Efficiency and memory usage depend on how large the vector size of the program is

**CPVECTOR** The code is vectorized and this key can be used to set the vector length. Default depends on the machine and should be set at the installation of the program.

**KGRPX** is an absolute upper bound on the number of k-points processed together. Specifying this key and CPVector you can override bands defaults.

CHAPTER

SIX

# STRUCTURE AND REACTIVITY

To study structure and reactivity common tasks are **geometry optimization**, **transition state search** and a **frequency run**. A frequency run can be done to obtain a good initial Hessian for a geometry optimization, or to check whether a proper minimum or transition state has been found.

The basis for locating stationary points on the PES are the nuclear gradients. (The user may assume that the program does that automatically when needed.)

## 6.1 Nuclear energy gradients

If you want the program to calculate the gradient of the energy w. r. t. nuclear displacements you should add the `Gradients` keyword. If the `SelectedAtoms` key is present, only the gradient of the selected atoms will be evaluated, and the rest set to zero.

Details about the theory of the analytical gradients within the BAND program can be found in the work of *Kadantsev* et al. [*19* (page 164)].

**`Gradients (block-type)`** Key to control the geometry optimization:

```
Gradients
  {oldio [0 | 1]}
  {LatticeGradients [false | true]}
  {LatticeStepSize step}
  {UseRelativeLatticeStep  [true | false]}
End
```

**`oldio`** (**Default: 1**) There are two slightly different implementations. The *oldio=1* implementation has a better scaling behavior for large systems, although it can be a bit slower for small ones. When used with MetaGGAs *oldio=1* is required.

**`LatticeGradeints`** (**Default: false**) This key handles whether the lattice gradients are evaluated numerically (false) or analytically (true).

**`latticeStepSize`** (**Default: 0.012**) With this keyword the step size for the numerical differentiation can be changed. When `UseRelativeLatticeStep` is set to true the step will be relative to the size of the displacement. (Unit is Bohr)

The user rarely needs to specify this key as it is automatically added for geometry optimizations and frequency runs.

This options honors the `SelectedAtoms` key, in which case only the forces will be calculated for the selected atoms.

## 6.2 Lattice gradients

The calculation of the forces, acting on the lattice vectors, is invoked by performing a geometry optimization, including lattice vectors. (see the *GeoOpt%OptimizeLattice* (page 44))

The step size for numerical differentiation is controlled with *Gradients%latticeStepSize* (page 43), and *Gradients%UseRelativeLatticeStep* (page 43).

**LatticeGradients (block-type)** Key to handle special options for the calculation of analytical and numerical lattice gradients.

```
LatticeGradients
   {AnalyticalPulay [true | false]}
   {AnalyticalKinetic [true | false]}
   {AnalyticalXC [true | false]}
   {AnalyticalElectrostatic [true | false]}
End
```

**AnalyticalElectrostatic** (**Default: true**) If true the electrostatic energy contribution to the lattice gradients is calculated analytically, else it is calculated numerically.

**AnalyticalKinetic** (**Default: true**) If true the kinetic energy contribution to the lattice gradients is calculated analytically, else it is calculated numerically.

**AnalyticalPulay** (**Default: true**) If true the Pulay contribution to the lattice gradients is calculated analytically, else it is calculated numerically.

**AnalyticalXC** (**Default: true**) If true the exchange-correlation energy contribution to the lattice gradients is calculated analytically, else it is calculated numerically.

## 6.3 Geometry optimization (GeoOpt)

The geometry can be optimized by adding the `GeoOpt` key block. Within the block you can specify the maximum number of cycles and the convergence criterion. The optimizer works with Cartesian coordinates and a Quasi Newton stepper. The initial Hessian is by default the unit matrix, but can also be loaded from a previous geometry optimization or frequency run. Various constraints are possible such as bond distances and angles. The GDIIS convergence accelerator is available but is disabled by default. A geometry optimization can be restarted from a previous result file. The geometry can be optimized non-relativistically, with scalar relativistic ZORA, or with spin-orbit coupling.

**GeoOpt (block-type)** Key to control the automatic geometry optimization:

```
GeoOpt
   {OptimizeLattice [false | true]}
   {Iterations n}
   {Converge {Grad=tolgrad} {E=tolE} {Step=tolStep}}
   {TrustRadius radius}
   {UseVariableTrustRadius var}
   {InitialHessian [UnitMatrix | filename | Swart]}
   {RestartSCF [true | false]}
   {RestartFit [true | false]}
   {GDIIS [true | false]}
   {StaticCosmoSurface [true | false]}
   {TSMode mode}
End
```

**OptimizeLattice** (**Default: false**) Whether or not to optimize the lattice vectors. The lattice gradients are obtained by numerical differentiation, see *GRADIENTS%LatticeStepSize* (page 43).

**Iterations** (**Default: 50**) maximum number of cycles.

**Converge {Grad=tolgrad} {E=tolE} {Step=tolStep}** various criteria to determine the convergence can be specified on line. Here *tolGrad* is the maximum gradient allowed (**Default: 1.0e-2** Hartree per Angstrom), *tolE* is the maximum energy change allowed (**Default: 1.0e-3** Hartree), *tolStep* is the maximum step size (**Default: 3e-2** Bohr)

**TrustRadius** (**Default: 0.2** Bohr) The step sizes taken by the optimizer will be limited to this value. If the proposed step is larger it will be scaled back.

**UseVariableTrustRadius** (**Default: false**) Automatic adjustment of the trust radius based on the observed energy changes.

**InitialHessian** (**Default: UnitMatrix**) The initial Hessian is read from a "RUNKF" file *filename* of a previous frequency calculation. Another option, *Swart*, is to use the empirical force field derived Swart Hessian.

**RestartSCF** (**Default: true**) During the optimization try to restart the SCF from the previous geometry step.

**RestartFit** (**Default: false**) During the optimization try to restart the SCF from fit coefficients of the previous geometry step. Can not be used simultaneously with RestartSCF.

**GDIIS** (**Default: false**) Use the GDIIS convergence accelerator.

**StaticCosmoSurface** (**Default: false**) Keep the Cosmo surface (if any) constant.

**TSMode** Hessian normal mode index to follow during transition state search. The specified mode is selected on the first iteration and is followed regardless of its index on subsequent iterations. Modes with zero frequencies are not counted.

Note that a (failed) geometry optimization can be continued with the Restart key by specifying as option GeometryOptimization.

## 6.4 Numerical frequencies (Hessian)

By specifying the `RunType` *Frequencies* you can calculate the Hessian which in turn yields the harmonic frequencies and vibrational modes. The Hessian is an important product that can be used in a geometry optimization, and in particular to start a transition state search. The second derivative of the energy (i.e. the Hessian) is obtained by numerically differentiating the analytical gradients. When your unit cell has N atoms in the unit cell and no symmetry (other than translational symmetry) the number of displacements is 2x3xN. For large systems this can be very time consuming, and you could consider to calculate only a partial Hessian. If you have a very symmetric unit cell, but are interested in asymmetric modes, set the subkeys `useA1Displacements` and `doA1Projection` to false. **Note**: the lattice vectors are assumed to be fixed.

A frequency run is invoked with

```
RunType
  Frequencies
End
```

The rest is controlled by the `Frequencies` key.

**Frequencies (block-type)** Key to control the numerical frequency run:

```
    Frequencies
      {Step size}
      {useA1Displacements [true | false]}
      {doA1Projection [true | false]}
      {StaticCosmoSurface [true | false]}
    End
```

**Step** (**Default: 0.01**) The step size (in Å) for the numerical differentiation.

**useA1Displacements** (**Default: true**) Determine only the total symmetric modes. When disabled, NOSYM calculations will be performed.

**doA1Projection** (**Default: true**) Symmetrize the Hessian. For most users the only sensible setting is to make it equal to the value of useA1Displacements.

**StaticCosmoSurface** (**Default: true**) Keep Cosmo surface (if any) constant. Although this is an approximation it is numerically much more stable. If you set it to *false* there is the risk that the number of Cosmo points is not constant for all finite displacements.

This options honors the `SelectedAtoms` key, in which case only the Hessian will be calculated for the selected atoms.

## 6.5 Transition state search

A transition state search is technically a geometry optimization. It is a search in the 3xN space for a point with vanishing gradients. The only difference is that it will try to go uphill in the direction of the lowest vibrational mode. The normal procedure is to guess a point that is as close as possible to the transition state. In that point you do a frequency run, which should hopefully produce a lowest vibrational mode in the direction of the transition state. You then start the Transition state search from that point, using the Hessian of the frequency run. At the end you can do again a frequency run to check that there is indeed a single negative vibrational mode.

The transition state search is invoked like this

```
RunType
   TS
End
```

The rest is controlled by the `GeoOpt` key as in a normal geometry optimization.

## 6.6 Partial Hessian and (pre)optimizations

If you consider the interaction of a molecule with a surface it may be initially convenient to freeze some of the lower layers in the slab, making calculations much cheaper. This can be done for the evaluation of the Hessian (see *SelectedAtoms* (page 13)) and during a geometry optimization or transition state search (see *Constraints* (page 46)). When using a partial Hessian to start a geometry optimization note this. **Note**: The atoms that you select during the frequency run, are the ones that should not be frozen in the geometry optimization. In a way the selection needs to be inverted.

## 6.7 Constrained optimization

During a geometry optimization certain constraints can be enforced with the `Constraints` key. The constraints refer to the coordinates of the unit cell as specified on input.

**Constraints (block-type)** Key to control constraints during a geometry optimization:

```
    Constraints
      {Atom aI {x y z}
      {Coord aI coordI {coordIvalue}
      {Dist aI aJ distance}
      {Angle aI aJ aK angle}
```

```
    {Dihed aI aJ aK aL angle}
End
```

**Atom** Freeze the position of atom *a1* to the current coordinate, or if specified to (*x y z*). This constraint will make the calculation cheaper, because the gradients of frozen atoms need not be calculated.

**Dist** Constrain the distance between atoms *a1* and *a2* to *distance*.

**Angle** Constrain the angle between atoms *a1*, *a2*, and *a3* to *angle*.

**Dihed** Constrain the dihedral angle between atoms *a1*, *a2*, *a3*, and *a4* to *angle*.

## 6.8 Selected atoms

When doing a frequency or geometry optimization run you can restrict it to a limited number of selected nuclei. The selection may not break the symmetry

```
SelectedAtoms a1 a2 ... an
```

The list of atoms with indices *a1 a2 ... an* are considered selected.

**Note**: Currently this option only has effect in a numerical frequency run and with the Gradients keyword.

## 6.9 Phonons and thermodynamics

Atoms vibrate about their equilibrium positions, giving rise to lattice vibrations, called *phonons*. BAND can calculate phonon dispersion curves within standard harmonic theory, implemented with a finite difference method in the spirit of the program PHON (http://www.homepages.ucl.ac.uk/~ucfbdxa/phon/) [*45* (page 165)]. Within the harmonic approximation we can calculate the partition function and from that thermodynamic properties, such as the specific heat and the free energy.

Our implementation can also handle 1D and 2D periodic systems.

To run a phonon calculation you need to do the following steps (**see also:** *Phonons example* (page 133)):

- *Optimize the structure* (page 44), **including the lattice vectors**. The resulting geometry is the starting geometry for the phonon run.
- Specify a super cell transformation. In principle this should be as large as possible. In practice one may want to start with a 2x2x2 cell. Set the `RunType` to Phonons:

```
RunType
   Phonons
End
```

- Examine with the GUI the dispersion curves, and check for negative frequencies. If these exist then either:
  - the geometry was not close enough to the minimum. Try specifying a smaller gradient convergence criteria in your *geometry optimization* (page 44)
  - the super cell transformation was too small
  - the *numerical precision* (page 27) of the phonon run was not good enough.

**PhononConfig (block-type)** Key to control the phonon run:

```
PhononConfig
  {SuperCell (Sub block type)}
  {StepSize step}
  {nSides [1|2]}
  {MinTempKelvin tmin}
  {MaxTempKelvin tmax}
  {NumTemperatures ntemp}
End
```

**SuperCell** This sub block key should hold the supercell transformation, which expresses the lattice vectors in terms of the vectors of the primitive cell.

**StepSize** (**Default: 0.076**) The step size taken to obtain all force constants.

**nSides** (**Default: 2**) By default a two-sided (or quadratic) numerical differentiation of the nuclear gradients is used. Using a single-sided (or linear) numerical differentiation is computationally faster but much less accurate (**Note**: in older versions of the program only the single-sided option was available).

**MinTempKelvin** (**Default: 0.0** Kelvin) Minimum temperature for thermodynamic plots.

**MaxTempKelvin** (**Default: 1000.0** Kelvin) Maximum temperature for thermodynamic plots.

**NumTemperatures** (**Default: 1000**) Number of temperatures for thermodynamic plots.

Here is an example input:

```
PhononConfig
  StepSize 0.0913
  SuperCell
    2 0 0
    0 2 0
    0 0 2
  SubEnd
End
```

In the standard output the thermodynamic functions are printed:

```
========================
ThermoDynamic Properties
========================
Zero-point Energy (Hartree)            0.00448537
Zero-point Energy (eV)                 0.12205313

=============================================================================================================
Temperature(K)  Internal energy(Hartree)              Entropy(kB)     Free Energy(Hartree)        Spec

  0.000000E+00             0.448537E-02             0.000000E+00             0.448537E-02
  0.100000E+01             0.448540E-02             0.116921E-01             0.448536E-02
  0.200000E+01             0.448566E-02             0.643295E-01             0.448525E-02
  ...                      ...                      ...                      ...
```

CHAPTER

SEVEN

# SPECTROSCOPIC PROPERTIES

## 7.1 Time-dependent DFT

In this section, the time-dependent density functional theory implementation in BAND is described. How to do a response calculation in BAND (which input keys to use), can be found in the list of keywords, see the key *Response* (page 49). The TDDFT module enables the calculation of real and imaginary parts of the material property tensor $\chi_e(\omega)$ called the electric susceptibility, and the macroscopic dielectric function $\epsilon_e(\omega)$ These are mutually related,

$$\epsilon_e(\omega) = 1 + 4\pi\chi_e(\omega)$$

In general $\chi_e(\omega)$ and $\epsilon_e(\omega)$ are tensors, which, however, simplify to scalars in isotropic systems. The above formula is valid in the case of insulators and semiconductors, where the bands are either fully occupied or fully unoccupied. It is defined as the interband part of the dielectric function and it is due to transitions from occupied bands to unoccupied bands. Also in the metallic case similar expressions can be found, the main difference is that there now is also an intraband contribution. Some examples are available in the $ADFHOME/examples/band directory and are discussed in the Examples document.

**References**

The three related Ph.D. theses, due to F. Kootstra (on TD-DFT for insulators), P. Romaniello (on TD-CDFT for metals), and A. Berger (on the Vignale-Kohn functional in extended systems) contain much background information, and can be downloaded from the SCM website (http://www.scm.com).

The most relevant publications on this topic due to the former "Groningen" group of P.L. de Boeij are [*22* (page 164)], [*23* (page 164)], [*24* (page 164)], [*25* (page 164)].

### 7.1.1 Response key

**`Response`** Perform a time-dependent DFT calculation to obtain real and imaginary parts of frequency-dependent dielectric function.

```
Response
   {nfreq   ival1}
   {strtfr  rval1}
   {endfr   rval2}
   {cnvi    rval3}
   {cnvj    rval4}
   {ebndtl  rval5}
   {shift   rval6}
   {isz     ival2}
   {iyxc    ival3}
   {static}
   {newvk}
```

```
   {cnt}
   {qv}
   {Berger2015}
End
```

Omitting the specific options in the Response block will cause default setting to be used during the calculation, as given above.

**nfreq** (**Default: 5**) the number of frequencies in a.u. for which a TDDFT calculation is performed when calculating the dielectric function $\epsilon_e(\omega)$ of a system.

**strtfr** (**Default: 0d0**) is the start frequency in a.u. of the frequency range over which the dielectric function is calculated.

**endfr** (**Default: 1d-2**) is the end frequency in a.u. of the frequency range over which the dielectric function is calculated.

**cnvi** (**Default: 1d-3**) the first convergence criterion for the change in the fitcoefficients for the fitfunctions, when fitting the density.

**cnvj** (**Default: 1d-3**) the second convergence criterion for the change in the fitcoefficients for the fitfunctions, when fitting the density.

**ebndtl** (**Default: 1d-3**) the energy band tolerance, for determination which routines to use for calculating the numerical integration weights, when the energy band posses no or to less dispersion.

**shift** (**Default: 0d0**) shift (in a.u.) of the virtual crystal orbitals.

**isz** (**Default: 0**) integer indicating whether or not scalar zeroth order relativistic effects are included in the TDDFT calculation. 0 = relativistic effects are not included, 1 = relativistic effects are included.

**iyxc** (**Default: 0**) integer for printing yxc-tensor (JCP 115, 1995 (2001)). 0 = not printed, 1 = printed.

**static** An alternative method that allows an analytic evaluation of the static response (Normally the static component is approximated by a finite small value). This option should only be used for non-relativistic calculations on insulators, and it has no effect on metals. Experience shows that KSPACE convergence can be slower. That is why it is not the default.

**newvk** Use the slightly modified version of the VK kernel.[*58* (page 166)] When using this option one uses effectively the static option, even for metals, so one should check carefully the convergence with the KSPACE parameter. An example response block for a vignale kohn calculation looks like

**qv/cnt** Use the **QV** or **CNT** parametrization for the longitudinal and transverse kernels of the xc-kernel of the homogeneous electron gas. Use this in conjunction with the newvk option.[*60,61* (page 166)]

```
    Response
       {...}
       newvk
       iyxc    1
       cnt
    END
```

**Berger2015** Use the parameter-free polarization functional by A. Berger.[*59* (page 166)] This is possible for 3D insulators and metals, but not in combination with relativistic approximations.

```
    Response
       {...}
       Berger2015
    END
```

### 7.1.2 Limitations

The method has not been implemented for slabs, so it can only be used for 1D and 3D systems.

### 7.1.3 References

[2] F. Kootstra, P. L. de Boeij, and J. G. Snijders, Phys. Rev. B 62, 7071 (2000).

[3] F. Kootstra, P. L. de Boeij, H. Aissa, and J. G. Snijders, J. Chem. Phys. 114, 1860 (2001).

[4] P. L. de Boeij, F. Kootstra, and J. G. Snijders, Int. J. Quantum Chem. 85, 449 (2001).

[5] P. L. de Boeij, F. Kootstra, J. A. Berger, R. van Leeuwen, and J. G. Snijders, J. Chem. Phys. 115, 1995 (2001).

[6] F. Kootstra, P. L. de Boeij, R. van Leeuwen, and J. G. Snijders, Festschrift in honour of R. G. Parr, Editor K. D. Sen, accepted.

[7] F. Kootstra, P. L. de Boeij, and J. G. Snijders, J. Chem. Phys. to be submitted.

[8] F. Kootstra, P. L. de Boeij, R. van Leeuwen, and J. G. Snijders, to be submitted.

[9] F. Kootstra, Ph.D. thesis, Rijksuniversiteit Groningen, Groningen (2001).

### 7.1.4 Time-dependent DFT for metals

For metals the interband part of the dielectric function is due to transitions from (partially)-occupied bands to (partially)-unoccupied bands. Now there is also a term, which is called the intraband part of the dielectric function, which is due to transitions within the same partially-occupied band. The macroscopic dielectric function $\epsilon_e(\omega)$ is now calculated as

$$\epsilon_e(\omega) = 1 + 4\pi\chi_e(\omega) - 4\pi i\sigma_e(\omega)/\omega$$

Convergence and reproducibility: For TD-DFT calculations on metals a dense sampling of reciprocal space is required, i.e. the results converge slowly with the KSPACE parameter. The dielectric function might even not reproduce well across different machines. (Usually results that are not yet converged with the KSPACE parameter, like the energy, are reproducible across different platforms). Nevertheless, when the KSPACE parameter is chosen sufficiently high, the same result will be obtained on all machines. For instance for Cu the machine dependence was less than 0.01 for the dielectric function with KSPACE=11. In short: check for the convergence of the dielectric function with respect to the KSPACE parameter.

### 7.1.5 Frequency dependent kernel

It is known that the exact Vignale Kohn kernel greatly improves the static polarizabilities of infinite polymers and nanotubes (see JCP 123 174910), but gives bad results for the optical spectra of semiconductors and metals. For the low frequency part one needs a frequency dependent kernel, because Drude-like tails are completely absent in the ALDA. With a modified Vignale Kohn kernel, neglecting $\mu_{xc}$ so that it reduces to the ALDA form in the static limit (see PRB 74 245117) much better results can be obtained. BAND currently only supports the modified VK kernel in either the QV or CNT parametrization, and it should only be used for metals.

### 7.1.6 EELS

Once the macroscopic dielectric function is known it is possible to calculate the electron energy loss function (EELS). In transmission electron energy loss spectroscopy one studies the inelastic scattering of a beam of high energy electrons by a target. The scattering rates obtained in these experiments is related to the dynamical structure factor $S(q, \omega)$ [1].

In the special case with wavevector $q = 0$, $S(q, \omega)$ is related to the longitudinal macroscopic dielectric function. This is the long-wave limit of EELS. For isotropic system the dielectric function is simply a scalar ( $1/3\mathrm{Tr}(\epsilon_e(\omega))$ ). In this case the long-wave limit of the electron energy loss function assumes the trivial form

$$\lim_{q \to 0} 2\pi \frac{S(q,\omega)}{q^2 V} = \frac{\epsilon_2}{\epsilon_1^2 + \epsilon_2^2}$$

with $\epsilon_1$ and $\epsilon_2$, respectively, the real and imaginary part of the dielectric function.

