



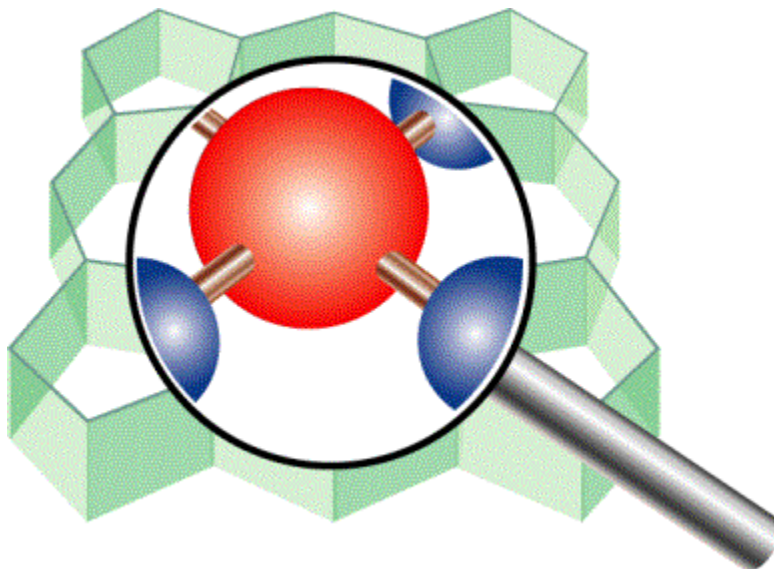
Scientific Computing & Modelling

# Examples BAND

**ADF Program System  
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# General notes on the Examples

The ADF package contains a series of sample runs. 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 ADF and 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 a UNIX type OS is used and a hierarchical structure of *directories* is assumed.

All sample files are stored in subdirectories under \$ADFHOME/examples/, where \$ADFHOME is the main directory of the ADF package. There are two main subdirectories in examples/: *adf/* for calculations with the molecular code ADF (and related utility programs) and *band/* for calculations with the periodic structures code BAND. Each sample run has its own directory (under *adf/* or *band/* respectively). For instance, \$ADFHOME/examples/band/NaCl/ contains an 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 Guides (ADF and BAND) 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.

# Model Hamiltonians

## NiCu surface alloy with GGA xc potential

Sample directory: band/NiCu\_XC/

This is an important example featuring many important keywords.

The line:  
Skip DOS

reduces the length of the output considerably.

A spin-unrestricted calculation can be done by using the keyword  
Unrestricted

The Becke Perdew generalized gradient approximation (GGA) for the exchange-correlation functional is invoked through the XC block:

```
| XC  
| GGA Always Becke Perdew  
| End
```

The subkey ALWAYS indicates that the Becke-Perdew xc potential should be used during the SCF. If this is not specified, the GGA energy will be calculated post-SCF using the LDA density.

```
| $ADFBIN/band << eor  
| Title Surface alloy: Cu slab with one surface Cu replaced by Ni (1:1)  
  
| Comment  
| Technical  
| Low quadratic K space integration  
| Reasonable real space integration accuracy  
| Features  
| Lattice : 2D  
| Unit cell : 4 atoms, sqrt(2) x sqrt(2), 2 layers  
| Basis : NO+STO w/ core  
| Options : XC functional in SCF  
| End  
  
| Skip DOS  
  
| Convergence  
| Degenerate default  
| End  
  
| DIIS  
| NCycleDamp 15  
| DiMix 0.25  
| End  
  
| SCF
```

```

Mixing 0.10
End

Accuracy 3.5
Kspace 3

Unrestricted

XC
  GGA Always Becke Perdew
End

Units
  Length Angstrom
End

Define
  latt=3.61 ! FCC lattice parameter
  halflatt=latt/2
End

Lattice
  latt 0 0
  0 latt 0
End

Atoms Ni
  0 0 0
End

Atoms Cu
  :: layer 1
  halflatt halflatt 0
  :: layer 2
  0 halflatt -halflatt
  halflatt 0 -halflatt
End

...
EndInput
eor

```

## MetaGGA functionals

*Sample directory:* band/LiMetaGGA/

Example for a post SCF metaGGA calculation.

```

$ADFBIN/band << eor
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
end

BasisDefaults
BasisType DZ
Core Large
end

end input
eor

```

## Relativistic effects: Platinum slab

Sample directory: `band/Pt_slab/`

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
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  
0 0 0 :: layer 1  
-ysh 0.0 -dlay :: layer 2  
ysh 0.0 -2.0*dlay :: layer 3  
End  
  
...  
  