[1] S. E. Schnatterly, in Solid State Physics Vol.34, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic Press, Inc., New York, 1979). [2] P. Romaniello, and P. L. de Boeij, Phys. Rev. B (accepted).

## 7.2 ESR

BAND is able to calculate electron paramagnetic resonance parameters of paramagnetic defects in solids: hyperfine A-tensor and the Zeeman g-tensor.

The implementation of EPR parameters in BAND are described in the publications by Kadantsev and coworkers [*20* (page 164)] and [*21* (page 164)].

**Hyperfine A-tensor**

The A-tensor is implemented within the non-relativistic and scalar relativistic spin-polarized Kohn-Sham scheme. The A-tensor calculation is invoked by block

```
ATENSOR
END
```

**Note**: the `Unrestricted` keyword should be present.

Two methods are used for A-tensor calculation.

Method 1 involves gradient of spin-polarization density and integration by parts. The isotropic component of A-tensor is obtained through integration, in a "nonlocal fashion".

In Method 2, the A-tensor is computed from spin-polarization density. Method 2 does not relies on the integration by parts. The isotropic component is obtained in a "local fashion" from the value of spin-polarization density on the grid points near the nuclei.

The user should be aware that numerical integration in A- and g-tensor routines is carried out over Wigner-Seitz (WS) cell, and, therefore, to obtain a meaningful result, the defect in question should lie at or, very close to, WS cell origin. This might require, on the user's part, some modification of the input geometry.

It also might happen that the size of the WS cell is not large enough for the adequate description of the paramagnetic defect in question. In this case, Method 1, which relies on the integration by parts and assumes that the spin-polarization density is localized inside the WS cell will fail. For the same reason, We recommend that the user removes diffuse basis set functions that describe the defect subsystem.

Finally, we note that the final result for A-tensor as presented by BAND is not scaled by the nuclear spin (as it is done in ADF) and the user is responsible for making necessary adjustments.

**g-tensor**

The calculation of Zeeman g-tensor is invoked with block

```
ESR
END
```

The Zeeman g-tensor is implemented using two-component approach of Van Lenthe and co-workers in which the g-tensor is computed from a pair of spinors related to each other by time-reversal symmetry.

**Note**: The keyword `Relativistic zora spin` should be present to invoke calculations with spin-orbital coupling. The user also has to specify

```
Kspace 1
```

($\Gamma$-point calculation). The g-tensor is then computed from the HOMO spinor at the $\Gamma$ point. In the output, the user can find two-contributions to g-tensor: one that stems from $K_\sigma$ operator and a second one, that stems from orbital angular momentum. By default, GIAO and spin-Zeeman corrections are not included, from our experience these corrections are quite small.

## 7.3 Electric Field Gradient (EFG)

```
EFG (block type)
```

The electronic charge density causes an electric field, and the gradient of this field couples with the nuclear quadrupole moment, that some (non-spherical) nuclei have and can be measured by several spectroscopic techniques. The EFG tensor is the second derivative of the Coulomb potential at the nuclei. For each atom it is a 3x3 symmetric and traceless matrix. Diagonalization of this matrix gives three eigenvalues, which are usually ordered by their decreasing absolute size and denoted as $|V_{zz}|$ , $|V_{yy}|$, $|V_{xx}|$. The result is summarized by the largest eigenvalue and the asymmetry parameter.

This options honors the `SelectedAtoms` key, in which case only the EFG will be calculated for the selected atoms.

## 7.4 NMR

With the NMR option the *shielding tensor* is calculated. There are essentially two methods: the super cell method and the single-dipole method.

1. The super cell method is according to the implementation by Skachkov *et al.*.[*37* (page 165)] The symmetry will automatically be set to `NOSYM`. The unit cell should not be chosen too small.
2. The other method is the single-dipole method. In principle one can now use the primitive cell.[*48* (page 165)] In practice also this method needs to be converged with super cell size. However, depending on the system the required super cell may be much smaller. At a given super cell size this method is more expensive than the super cell method.

```
NMR (block type)
   {SuperCell [true | false]}
End
```

**`SuperCell`** (**Default: true**) This is the switch between the two methods, either the super cell (true), or the single-dipole method (false).

This options honors the `SelectedAtoms` key, in which case only the NMR properties will be calculated for the selected atoms only.

CHAPTER

# EIGHT

# MORE ANALYSIS

If you are interested in the DOS or a partitioning of the DOS, look for the description of the keys `DOS`, `GrossPopulations` for partial DOS, and `OverlapPopulations` for overlap DOS.

The eigen system can be printed with `Print Eigens` and the Mulliken populations per orbital per k-point can be printed with `Print OrbPop`.

A list of the basis functions will be printed with `Print OrbLabels`.

## 8.1 Charges

BAND prints always three charge analyses. Namely the Voronoi charges, the Mulliken analysis, and the Hirshfeld charges. The calculation comes at virtually no cost, so there are no keys associated with it. This is different for the Bader analysis.

### 8.1.1 Bader Analysis (AIM)

**`GridBasedAIM (block-type)`** Invoke the ultra fast grid based Bader analysis.[*33,34* (page 165)]

```
GridBasedAIM
   {SmallDensity rhosmall }
   {Iterations n }
   {UseStartDensity [false | true] }
End
```

**`SmallDensity`** (**Default: 1e-6**) Where *rhosmall* is the value below which the density is ignored. This should not be chosen too small because it may lead to unassignable grid points.

**`Iterations`** (**Default: 40**) The number *n* determines the maximum number of steps that may be taken to find the nuclear attractor for a grid point.

**`UseStartDensity`** (**Default: false**) handles whether the analysis is performed on the startup density (true) rather than on the final density (false).

**`AIMCriticalPoints (block-type)`** Also the critical points of the density can be determined. The algorithm starts from a regular mesh of points, and from each of these it walks towards its corresponding critical point.

```
AIMCriticalPoints
    { GridPadding pad }
    { GridSpacing space }
    { eqvPointsTol tol }
End
```

**GridPadding** (**Default: 0.7** Bohr) *pad* determines how much extra space is added to the starting guess domain in the search for the critical points.

**GridSpacing** (**Default: 0.5** Bohr) The variable *space* determines the distance between the initial trial points.

**eqvPointsTol** (**Default: 0.27** Bohr) *tol* is used as a criterion to whether or not two critical points are the same.

## 8.2 Density of States

**DOS (block-type)** General Density-Of-States (DOS) information.

```
DOS
   { File filename }
   { Energies n }
   { Min emin }
   { Max emax }
   { IntegrateDeltaE [true | false] }
End
```

**File** (**Optional**) handles the name of the output file with the DOS results.

**Energies** (**Default: 300**) number of equidistant energy-values.

**Min** (**Default: -0.75** a.u.) lower bound energy (w.r.t. Fermi level).

**Max** (**Default: +0.75** a.u.) upper bound energy (w.r.t. Fermi level).

**IntegrateDeltaE** (**default=true**) This subkey handles which algorithm is used to calculate the data-points in the plotted DOS. *If the argument is true*: the data-points represent an integral over the states in an energy interval. Here, the energy interval depends on the number of Energies and the user-defined upper and lower energy for the calculation of the DOS. The result has as unit [number of states / (energy interval * unit cell)]. *If the argument is false*: the data-points do represent the number of states for a specific energy and the resulting plot is equal to the DOS per unit cell (unit: [1/energy]). Since the resulting plot can be a wild function and one might miss features of the DOS due to the step length between the energies, the default is set to the integration algorithm.

**An example input:**

```
DOS
   FILE        plotfile
   ENERGIES      500
   MIN          -.35
   MAX          1.05
End
```

According to this example, DOS values will be generated in an equidistant mesh of 500 energy values, ranging from 0.35 a.u. below the Fermi level to 1.05 a.u. above it. All information will be written to a file plotfile. The information on the plot file is a long list of pairs of values (energy and DOS), with some informative text-headers and general information. DOS values are generated for the total DOS and optionally also for some partial DOS (see the keys *GrossPopulations* (page 56) and *OverlapPopulations* (page 57)).

### 8.2.1 Gross populations

**GrossPopulations (block-type)** *Partial* densities-of-states (**pDOS**) are generated for the gross populations listed under this key.

```
    GrossPopulations
       {iat lq}
       {FragFun jat ifun}
       {Frag kat}
       {Sum
        ...
        EndSum}
    End
```

**iat** pDOS is generated for atom *lg*.

**FragFun** pDOS is generated for atom *jat* with all real spherical harmonics belonging to *l*-value *ifun*.

**Frag** pDOS of the functions belonging to atom *kat* will be calculated.

**Sum** sum all pDOS, specified in this block.

Example:

```
GrossPopulations
   FragFun 1 2:: Second function of first atom
   Frag 2 :: Sum of all functions from second atom
   SUM:: sum following PDOSes
      Frag 1::Atom nr.1
      FragFun 2 1::First function of second atom
      5 1:: All pfunctions of fifth atom
   EndSum
End
```

### 8.2.2 Overlap populations

**OverlapPopulations (block-type)** *Overlap population weighted* DOS (**OPWDOS**) are generated for the overlap populations listed

```
    OVERLAPPOPULATIONS
       Left
          { iat lq }
          { FragFun jat ifun }
          { Frag kat }
       Right
          ...
    End
```

You can use this to get the OPWDOS, also known as the crystal orbital overlap population (**COOP**), of two functions, or, if you like, one bunch of functions with another bunch of functions. The key-block should consist of left-right pairs. After a line with left you enter lines that specify one or more functions (according to *GrossPopulations* (page 56)), followed by a similar structure beginning with right, which will produce the OPWDOS of the left functions with the right functions. Example:

```
OVERLAPPOPULATIONS
   LEFT::First OPWDOS
      Frag 1
   RIGHT
      Frag 2
   LEFT:: Next OPWDOS
      FragFun 1 1
   RIGHT
      2 1
```

```
      FragFun 3 5
End
```

## 8.3 Band structure

The band structure is best examined with the GUI module "Bandstructure". The band gap (if any) is printed in the output. Here is an example for the NaCl crystal

```
---------------------------------------
Band gap information
---------------------------------------
Number of valence electrons                  16
Valence Band index                            8
Top of valence Band (a.u.)                -0.192
Bottom of conduction Band (a.u.)          -0.039
Band gap (a.u.)                            0.153
Band gap (eV)                              4.173
Band gap (kcal)                           96.235
```

With the normal k-points the band structure looks rather coarse. The brute force solution is simply to crank up the KSPACE parameter, but this is very expensive and not needed for the precision. BAND has an option to interpolate the band curves for the path through the Brillouin zone.

### 8.3.1 Band structure interpolation

**`BZStruct (block-type)`** Influences how BAND outputs the band structure to the RUNKF file.

```
    BZStruct
      Interpol ipol
      {Enabled [true | false]}
      {Automatic [true | false]}
    End
```

**`Interpol`** The higher the value of *ipol* the more refined the interpolation.

**`Enabled`** (**Default: true**) Whether or not to generate band structure data.

**`Automatic`** (**Default: true**) Whether or not to use the automatic path along high symmetry lines in the BZ.

**`BZPath (block-type)`** User defined path through the Brillouin zone.

```
    BZPath
      kmesh mesh
      path
    End
```

When `BZStruct%Automatic` is false you can specify manually a path. Increasing *mesh* leads to more points per line segment. The line segments are specified by some path subkeys. The coordinates are in terms of reciprocal lattice vectors. If you want to make a jump in the BZ, you need to specify a new path. Here is an example:

```
    bzpath
      kmesh 2
      path
        0.25 0.25 0.25
        0 0 0.5
        0 0 0
```

```
      0.5 -0.5 0.5
      0.25 0.25 0.25
      0 0 0
    subend
    path
      0 0 0.5
      0.5 -0.5 0.5
    subend
  end
```

## 8.4 Effective Mass

**EffectiveMass (block-type)** In a semi conductor the mobility of the 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 with 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 subkeys.

```
  EffectiveMass
    StepSize step
    NumAbove na
    NumBelow nb
    UniqueKPoints k1 k2 ...
  End
```

**StepSize** (**Default: 1e-3**) Size of the step taken in reciprocal space to perform the numerical differentiation.

**NumAbove** (**Default: 1**) Number of bands to take into account above the Fermi level.

**NumBelow** (**Default: 1**) Number of bands to take into account below the Fermi level.

**UniqueKPoints** List of unique k-points where to print the effective mass. If this option is omitted, it will use the top of valence band and the bottom of the conduction band.

## 8.5 Properties at Nuclei

**PropertiesAtNuclei (block-type)** A number of properties can be obtained near the nucleus. An average is taken over a tiny sphere around the nucleus. Technically the following properties are available.

```
  PropertiesAtNuclei
    vxc[rho(fit)]
    rho(fit)
    rho(scf)
    v(coulomb/scf)
    rho(deformation/fit)
    rho(deformation/scf)
  End
```

Physically `rho(scf)`, being the electronic density, is the most relevant one.

## 8.6 Form Factors

**FormFactors** X-ray structure factors (Fourier analysis of the charge density) are computed after termination of the SCF procedure.

```
{FormFactors ival}
```

The key is followed by an integer specifying the number of stars of K-vectors for which the structure factors are computed. (**Default: 2**)

## 8.7 Fragments

A fragment feature is available albeit rather primitive. It allows for the analysis of the DOS in a fragment basis and for the calculation of the deformation density with respect to fragment densities. A typical application is the periodical adsorption of one or more molecules on a surface. For instance, consider periodic adsorption of hydrogen molecules over a surface. First you calculate the free molecule in the same orientation as when adsorbed to the substrate. Since you would like to use a molecular fragment, it makes sense to put the molecules far apart (large lattice spacing) and force dispersion to be neglected (KSPACE 1). To use the fragment in the next run you need to rename the result file ("RUNKF"), to something like "frag.runkf", see the example script discussed below.

Specifying

```
Print Eigens
```

for this calculation produces output concerning the eigen states, thereby providing a means to identify the eigen states (e.g. to be sigma, pi, et cetera).

Next, prepare the input for the overlayer with the substrate. With one or more `Fragment` keys you specify which fragment file(s) to use and to which atoms they should be mapped. It is allowed to have more than one fragment. The subkey `Labels` of a fragment gives you the possibility to introduce labels for the fragment orbitals. Finally you can specify which fragments to use in the DOS analysis, via the `DosBas` key.

An example of using the fragments feature in BAND is provided in one of the sample runs (CO on a Cu surface) in the directory $ADFHOME/examples/band/Frags_COCu, see the *example* (page 135). The provided example is a slab calculation of Cu with a CO molecule adsorbed. A DOS analysis is performed in terms of the Cu atomic orbitals and the CO molecular orbitals. Note in the first step the use of `KSPACE 1`, together with a large lattice spacing. In this way a 'molecular' solution is obtained, which can be used as a fragment. This fragment is saved as CO.runkf, and is input for the second step of this example. Some of the orbital labels are adapted by specifying Labels. In the remaining steps this example demonstrates how to obtain the deformation density with respect to the sum of fragments (CO molecule + bare Cu slab) densities.

### 8.7.1 Fragment key

**Fragment (block-type)** Define a fragment. This key takes as argument the fragment file name (absolute path or path relative to the executing directory) and its contents are for each atom in the fragment two integers: atom number in the fragment versus atom number in this calculation. It has a subkey Labels so that you can assign meaningful names to the orbitals. You can define several fragments. Example

```
Fragment
  1 3 !  atom 1 of this fragment is assigned to third atom
  2 4 !  atom 2 of this fragment is assigned to fourth atom
  Labels
   Sigma
   Sigma*
```

```
   Pi_x
   Pi_y
   Pi_x*
   Pi_y*
  Subend
End
```

In this example the first four fragment orbitals will be labeled as stated in the body of this key. The remaining orbitals are labeled by the default labeling system (e.g. 1/FO/5, etc.). The labels are used in combination with options like Print Eigens and Print OrbPop. (See also Print OrbLabels). This key can be given once for each fragment.

## 8.8 Energy Decomposition Analysis Methods

In BAND there are two fragment-based energy decomposition methods available: the periodic energy decomposition analysis (PEDA)[*56* (page 166)] and the periodic energy decomposition analysis combined with the natural orbitals of chemical valency method (PEDA-NOCV)[*56* (page 166)].

### 8.8.1 Periodic Energy Decomposition Analysis (PEDA)

**PEDA**

```
    PEDA
```

If present in combination with the fragment key blocks the decomposition of the interaction energy between fragments is invoked and the resulting energy terms ($\Delta E_{int}$, $\Delta E_{disp}$, $\Delta E_{Pauli}$, $\Delta E_{elstat}$, $\Delta E_{orb}$) presented in the output file. (See the *example* (page 140) or the tutorial)

### 8.8.2 Periodic Energy Decomposition Analysis and natural orbitals of chemical valency (PEDA-NOCV)

**PEDANOCV (block-type)**

```
    PEDANOCV
       {EigValThresh rval}
    End
```

**EigValThresh** (**Default: 0.001**) The threshold controls that for all NOCV deformation densities with NOCV eigenvalues larger than *rval* the energy contribution will be calculated and the respective pEDA-NOCV results will be printed in the output

If present in combination with the fragment key blocks and the PEDA the decomposition of the orbital relaxation term is performed. The binary result file will contain the information to plot NOCV Orbitals and NOCV deformation densities. (See the *example* (page 143) or the tutorial)

**General Remark:** In case of the error message "Fragments cannot be assigned by a simple translation!", BAND does only allow for fragments which can be transformed to the structure in the PEDA calculation by a simple translation. So, a rotation is not allowed. Furthermore, one has to keep in mind that BAND will use a centralized version of the coordinates with respect to the geometrical center. During this routine, the atoms of a not centralized structure can end up at one or the other side of the unit cell. Hence, the same error message will appear. - Here, the whole structure should be centralized with respect to the geometrical center of the problematic fragment!

CHAPTER

NINE

# RESTARTS

The main results of a BAND calculation are stored in the RUNKF file. If you save this file you can use it to restart your calculation. The input for the restart calculation is essentially the same, except for some extra keys, like `Restart`, `Grid`, and `DensityPlot`.

The DOS section that outputs information of the SCF solution can be executed with key `Restart`, subkey `DOS` and orbital plots can be obtained with subkey `OrbitalPlot`. Likewise, plots of the density (and many other symmetric properties) can can be obtained with the key `DensityPlot`. Density and orbital plot restarts require the specification of the `Grid` key. With the subkey `SCF` you can start the SCF procedure with the last solution from the restart file. This can be useful if the SCF did not converge. Also if you have changed some settings that should have little effect, like the integration accuracy, the restart SCF option can help you to save a few cycles. Similarly, a geometry optimization can be restarted with the subkey `GeometryOptimization` You can use the geometry of a previous calculation.

## 9.1 Restart key

**`Restart`** Tells the program that it should restart with the restart file.

```
Restart
   File filename
   {option}
End
```

**`File`** *filename* is the name of the restart file

*options* is the program part to do a restart for:

- SCF
- GeometryOptimization
- Geometry
- DOS
- *OrbitalPlot* (page 65)
- *DensityPlot* (page 64)
- *NOCVdRhoPlot* (page 66)
- *NOCVOrbsPlot* (page 65)

Usually the input for a restart is the same as for the original calculation, where you add some extra options.

## 9.2 Grid

**Grid (block-type)** Used for restart options `OrbitalPlot`, `DensityPlot`, `NOCVOrbsPlot` and `NOCVdRhoPlot`. There are two ways to define your grid. The most easy way is to use the Type key which can have the values **Coarse**, **Medium**, and **Fine**, for example

```
Grid
   Type Coarse
End
```

This generates automatically a grid around the atoms in the unit cell. The alternative is to specify everything by hand. The following input would create a cube from (-1,-1,-1) to (1,1,1)

```
Grid
   -1 -1 -1 ! Starting point
   1 0 0 0.1   ! vec1 and dvec1
   0 1 0 0.1   ! vec2 and dvec2
   0 0 1 0.1   ! vec3 and dvec3
   20 20 20    ! nr. of steps along three directions
End
```

## 9.3 Plots of the density, potential, and many more properties

**DensityPlot (block-type)** Goes together with the `Restart%DensityPlot` and `Grid` keys. Example input

```
...
Restart vi
   File my.runkf
   DensityPlot
End

Grid
   Type Coarse
End

DensityPlot
   rho(fit)
   vxc[rho]
End
...
```

After such a run you get a TAPE41 file that you should rename to my.t41, and view with adfview.

The most common properties to plot are:

- `rho(fit)` The fitted density.
- `v(coulomb)` The Coulomb potential.
- `vxc[rho(fit)]` the XC potential (using the fitted density)
- `vxc[rho]` XC potential of the exact density
- `rho` The density
- `|gradRho|` The norm of the gradient of the density
- `tau` The symmetric kinetic energy density

- `LDOS` The local density of states. (See *LDOS key* (page 66))
- `elf[rho]` The electron localization function

Some more specialized options are:

- `rho(deformation/fit)` the fitted deformation density
- `rho(atoms)` The density of the startup atoms
- `v(coulomb/atoms)` The Coulomb potential of the start density

In the BAND example directory there is the *Frags_COCu* (page 135) example which shows how this can be used in combination with the `Fragment` key.

## 9.4 Orbital plots

**`OrbitalPlot (block-type)`** Goes together with the `Restart%OrbitalPlot` and `Grid` keys. In the BAND example directory there is the *Cu_slab* (page 148) example that shows how this can be used. Example input

```
...
Restart
   File my.runkf
   OrbitalPlot
End

Grid
   Type Coarse
End

OrbitalPlot
   1 Band 5 8  ! for k-point 1 plot bands 5 to 8
   5 Band 6    ! for k-point 5 plot band 6
   6 -0.2 +0.3 ! for k-point 6 plot bands between -0.2 and +0.3 a.u. w.r.t Fermi level
End
...
```

After such a run you get a TAPE41 file that you should rename to my.t41, and view with adfview.

## 9.5 NOCV Orbital Plots

**`NOCVOrbsPlot (block-type)`** Goes together with the `Restart%NOCVOrbsPlot` and `Grid` keys. See example *PEDANOCV_MgO+CO* (page 143). Example input

```
...
Restart
   File my.runkf
   NOCVOrbsPlot
End

Grid
   Type Coarse
End

NOCVOrbsPlot
   1 Band 5 8 ! for k-point 1 plot NOCV Orbitals 5 to 8
```

```
End
...
```

After such a run you get a TAPE41 file that you should rename to my.t41, and view with adfview.

## 9.6 NOCV Deformation Density Plots

**NOCVdRhoPlot (block-type)** Goes together with the `Restart%NOCVdRhoPlot` and `Grid` keys. See example *PEDANOCV_MgO+CO* (page 143). Example input

```
...
Restart
   File my.runkf
   NOCVdRhoPlot
End

Grid
   Type Coarse
End

NOCVdRhoPlot
   1 Band 5 8 ! for k-point 1 plot NOCV deformation densities 5 to 8
End
...
```

After such a run you get a TAPE41 file that you should rename to my.t41, and view with adfview.

## 9.7 LDOS (STM)

**LDOS (block-type)** Local Density-Of-States information. This can be used to generate STM images in the Tersoff-Hamann approximation.[*35* (page 165)]

```
LDOS
   { Shift eshift }
   { DeltaNeg deneg }
   { DeltaPos depos }
End
```

**Shift** (**Default: 0.0** a.u.) The energy bias with respect to the fermi level in a.u..

**DeltaNeg** (**Default: 1e-4** a.u.) defines the lower bound energy as *eshift-deneg*.

**DeltaPos** (**Default: 1e-4** a.u.) defines the upper bound energz as *eshift+depos*.

The local density of states is integrated over the resulting interval. Example of an LDOS restart

```
Restart
   File my.runkf
   DensityPlot
End

Grid
   Type Coarse
End

DensityPlot
```

```
        LDOS
        Shift      0.1
        DeltaNeg .001
        DeltaPos 0
     End
```

According to this example, we restart from the result file of a previous calculation. The calculation will generate a file TAPE41 which can be viewed with adfview. (Rename the file to my.t41)

See also *Restart* (page 63), and *DensityPlot* (page 64).

## 9.8 Complete example scripts for visualization

Below follows a complete example how to use BAND for visualizing. We start with the normal calculation for e.g. a Li slab

```
#!/bin/sh
# Contents of the file LiSlab.job

"$ADFBIN/band" << eor
TITLE Li Slab

UNITS
    length Angstrom
    angle Degree
END

ATOMS Li
   Li  0.0    0.0    0.0
   Li -1.745 -1.745 -1.745
END

Lattice
   3.49 0.000000 0
   0.000000 3.49 0
End

BasisDefaults
   BasisType DZ
   Core Large
End

XC
   LDA SCF VWN
END

end input
eor

# store the result file
mv RUNKF LiSlab.runkf
```

Note that we store the result file in “LiSlab.runkf”. In the next run we use this file to generate the plot file. The job is essentially a copy of the first job with some extra lines. In this case we instruct the program to generate plot information for the density and the LDOS

```
#!/bin/sh
# Contents of the file LiSlab_restart.job

"$ADFBIN/band" << eor
TITLE Li Slab

UNITS
    length Angstrom
    angle Degree
END

Restart
   File LiSlab.runkf
   DensityPlot
End

Grid
   Type Coarse
End

DensityPlot
   rho(fit)
   LDOS
End

LDOS
   shift 0.0
End

ATOMS
   Li  0.0    0.0    0.0
   Li -1.745 -1.745 -1.745
END

Lattice
   3.49 0.000000 0
   0.000000 3.49 0
End

BasisDefaults
   BasisType DZ
   Core Large
End

XC
   LDA SCF VWN
END

end input
eor

# Store the result file, and more importantly, the plot file (.t41)
mv RUNKF LiSlab_restart.runkf
mv TAPE41 LiSlab.t41
```

And then you can visualize the result with adfview.

```
$ADFBIN/adfview  LiSlab.runkf
```

It is most convenient to start adfview from the .runkf file rather than from the .t41.

CHAPTER

TEN

# EXPERT OPTIONS

## 10.1 Symmetry

The symmetry of the system is automatically detected. Normally the symmetry of the initial system is maintained. One can lower the symmetry with the `Symmetry` key. In such cases the keyword `POTENTIALNOISE` can force the solution away from the initial symmetry.

**SYMMETRY** The most common option is **NOSYM** forcing the program to run without any symmetry. It is also possible to run in a lower symmetry other than NOSYM but this is more involved. The argument should be a list of numbers, representing the operators to maintain. The way to proceed is as follows. First run the calculation with the following added to your input

```
print symmetry
stopafter gemtry
```

and then you look in the output for (here the first four operators are listed)

```
   64    SYMMETRY OPERATORS:

NO               MATRIX              TRANSL        AXIS    DET   ROTATION
-------------------------------------------------------------------------

1)        1.000   0.000   0.000       0.000       0.000    1.0       1
          0.000   1.000   0.000       0.000       0.000
          0.000   0.000   1.000       0.000       1.000

2)        1.000   0.000   0.000       0.000       0.000    1.0       1
          0.000   1.000   0.000       5.400       0.000
          0.000   0.000   1.000       0.000       1.000

3)        1.000   0.000   0.000       5.400       0.000    1.0       1
          0.000   1.000   0.000       0.000       0.000
          0.000   0.000   1.000       0.000       1.000

4)        1.000   0.000   0.000       5.400       0.000    1.0       1
          0.000   1.000   0.000       5.400       0.000
          0.000   0.000   1.000       0.000       1.000
```

from this list you should select the desired operators and use that in your final calculation, for example

```
Symmetry 1 7 21 31
```

**POTENTIALNOISE** The initial potential for the SCF procedure is constructed from a sum-of-atoms density. Added to this is some small noise in the numerical values of the potential in the points of the integration grid. The

purpose of the noise is to help the program break the initial symmetry, if that would lower the energy, by effectively inducing small differences between (initially) degenerate orbitals.

```
PotentialNoise rval
```

The noise in the potential is randomly generated between zero and an upper limit *rval* (**Default: 1e-4** a.u.). This can be used therefore to suppress the noise by choosing zero, or to increase it by specifying some large number.

## 10.2 Excited States

By default the levels are occupied according to the aufbau principle. In some cases it is possible to create holes below the Fermi level or uneven occupation for up and down spin with the `Occupations` ($\Gamma$-only) and alternatively the `EnforcedSpinPolarization` (for an arbitrary number of k-points) key.

**`OCCUPATIONS (block-type)`** Allows one to input specific occupations numbers. Applies only for calculations that use only one k-point (i.e. pseudo-molecule calculations).

```
OCCUPATIONS
   1 occupations_alpha {// occupations_beta}
End
```

- `occupations_beta` and the separating double slash (//) must not be used in a spin-restricted calculation.
- `occupations_alpha/beta` is a sequence of values assigned to the states ('bands') in energy ordering.

**`EnforcedSpinPolarization`** Allows one to specify the excess of up spin w.r.t. down spin number of electrons.

```
EnforcedSpinPolarization rval
```

Is *rval* larger than zero then is the number of up spin electrons larger than the number of down spin electron. Is *rval* smaller than zero it is the other way around.

**`ElectronHole (block-type)`** Allows one to specify an occupied band which shall be depopulated, where the electrons are then moved to the Fermi level. For a spin-restricted calculation 2 electrons are shifted and for a spin-unrestricted calculation only one electron is shifted.

```
ElectronHole
  BandIndex ival1
  SpinIndex ival2
End
```

**`BandIndex`** *ival1* defines which occupied band shall be depopulated.

**`SpinIndex`** *ival2* defines the spin of the shifted electron. (1 or 2)

**General Remark**: To accomplish the excitation of a specific low-lying AO of one atom it helps to define for all other atoms a basis set with frozen core and for the chosen one an all-electron basis set. Then the lowest bands are equal to the AOs of the chosen atom. (See the example *Si_ElectronHole* (page 156))

## 10.3 The programmer key

The programmer has many options, most of which are set automatically. However, with the programmer key you can override many default behaviors. An overview is printed early in the output, and looks like

```
====================
 R U N    C O N F I G
 ====================

 Calculate gradient of basis  .  .  .  .  .  .  .  .  .  .  .  .  T
 Calculate sec. der. of basis .  .  .  .  .  .  .  .  .  .  .  .  F
 Calculate operator T working on basis .  .  .  .  .  .  .  .  .  T
 Calculate gradient of fit .  .  .  .  .  .  .  .  .  .  .  .  .  T
 Calculate sec. der. of fit.  .  .  .  .  .  .  .  .  .  .  .  .  F
 Calculate gradient of fit pot.  .  .  .  .  .  .  .  .  .  .  .  T
 Kin. energy via grad.  .  .  .  .  .  .  .  .  .  .  .  .  .  .  F
 Calculate gradient of energy .  .  .  .  .  .  .  .  .  .  .  .  T
 Calculate kin. energy density.  .  .  .  .  .  .  .  .  .  .  .  F
 Calculate nuc. grad of kin. energy density  .  .  .  .  .  .  .  F
 Calculate der. of density .  .  .  .  .  .  .  .  .  .  .  .  .  T
 Calculate second der. of density.  .  .  .  .  .  .  .  .  .  .  F
 Calculate nuc. grad. of density .  .  .  .  .  .  .  .  .  .  .  T
 Calculate nuc. grad. of grad. density .  .  .  .  .  .  .  .  .  F
 Exact rho during SCF.  .  .  .  .  .  .  .  .  .  .  .  .  .  .  T
 Exact grad. rho during SCF.  .  .  .  .  .  .  .  .  .  .  .  .  F
 Exact grad. rho post SCF  .  .  .  .  .  .  .  .  .  .  .  .  .  T
 Store history of dens. matrix.  .  .  .  .  .  .  .  .  .  .  .  F
 Store original Bloch functions  .  .  .  .  .  .  .  .  .  .  .  T
 Direct  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  F
 Direct basis  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  F
 Calculate DOS .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  T
 Calculate Band structure  .  .  .  .  .  .  .  .  .  .  .  .  .  T
 Calculate EFG .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  F
```

Some of these option are controllable via the Programmer key.

**Programmer (block-type)**

**UseZlmFit [true | false]** Determines whether or not to use ZlmFit. When using this the DirectBas key will be enabled.

**FlioSinglePrecision [true | false]** The basis and fit functions are written and read to so-called FLIO files. With this option the double precision numbers can be converted to single precision, saving half of the IO. The results tend to be still fairly accurate. SCF convergence is usually possible to 1e-5. For deeper convergence disable this option.

**DirectBas [true | false]** Normally basis functions (and possibly derivatives) are calculated once and stored on disk. Enabling this option causes BAND not to store the basis functions but to recalculate them when needed. This reduces the amount of IO, at the cost of increased CPU. Also disables FlioSinglePrecision.

**ExactGradRho [true | false]** The gradient (and second derivative) of the density are usually obtained via the fitted density. With this option you force the program to use the exact density gradient. This requires the calculation of basis set derivatives.

**KinViaGrad [true | false]** Matrix elements of the kinetic energy operator are normally calculated as

$$T_{ij} = \frac{1}{2} \int \Psi_i \nabla \cdot \nabla \Psi_j$$

Using partial integration this can be rewritten as

$$T_{ij} = -\frac{1}{2} \int (\nabla \Psi_i) \cdot \nabla \Psi_j$$

and requires the calculation of the gradient of the basis functions.

**UseSharedMemory [true | false]** Whether or not to use shared memory in a BAND calculation. Doing so might reduce the memory requirement. A reason to disable it might be a bug (like a hangup or race condition) due to this feature.

**DidervCompat [true | false]** Originally all radial derivatives of NAOs were done numerically. However, more accurate derivatives are available from the DIRAC subroutine. To get the old (and slightly worse) derivatives set this option to *true*.

CHAPTER

ELEVEN

# RECOMMENDATIONS AND TROUBLE SHOOTING

## 11.1 Recommendations

### 11.1.1 Model Hamiltonian

The most important ingredients are the kinetic energy (relativistic effects) and the XC functional.

#### Relativistic model

By default we do not use relativistic effects. The best approximation is to use spin-orbit coupling, however that is very expensive. The scalar relativistic option comes for free, and for light elements will give very similar results as non-relativistic theory, and for heavy ones better results w. r. t. experiment. We recommend to always use this (scalar ZORA). To go beyond to the spin-orbit level can be important when there are heavy elements with *p* valence electrons. Also the band gap appears quite sensitive for the spin-orbit effect.

#### XC functional

The default functional is the LDA, that gives quite good geometries but terrible bonding energies. GGA functionals are usually better at bonding energies, and among all possibilities the PBE is a common choice. Using a GGA is not more expensive than using plain LDA. This is even more so for metaGGAs (such as TPSS). For the special problem of band gaps there are two model Hamiltonians available (TB-mBJ and GLLC-SC). The Unrestricted option will be needed when the system is not closed shell. For systems interacting through dispersion interactions it is advised to use the Grimme corrections. Unfortunately there is no clear-cut answer to this problem, and one has to try in practice what works best.

### 11.1.2 Technical Precision

In principle it is simple to control the technical precision with the NumericalQuality key. Here is an example how you could tweak a bit more

```
NumericalQuality Normal ! this is the easy knob, sets the default quality for the keys below

BeckeGrid
  Quality Basic ! tweak the grid
End
KSpace
  Quality Good  ! tweak the k-space grid
End
ZlmFit
```

```
  Quality Basic   ! tweak the density fit
End
SoftConfiment
  Quality VeryGood   ! tweak the radial confinement of basis functions
End
```

Here are per issue hints for when to go for a better quality (but it is by no means complete)

- **BeckeGrid**: Increase quality if there are geometry convergence problems. Also negative frequencies can be caused by the grid.
- **KSpace**: Increase quality for metals
- **ZlmFit**: Increase quality if the SCF does not converge.
- **SoftConfinment**: Increase quality for weakly bonded systems, such as layered materials

The other important issue is the basis set. For geometry optimization the TZP is advised. For properties TZ2P. The best available basis set is QZ4P. All these are quite big, and therefore the DZ basis set is an attractive basis set for quick scans. For geometry optimization the DZP basis works quite well, but it is available only for light elements, and defaults to the TZP basis for other elements.

### 11.1.3 Performance

The performance is influenced by the model Hamiltonian and basis set, discussed above. Here follow more technical tips.

#### Reduced precision

One of the simplest things to try is to run your job with NumericalQuality Basic. For many systems this will work well, and it can be used for instance to pre-optimize a geometry. However, it can also cause problems such as problematic SCF convergence, geometry optimization, or simply bad results. See above how to tweak more finely the *Technical Precision* (page 75).

#### Memory usage

Another issue that is the choice CPVector (say the vector length of you machine) and the number of k-points processed together during the calculation of the parameters. In the output you see the used value

```
                  =========================
                  = Numerical Integration =
                  =========================

TOTAL NR. OF POINTS                                4738
BLOCK LENGTH                                        256
NR. OF BLOCKS                                        20
MAX. NR. OF SYMMETRY UNIQUE POINTS PER BLOCK         35
NR. OF K-POINTS PROCESSED TOGETHER IN BASPNT          5
NR. OF SYMMETRY OPERATORS (REAL SPACE)               48
SYMMETRY OPERATORS IN K-SPACE                        48
```

If you want to change the default settings you can specify the `CPVector` and `KGRPX` keywords. The optimal combination depends on the calculation, on the machine. **Note**: bigger is not necessarily better. Example

```
CPVector 512
KGRPX 3
```

#### Reduced basis set

When starting work on a large unit cell it is wise to start with a DZ basis. With such a basis, one can test for instance the quality of the k-space integration. However, for most properties, the DZ basis is probably not very accurate. You can next go for the DZP (if available) or TZP basis set, but that may be a bit of overkill.

#### Frozen core for 5d elements

The standard basis sets TZ2P are not optimal for third-row transition elements. The V basis offers the possibility to freeze the 4f,5s, and 5p functions. With this you can usually still get quite good results. Sometimes you need to relax the frozen core dependency criterion

```
Dependency Core=0.8 ! The frozen core overlap may not be exactly 1
```

If you want to use the TZ2P you can change it like this one for Au

```
AtomType AuDIRAC Au14 12 ! note: now 12 core functions, was 10
VALENCE
1S
2S
2P
3S
3P
3D
4S
4P
4D
4F
5S
5P
5D    ! from here on valence
6S  1
SubEnd
BasisFunctions
!  5S     4.600000
  6S     3.150000
  6S     1.210000
!  5P     6.650000
!  5P     3.100000
  5D     5.050000
  5D     1.500000
  6P     1.950000
  5F     2.500000
SubEnd
```

## 11.2 Trouble Shooting

### 11.2.1 SCF does not converge

Some systems are more difficult to converge than others. A Pd slab for instance is easier to converge than an Fe slab. Generally, what you do in a problematic case is to go for more conservative settings. The two main option are to decrease `SCF%Mixing` and/or `DIIS%Dimix`.

```
SCF
   Mixing 0.05 ! more conservative mixing
End

Diis
   DiMix 0.1 ! also more conservative strategy for DIIS procedure
   Adaptable false ! disable automatic changing of dimix
End

Convergence
   Degenerate Default ! For most calculations this is quite a good idea anyway
End
```

Sometimes SCF convergence problems are caused by bad precision. An indication of this is when there are many iteration after the HALFWAY message. The simplest thing to try is to see whether increasing the NumericalAccuracy helps. Specifically an insufficient quality of the **density fit** may cause problems. For systems with heavy elements the quality of the **Becke grid** may also play a role. Another potential problem when **only one k-point** is used. The following could be a typical example

```
NumericalQuality Basic ! this is an expensive calculation, like to keep it basic

KSpace
  Quality Normal ! add this when basic gives you only one k-point
End

ZlmFit
  Quality Normal   ! but we do a better density fit (you can also try Good)
End

BeckeGrid
  Quality Normal ! better grid especially for heavy atoms (you can also try Good)
End
```

An alternative is to try a **LIST** method. For sure the cost of a single SCF iteration will increase, but it may reduce the number of SCF cycles, see *Diis%Variant* (page 37).

```
Diis
  Variant LISTi ! invoke the LISTi method
End
```

For heavy elements the use of a small or no frozen core may complicate the SCF convergence.

### 11.2.2 Geometry does not converge

One thing that you should make sure is that at least the **SCF converges**. If that is so, then maybe the **gradients are not accurate enough**. Here are some settings to improve the accuracy of the gradients

```
RadialDefaults
  NR 10000   ! more radial points
End

NumericalQuality Good
```

### 11.2.3 Negative frequencies phonon spectrum

When doing a phonon calculation one sometimes encounters unphysical negative frequencies. There are two likely causes: either the **geometry was not in the minimum geometry** (see `GeoOpt%Converge`), or the **step size** used in the Phonon run is too large (see *PhononConfig%StepSize* (page 47)). Also **general accuracy** issues may be the cause, such as numerical integration, k-space integration and fit error.

### 11.2.4 Basis set dependency

A calculation aborts with the message: dependent basis. It means that for at least one k-point in the BZ the set of Bloch functions, constructed from the elementary basis functions is so close to linear dependency that the numerical accuracy of results is in danger. To check this, the program computes, for each k-point separately, the overlap matrix of the Bloch basis (normalized functions) and diagonalizes it. If the smallest eigenvalue is zero, the basis is linearly dependent. (Negative values should not occur at all!). Given the limited precision of numerical integrals and other aspects in the calculation, you are bound for trouble already if the smallest eigenvalue is very small, even if not exactly zero. The program compares it against a criterion that can be set in input (key `Dependency` option *Bas*).

If you encounter such an error abort, you are strongly advised not to adjust the criterion so as to pass the internal test: there were good reasons to implement the test and to set the default criterion at its current value. Rather, you should adjust your basis set. There are two ways out: using confinement or removing basis functions.

#### Using confinement

Usually the dependency problem is due to the diffuse basis functions. This is especially so for highly coordinated atoms. One way to reduce the range of the functions is to use the Confinement key. In a slab you could consider to use confinement only in the inner layers, and to use the normal basis to the surface layers. The idea is that basis functions of the surface atoms can describe the decay into the vacuum properly, and that inside the slab the diffuseness of the functions is not needed. If all the atoms of the slab are of the same type, you should make a special type for the inner layers: simply put them in a separate Atoms block. The confinement can be specified per type.