END INPUT  
eor
```

# Precision and performance

## Convenient way to specify a basis set

*Sample directory:* band/BasisDefaults/

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
Title CO + H2: fine tuning the basis defaults

KSpace 1

Accuracy 4

Define
far=20
End

Lattice
far
End

! So we have cheap defaults
BasisDefaults
BasisType DZ
Core Large
End

Atoms C ! This C has no frozen core
0
Core None
End

Atoms O ! This O with a larger basis
0 2.13
BasisType TZ2P
End

Atoms H ! This one also with a larger basis
4 0
BasisType V
End

Atoms H ! Let us use the default settings for this atom
4 1.43
End
```

```
END INPUT  
eor
```

## Confinement and tails options for copper dimer

Sample directory: band/Cu2\_Confine/

This example illustrates two keywords to speed up BAND calculations and reduce the required disk space to some extent, without significant loss of accuracy.

The TAILS keyword implies that cutoffs will be applied to the (basis) functions. Basis functions will be assumed to be zero outside the radius where the remaining relative norm of the function is smaller than 0.00001, in this example. The shape of the function is slightly modified, in a 'soft' way, beyond the radius where the relative norm of the function outside the radius is 0.01. The Coulomb option is always recommended in this line as it gives more accurate results for core functions.

The CONFINEMENT option can be specified for each atom type separately. It is based on a soft cut-off related to a distance criterion. In this sense it is quite different from the tails option. The CONFINEMENT option can be useful in itself, for avoiding near linear dependency in the basis. However, its use in making BAND calculations more efficient is primarily in combination with the tails option.

```
$ADFBIN/band << eor  
  
Title Copper dimer - confinement and tails options  
  
KSpace 1  
  
Accuracy 4.5  
  
Dependency Basis=1E-10 Fit=1E-7  
  
Units  
  Angle Radian  
End  
  
SCF  
  Mixing 0.05  
  Iterations 20  
End  
  
Convergence  
  Degenerate default  
End  
  
DIIS  
  NCycleDamp 0  
  DiMix 0.15  
End  
  
Define  
  bbb=20  
  ccc=4.2
```

```
End
Lattice
  bbb bbb 0
 -bbb bbb 0
End
Atoms Cu
  0 0 0
  0 0 ccc
End
....
END INPUT
eor
```

The output file prints some information on how much was gained because of the tails and confinement options in various routines, for example:

Compression due to negligible tails in baspnt

max. percentage stored per node 98.23%

min. percentage stored per node 95.45%

# Restarts

## Restart the SCF

*Sample directory:* band/RestartSCF/

This very simple 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
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 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  
End  
  
BasisDefaults  
BasisType TZ2P  
Core Large  
End  
  
END INPUT  
eor
```

# Structure and Reactivity

## NaCl: Bulk Crystal

*Sample directory:* band/NaCl/

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 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
```

# Polyacetylene polymer calculation

*Sample directory:* band/CnHn/

This example illustrates how a one-dimensional periodic system can be treated by specifying only one lattice vector. It further shows how variables can be defined with the DEFINE keyword. The rest more or less speaks for itself. The Kspace integration is taken very accurate, whereas real space integration (ACCURACY keyword) is not so accurate.

Here and in the following BAND examples, we will leave out some space consuming parts of the input file which have been discussed already. Please check the actual input files if you wish to repeat one of the calculations.

```
$ADFBIN/band << eor
Title Polymer
Comment
  Technical
    Quadratic k space integration (1D)
    Low real space integration accuracy
    Definitions of variables
  Features
    Lattice : 1D, polymer
    Unit cell : 4 atoms
    Basis : NO+STO w/ core
End
Kspace 5
Accuracy 3
Units
  Length Angstrom
  Angle Radian
End
Define
  dCCd=1.3386
  dCCs=1.4510
  dCH=1.0770
  aCCC=124.5/180*pi
  arC=aCCC-pi/2
  aCCH=119.2/180*pi ! double bonded CC
  arH=aCCH-pi/2
End
Lattice
dCCd+sin(arC)*dCCs cos(arC)*dCCs 0.0
End
Atoms C
```

```

dCCd/2 0.0 0.0
-dCCd/2 0.0 0.0
End

Atoms H
dCCd/2+sin(arH)*dCH -cos(arH)*dCH 0.0
-dCCd/2-sin(arH)*dCH cos(arH)*dCH 0.0
End