#### Removing basis functions

You should remove one or more basis functions and maybe modify some of the (other) STO basis functions. The program prints information that helps you determine which basis functions should be modified/removed. Another way to modify your basis set, is to use the confinement keyword. This has the effect of making the diffuse basis functions more localized, thus reducing problematically large overlap with similar functions on neighboring atoms.

In the standard output file, after the error message, you will find a list of eigenvalues of the overlap matrix. If only the first is smaller than the threshold, you should remove one basis function. If more eigenvalues are very small, it is likely that you have to remove more than one function, although you can of course try how far you can get by eliminating just one.

Next the program prints the so-called Dependency Coefficients: a list of numbers, one for each basis function. Those with a large value are the suspicious ones. If you find two coefficients that are significantly larger than the others, you should replace the two corresponding functions by one. Easiest is to remove one of them (take the one with the bigger coefficient). If one of them is a numerical orbital from Dirac and the other an STO, remove the STO. If both are STOs, remove one and replace the other by some kind of average (regarding the radial characteristic: exponential factor and power of radial coordinate).

To identify how the functions in your input correspond to the list the underlies the series of Dependency Coefficients, you have to set up the list of basis functions as follows:

- Consider an outer loop over all atom TYPES. These correspond, in order as well as in number, to the sequence of AtomType keys in your input file.

- For each type, consider a loop over all atoms of that type, i.e. the atoms in the ATOM block corresponding to the AtomType key at hand.
- For each atom (each AtomType key), first write down all DIRAC basis functions, then all STOs. When writing down the functions, be aware that each entry in your input file specifies a function *set*, by the quantum number L and hence corresponds to 2L+1 actual basis functions.
- Regarding the DIRAC basis functions: they belong to the list of basis functions only if the key Valence occurs in the pertaining DIRAC input block. If not, no DIRAC functions of that type are included in the basis. *If* the Dirac functions are included, you must omit the Core functions and include only the Valence functions from that DIRAC block. The first record in your DIRAC block with two numbers defines (by the first number) the total number of function sets in the DIRAC block (which you can verify by simple counting) and (by the second number) the number of Core function sets among them. The Core function sets, if any, are always the first so many in the list in the DIRAC block.

The program stops as soon as it encounters a dependency problem. This may happen for the first k-point. After you have adjusted the basis set following the above guidelines, you will have solved it. However, it may easily happen that the problem shows up again, but now for another (later) k-point, where other entries in the basis set may cause trouble. Do not think you have repaired the first problem incorrectly. Just repeat the procedure until you pass all k-points in the basis set construction without errors. Typically (as a last remark), although not necessarily, the first k-point may have a dependency problem from too many *s*-type functions, while other k-points may be more sensitive to the series of *p*-functions in your basis.

### 11.2.5 Frozen core too large

BAND calculates the overlap matrix of the core functions, and this should approximate the unit matrix. When the deviation is larger then the frozen-core overlap criterion the program stops. The default criterion (0.98) is fairly strict. The safest solution is to choose a smaller frozen core. For performance reasons, however, this may not be the preferred option. In practice you might still get reliable results by setting the criterion to 0.8, see the *Dependency* (page 39) keyword. For the *5d* transition metals, for instance, you can often freeze the 4f orbital, thus reducing the basis set considerably. We strongly advise you to compare these results to a calculation with a smaller core. Such tests can be performed with a smaller unit cell or with a lower qualitz for the `KSPACE` block key.

## 11.3 Various issues

### 11.3.1 Understanding the logfile

In practice you will look often at the logfile to see whether the calculation is going fine. Here is a logfile for a single point calculation.

```
10:04:09   INIT
10:04:09  BAND development version  RunTime: Sep30-2014 10:04:09  Nodes: 1  Procs: 8
10:04:09  Specify title in input
10:04:09  using 2014 defaults convention
10:04:09  All basis functions smoothly confined at radius:  7.0
10:04:10   RADIAL
10:04:10   POINTS
10:04:11   CELLS
10:04:11   NUMGRD
10:04:11   ELSTAT
10:04:11   ATMFNC
10:04:11  CalcAtomicProperties
10:04:11   PREPAREBAS
10:04:11  ------ K ..   6
```

```
10:04:12   PREPAREHAM
10:04:12  ------ K ..   6
10:04:12   PREPAREFIT
10:04:13  start of SCF loop
10:04:13  initial density from psi
10:04:14  cyc=  0 err=0.00E+00 cpu=   1s ela=   2s
10:04:16  cyc=  1 err=7.83E-01 meth=m nvec= 1 mix=0.0750 cpu=   1s ela=   2s fit=5.02E-02
10:04:17  cyc=  2 err=7.14E-01 meth=d nvec= 2 mix=0.2000 cpu=   1s ela=   1s fit=2.12E-02
10:04:19  cyc=  3 err=9.39E-02 meth=d nvec= 3 mix=0.2000 cpu=   1s ela=   2s fit=2.72E-02
10:04:20  cyc=  4 err=2.82E-02 meth=d nvec= 3 mix=0.2200 cpu=   1s ela=   1s fit=2.92E-02
10:04:22  cyc=  5 err=4.48E-03 meth=d nvec= 3 mix=0.2420 cpu=   1s ela=   2s fit=2.92E-02
10:04:23  HALFWAY
10:04:23  cyc=  6 err=3.07E-03 meth=d nvec= 4 mix=0.2420 cpu=   1s ela=   1s fit=2.93E-02
10:04:25  cyc=  7 err=6.90E-04 meth=d nvec= 4 mix=0.2662 cpu=   1s ela=   1s fit=2.93E-02
10:04:26  cyc=  8 err=2.68E-04 meth=d nvec= 4 mix=0.2928 cpu=   1s ela=   2s fit=2.93E-02
10:04:28  cyc=  9 err=1.28E-04 meth=d nvec= 4 mix=0.3221 cpu=   1s ela=   1s fit=2.93E-02
10:04:29  cyc= 10 err=6.90E-05 meth=d nvec= 4 mix=0.3543 cpu=   1s ela=   1s fit=2.93E-02
10:04:30  SCF CONVERGENCE
10:04:31  cyc= 11 err=3.43E-06 meth=d nvec= 5 mix=0.3543 cpu=   1s ela=   1s fit=2.93E-02
10:04:32  cyc= 12 err=3.43E-06 meth=d nvec= 1 mix=1.0000 cpu=   1s ela=   1s fit=2.93E-02
10:04:32  ------ K ..   6
10:04:34
10:04:34  Max. cycle time CP:       1.379
10:04:34                 IO:       0.309
10:04:34
10:04:34  Mean cycle time CP:       1.459
10:04:34                 IO:       0.151
10:04:34                 EL:       1.636
10:04:34
10:04:34  final mix.par.            0.083
10:04:34  Approx. conv.rate:        0.000
10:04:34
10:04:34  FERMI ENERGY:          -0.2198 A.U.
10:04:34                         -5.9802 E.V
10:04:34  Band gap:                0.1394 A.U.
10:04:34                          3.7943 E.V
10:04:34   ENERGY
10:04:34  ENERGY OF FORMATION:   -1.3496 A.U.
10:04:34                        -36.7236 E.V.
10:04:34                       -846.8654 KCAL/MOL
10:04:34   CHARGE
10:04:34   HIRSH
10:04:34   CM5CHARGES
10:04:34   GRADIENTS
10:04:38   DOS
10:04:38  cannot use good scaling dos routines
10:04:38  storing all partial DOS
10:04:38  integrate over delta E
10:04:39   BZSTRUCT
10:04:39   PREPAREBAS
10:04:39  ------ K ..   6
10:04:39   PREPAREHAM
10:04:39  ------ K ..   6
10:04:41  copy T(V/VOC)
10:04:41  copy eigensystem
10:04:41  NORMAL TERMINATION
10:04:41  END
```

There are three different phases. The first phase is the preparation phase. The second phase is the SCF procedure. The third part is the properties phase. Particularly important are the SCF CONVERGENCE and NORMAL TERMINATION messages.

Let us take a closer look at a line during the SCF.

```
10:04:19  cyc=  3 err=9.39E-02 meth=d nvec= 3 mix=0.2000 cpu=   1s ela=   2s fit=2.72E-02
```

The meaning of cyc is the iteration number, so it is the third iteration. The self consistent error (err) is 9.4e-2. The method (meth) to guess the density for the next cycle is d, meaning DIIS, being a linear combination (nvec) of three vectors. The density is biased (mix) by 0.2 towards output densities. The SCF cycle took 1 second of cpu time (per core), and needed 2 seconds of real time. Finally the error of the density fitting was 2.7e-2.

### 11.3.2 Breaking the symmetry

In some cases you want to break the symmetry. An example of this is when you want to get the antiferromagnetic state of Fe. Another common example is when you want to apply geometry constraints on atoms.

The easiest way to do this is of course to disable all symmetry, see *SYMMETRY%NOSYM* (page 71), but this might make your calculation more expensive than is needed. A bit more elegant way is to define separate types for the equivalent atoms. Here follows an example input for antiferrmomagnetic iron

```
Atoms Fe
  0.0 0.0 0.0
end

! second iron as new type to break the symmetry
Atoms Fe
 -1.435 -1.435 1.435
End

Lattice
 -1.435  1.435  1.435
  1.435 -1.435  1.435
  2.87   2.87  -2.87
End

CONVERGENCE
  CRITERION 1.0e-4
  Degenerate default
  SpinFlip 2  ! Flip (startup) spin density at second atom
END
```

Another solution is to use the expert SYMMETRY keyword.

### 11.3.3 Labels for the basis functions

You see the labels for the basis functions in for instance the DOS section of the output. The labels are also used in combination with options like `Print Eigens` and `Print OrbPop`. (See also `Print Orbitallabels`).

What do the labels look like? A normal atomic basis function, i.e. a numerical orbital or a Slater type orbital, gets a label like <atom number>/<element>/<orbital type>/<quantum numbers description>/<exp in sto>

Example with a Li and a H atom:

```
1/LI/NO/1s
1/LI/NO/2s
1/LI/STO/2s/1.4
```

```
1/LI/STO/2p_y/1.3
1/LI/STO/2p_z/1.3
1/LI/STO/2p_x/1.3
2/H/NO/1s
2/H/STO/1s/1.9
...
```

Core states will just get simple numbers as labels:

```
CORE STATE 1
CORE STATE 2
```

With the `Fragment` key you can give meaningful names to the fragment option, see `Fragment%Labels` and `DosBas`.

### 11.3.4 Reference and Startup Atoms

The formation energy of the crystal is calculated with respect to the reference atoms. BAND gives you the formation energy with respect to the spherically symmetric spin-*restricted* LDA atoms. If you want the program to do the spin-unrestricted calculation for the atoms you can give key Unrestricted the extra option Reference. We do not recommend this as it would give you the false (except in special cases) feeling that you've applied the right atomic correction energy so as to obtain the 'true' bonding energy with respect to isolated atoms. The true atomic correction energy is the difference in energy between the used artificial object, i.e. the spherically symmetric, spin-restricted atom with possibly fractional occupation numbers, and the appropriate multiplet state. The spin-*un*restricted reference atom would still be spherically symmetric, with possibly fractional occupations: it would only have the probably correct (Hund's rule) net spin polarization.

The startup density is normally the sum of the restricted atoms. In case you do an unrestricted calculation you may want to get the sum of the unrestricted atoms as startup density by giving key Unrestricted the extra option StartUp. This does not always provide a better startup density since all atoms will have their net-spins pointing up. If a frozen core is used this option can sometimes lead to a negative valence density, because the frozen core is derived from the restricted atom. The program will stop in such a case.

No matter what reference or startup atoms you use, core orbitals and NOs originate always from the restricted free-atom calculation, because we don't want a spatial dependence of the *basis functions* on spin.

### 11.3.5 Numerical Atoms, Basis functions, and Fit functions

The program starts with a calculation of the free atoms, assuming spherical symmetry. The formation energy is calculated w.r.t such atoms. You have to specify the configuration (i.e. which orbitals are occupied) in the Dirac subkey of the block key AtomType, and you can for instance use the experimental configuration. Keep in mind, however, that this is not necessarily the optimal configuration for your density functional. For instance, Ni has experimentally two electrons in the 4s shell, but with LDA you will find that it is energetically more profitable to move one electron from the 4s to the 3d. The configuration of the reference atoms does not (i.e. should not) affect the final (SCF) density.

Besides the available basis sets in $ADFHOME/atomicdata/band, you could in principle use the basis functions from the database of the molecular ADF program (see the documentation of ADF for how this database is organized). The functions you will find there are STOs, which is not optimal since BAND offers you the option to use NOs from the numerical atom. The most efficient approach is to use the NOs and remove from the ADF basis set those STOs that are already well described by the NOs.

As an example we will construct a basis for the Ni atom with orbitals frozen up to the *2p* shell, derived from a triple-zeta ADF basis. In the Dirac subkey of the block key AtomType you specify that the NOs up to *2p* should be kept frozen and that the 3d and *4s* NOs be included in the valence basis. Copy from the ADF database all *3d*, *4s* and the

polarization functions into the BasisFunctions subkey of the block key AtomType and remove the middle STOs of the *3d* and the *4s*.

Usually it is already quite adequate for a good-quality basis to augment each NO with one STO. You could then take a double zeta ADF basis and remove one of the 3d and one of the 4s STOs. We often find that such a basis, with one STO added per NO, has a quality that is comparable to *triple* zeta STO sets. We strongly recommend that you use combined NO/STO bases. Of course, you may want to verify the quality of the basis set by calculations on a few simple systems.

You can copy the fit functions from the ADF database into the FitFunctions subkey of the block key AtomType. As a matter of experience (and justified by a somewhat different handling of fit functions between the two programs), BAND is in most cases (we have not yet seen an exception) less sensitive to the quality of the fit set than ADF is.

CHAPTER

# TWELVE

# EXAMPLES

## 12.1 Introduction

The ADF package contains a series of sample runs for the BAND program. Provided are UNIX scripts to run the calculations and the resulting output files.

The examples serve:

- To check that the program has been installed correctly: run the sample inputs and compare the results with the provided outputs. *Read the remarks below about such comparisons.*
- To demonstrate how to do calculations: an illustration to the User manuals. The number of options available in BAND is substantial and the sample runs do not cover all of them. They should be sufficient, however, to get a feeling for how to explore the possibilities.
- To work out special applications that do not fit well in the User's Guide.

Where references are made to the operating system (OS) and to the file system on your computer the terminology of UNIX type OSs is used.

All sample files are stored in subdirectories under $ADFHOME/examples/, where $ADFHOME is the main directory of the ADF package. The main subdirectory for the BAND examples is $ADFHOME/examples/band. Each sample run has its own directory. For instance, $ADFHOME/examples/band/NaCl/ contains a BAND calculation on the NaCl bulk crystal. Each sample subdirectory contains:

- A file TestName.run: the UNIX script to execute the calculation or sequence of calculations of the example
- A file TestName_orig.out: the resulting output(s) against which you can compare the outcome of your own calculation.

Notes:

- Running the examples on Windows: You can run an example calculation by double-clicking on the appropriate .run file. After the calculation has finished, you can compare the TestName.out file with the reference TestName_orig.out file. See remarks about comparing output files below.
- The UNIX scripts make use of the *rm* (remove) command. Some UNIX users may have aliased the *rm* command. They should accordingly adapt these commands in the sample scripts so as to make sure that the scripts will remove the files. New users may get stuck initially because of files that are lingering around after an earlier attempt to run one of the examples. In a subsequent run, when the program tries to open a similar (temporary or result) file again, an error may occur if such a file already exists. Always make sure that no files are left in the run-directory except those that are required specifically.
- It is a good idea to run each example in a separate directory that contains no other important files.
- The run-scripts use the environment variables ADFBIN and ADFRESOURCES. They stand respectively for the directory that contains the program executables and the main directory of the database. To use the scripts as they are you must have defined the variables ADFBIN and ADFRESOURCES in your environment. If a parallel

(PVM or MPI) version has been installed, it is preferable to have also the environment variable NSCM. This defines the default number of parallel processes that the program will try to use. Consult the Installation Manual for details.

- As you will note the sample run scripts refer to the programs by names like 'adf', 'band', and so on. When you inspect your $ADFBIN directory, however, you may find that the program executables have names 'adf.exe', 'band.exe'. There are also files in $ADFBIN with names 'adf', 'band', but these are in fact scripts to execute the binaries. We strongly recommend that you use these scripts in your calculations, in particular when running parallel jobs: the scripts take care of some aspects that you have to do otherwise yourself in each calculation.
- You need a license file to run any calculations successfully. If you have troubles with your license file, consult the Installation manual. If that doesn't help contact us at support@scm.com

Many of the provided samples have been devised to be short and simple, at the expense of physical or chemical relevance and precision or general quality of results. They serve primarily to illustrate the use of input, necessary files, and type of results. The descriptions have been kept brief. Extensive information about using keywords in input and their implications is given in the User's Guide and the Utilities and Property Programs documents (NMR, DIRAC, and other utility programs).

When you compare your own results with the sample outputs, you should check in particular (as far as applicable):

- Occupation numbers and energies of the one-electron orbitals;
- The optimized geometry;
- Vibrational frequencies;
- The bonding energy and the various terms in which it has been decomposed;
- The dipole moment;
- The logfile. At the end of a calculation the logfile is automatically appended (by the program itself) to the standard output.

General remarks about comparisons:

- For technical reasons, discussion of which is beyond the scope of this document, differences between results obtained on different machines, or with different numbers of parallel processes, may be much larger than you would expect. They may significantly exceed the machine precision. What you should check is that they fall well (by at least an order of magnitude) within the *numerical integration* precision used in the calculation.
- For similar reasons the orientation of the molecule used by the program may be different on different machines, even when the same input is supplied. In such cases the different orientations should be related and only differ in some trivial way, such as by a simple rotation of all coordinates by 90 degrees around the z-axis. When in doubt, contact an ADF representative.
- A BAND run may generate, apart from result files that you may want to save, a few scratch files. The UNIX scripts that run the samples take care of removing these files after the calculations have finished, to avoid that the program aborts in the next run by attempting to open a 'new' file that is found to exist already.
- A sample calculation may use one or more data files, in particular *fragment* files. The samples are self-contained: they first run the necessary pre-calculations to produce the fragment files. In 'normal' research work you may have libraries of fragments available, first for the 'basic atoms', and later, as projects are developing, also for larger fragments so that you can start immediately on the actual system by attaching the appropriate fragment files.

Default settings of print options result in a considerable amount of output. This is also the case in some of the sample runs, although in many of them quite a bit of 'standard' output is suppressed by inserting applicable print control keys in the input file. Consult the User's Guide about how to regulate input with keys in the input file.

## 12.2 Model Hamiltonians

### 12.2.1 Example: MetaGGA functionals

Download LiMetaGGA.run

Example for a post SCF metaGGA calculation.

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title Li bulk

KSpace 3

accuracy 5

DIIS
   dimix 0.3
   ncycledamp 0
end

scf
   mixing 0.6
end

xc
   metaGGA postscf
end

define
   ha=6.60/2
end

Lattice
   -ha  ha  ha
    ha -ha  ha
    ha  ha -ha
end

Atoms
   Li   0.0  0.0  0.0
end

BasisDefaults
   BasisType DZ
   Core Large
end

end input
eor
```

### 12.2.2 Example: Relativistic effects: Platinum slab

Download Pt_slab.run

This example can of course be compared directly to the Cu slab. This example is important, as SCF convergence is

frequently difficult in slab calculations. The specifications in the CONVERGENCE, SCF, and DIIS blocks are typical. Such settings are recommended in slab calculations with convergence problems.

The DEGENERATE subkey specifies that bands with the same energy should have the same occupation numbers. This helps SCF convergence. The same is true for the values for the MIXING subkey in the SCF block and the DIMIX subkey in the DIIS block. Please note that the recommended value for Mixing is approximately half of the value for Dimix.

Another important feature in BAND is that it enables relativistic treatments for heavy nuclei. Both the ZORA scalar relativistic option and spin-orbit effects have been implemented. The line

```
Relativistic ZORA SPIN
```

specifies that in this case both the scalar relativistic effects (ZORA) and spin-orbit effects (SPIN) will be taken into account. Whereas the ZORA keyword does not make the calculation much more time-consuming, the same cannot be said for the spin-orbit option. Usually the ZORA keyword will give the most pronounced relativistic effects and the spin-orbit effects will be a fairly minor correction to that. We therefore recommend scalar ZORA as a good default method for treating heavy nuclei.

The DEPENDENCY keyword means that the calculation should continue even if the basis is nearly linearly dependent (as measured by the eigenvalues of the overlap matrix).

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title Platinum slab

Comment
 Technical
   Low quadratic K space integration
   Low real space integration accuracy
 Features
   Lattice   : 2D
   Unit cell : 3 atoms, 1x1
   Basis     : NO+STO w/ core
   Options   : Spinorbit ZORA
End

Convergence
   Degenerate 1.0E-03
End

SCF
   Iterations 60
   Mixing 0.06
End

DIIS
   NCycleDamp 15
   DiMix 0.15
End

KSpace 3
Accuracy 3

Relativistic ZORA SPIN

Dependency Basis=1E-8
```

```
Define
   latt=7.41
   lvec=latt/SQRT(2.0)
   ysh=lvec/SQRT(3.0)
   dlay=latt/SQRT(3.0)
End

Lattice
   SQRT(3.0)*lvec/2.0  0.5*lvec
   SQRT(3.0)*lvec/2.0 -0.5*lvec
End

Atoms Pt
   Pt   0   0        0    :: layer 1
   Pt  -ysh 0.0     -dlay :: layer 2
   Pt   ysh 0.0 -2.0*dlay :: layer 3
End

END INPUT
eor
```

### 12.2.3 Example: Spin polarization: antiferromagnetic iron

`Download BetaIron.run`

With the `UNRESTRICTED` keyword we do a spin polarized calculation. Normally this would converge to the ferromagnetic solution.

With the `SpinFlip` keyword we make sure that we start with an antiferrmagnetic density.

For antiferromagnetic iron we need a larger unit cell of two atoms. Because these atoms appear to the program as symmetry equivalent we have to specify them as separate types.

```
$ADFBIN/band << eor
TITLE Beta iron

UNITS
    length Angstrom
    angle Degree
END

ATOMS Fe
     0.0 0.0 0.0
end

! second iron as new type to break the symmetry
Atoms Fe
   -1.435 -1.435 1.435
END

Lattice
   -1.435  1.435  1.435
    1.435 -1.435  1.435
    2.87   2.87  -2.87
End

CONVERGENCE
   CRITERION 1.0e-4
```

```
   Degenerate default
   SpinFlip 2  ! Flip (startup) spin density at second atom
END

BasisDefaults
   BasisType DZ
   Core Large
End

UNRESTRICTED

end input
eor
```

### 12.2.4 Example: Graphene sheet with dispersion correction

Download Graphene_Dispersion.run

A normal GGA would give no interaction between two graphene sheets.

Use the dispersion option in the XC keyblock.

In the first run we use BP86-D, and in the second BLYP-D3.

```
$ADFBIN/band << eor
TITLE Dispersion energy with two parallel graphene sheets

kspace 3
accuracy 4.5

XC
gga scf bp86
dispersion default
end

dependency basis=1e-6

UNITS
    length Angstrom
    angle Degree
END

ATOMS
   C    0.00  0.0000000000  0.000
   C    0.00  0.0000000000 -3.355
   C    1.23  0.7101408312  0.000
   C   -1.23 -0.7101408311 -3.355
END

Lattice
   2.46 0.000000000 0.00
   1.23 2.130422493 0.00
End

CONVERGENCE
CRITERION 1.0e-4
Degenerate default
END
```

```
DIIS
CLARGE 10
CHUGE 30
DIMIX 0.3
NVCTRX 10
NCYCLEDAMP 5
END

SCF
iterations 50
mixing 0.2
END

BasisDefaults
BasisType TZP
Core Large
End
end input
eor

rm RUNKF

$ADFBIN/band << eor
TITLE Grimme3 dispersion energy with two parallel graphene sheets

kspace 3
accuracy 4.5

XC
gga scf blyp
dispersion Grimme3
end

dependency basis=1e-6

Gradients
End

UNITS
    length Angstrom
    angle Degree
END

ATOMS
   C    0.00  0.0000000000  0.000
   C    0.00  0.0000000000 -3.355
   C    1.23  0.7101408312  0.000
   C   -1.23 -0.7101408311 -3.355
END

Lattice
   2.46 0.000000000 0.00
   1.23 2.130422493 0.00
End

CONVERGENCE
CRITERION 1.0e-4
Degenerate default
```

```
END

DIIS
CLARGE 10
CHUGE 30
DIMIX 0.3
NVCTRX 10
NCYCLEDAMP 5
END

SCF
iterations 50
mixing 0.2
END

BasisDefaults
BasisType TZP
Core Large
End

end input
eor
```

### 12.2.5 Example: H on perovskite with the COSMO solvation model

`Download HonPerovskite_Solvation.run`

We want to model H adsorption on a Perovskite surface in a solution, modeled by a COSMO surface.

We create only the COSMO surface above the slab with the `RemovePointsWithNegativeZ` option.

```
$ADFBIN/band << eor
DefaultsConvention 2014

TITLE Hydrogen on Perovksite wit solvation

Solvation
   Surf Delley
   charge method=inver
End

PeriodicSolvation
   nstar 3
   RemovePointsWithNegativeZ true
End

Screening
   rmadel 30 ! to speed up the calculation
End

Units
    length Angstrom
    angle Degree
End

Atoms
   H    0.0  0.000000000  0.900000000
   Ca   0.0  0.000000000  0.000000000
```

```
   Ca   0.0  3.535533906 -3.535533906
   Ti  -2.5 -3.535533906  0.000000000
   Ti  -2.5  0.000000000 -3.535533906
   O    0.0 -3.535533906  0.000000000
   O    2.5  1.767766953 -1.767766953
   O    2.5 -1.767766953 -1.767766953
End

Lattice
   5.0  0.000000000  0.0
   0.0  7.071067812  0.0
End

Convergence
   Criterion 1.0e-4
End

BasisDefaults
   BasisType SZ
   Core Large
End

end input
eor
```

### 12.2.6 Example: Applying a homogeneous electric field

Download EField.run

With the EFIELD keyword you can specify a static electric field in the z-direction.

```
$ADFBIN/band << eor
DefaultsConvention 2014

Title Electric Field (field in a.u.)

EField
   Unit a.u.
   eZ=0.03
end

KSpace 1

Gradients
End

lattice
   15.0  0.00  0.00
   0.00  15.0  0.00
End

Atoms
   H   0.0 0.0 0.0
   Li  0.0 1.0 3.0
End

BasisDefaults
```

```
   BasisType TZP
   Core Large
End

end input
eor
```

### 12.2.7 Example: Finite nucleus

Download FiniteNucleus.run

Normally the nucleus is approximated as a point charge, however we can change this to a finite size. Properties that might be affected are EFG, and the a-tensor. For such calculations one needs to crank up the precision and also use a relativistic Hamiltonian.

```
"$ADFBIN/band" << eor
TITLE Au atom with point charge nucl.

programmer
flioSinglePrecision false
end

relativistic zora

PropertiesAtNuclei
  rho(scf)
  rho(deformation/scf)
  vxc[rho(fit)]
  rho(fit)
  v(coulomb/scf)
End

RadialDefaults
nr 10000
end

kspace 1

Accuracy 6

integration
  allElectron true
end

Unrestricted

efg
end

atensor
end

UNITS
    length Angstrom
    angle Degree
END
```

```
NuclearModel PointCharge

lattice
   30 0 0
end

screening
   rcelx 5
end

ATOMS
   Au    0.000000      0.000000      0.000000
end

CONVERGENCE
Degenerate default
END

DIIS
CLARGE 10
CHUGE 10
DIMIX 0.1
NVCTRX 20
NCYCLEDAMP 0
END

scf
mixing 0.3
end

BasisDefaults
BasisType TZ2P
Core None
End

XC
gga always pbe
END

Dependency basis=1e-8
end input
eor

rm RUNKF
rm Points

"$ADFBIN/band" << eor
TITLE Au atom with finite nucl.

programmer
flioSinglePrecision false
end

relativistic zora

PropertiesAtNuclei
  rho(scf)
  rho(deformation/scf)
```

```
  vxc[rho(fit)]
  rho(fit)
  v(coulomb/scf)
End

RadialDefaults
nr 10000
end

kspace 1

Accuracy 6

integration
  allElectron true
end

Unrestricted

efg
end

atensor
end

UNITS
    length Angstrom
    angle Degree
END

NuclearModel Gaussian

lattice
30 0 0
end

screening
rcelx 5
end

ATOMS
   Au    0.000000      0.000000      0.000000
end

CONVERGENCE
Degenerate default
END

DIIS
CLARGE 10
CHUGE 10
DIMIX 0.1
NVCTRX 20
NCYCLEDAMP 0
END

scf
mixing 0.3
```

```
end

BasisDefaults
BasisType TZ2P
Core None
End

XC
gga always pbe
END

Dependency basis=1e-8
end input
eor
```

### 12.2.8 Example: Fixing the Band gap of NiO with GGA+U

`Download NiO_Hubbard.run`

With the `UNRESTRICTED` keyword we do a spin polarized calculation.

With the `HubbardU` key block we set up the GGA+U calculation. You need to specify per atom type (only two here, Ni, and O) the U and the $l$-value to which it should be applied.

```
$ADFBIN/band << eor
TITLE NiO

UNITS
    length Angstrom
    angle Degree
END

HubbardU
   printOccupations true
   Enabled true
   uvalue 0.3 0.0  ! Type 1 (Ni) will get U=0.3
   lvalue 2 -1     ! Will be used for the d-orbitals of Ni
End

ATOMS Ni
   0.0 0.0 0.0
END

ATOMS O
   2.085 2.085 2.085
END

Lattice
   0.000 2.085 2.085
   2.085 0.000 2.085
   2.085 2.085 0.000
End

CONVERGENCE
   CRITERION 1.0e-4
   Degenerate default
END
```

```
DIIS
   CLARGE 10
   CHUGE 10
   DIMIX 0.2
   NVCTRX 20
   NCYCLEDAMP 0
END

SCF
   iterations 50
   mixing 0.1
END

BasisDefaults
   BasisType TZP
   Core Large
End

XC
   GGA Becke Perdew
END

UNRESTRICTED

Dependency basis=1e-6

end input
eor
```

### 12.2.9 Example: Fixing the band gap of ZnS with the TB-mBJ model potential

Download ZnS_ModelPotential.run

With the XC subkey model we invoke the so-called TB-mBJ model potential, which increases band gaps for solids.

```
$ADFBIN/band << eor
DefaultsConvention 2014

TITLE ZnS pot=TB-mBJ

XC
   model TB-mBJ
END

UNITS
   length Angstrom
   angle Degree
END

ATOMS
   Zn  0.0000  0.0000  0.0000
   S   1.3525  1.3525  1.3525
END

Lattice
   0.000000 2.705 2.705
   2.705 0.000000 2.705
```

```
   2.705 2.705 0.000000
End

BasisDefaults
   BasisType DZ
   Core Large
End

end input
eor
```

## 12.3 Precision and performance

### 12.3.1 Example: Convenient way to specify a basis set

Download BasisDefaults.run

This example shows some of the flexibility of the BasisDefaults key. The defaults are set to a DZ basis and a Large core. As the example shows, it is possible to override the defaults per atom type by specifying subkeys in Atoms blocks.

```
$ADFBIN/band << eor
DefaultsConvention 2014

Title CO + H2: fine tuning the basis defaults

NumericalQuality Basic

! So we have  cheap defaults
BasisDefaults
   BasisType DZ
   Core Large
End

Atoms C ! This C has no frozen core
   0.0 0.0 0.0
   Core None
End

Atoms O ! This O with a larger basis
   0.0 2.13 0.0
   BasisType TZ2P
End

Atoms H ! This one also with a larger basis
   4.0 0.0 0.0
   BasisType V
End

Atoms H ! Let us use the default settings for this atom
   4.0 1.43 0.0
End

END INPUT
eor
```

### 12.3.2 Example: Tuning precision and performance

Download Peptide_NumericalQuality.run

This example shows how to tune the numerical quality of the calculation. This will influence both efficiency and accuracy of the calculation.

```
$ADFBIN/band << eor

NumericalQuality Normal

ZlmFit
   Quality Normal
End

BeckeGrid
   Quality Basic
End

KSpace
   Quality Basic
End

SoftConfinement
   Quality VeryGood
End

UNITS
   length Angstrom
END

ATOMS
   C  -2.543276676    0.646016253   -0.226282061
   C  -1.380007216   -0.349821933   -0.099968062
   C   1.066549862   -0.581911934   -0.064823014
   C   2.223931363    0.423839954   -0.118070453
   N  -0.149937993    0.193000383   -0.179010633
   N   3.452833267   -0.128914507   -0.101813389
   O  -1.589886979   -1.564606357    0.062390357
   O   2.010772661    1.647347397   -0.186192833
   H  -2.480330907    1.422845016    0.554868474
   H   3.629655835   -1.142731500   -0.018098016
   H  -2.511564496    1.180719545   -1.193540463
   H   0.024515371    1.206808884   -0.244500253
   H   1.160598100   -1.320381370   -0.884522980
   H   1.071343640   -1.136930542    0.888913220
END

Lattice
       7.211585775    0.000000000    0.000000000
End

BasisDefaults
   BasisType DZ
   Core Large
End

XC
   GGA PBE
```

```
END

end input
eor
```

### 12.3.3 Example: Multiresolution

Download H2O_Multiresolution.run

This example demonstrates how to use different levels of numerical precision for different regions, with the aim of increasing computational efficiency.

Let us assume that we are interested in having an accurate description only for a subregion of a large chemical system (in this simple example, the central water molecule embedded in a small water cluster). The system can be divided into sub-regions and different levels of numerical accuracy can be used for each of these sub-regions.[*53* (page 166)]

In this example we will tweak the basis set (BasisType), the numerical integration quality (BeckeGrid) and the density fitting quality (ZlmFit):

- Region_1 (central water molecule): All-electron TZP basis set, good integration and fitting quality;
- Region_2 (nearby water molecules): DZP basis set, normal integration and fitting quality;
- Region_3 (far away water molecules): DZ basis set, basic integration and fitting quality.

Note: For the atoms that have not been explicitly defined in the AtomDepQuality sub-blocks, the quality defined in NumericalQuality will be used (Basic in this example).

```
$ADFBIN/band << eor

UNITS
   length Angstrom
END

! Region 1

Atoms O
   O       0.00000000       0.00000000       0.00000000
   BasisType TZP
   Core None
End
Atoms H
   H       0.95598067      -0.00675125       0.0469560
   H      -0.27235084       0.54445503       0.7386041
   BasisType TZP
   Core None
End

! Region 2

Atoms O
   O      -0.60494216       1.46490169       2.08012471
   O       2.20300071      -1.46837786      -1.32565612
   O      -1.50296488       0.38335767      -2.26270407
   O      -1.26586015      -2.22743706       0.52905656
   O       2.56741860      -1.62760305       1.40348274
   BasisType DZP
End
Atoms H
```

```
   H      -1.36174124       1.46490169       2.66613184
   H       0.15185693       1.46490169       2.66613184
   H       1.41269969      -1.75817168      -1.78128023
   H       2.91509001      -1.94050071      -1.75713167
   H      -1.22374034       1.23595156      -2.59627085
   H      -0.94183314       0.22778137      -1.50305317
   H      -1.86350326      -2.02544308       1.24889726
   H      -0.71759486      -1.44720433       0.44668931
   H       2.62568379      -1.68307735       0.44971272
   H       3.11146028      -0.87440516       1.63338252
   BasisType DZP
End

! Region 3

Atoms O
   O       1.85561863       3.40985337       0.07797373
   O       2.15143451      -2.15387984       4.03356174
End
Atoms H
   H       2.20215679       2.60864811      -0.31462138
   H       1.19434847       3.10556187       0.69948059
   H       2.18159460      -2.07271050       3.08032966
   H       2.77736140      -1.50229172       4.34945851
End

NumericalQuality Basic

SoftConfinement
   Quality Normal
End

BeckeGrid
   AtomDepQuality
      1  Good
      2  Good
      3  Good
      4  Normal
      5  Normal
      6  Normal
      7  Normal
      8  Normal
      9  Normal
      10 Normal
      11 Normal
      12 Normal
      13 Normal
      14 Normal
      15 Normal
      16 Normal
      17 Normal
      18 Normal
   SubEnd
End

ZlmFit
   AtomDepQuality
      1  Good
```

```
      2  Good
      3  Good
      4  Normal
      5  Normal
      6  Normal
      7  Normal
      8  Normal
      9  Normal
      10 Normal
      11 Normal
      12 Normal
      13 Normal
      14 Normal
      15 Normal
      16 Normal
      17 Normal
      18 Normal
   SubEnd
End

BasisDefaults
   BasisType DZ
End

END INPUT
eor

end input
eor
```

## 12.4 Restarts

### 12.4.1 Example: Restart the SCF

`Download RestartSCF.run`

This example shows how you can continue with an unfinished calculation. It consists of two runs. After the first run the RUNKF file is saved, and the renamed file is used in the second run. The second run is almost a copy for the first, except for the `Restart` key. You can, however, change more, as long as the basis set remains the same.

```
# ----------------------------- first run --------------------------

$ADFBIN/band << eor
Title B chain

KSpace 3

Accuracy 4

skip dos

XC
   GGA Becke Perdew
END

UNRESTRICTED
```

```
SCF
   Mixing 0.4
   Iterations 40
End

Convergence
   Degenerate default
End

DIIS
   NCycleDamp 0
   DiMix 0.5
End

Define
   ddd=4.0
   ccc=1.5
End

Lattice
   ddd
End

Atoms
   B   0.00  0.00  0.00
End

BasisDefaults
   BasisType TZ2P
   Core Large
End

END INPUT
eor

mv RUNKF BChain.runkf
rm Points

# ----------------------------- second run --------------------------

$ADFBIN/band << eor
Title B chain restart

KSpace 3

Accuracy 4

XC
   GGA Becke Perdew
END

UNRESTRICTED

Restart
   File BChain.runkf
   scf
end
```

```
SCF
   Mixing 0.4
   Iterations 40
End

Convergence
   Degenerate default
End

DIIS
   NCycleDamp 0
   DiMix 0.5
End

Define
   ddd=4.0
   zzz=3
End

Lattice
   ddd
End

Atoms
   B   0.00  0.00  0.00
End

BasisDefaults
   BasisType TZ2P
   Core Large
End

END INPUT
eor
```

### 12.4.2 Example: Properties on a grid

`Download BeO_tape41.run`

If we save the RUNKF file of a calculation we can restart it to calculate properties on a grid.

In the second run we restart from the file BeO.runkf. We specify to use a regular grid and ask the program to calculate a bunch of properties on that grid.

First job:

```
$ADFBIN/band << eor
Title BeO

Comment
   in the "ideal" most symmetric configuration: u=3/8, and c=sqrt(8/3)*a
End

DefaultsConvention 2014

NumericalQuality Basic

xc
```

```
  gga scf bp86
end

Define
  uuu=3/8
  aaa=5.10
  ccc=sqrt(8/3)*aaa
End

Coordinates Natural

ATOMS
  Be  0 0 0
  Be  1/3 1/3 1/2
  O   0 0 uuu
  O   1/3 1/3 uuu+1/2
END

Lattice
  aaa 0 0
  0.5*aaa 0.5*sqrt(3)*aaa 0
  0 0 ccc
End

BasisDefaults
  BasisType DZ
  Core large
end

end input
eor

mv RUNKF BeO.runkf
```

Second job:

```
$ADFBIN/band << eor
DefaultsConvention 2014

Title BeO

Comment
 in the "ideal" most symmetric configuration: u=3/8, and c=sqrt(8/3)*a
End

Restart
  File BeO.runkf
  DensityPlot
End

Grid
   Type Coarse
End

DensityPlot
   rho(deformation/fit)
   rho(fit)
   rho(atoms)
   v(coulomb/atoms)
```

```
   v(coulomb)
   vxc[rho(fit)]
End

NumericalQuality Basic

xc
  gga scf bp86
end

Define
  uuu=3/8
  aaa=5.10
  ccc=sqrt(8/3)*aaa
End

Coordinates Natural

ATOMS
  Be  0 0 0
  Be  1/3 1/3 1/2
  O   0 0 uuu
  O   1/3 1/3 uuu+1/2
END

Lattice
  aaa 0 0
  0.5*aaa 0.5*sqrt(3)*aaa 0
  0 0 ccc
End

BasisDefaults
  BasisType DZ
  Core large
end

end input
eor
```

## 12.5 Structure and Reactivity

### 12.5.1 Example: NaCl: Bulk Crystal

`Download NaCl.run`

A bulk crystal computation for Sodium Chloride (common salt), with a subsequent DOS analysis, using a Restart facility to use the results from a preceding calculation.

Calculations on periodic systems are carried out with the BAND program. Its input format has recently been changed substantially. It is now more similar in style to ADF. Old BAND input files are no longer compatible with the new version however.

The BAND input still follows slightly different conventions from the ADF input, for historical reasons.

The `COMMENT` keyword allows users to provide some information about the run which may be of use later. Usually a brief summary of the run is given here.

Numerical integration precision is controlled with the key `Accuracy` (in ADF: Integration)

The accuracy for integrals over the Brillouin Zone is set by the `Kspace` key. The latter should, generally, take as value an *odd* number (3, 5...) to invoke the accurate *quadratic* tetrahedron integration procedure. For *even* values it will revert to the *linear* tetrahedron method, which is almost always inferior in accuracy.

The key `Angstroms` specifies that geometric data, such as lattice constants are in angstrom units.

Since there are 3 data records in the `Lattice` block, the calculation will assume 3-dimensional periodicity, with lattice vectors as indicated. Note that lattice vectors are undefined up to linear combinations among themselves. Internally, the program will recombine the input vectors so as to minimize the size of the actually used vectors.

The input line `Coordinates NATURAL` means that atomic positions are input as coefficients in terms of the lattice vectors, rather than as absolute (Cartesian) coordinate values.

For each of the atoms in the calculations, Na and Cl here, there must be data blocks to specify various items. First, their positions in the crystal unit cell (key `Atoms`). Second, the single isolated atom computation that will serve as start-up (`Dirac`). Third, any Slater-type orbital basis functions (`BasisFunctions`) for that atom. Fourth, the fit functions (`FitFunctions`) for the calculation of the Coulomb potential and. The third item (`BasisFunctions`) is optional and not present in this example.

It is recommended to include the numerical atomic orbitals that are computed by the Herman-Skillman type subprogram DIRAC as basis functions for the periodic structure calculation. This is effectuated by putting the word VALENCE in the Dirac data blocks. If that is done, additional STO basis functions (key `BasisFunctions`) are optional and are used to increase the basis set flexibility. In absence of the numerical (DIRAC/VALENCE) orbitals, a minimal STO set is necessary of course, lest we wouldn't have any basis set at all.

In an equivalent ADF calculation, basis and fit functions would be provided through the Create runs, which pick up the basis and fit functions from a database file. The Create runs would also serve to provide the start-up density, as the DIRAC runs do in BAND.

The basis and fit sets that one has to insert into the BAND input files can be taken from the corresponding ADF database. Note, however, that ADF does not use any numerical orbitals. Since it is recommended to include such numerical orbitals in a BAND calculation, one has to adjust the STO-type basis set for BAND, in comparison with ADF, so as to avoid linear dependency with the numerical orbitals. As a general guideline: for each of the included numerical orbitals (the occupied valence orbitals of the DIRAC calculation), one should remove one STO of the appropriate (n,l)-value. This keeps the overall size and flexibility of the basis at the same level and is usually sufficient to avoid dependency troubles.

The RUNKF key, early in the input, specifies that this standard result file from BAND must be saved under the name 't21.NaCl'. This file will be used in the follow-up calculation of Density-of-States properties.

Note, finally, that the data blocks of block type keys in the input for BAND end with a record 'END', as in ADF, whereas previously '==' was used in BAND to end a record.

```
$ADFBIN/band << eor
Title Title NaCl (from neutral atoms)

Comment
 Technical
   Hybrid K space integration (3D)
   Low real space integration accuracy
   Natural coordinates
   Lengths in Angstrom
   Parameters Dirac procedure
 Features
   Lattice   : 3D
   Unit cell : 2 atoms
   Basis     : NO w/ core
   Options   : Save restart file
```

```
End

Accuracy 3.5
Kspace 3

Units
 Length Angstrom
End

Lattice
0    2.75   2.75
2.75  0     2.75
2.75  2.75   0
End

ATOMS NA
0
End

Coordinates Natural
Atoms Cl
  .5  .5  .5
End

AtomType Na
Dirac   Na
  4 1
  Radial  2000
  RMin    1E-4
  RMax    60
  VALENCE
  1 0
  2 0
  2 1
  3 0 1.0
SubEnd

FitFunctions
  1 0 18.9
  2 0 30.3
  2 0 15.5
  3 0 14.9
  3 0  8.9
  4 0  7.8
  4 0  5.1
  4 0  3.3
  5 0  2.8
  5 0  1.9
  5 0  1.3
  2 1 14.3
  3 1  9.9
  4 1  6.7
  4 1  3.4
  5 1  2.4
  5 1  1.3
  3 2 10.5
  4 2  5.4
  5 2  3.0
```

```
  5 2  1.3
  4 3  5.8
  5 3  1.7
  5 4  2.0
SubEnd
End

AtomType Cl
Dirac  Cl
  5 3
  VALENCE
  1 0
  2 0
  2 1
  3 0
  3 1  5.0
SubEnd

FitFunctions
  1 0 29.1
  2 0 49.5
  2 0 26.1
  3 0 25.8
  3 0 15.8
  4 0 14.2
  4 0  9.4
  4 0  6.2
  5 0  5.4
  5 0  3.8
  5 0  2.6

  2 1 21.2
  3 1 16.5
  4 1 12.4
  4 1  6.8
  5 1  5.1
  5 1  3.1

  3 2 16.6
  4 2  9.4
  5 2  5.5
  5 2  2.6

  4 3  8.7
  5 3  3.3

  5 4  4.0
SubEnd
End

End Input
eor

mv RUNKF t21.NaCl

rm Points
```

The next run has largely the same input and provides a restart of the previous run.

The key RESTARTDOS tells the program to pick up the indicated file as restart file *and* to use it for DOS analysis purposes.

The DOS key block details the energy grid (and range) and the file to write the data to. The optional keys GROSSPOPULATIONS and OverlapPopulations invoke the computation of, respectively, gross populations and overlap populations (i.e. for each of these the density-of-states values in the user-defined energy grid).

```
$ADFBIN/band << eor
Title Title NaCl (from neutral atoms)   DOS analysis (restart)

Comment
 Technical
   Hybrid K space integration (3D)
   Low real space integration accuracy
   Natural coordinates
   Lengths in Angstrom
   Parameters Dirac procedure
 Features
   Lattice   : 3D
   Unit cell : 2 atoms
   Basis     : NO w/ core
   Options   : Use restart file for DOS
               Analysis: DOS, PDOS, COOP
End

Restart
  File t21.NaCl
  DOS
End

Accuracy 3.5
Kspace 3

SCF
 Iterations 15
End

Units
 Length Angstrom
End

Lattice
  0    2.75   2.75
  2.75  0     2.75
  2.75  2.75   0
End

DOS
  File NaCl.dos
  Energies 1000
  Min -0.5
  Max  0.5
End

GROSSPOPULATIONS
 FRAG 1
 FRAG 2
 SUM
   1 0
```

```
   2 0
 ENDSUM
End

OVERLAPPOPULATIONS
LEFT
 FRAG 1
RIGHT
 FRAG 2
LEFT
  1 0
  1 1
RIGHT
  2 0
  2 1
End

Atoms NA
  0
End

Coordinates Natural

Atoms Cl
  .5  .5  .5
End

AtomType Na
Dirac   Na
  4 1
  Radial  2000
  RMin    1E-4
  RMax    60
  VALENCE
  1 0
  2 0
  2 1
  3 0 1.0
SubEnd

FitFunctions
  1 0 18.9
  2 0 30.3
  2 0 15.5
  3 0 14.9
  3 0  8.9
  4 0  7.8
  4 0  5.1
  4 0  3.3
  5 0  2.8
  5 0  1.9
  5 0  1.3
  2 1 14.3
  3 1  9.9
  4 1  6.7
  4 1  3.4
  5 1  2.4
  5 1  1.3
```

```
  3 2 10.5
  4 2  5.4
  5 2  3.0
  5 2  1.3
  4 3  5.8
  5 3  1.7
  5 4  2.0
SubEnd
End

AtomType Cl
Dirac  Cl
  5 3
  VALENCE
  1 0
  2 0
  2 1
  3 0
  3 1  5.0
SubEnd

FitFunctions
  1 0 29.1
  2 0 49.5
  2 0 26.1
  3 0 25.8
  3 0 15.8
  4 0 14.2
  4 0  9.4
  4 0  6.2
  5 0  5.4
  5 0  3.8
  5 0  2.6

  2 1 21.2
  3 1 16.5
  4 1 12.4
  4 1  6.8
  5 1  5.1
  5 1  3.1

  3 2 16.6
  4 2  9.4
  5 2  5.5
  5 2  2.6

  4 3  8.7
  5 3  3.3

  5 4  4.0
SubEnd
End

End Input
eor
```

Finally, we copy the contents of the DOS result file to standard output

```
echo Contents of DOS file
cat NaCl.dos
```

### 12.5.2 Example: Atomic energies

Download H_ref.run

This example consists of several atomic energy calculations:

- Formation energy of the H-atom w.r.t. spherical atom.
- Formation energy of the H-atom w.r.t. spherical atom
- Spin polarization energy of the H-atom w.r.t. spherical atom
- Spin polarization (relativistic) energy of the H-atom w.r.t. spherical atom
- Spin polarization energy of the H-atom w.r.t. spin unrestricted atom
- Spin polarization (relativistic) energy of the H-atom w.r.t. spin unrestricted atom

Only the first run is given here:

```
$ADFBIN/band << eor
Title Formation energy of the H-atom w.r.t. spherical atom

Comment
 Technical
   Quadratic K space integration
   High real space integration accuracy
 Features
   Lattice   : 2D, quasi atom
   Unit cell : 1 atom, 1x1
   Basis     : NO+STO
End

Kspace 5
Accuracy 5.0

Convergence
   Criterion 1E-6
End

Define
   far=20.0
End

Lattice
   far 0.0 0.0
   0.0 far 0.0
End

Atoms
   H   0.0 0.0 0.0
End

AtomType H
Dirac H
1  0
VALENCE
```

```
1S 1
SubEnd

BasisFunctions
1S   1.58
2P   1.0
SubEnd

FitFunctions
 1S   3.16
 1S   2.09
 1S   1.38
 2S   1.50
 2P   4.00
 2P   2.65
 2P   1.75
 3D   4.00
 3D   2.50
 4F   3.00
 5G   4.00
SubEnd

End

END INPUT
eor
```

### 12.5.3 Example: Hydrogen on Pt surface

`Download H_on_Pt.run`

This example is in many ways similar to the Pt slab example. We refer to the explanations in that example for details. Suffice it to say here that the convergence criteria have again been chosen such that also difficult slab calculations have a good chance to converge. Further, this calculation is once again at the spin-orbit relativistic level. The geometry is such that two layers of Pt are covered by a hydrogen layer.

...

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title Hydrogen on platinum

Comment
 Technical
   Low quadratic K space integration
   Low real space integration accuracy
 Features
   Lattice   : 2D
   Unit cell : 4 atoms, 1x1
   Basis     : NO+STO
   Options   : Spinorbit ZORA
End

SCF
   Mixing 0.1
   Iterations 100
```

```
End

Convergence
   Degenerate default
   Criterion 1e-6
End

DIIS
   NCycleDamp 0
   DiMix 0.15
End

KSpace 3
Accuracy 3

Relativistic ZORA SPIN

Dependency Basis=1E-8

Define
   latt=7.41
   lvec=latt/SQRT(2.0)
   ysh=lvec/SQRT(3.0)
   dlay=latt/SQRT(3.0)
   height=3.0
End

Lattice
   SQRT(3.0)*lvec/2.0  0.5*lvec
   SQRT(3.0)*lvec/2.0 -0.5*lvec
End

Atoms
   Pt    0.0  0.0    0     :: layer 1
   Pt  -ysh   0.0  -dlay :: layer 2
   H     0.0  0.0    height
End

END INPUT
eor
```

### 12.5.4 Example: Calculating the atomic forces

`Download BNForce.run`

This example shows how to calculate the gradient of the energy with respect to atomic displacements, using the `GRADIENTS` key block.

```
$ADFBIN/band << eor
Title BN zincblende structure (force calculation)

DefaultsConvention 2014

Gradients
End

NumericalQuality Basic  ! for speed, not very accurate
```

```
Units
   Length Angstrom
End

Define
   a = 3.60
End

Lattice
   0.0   0.5*a 0.5*a
   0.5*a 0.0   0.5*a
   0.5*a 0.5*a 0.0
End

Atoms
   B  0.000000 0.000000 0.000000
   N  0.2404*a 0.2404*a 0.2404*a
end

BasisDefaults
   BasisType TZ2P
   Core Large
End

END INPUT
eor
```

In the output you will find the result

```
FINAL GRADIENTS
   1  B  0.017517  0.017517  0.017517
   2  N -0.017517 -0.017517 -0.017517
```

### 12.5.5 Example: Optimizing the geometry

`Download H2BulkGeo.run`

This example shows how to optimize the geometry, using the `GEOOPT` key block, including a restart of a previous optimization. It consists of two runs.

```
$ADFBIN/band << eor
DefaultsConvention 2014

Title H2 bulk geometry optimization

Comment
    Demonstrates the GeoOpt block
    GoeOpt iterations limited to make it faster
End

GeoOpt
  Iterations 5
  Converge Grad=1e-6
End

Units
   Angle Radian
```

```
End

Define
   aaa=1
End

ATOMS
  H   0.0 0.0 0.0
  H   aaa 0.0 0.0
End

Lattice
  5.0*aaa  0        0
  0        5.0*aaa  0
  0        0        5.0*aaa
End

BasisDefaults
   BasisType DZP
End

END INPUT
eor

rm logfile

mv RUNKF H2BulkGeo.runkf
```

Note that the RUNKF file is saved. In the next run we use the result file to continue the geometry optimization.

```
$ADFBIN/band << eor
DefaultsConvention 2014

Title H2 bulk geometry optimization

Comment
    Restarting the geometry optimization
End

Restart
  File H2BulkGeo.runkf
  GeometryOptimization
end

GeoOpt
  Iterations 5
  Converge Grad=1e-6
End

Units
   Angle Radian
End

Define
   aaa=1
End

ATOMS
  H   0.0 0.0 0.0
```

```
  H   aaa 0.0 0.0
End

Lattice
  5.0*aaa  0        0
  0        5.0*aaa  0
  0        0        5.0*aaa
End

BasisDefaults
   BasisType DZP
End

END INPUT
eor
```

### 12.5.6 Example: Nuclear gradient with a MetaGGA functional

Download CO_MetaGGA_Force.run

This example shows how to calculate the gradient of the energy with respect to atomic displacements for a metaGGA functional, using the GRADIENTS and XC key block.

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title CO chain

KSpace 3

accuracy 5

DIIS
   dimix 0.2
   ncycledamp 0
end

SCF
   Mixing 0.3
end

XC
   metaGGA scf force tpss
end

gradients
end

Lattice
   6.00  0.00  0.00
end

Atoms
   C  0.00  0.00  0.00
   O  2.20  0.00  0.00
end
```

```
BasisDefaults
   BasisType DZ
   Core Large
end

end input
eor
```

### 12.5.7 Example: Frequency run and transition state search

Download H2SlabFreqTS.run

First run: $H_2$ slab frequency calculation near minimum. Second run: transition state search, using as restart the results of the first run.

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title H2 slab frequency calculation near minimum
Comment
    Optimized for speed / Accuracy low
    Basis very small
    Demonstrates the frequencies runtype
End

KSpace 2

Accuracy 4

screening
  RMadel 9
end

Dependency Basis=1e-8

RunType
  Frequencies
End

GeoOpt
  RestartSCF true
End

SCF
  Mixing 0.2
End

Convergence
  Degenerate default
End

DIIS
  NCycleDamp 0
  DiMix 0.5
End

Units
```

```
  Length Angstrom
  Angle Radian
End

ATOMS
:: TS coords
:: 0.408818   -0.059284    0.374229
:: 0.305357    0.059284   -0.374229
:: Local minimum coords:
   H   -0.4  0   0.1
   H    0.4  0  -0.1
End

Lattice
   2.645886  0         0
   0         2.645886  0
End

AtomType H

DIRAC H
 1  0
 VALENCE
 1S 1
SubEnd

BasisFunctions
 1S   0.69

2P   1.25
SubEnd

FitFunctions
 1S   3.16
 1S   2.09
 1S   1.38
 2S   1.50
 2P   4.00
 2P   2.65
 2P   1.75
 3D   4.00
 3D   2.50
SubEnd

End

END INPUT
eor
mv RUNKF H2SlabFreq.runkf

rm Points
```

Here comes the second run where the Hessian (from the frequency run) is used to find the transtition state

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title H2 slab TS search
Comment
```

```
    Optimized for speed / Accuracy low
    Basis very small
    Demonstrates the GeoOpt block
End

KSpace 2

Accuracy 5.0

screening
  RMadel 9
end

Dependency Basis=1e-8

RunType
 TS
End

GeoOpt
  Iterations 50
  Converge Grad=1e-3
  RestartSCF true
  InitialHessian H2SlabFreq.runkf
End

SCF
  Mixing 0.2
End

Convergence
  Degenerate default
End

DIIS
  NCycleDamp 0
  DiMix 0.5
End

Units
  Length Angstrom
  Angle Radian
End

ATOMS
  H   -0.4  0  0.1
  H    0.4  0 -0.1
End

Lattice
  2.645886   0.000000   0.000000
  0.000000   2.645886   0.000000
End

AtomType H

DIRAC H
 1  0
```

```
 VALENCE
 1S 1
SubEnd

BasisFunctions
 1S   0.69
2P   1.25
SubEnd

FitFunctions
 1S   3.16
 1S   2.09
 1S   1.38
 2S   1.50
 2P   4.00
 2P   2.65
 2P   1.75
 3D   4.00
 3D   2.50
SubEnd

End

END INPUT
eor

mv RUNKF H2SlabTS.runkf

rm Points
```

## 12.6 Time dependent DFT

### 12.6.1 Example: Time-dependent DFT calculations for bulk silicon

`Download Silicon.run`

The time-dependent DFT functionality is an important functionality. It enables you to calculate frequency-dependent dielectric functions for 1-dimensional and 3-dimensional periodic systems. In the present example, a standard geometry for bulk Silicon is given. The `Accuracy` and `Kspace` variables can keep their normal values. The important part in this example is of course the `RESPONSE` block. It specifies that 7 frequencies should be treated, with an even spacing between 0.0 Hartree and 0.25 Hartree. In this example scalar ZORA relativistic effects are switched on with the `isz` line in the `RESPONSE` block.

```
$ADFBIN/band << eor
DefaultsConvention pre2014

TITLE Silicon

ACCURACY 5
KSPACE 2

DEPENDENCY BASIS 1e-10

UNITS
   LENGTH ANGSTROM
```

```
END

RESPONSE
   nfreq   7
   strtfr  0d0
   endfr   25d-2
   isz     1
END

DEFINE
   AAA=5.43
   HA=AAA/2
END

LATTICE
   0   HA  HA
   HA  0   HA
   HA  HA  0
END

ATOMS
   Si  0.0   0.0   0.0
   Si  HA/2  HA/2  HA/2
END

END INPUT
eor
```

For Silicon the real and imaginary parts of the dielectric function: epsilon(omega) = 1 + 4 Pi Chi(omega) are calculated.

In the output file, the results will look something like the fragment below. The output specifies for which frequency the dielectric function is determined, and then proceeds to print the values for the 3x3 tensors.

The real and imaginary parts are printed separately. At this frequency, the imaginary part is still zero. Because of the high symmetry of the system, the real part is a constant times the unit matrix except for numerical noise.

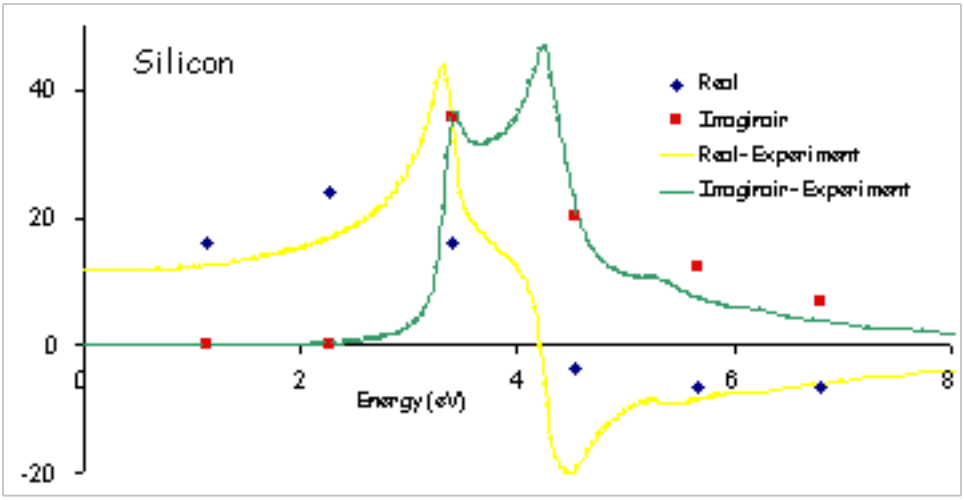
```
 Frequency    0.833333E-01 au    2.26756     eV
 Start the SCF procedure
* Real
 Chi_jj   X     -12.8363       0.142802E-18   0.547977E-17
 Chi_jj   Y     0.202883E-17   -12.8363       0.121052E-17
 Chi_jj   Z     0.124042E-16   0.215311E-17   -12.8363
* Imag
 Chi_jj   X     0.000000E+00   0.000000E+00   0.000000E+00
 Chi_jj   Y     0.000000E+00   0.000000E+00   0.000000E+00
 Chi_jj   Z     0.000000E+00   0.000000E+00   0.000000E+00
*
```

After each frequency has been treated, the results are summarized in a table, for each component separately. For the xx-component, this looks as in the table below. The frequency/energy is again printed in two different units, the Dielectric Function is printed in a.u. The values for Chi, which are trivially related to those printed here, are summarized in a separate table.

```
=============================================================
==          Frequency          ===       Dielectric Function     ==
==     a.u.    ==       e.V.    ===         Re    ==         Im     ==
============XX-dir=============================================
    0.416667E-01     1.13378          16.1119         0.000000E+00
    0.833333E-01     2.26756          23.7904         0.000000E+00
    0.125000         3.40134          15.8529          35.8574
```

```
    0.166667          4.53512         -3.49949          20.2221
    0.208333          5.66890         -6.60897          12.3661
    0.250000          6.80268         -6.42943          6.87957
============YY-dir================================================
    0.416667E-01      1.13378          16.1119         0.000000E+00
    0.833333E-01      2.26756          23.7904         0.000000E+00
    0.125000          3.40134          15.8529          35.8574
    0.166667          4.53512         -3.49949          20.2221
    0.208333          5.66890         -6.60897          12.3661
    0.250000          6.80268         -6.42943          6.87957
============ZZ-dir================================================
    0.416667E-01      1.13378          16.1119         0.000000E+00
    0.833333E-01      2.26756          23.7904         0.000000E+00
    0.125000          3.40134          15.8529          35.8574
    0.166667          4.53512         -3.49949          20.2221
    0.208333          5.66890         -6.60897          12.3661
    0.250000          6.80268         -6.42943          6.87957
```

Results of the test calculation (red/blue) are plotted in next Figure together with experimental data (yellow/green). The results for the seven specified frequencies are given. It should be obvious that more frequencies are needed (resulting in longer run times) to obtain a smooth curve in which peaks cannot be missed because of too coarse interpolation.




### 12.6.2 Example: Time-dependent DFT calculations for bulk helium

Download He_crystal.run

```
$ADFBIN/band << eor
DefaultsConvention pre2014

TITLE HELIUM CUBIC

ACCURACY 5
KSPACE 3

RESPONSE
   nfreq  10
   strtfr 0d0
   endfr  2d-1
   ebndtl 1d-2
```

```
END

DEFINE
   HA = 12
END

LATTICE
   HA    0    0
    0   HA    0
    0    0   HA
END

ATOMS
   He   0.0   0.0   0.0
END

BASISDEFAULTS
BASISTYPE V
END

END INPUT
eor
```

### 12.6.3 Example: Time-dependent DFT calculations for bulk diamond

Download Diamond.run

```
$ADFBIN/band << eor
DefaultsConvention pre2014

TITLE DIAMOND

ACCURACY 5
KSPACE 2

Dependency  Basis=1.e-6

UNITS
   LENGTH ANGSTROM
END

RESPONSE
   nfreq    7
   strtfr   0d0
   endfr    7d-1
END

DEFINE
   AAA=3.57
   HA=AAA/2
END

LATTICE
   0   HA  HA
   HA  0   HA
   HA  HA  0
END
```

```
ATOMS
   C  0.00  0.00  0.00
   C  HA/2  HA/2  HA/2
END

BasisDefaults
   BasisType DZ
End

END INPUT
eor
```

### 12.6.4 Example: Time-dependent DFT calculations for hydrogen chain

Download H_chain.run

The input for a one-dimensional system is no different from that for a three-dimensional system. No tests have been performed on two-dimensional systems yet in combination with the TDDFT code. It is therefore not expected to work. Besides the number of frequencies, and the beginning and end frequency of the frequency range, the RESPONSE block also contains stricter than default convergence criteria (cnvi and cnvj) for the fit coefficients describing the density change.

...

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title H2-chain

ACCURACY 5
KSPACE 3

DEPENDENCY BASIS 1e-10

RESPONSE
   nfreq  10
   strtfr 0d0
   endfr  15d-3
   cnvi   1d-5
   cnvj   1d-5
END

DEFINE
   HX = 4.5
END

LATTICE
   HX
END

ATOMS
   H    1.0  0.001 0.0
   H   -1.0 -0.001 0.0
END

END INPUT
eor
```

The output for this calculation will give rise to a table like the following one:

```
============================================================
==          Frequency          ===       Polarizability(xx)      ==
==     a.u.    ==       e.V.    ===         Re     ==         Im      ==
============================================================
   0.166667E-02   0.453512E-01    127.119         0.00000
   0.333333E-02   0.907023E-01    127.201         0.00000
   0.500000E-02   0.136054        127.338         0.00000
   0.666667E-02   0.181405        127.530         0.00000
   0.833333E-02   0.226756        127.778         0.00000
   0.100000E-01   0.272107        128.083         0.00000
   0.116667E-01   0.317458        128.446         0.00000
   0.133333E-01   0.362809        128.868         0.00000
   0.150000E-01   0.408161        129.351         0.00000
============================================================
==          Frequency          ===             Chi_JJ (xx)         ==
==     a.u.    ==       e.V.    ===         Re     ==         Im      ==
============================================================
    0.00000         0.00000       -2.74118         0.00000
   0.166667E-02   0.453512E-01   -2.74153         0.00000
   0.333333E-02   0.907023E-01   -2.74259         0.00000
   0.500000E-02   0.136054       -2.74436         0.00000
   0.666667E-02   0.181405       -2.74685         0.00000
   0.833333E-02   0.226756       -2.75005         0.00000
   0.100000E-01   0.272107       -2.75399         0.00000
   0.116667E-01   0.317458       -2.75866         0.00000
   0.133333E-01   0.362809       -2.76409         0.00000
   0.150000E-01   0.408161       -2.77028         0.00000
============================================================
```

### 12.6.5 Example: Time-dependent current DFT calculations for a metal

Download Cu_resp_NR_ALDA.run

This example shows how to calculate the dielectric function for a metal. The RESPONSE keyblock is as usual. In the manual it is explained that the KSPACE parameter should be chosen with care.

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title: response of Cu within ALDA

Comment
 Technical
   Hybrid k space integration (3D)
   Reasonable real space integration accuracy
   Definitions of variables
 Features
   Lattice   : 3D
   Unit cell : 1 atom
   Basis     : NO+STO w/ core (DZ/Cu.2p)
   Options   : ALDA
End

kspace  7
Accuracy 4.0
```

```
RESPONSE
   nfreq   2
   strtfr  0.10d0
   endfr   0.25d0
END

Units
   Length Angstrom
End

Define
   halflatt=3.61/2
End

Lattice :: FCC
   0        halflatt halflatt
   halflatt 0        halflatt
   halflatt halflatt 0
End

Atoms
   Cu  0.00  0.00  0.00
End

BasisDefaults
   BasisType DZ
   Core Large
End

END INPUT
eor
```

## 12.7 Spectroscopy

### 12.7.1 Example: Hyperfine A-tensor

Download TiF3a.run

Sample calculation for an ESR A-tensor calculation. The calculation should be spin unrestricted and have the ATENSOR keyword.

```
$ADFBIN/band << eor
DefaultsConvention 2014

Title TiF3

Units
   Length Angstrom
End

Define
   a = 25
   RTIF = 1.78
   RY = RTIF*SQRT(3)/2
End
```

```
Unrestricted

EFG
End

ATensor
End

Atoms
   Ti  0.0     0.0  0.0
   F   RTIF    0.0  0.0
   F  -RTIF/2  RY   0.0
   F  -RTIF/2 -RY   0.0
end

BasisDefaults
   BasisType TZP
   Core None
End

END INPUT
eor
```

### 12.7.2 Example: Zeeman g-tensor

Download TiF3g.run

Sample calculation for an ESR g-tensor calculation. This makes only sense for a relativistic spin orbit calculation.

```
$ADFBIN/band << eor
DefaultsConvention 2014

Title TiF3

Relativistic ZORA SPIN

esr
end

Units
   Length Angstrom
End

Define
   RTIF = 1.78
   RY  = RTIF*SQRT(3)/2
End

Atoms
   Ti  0.0  0.0     0.0
   F   0.0  RTIF    0.0
   F  -RY  -RTIF/2  0.0
   F   RY  -RTIF/2  0.0
end

BasisDefaults
   BasisType DZ
```

```
   Core None
End

END INPUT
eor
```

### 12.7.3 Example: NMR

`Download PE-NMR.run`

With the `NMR` keyblock you can specify for which atom you want the shielding tensor.

The NMR option is not implemented with the frozen core approximation, hence we set core to NONE.

```
$ADFBIN/band << eor
DefaultsConvention pre2014

TITLE PE

NMR
   nmratom=1
   ms0=1.
end

Units
   Length Angstrom
   Angle  Degree
end

XC
   GGA Always Becke Perdew
end

DEPENDENCY BASIS 1e-10

KSPACE 3
Accuracy 5

define
   aCCC = 112.777
   aHCH = 109.47
   alf2 = aCCC/2
   bet  = aHCH/2.
   rcc=1.533
   rch=1.09
   z3 = rch*cos(bet)
   y3 = rch*sin(bet)
   T = 2*rcc*sin(alf2)
   C2x =  rcc*sin(alf2)
   C2z = -rcc*cos(alf2)
end

Lattice
   T          0.        0.
end

Atoms C
   0.         0.        0.
```

```
   C2x        0.        C2z
end

Atoms H
   0.          y3       z3
   0.         -y3       z3
   C2x         y3       C2z-z3
   C2x        -y3       C2z-z3
end

BasisDefaults
   BasisType TZ2P
   Core NONE
End

end input
eor
```

### 12.7.4 Example: EFG

Download SnO_EFG.run

The calculation of the electric field gradient is invoked by the EFG keyblock.

Because Sn is quite an heavy atom we use the scalar relativistic option.

```
$ADFBIN/band << eor
DefaultsConvention 2014

Title SnO EFG

NumericalQuality Basic ! Only for speed

Relativistic ZORA

! useful for Moessbauer spectroscopy: density and coulomb pot. at nuclei
PropertiesAtNuclei
End

EFG
End

Units
   Length Angstrom
End

Coordinates Natural

Define
   aaa=3.8029
   ccc=4.8382
   vvv=0.2369
End

Lattice
   aaa  0.0  0.0
   0.0  aaa  0.0
   0.0  0.0  ccc
```

```
End

Atoms
   O   0.0  0.0  0.0
   O   0.5  0.5  0.0
   Sn  0.0  0.5  vvv
   Sn  0.5  0.0 -vvv
End

BasisDefaults
   BasisType DZ
   Core none
End

End input
eor
```

### 12.7.5 Example: Phonons

Download GraphenePhonons.run

A phonon calculation should be performed at the equilibrium geometry.

In the first calculation we optimize the geometry, including the lattice vectors. We also set the criteria a bit more strict.

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title Graphene geometry optimization

kspace 5

integration
  accint 5
end

Units
  length angstrom
end

ATOMS
  C   0.00 0.0000000000 0.00
  C   1.23 0.7101408312 0.00
END

Lattice
   2.46 0.000000000 0.00
   1.23 2.130422493 0.00
End

GeoOpt
  OptimizeLattice true
  Converge grad=1e-5
End

BasisDefaults
  BasisType DZ
end
```

```
end input
eor

mv RUNKF Graphene.runkf
```

In the second calculation we use the geometry from the optimization. Then we define a supercell and can do the phonon run. Note that `KSpace` can be chosen a bit lower, because we have now a bigger unit cell.

```
echo "Phonon calculation"

$ADFBIN/band << eor
DefaultsConvention pre2014

Title Graphene phonon calc

kspace 3

Restart
  File Graphene.runkf
  Geometry
End

integration
  accint 5
end

runtype
  phonons
end

phononConfig
  stepSize 0.0913
  superCell
    2 0
    0 2
  subend
end

Units
  length angstrom
end

ATOMS
  C   0.00 0.0000000000 0.00
  C   1.23 0.7101408312 0.00
END

Lattice
   2.46 0.000000000 0.00
   1.23 2.130422493 0.00
End

BasisDefaults
  BasisType DZ
end

end input
eor
```

## 12.8 Analysis

### 12.8.1 Example: CO absorption on a Cu slab: fragment option and densityplot

Download Frags_COCu.run

This example illustrates the usage of fragments in a BAND calculation for analysis purposes. It takes two runs to do the DOS analysis in a fragment basis, and an extra two runs to get the deformation density with respect to the fragment densities. The setup involves first the computation of the free CO overlayer, which is to be absorbed on a Cu surface. To suppress (most of the) interactions between the CO molecules, i.e. to effectively get the *molecular* CO, the KSpace parameter is set to 1 (= no dispersion), and the lattice parameters are set so large that the CO molecules are far apart. The standard result file RUNKF is saved under the name 'CO.runkf'.

```
# ---------------------------- CO molecule -------------------------

$ADFBIN/band << eor
DefaultsConvention pre2014

Title The CO fragment

Comment
 Technical
   Zero order k space integration
   Good real space integration accuracy
   Definitions of variables
 Features
   Lattice   : 2D, large lattice vectors
   Unit cell : 2 atoms, 1x1, quasi molecular
   Basis     : NO+STO w/ core
End

PRINT EIGENS

Kspace   1  ! neglect dispersion
Accuracy   4

Define
  bond=2.18
  far=25
End

Lattice     ! CO molecules far apart
  far  0.0
  0.0  far
End

Atoms
  C   0 0 0
  O   0 0 bond
End

BasisDefaults
BasisType DZ
Core Large
End

End Input
```

```
eor

mv RUNKF CO.runkf
```

Now we can use the result file to do a DOS analysis for CO on a copper surface treating the molecule as a fragment. With Fragment%Labels we assign names to the different symmetry orbitals. The Density-of-States analysis details are given with the keys DOS (energy grid, result file with DOS data) and, optionally, GrossPopulations and OverlapPopulations.

```
# ---------------------------- CO + Cu slab -------------------------

$ADFBIN/band << eor
DefaultsConvention pre2014

Title Cu slab with CO adsorbed

Comment
 Technical
   Quadratic K space integration (low)
   Good real space integration accuracy
   Definitions of variables
 Features
   Lattice   : 2D
   Unit cell : 3 atoms, 1x1
   Basis     : NO+STO w/ core
   Options   : Molecular fragment
               Analysis: DOS, PDOS, COOP
End

KSpace 3
Accuracy 4

! fragment specification

Fragment CO.runkf
  1 1
  2 2
Labels ! let us give them some labels
  2Sigma
  2Sigma*
  1Pi_x
  1Pi_y
  3Sigma
  1Pi_x*
  1Pi_y*
  3Sigma*
SubEnd
End

! use fragment basis in dos
DosBas
Fragment 1
End

DOS   ! Analysis
  File  pdos.CO_Cu
  Energies 500
  Min -0.750
```

```
  Max 0.300
End

GrossPopulations
  3 2    ! All metal d states
  Sum     ! ALl metal sp states
    3 0
    3 1
  EndSum

  Frag 1   ! All CO states
  Sum   ! CO 1pi
    FragFun 1 5
    FragFun 1 6
  EndSum
  FragFun 1 7  ! CO 5-sigma
End

OverlapPopulations
  Left   ! Metal d with CO
    3 2
  Right
    Frag 1
End

Define
  dist=3.44
  bond=2.18
End

Lattice
  4.822 0.0
  0.0   4.822
End

Atoms
  C   0 0 dist
  O   0 0 dist+bond
  Cu  0.0   0.0   0.0
End

BasisDefaults
BasisType DZ
Core Large
End

End Input
eor
```

After this run we copy the computed DOS data from the DOS result file to standard output. We also save the restart file for later use.

```
echo Contents of DOS file
cat pdos.CO_Cu

mv RUNKF COCu.runkf
```

Next we want to know the deformation density with respect to the two fragments: 1) The CO molecule and 2) the bare Cu surface. We haven't done the bare Cu surface yet, so that is what happens next.

```
# ---------------------------- Cu slab --------------------------

$ADFBIN/band << eor
DefaultsConvention pre2014

Title Cu slab

Comment
 Technical
   Quadratic K space integration (low)
   Good real space integration accuracy
   Definitions of variables
 Features
   Lattice   : 2D
   Unit cell : 3 atoms, 1x1
   Basis     : NO+STO w/ core
   Options   :
End

Kspace 3
Accuracy 4

Define
  dist=3.44
  bond=2.18
End

Lattice
  4.822 0.0
  0.0   4.822
End

Atoms
  Cu  0.0   0.0   0.0
End

BasisDefaults
BasisType DZ
Core Large
End

End Input
eor

mv RUNKF Cu.runkf
```

Now we are all set to do our final calculation. We have the two fragment files CO.runkf and Cu.runkf, and the restart file COCu.runkf. Next we want to know the deformation density with respect to the two fragments: 1) The CO molecule and 2) the bare Cu surface. The visualization options like OrbitalPlot and Densityplot require a regular set of points (a grid). Here is how it works

```
# ---------------------------- CO + Cu slab restart --------------------------

$ADFBIN/band -n 1 << eor
DefaultsConvention pre2014

Title Cu slab with CO adsorbed (restart density plot)
```

```
Kspace 3
Accuracy 4

Restart
  File COCu.runkf
  DensityPlot
End

Grid
  Type Coarse
End

DensityPlot
  rho(deformation/fit)
End

! fragment specification

Fragment CO.runkf
  1 1
  2 2
End

Fragment Cu.runkf
  1 3
End

Define
  dist=3.44
  bond=2.18
End

Lattice
  4.822 0.0
  0.0   4.822
End

Atoms
  C   0 0 dist
  O   0 0 dist+bond
  Cu  0.0   0.0   0.0
End

BasisDefaults
BasisType DZ
Core Large
End

End Input
eor
```

This particular restart options does not work in parallel, hence the "-n 1" on the first line.The result of the last run is a file named TAPE41. Normally you would save that to COCu.t41

```
mv TAPE41 COCu.t41
```

and view it with adfview. On the TAPE41 file are now three fields shown in adfview as

- FITDENSITY_deformation_scf

- FITDENSITY_deformation_scf_frag1
- FITDENSITY_deformation_scf_frag2

being the deformation density of CO+Cu with respect to the atoms, and the same for the two fragments CO and the Cu slab. In adfview you can add the fields of the two fragments, and then create another field that holds the difference.

### 12.8.2 Example: CO absorption on a MgO slab: fragment option and PEDA

`Download PEDA_MgO+CO.run`

This example shall illustrate the use of the `Fragment` keywords in combination with the `PEDA` keyword to perform the PEDA. For this example two fragment calculations are necessary to calculate the unperturbed eigensystems of the MgO slab and CO fragment.

#### Fragment calculations

```
# ---------------------------- MgO slab --------------------------

$ADFBIN/band << eor
Title MgO surface

KSpace
  Grid 3 3
End

BeckeGrid
   quality basic
End

XC
   GGA PBE
End

Units
   length angstrom
end

Atoms
   Mg  0.00000000       0.00000000       0.00000000
   Mg  1.50260191      -1.50260191      -2.12400000
   Mg  0.00000000       0.00000000      -4.24800000
   Mg  3.00520382       0.00000000       0.00000000
   Mg  1.50260191       1.50260191      -2.12400000
   Mg  3.00520382       0.00000000      -4.24800000
   O   1.50260191      -1.50260191       0.00200000
   O   0.00000000       0.00000000      -2.12400000
   O   1.50260191      -1.50260191      -4.25000000
   O   1.50260191       1.50260191       0.00200000
   O   3.00520382       0.00000000      -2.12400000
   O   1.50260191       1.50260191      -4.25000000
End

Lattice
       3.00520382      -3.00520382       0.00000000
       3.00520382       3.00520382       0.00000000
End
```

```
BasisDefaults
   BasisType TZP
   Core small
End

END INPUT
eor

mv RUNKF MgO.runkf
```

```
# ---------------------------- CO fragment ------------------------

$ADFBIN/band << eor
Title CO molecule

KSpace
  Grid 3 3
End

BeckeGrid
  quality basic
End

XC
  GGA PBE
End

Units
   length angstrom
end

Atoms
   C   0.00000000       0.00000000       2.61000000
   O   0.00000000       0.00000000       3.73700000
End

Lattice
       3.00520382      -3.00520382       0.00000000
       3.00520382       3.00520382       0.00000000
End

BasisDefaults
   BasisType TZP
   Core small
End

END INPUT
eor

mv RUNKF CO.runkf
```

### PEDA calculation

The two result files, MgO.runkf and CO.runkf, can now be used to perform the PEDA. Here, the mapping of the atoms of the PEDA calculation and the fragment calculations is necessary. And the used grid points in reciprocal space have to be identical in all three calculations.

```
# ----------------------------- PEDA calculation ------------------------

$ADFBIN/band << eor
Title PEDA

KSpace
   Grid 3 3
End

BeckeGrid
   quality basic
End

XC
   GGA PBE
End

fragment MgO.runkf
   1  1
   2  2
   3  3
   4  4
   5  5
   6  6
   7  7
   8  8
   9  9
   10 10
   11 11
   12 12
end

fragment CO.runkf
   2 13
   1 14
end

PEDA

units
   length angstrom
end

Atoms
   Mg  0.00000000       0.00000000       0.00000000
   Mg  1.50260191      -1.50260191      -2.12400000
   Mg  0.00000000       0.00000000      -4.24800000
   Mg  3.00520382       0.00000000       0.00000000
   Mg  1.50260191       1.50260191      -2.12400000
   Mg  3.00520382       0.00000000      -4.24800000
   O   1.50260191      -1.50260191       0.00200000
   O   0.00000000       0.00000000      -2.12400000
   O   1.50260191      -1.50260191      -4.25000000
   O   1.50260191       1.50260191       0.00200000
   O   3.00520382       0.00000000      -2.12400000
   O   1.50260191       1.50260191      -4.25000000
   O   0.00000000       0.00000000       3.73700000
   C   0.00000000       0.00000000       2.61000000
```

```
End

Lattice
       3.00520382      -3.00520382       0.00000000
       3.00520382       3.00520382       0.00000000
End

BasisDefaults
   BasisType TZP
   Core small
End

END INPUT
eor
```

In the output file the results can be found in the PEDA block after the Energy Analysis.

### 12.8.3 Example: CO absorption on a MgO slab: fragment option, PEDA and PEDANOCV

Download PEDANOCV_MgO+CO.run

This example shall illustrate the use of the `Fragment` keywords in combination with the `PEDA` and `PEDANOCV` keywords to perform the PEDANOCV calculation. For this example two fragment calculations are necessary to calculate the unperturbed eigensystems of the MgO slab and CO fragment. Here, the sampling of the reciprocal space is restricted to $\Gamma$ point.

#### Fragment calculations

```
!----------------------------- MgO slab ------------------------

$ADFBIN/band << eor
Title MgO fragment

KSpace
   Grid 1 1
end

BeckeGrid
   quality basic
End

relativistic zora

XC
   GGA PBE
End

Units
   length angstrom
end

Atoms
   Mg  0.00000000       0.00000000       0.00000000
   Mg  1.50260191      -1.50260191      -2.12400000
   Mg  0.00000000       0.00000000      -4.24800000
```

```
   Mg  3.00520382       0.00000000       0.00000000
   Mg  1.50260191       1.50260191      -2.12400000
   Mg  3.00520382       0.00000000      -4.24800000
   O   1.50260191      -1.50260191       0.00200000
   O   0.00000000       0.00000000      -2.12400000
   O   1.50260191      -1.50260191      -4.25000000
   O   1.50260191       1.50260191       0.00200000
   O   3.00520382       0.00000000      -2.12400000
   O   1.50260191       1.50260191      -4.25000000
End

Lattice
       3.00520382      -3.00520382       0.00000000
       3.00520382       3.00520382       0.00000000
End

BasisDefaults
   BasisType TZP
   Core none
End

END INPUT
eor

mv RUNKF MgO.runkf
```

```
!------------------------------ CO fragment ------------------------

$ADFBIN/band << eor
Title CO fragment

KSpace
   Grid 1 1
End

BeckeGrid
   quality basic
End

relativistic zora

XC
   GGA PBE
End

Units
   length angstrom
end

Atoms
   C   0.00000000       0.00000000       2.61000000
   O   0.00000000       0.00000000       3.73700000
End

Lattice
       3.00520382      -3.00520382       0.00000000
       3.00520382       3.00520382       0.00000000
End
```

```
BasisDefaults
   BasisType TZP
   Core none
End

END INPUT
eor

mv RUNKF CO.runkf
```

### PEDANOCV calculation

The two result files, MgO.runkf and CO.runkf, can now be used to perform the PEDANOCV. Here, the mapping of the atoms of the PEDA calculation and the fragment calculations is necessary. And the used grid points in reciprocal space have to be identical in all three calculations.

```
!------------------------------ PEDANOCV calculation ------------------------

$ADFBIN/band << eor
Title H-H chain

KSpace
   Grid 1 1
End

BeckeGrid
   quality basic
End

relativistic zora

XC
   GGA PBE
End

fragment MgO.runkf
   1  1
   2  2
   3  3
   4  4
   5  5
   6  6
   7  7
   8  8
   9  9
   10 10
   11 11
   12 12
end

fragment CO.runkf
   2  13
   1  14
end

PEDA
```

```
PEDANOCV
  EigvalThresh 0.001
End

units
  length angstrom
end

Atoms
   Mg  0.00000000       0.00000000       0.00000000
   Mg  1.50260191      -1.50260191      -2.12400000
   Mg  0.00000000       0.00000000      -4.24800000
   Mg  3.00520382       0.00000000       0.00000000
   Mg  1.50260191       1.50260191      -2.12400000
   Mg  3.00520382       0.00000000      -4.24800000
   O   1.50260191      -1.50260191       0.00200000
   O   0.00000000       0.00000000      -2.12400000
   O   1.50260191      -1.50260191      -4.25000000
   O   1.50260191       1.50260191       0.00200000
   O   3.00520382       0.00000000      -2.12400000
   O   1.50260191       1.50260191      -4.25000000
   O   0.00000000       0.00000000       3.73700000 ! BAND will automatically block
   C   0.00000000       0.00000000       2.61000000 ! atoms of same type together!!!!!!
End

Lattice
       3.00520382      -3.00520382       0.00000000
       3.00520382       3.00520382       0.00000000
End

BasisDefaults
   BasisType TZP
   Core none
End

END INPUT
eor

mv RUNKF decomp.runkf
```

In the output file the results can be found in the PEDANOCV block after the Energy Analysis and PEDA block.

The NOCV orbitals and NOCV deformation densities can be visualized using adfview or by a restart calculation. In the latter case, one adds the `Restart` block key with the options `File decomp.runkf` and the `NOCVdRhoPlot` and `NOCVOrbsPlot` keys. These will trigger the calculation of the plot properties. To specifiy which NOCV deformation densities and NOCV orbitals are plotted, one adds the `NOCVdRhoPlot` and `NOCVOrbsPlot` block key. In both blocks the line `1 Band 1 5` means, that for k-point 1 the densities/orbitals 1 to 5 are calculated.

```
$ADFBIN/band << eor
Title Restart Calculation

Restart
   File decomp.runkf
   NOCVdRhoPlot
   NOCVOrbsPlot
End

NOCVdRhoPlot
```

```
   1 Band 1 5
End

NOCVOrbsPlot
   1 Band 1 5
End

Grid
   Type coarse
End

KSpace
   Grid 1 1
End

BeckeGrid
   quality basic
End

relativistic zora

XC
   GGA PBE
End

units
   length angstrom
end

Atoms
   Mg  0.00000000       0.00000000       0.00000000
   Mg  1.50260191      -1.50260191      -2.12400000
   Mg  0.00000000       0.00000000      -4.24800000
   Mg  3.00520382       0.00000000       0.00000000
   Mg  1.50260191       1.50260191      -2.12400000
   Mg  3.00520382       0.00000000      -4.24800000
   O   1.50260191      -1.50260191       0.00200000
   O   0.00000000       0.00000000      -2.12400000
   O   1.50260191      -1.50260191      -4.25000000
   O   1.50260191       1.50260191       0.00200000
   O   3.00520382       0.00000000      -2.12400000
   O   1.50260191       1.50260191      -4.25000000
   O   0.00000000       0.00000000       3.73700000
   C   0.00000000       0.00000000       2.61000000
End

Lattice
       3.00520382      -3.00520382       0.00000000
       3.00520382       3.00520382       0.00000000
End

BasisDefaults
   BasisType TZP
   Core none
End

debug BlockPropertyModule
```

```
END INPUT
eor
```

The important output of this calculation is the TAPE41 file. Renaming it to foobar.t41 will allow adfview to read and interpret the data stored on this file.

### 12.8.4 Example: Cu_slab: 2-dim. Finite temperature and orbital plot

Download Cu_slab.run

A two-dimensional infinite (periodic boundary conditions) slab calculation is performed for Cu. The dimensionality is simply defined by the number of records in the Lattice data block. In a 2-dimensional calculation the lattice vectors are put in the xy-plane. (In a one-dimensional calculation (polymer), the lattice vector is taken along the x-axis in the program.)

Slab calculations for metals frequently suffer from SCF convergence problems, as a result of the open valence band(s). To help the program converge it is often useful or even necessary to use some special features, such as the ElectronicTemperature key. This particular key requires a numerical value (0.025 in the example) and implies that a finite-temperature electronic distribution is used, rather than a sharp cut-off at the Fermi level. The numerical value is the applied energy width, in hartree units.

The so-modified electronic distribution also affects the energy. The 'true' zero-T energy is computed, approximately, by an interpolation formula. The interpolation is not very accurate and one should try to use as small as possible values for the ElectronicTemperature key so as to avoid increasing uncertainty in the results. The program prints, in the energy section of the output file, the finite-T correction term that has been applied through the interpolation formula. This gives at least an indication of any remaining uncorrected deviation of the outcome from a true zero-T calculation.

In the second run the runkf file of the first run is used to do an orbital plot restart. Normally you would rename the resulting TAPE41 to "myslab.t41" and watch the orbitals with adfview.

```
# ---------------------------- first run -------------------------

$ADFBIN/band << eor
Title Cu slab

Comment
 Technical
   Quadratic K space integration
   Good real space integration accuracy
 Features
   Lattice   : 2D
   Unit cell : 1 atom, 1x1
   Basis     : NO+STO w/ core
   Options   : ElectronicTemperature (temperature effect)
End

Kspace 5
Accuracy 4

Convergence
   ElectronicTemperature  0.025
End

Lattice
   4.822 0.0
   0.0   4.822
End
```

```
Atoms
   Cu  0.0   0.0   0.0
End

BasisDefaults
   BasisType DZ
End

EndInput
eor

mv RUNKF CuSlab.runkf
rm Points

# ----------------------------- orbital plot --------------------------
export NSCM=1

$ADFBIN/band -n 1 << eor
Title Cu slab orbital plot

Comment
 Technical
   Quadratic K space integration
   Good real space integration accuracy
 Features
   Lattice   : 2D
   Unit cell : 1 atom, 1x1
   Basis     : NO+STO w/ core
   Options   : ElectronicTemperature (temperature effect)
End

Kspace 5
Accuracy 4

Restart
   File CuSlab.runkf
   OrbitalPlot
End

Grid
   Type Coarse
End

OrbitalPlot
   1 Band 2 4 ! k-point 1, bands 2 to 4
   3  -0.1 0.1 ! k-point 3 orbitals within 0.1 Hartree from Fermi Level
End

Convergence
   ElectronicTemperature  0.025
End

Lattice
   4.822  0.000
   0.000  4.822
End

Atoms
```

```
   Cu  0.0   0.0   0.0
End

BasisDefaults
   BasisType DZ
End

EndInput
eor

echo "Begin TOC of tape41"

$ADFBIN/dmpkf -n 1 TAPE41 --toc

echo "End TOC of tape41"
```

### 12.8.5 Example: Bader analysis

Download Li2O_Bader.run

To get the Atoms In Molecules (or Bader) analysis use the GridBasedAIM block key.

The grid-based AIM method is very fast, but a bit inaccurate. Therefore we force extra integration points.

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title Li2O bulk (fluorite structure)

KSpace 3

accuracy 4

Integration
   accsph 6
   accpyr 6
end

GridBasedAIM
End

Dependency basis=1e-9 fit=1e-8

tails bas=0 core=0 fit=0

DIIS
   dimix 0.2
   ncycledamp 0
end

scf
   mixing 0.4
end

xc
   gga scf bp86
end
```

```
define
   ha=8.73/2
   qa=8.73/4
end

Lattice
   0  ha ha
   ha 0  ha
   ha ha 0
end

Atoms
   O   0.0   0.0  0.0
   Li  qa    qa   qa
   Li  3*qa  qa   qa
end

BasisDefaults
   BasisType TZ2P
   Core small
end

end input
eor
```

### 12.8.6 Example: Properties at nuclei

Download PropertiesAtNuclei.run

One can obtain the values of some properties near the nucleus. The average is taken over a tiny sphere.

```
$ADFBIN/band << EOF
DefaultsConvention pre2014

Title O2

PropertiesAtNuclei
   vxc[rho(fit)]
   rho(fit)
   rho(scf)
   v(coulomb/scf)
   rho(deformation/fit)
   rho(deformation/scf)
End

unrestricted

Accuracy 6

UNITS
   length Angstrom
   angle Degree
END

Atoms
   O   0.000  0.000  0.000
   O   0.000  0.000  1.208
```

```
end

BasisDefaults
   BasisType DZ
   Core None
End

XC
   gga always pbe
END

end input
EOF
```

### 12.8.7 Example: Band structure plot

Download Li_BZPlot.run

First run: automatic generation of band structure data on the result file (to be viewed with the GUI). We use a little bit of interpolation for smoother curve.

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title Li Bulk

kspace 5

units
   length angstrom
end

ATOMS
    Li 0.0 0.0 0.0
END

BZStruct
   Interpol 1
   Enabled true
   Automatic true
end

Lattice
   -1.745  1.745  1.745
    1.745 -1.745  1.745
    1.745  1.745 -1.745
End

SCF
   Mixing 0.3
end

diis
   dimix 0.3
   ncycledamp 0
end
```

```
BasisDefaults
   BasisType DZ
   Core Large
end

end input
eor
```

Second run: specifying the path through the BZ zone by hand. We set automatic to false and then specify the path with the `BZPath` keyblock, using one or more path subkeys. This run will actually produce exactly the same path as the automatic one.

```
$ADFBIN/band << eor
DefaultsConvention pre2014

Title Li Bulk

kspace 5

units
   length angstrom
end

ATOMS
   Li 0.0 0.0 0.0
END

BZStruct
   Enabled true
   Automatic false
end

bzpath
   kmesh 2
   path
      0.25  0.25  0.25
      0.00  0.00  0.50
      0.00  0.00  0.00
      0.50 -0.50  0.50
      0.25  0.25  0.25
      0.00  0.00  0.00
   subend
   path
      0.00  0.00  0.50
      0.50 -0.50  0.50
   subend
end

Lattice
   -1.745  1.745  1.745
    1.745 -1.745  1.745
    1.745  1.745 -1.745
End

SCF
   Mixing 0.3
end
```

```
diis
   dimix 0.3
   ncycledamp 0
end

BasisDefaults
   BasisType DZ
   Core Large
end

end input
eor
```

### 12.8.8 Example: Effective Mass (electron mobility)

`Download EffectiveMass.run`

An effective mass calculation is about the curvature of band at the top of the valence band and the bottom of the conduction band. This is obtained by numerical differentiation.

It can be done for systems with 1D, 2D, or 3D translational symmetry.

The easiest way to use this feature is to specify an empty `EffectiveMass` key-block (so leave out the `NumAbove`, `NumBelow`, and `UniqueKPoints`).

Example 1D:

```
"$ADFBIN/band"  << eor
DefaultsConvention 2014

TITLE 1D Al Chain

EffectiveMass
   StepSize 0.001
   NumAbove 4
   NumBelow 2
   UniqueKPoints 1 2 3
End

UNITS
   length Angstrom
   angle Degree
END

ATOMS
   Al  0.0 0.0 0.0
END

Lattice
   2.12440502 -0.000000 0.0
End

BasisDefaults
   BasisType DZ
   Core Large
End

XC
```

```
   LDA SCF VWN
END

end input
eor

rm -f RUNKF
```

Example 2D:

```
"$ADFBIN/band"  << eor
DefaultsConvention 2014

TITLE MoS2Slab

relativistic zora

EffectiveMass
End

UNITS
   length Angstrom
   angle Degree
END

Atoms Mo
   Mo     -1.626960686     0.313108730     0.000000000
   S       0.000000000     1.252434919     1.547040825
   S       0.000000000     1.252434919    -1.547040825
End

Lattice
           1.626960686    -2.817978569     0.000000000
           1.626960686     2.817978569     0.000000000
End

BasisDefaults
   BasisType DZ
   Core Large
End

end input
eor

rm -f RUNKF
```

Example 3D:

```
"$ADFBIN/band"  << eor

DefaultsConvention 2014

NumericalQuality Basic

KSpace
   Quality Normal
End

TITLE ZnO
```

```
Tails bas=1e-8

EffectiveMass
   NumAbove 2
   NumBelow 2
End

UNITS
    length Angstrom
    angle Degree
END

ATOMS
   Zn  1.625 0.9381941876 0.0
   Zn  1.625 -0.9381941878 2.615
   O   1.625 0.9381941876 1.96125
   O   1.625 -0.9381941878 4.57625
END

Lattice
   1.625 -2.814582562 0.000000
   1.625 2.814582562 0.000000
   0.000000 0.000000 5.23
End

BasisDefaults
   BasisType DZ
   Core Large
End

end input
eor
```

### 12.8.9 Example: Generating an Excited State with and Electron Hole

Download Si_ElectronHole.run

There is the possibility define the excitation of an electron from a low lying, localized band to a virtual band. The *ElectronHole* (page 72) key does allow the specification of the original band and the spin of the electron. The *EnforcedSpinPolarization* (page 72) key allows to restrict the spin polarization of the whole system.

```
"$ADFBIN/band" <<eor
TITLE Untitled

UNITS
    length Angstrom
    angle Degree
END

ATOMS Si
    -0.67875 -0.67875 -0.67875
    File $ADFRESOURCES/band/DZP/Si.2p
END

ATOMS Si
    0.67875 0.67875 0.67875
    File $ADFRESOURCES/band/DZP/Si
```

```
END

Lattice
    0.000  2.715  2.715
    2.715  0.000  2.715
    2.715  2.715  0.000
End

BasisDefaults
    BasisType DZP
    Core Large
End

XC
    LDA SCF VWN
END

UNRESTRICTED

ElectronHole
    BandIndex 1
    SpinIndex 1
End

EnforcedSpinPolarization 0

end input
eor
```

## 12.9 List of Examples

- *LiMetaGGA* (page 87)
- *Li_BZPlot* (page 152)
- *NaCl* (page 107)
- *NiO_Hubbard* (page 97)
- *PE-NMR* (page 131)
- *Peptide_NumericalQuality* (page 100)
- *PropertiesAtNuclei* (page 151)
- *Pt_slab* (page 87)
- *RestartSCF* (page 103)
- *Silicon* (page 123)
- *Si_ElectronHole* (page 156)
- *SnO_EFG* (page 132)
- *TiF3a* (page 129)
- *TiF3g* (page 130)
- *ZnS_ModelPotential* (page 98)

CHAPTER

# THIRTEEN

# REQUIRED CITATIONS

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

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

## 13.1 General References

For calculations with the periodic structures BAND program, version 2016:

1. G. te Velde and E.J. Baerends, *Precise density-functional method for periodic structures*, Physical Review B 44, 7888 (1991) (http://link.aps.org/doi/10.1103/PhysRevB.44.7888)
2. G. Wiesenekker and E.J. Baerends, *Quadratic integration over the three-dimensional Brillouin zone*, Journal of Physics: Condensed Matter 3, 6721 (1991) (http://www.iop.org/EJ/abstract/0953-8984/3/35/005)
3. M. Franchini, P.H.T. Philipsen, L. Visscher, *The Becke Fuzzy Cells Integration Scheme in the Amsterdam Density Functional Program Suite*, Journal of Computational Chemistry 34, 1818 (2013) (http://dx.doi.org/10.1002/jcc.23323).
4. M. Franchini, P.H.T. Philipsen, E. van Lenthe, L. Visscher, *Accurate Coulomb Potentials for Periodic and Molecular Systems through Density Fitting*, Journal of Chemical Theory and Computation 10, 1994 (2014) (http://dx.doi.org/10.1021/ct500172n).
5. BAND2016, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com Optionally, you may add the following list of authors and contributors: P.H.T. Philipsen, G. te Velde, E.J. Baerends, J.A. Berger, P.L. de Boeij, M. Franchini, J.A. Groeneveld, E.S. Kadantsev, R. Klooster, F. Kootstra, P. Romaniello, D.G. Skachkov, J.G. Snijders, C.J.O. Verzijl, G. Wiesenekker, T. Ziegler

**Note:** if you have used a modified (by yourself, for instance) version of the code, you should mention in the citation that a modified version has been used.

## 13.2 Feature References

**Lead** See key references above, for all work with BAND

**Suggested** G. Wiesenekker, G. te Velde and E.J. Baerends, *Analytic quadratic integration over the two-dimensional Brillouin zone*, Journal of Physics C: Solid State Physics 21, 4263 (1988) (http://www.iop.org/EJ/abstract/0022-3719/21/23/012)

### 13.2.1 Geometry optimization

**Lead** E.S. Kadantsev, R. Klooster. P.L. de Boeij and T. Ziegler, *The Formulation and Implementation of Analytic Energy Gradients for Periodic Density Functional Calculations with STO/NAO Bloch Basis Set*, Molecular Physics 105, 2583 (2007) (http://www.informaworld.com/smpp/content~content=a785133384~db=all~order=page)

### 13.2.2 TDDFT

**Lead** F. Kootstra, P.L. de Boeij and J.G. Snijders, *Efficient real-space approach to time-dependent density functional theory for the dielectric response of nonmetallic crystals*, Journal of Chemical Physics 112, 6517 (2000) (http://link.aip.org/link/?JCPSA6/112/6517/1)

P. Romaniello and P.L. de Boeij, *Time-dependent current-density-functional theory for the metallic response of solids*, Physical Review B 71, 155108 (2005) (http://link.aps.org/doi/10.1103/PhysRevB.71.155108)

**Main applications** F. Kootstra, P.L. de Boeij, and J.G. Snijders, *Application of time-dependent density-functional theory to the dielectric function of various nonmetallic crystals*, Physical Review B 62, 7071 (2000) (http://link.aps.org/doi/10.1103/PhysRevB.62.7071)

P. Romaniello, P.L. de Boeij, F. Carbone, and D. van der Marel, *Optical properties of bcc transition metals in the range 0.40 eV*, Physical Review B 73, 075115 (2006) (http://link.aps.org/doi/10.1103/PhysRevB.73.075115)

**Suggested book references** F. Kootstra, Ph.D. thesis (http://www.scm.com/Doc/ft439.pdf), Rijksuniversiteit Groningen, Groningen (2001).

P. Romaniello, Ph.D. thesis (http://www.scm.com/Doc/Thesis_Pina.pdf), Rijksuniversiteit Groningen, Groningen (2006).

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### 13.2.3 Relativistic TDDFT

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### 13.2.4 Vignale Kohn

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### 13.2.5 NMR

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### 13.2.6 ESR

**A-tensor: Nuclear magnetic dipole hyperfine interaction** E.S. Kadantsev and T. Ziegler, *Implementation of a Density Functional Theory-Based Method for the Calculation of the Hyperfine A-tensor in Periodic Systems with the Use of Numerical and Slater Type Atomic Orbitals: Application to Paramagnetic Defects*, Journal of Physical Chemistry A 112, 4521 (2008) (http://pubs.acs.org/doi/abs/10.1021/jp800494m)

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## 13.3 External programs and Libraries

Click here for the list of programs and/or libraries used in the ADF package. On some platforms optimized libraries have been used and/or vendor specific MPI implementations.

CHAPTER

# FOURTEEN

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CHAPTER

# FIFTEEN

# KEYWORDS

## Q



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