```

A larger unit cell can of course be specified as well. In the second part of the example a supercell of 5 units is used. Another new feature introduced in this example is the TAILS keyword, which similar to ADF implies that distance cut-offs are applied to make the calculation cheaper. At the moment no big gains are yet to be expected from this, but this situation is expected to change in future versions of the code.

in the BASIS key. This subkey is actually mandatory at the moment if the TAILS keyword is used.

```

$ADFBIN/band << eor
Title Polymer with big unit cell (5 units)

Comment
Technical
  Low quadratic k space integration (1D)
  Low real space integration accuracy
Definitions of variables
Features
  Lattice : 1D, polymer
  Unit cell : 4 atoms
  Basis : NO+STO w/ core
End

Kspace 3
Accuracy 3

Units
Length Angstrom
Angle Radian
End

Tails Bas=1E-2

Define
dCCd=1.3386
dCCs=1.4510
dCH=1.0770
aCCC=124.5/180*pi
arC=aCCC-pi/2
aCCH=119.2/180*pi ! double bonded CC
arH=aCCH-pi/2
Latx(nlatt)=nlatt*(dCCd+sin(arC)*dCCs)
Laty(nlatt)=nlatt*(cos(arC)*dCCs)
Laty(nlatt)=nlatt*(cos(arC)*dCCs)
End

Lattice

```

```

Latx(5) Laty(5) 0.0
End

Atoms C
dCCd/2 0.0 0.0
-dCCd/2 0.0 0.0
dCCd/2+Latx(1) Laty(1) 0.0
-dCCd/2+Latx(1) Laty(1) 0.0
dCCd/2+Latx(2) Laty(2) 0.0
-dCCd/2+Latx(2) Laty(2) 0.0
dCCd/2+Latx(3) Laty(3) 0.0
-dCCd/2+Latx(3) Laty(3) 0.0
dCCd/2+Latx(4) Laty(4) 0.0
-dCCd/2+Latx(4) Laty(4) 0.0
End

Atoms H
dCCd/2+sin(arH)*dCH -cos(arH)*dCH 0.0
-dCCd/2-sin(arH)*dCH cos(arH)*dCH 0.0
dCCd/2+sin(arH)*dCH+Latx(1.0) -cos(arH)*dCH+Laty(1.0) 0.0
-dCCd/2-sin(arH)*dCH+Latx(1.0) cos(arH)*dCH+Laty(1.0) 0.0
dCCd/2+sin(arH)*dCH+Latx(2.0) -cos(arH)*dCH+Laty(2.0) 0.0
-dCCd/2-sin(arH)*dCH+Latx(2.0) cos(arH)*dCH+Laty(2.0) 0.0
dCCd/2+sin(arH)*dCH+Latx(3.0) -cos(arH)*dCH+Laty(3.0) 0.0
-dCCd/2-sin(arH)*dCH+Latx(3.0) cos(arH)*dCH+Laty(3.0) 0.0
dCCd/2+sin(arH)*dCH+Latx(4.0) -cos(arH)*dCH+Laty(4.0) 0.0
-dCCd/2-sin(arH)*dCH+Latx(4.0) cos(arH)*dCH+Laty(4.0) 0.0
End

```

## Pd bulk

Sample directory: band/Pd/

The main things to note are the specification of a scalar relativistic ZORA calculation, and the fact that symmetry information will be printed on output.

This example also shows incidentally how to override optimization memory parameters KGRPX and CPVector.

```

$ADFBIN/band << eor
Title Pd bulk

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

```

```

Options : spin restricted, scalar relativistic,
         numerical fit functions
         Full symmetry
End

KGRPX 2
CPVector 256
Kspace 5
Accuracy 4.0

Print SYMMETRY

Relativistic ZORA

Define
  halflatt=7.35/2
End

Lattice :: FCC
  0   halflatt halflatt
  halflatt 0   halflatt
  halflatt halflatt 0
End

Atoms Pd
  0.0
End

...
END INPUT
eor

```

## Ne bulk

*Sample directory:* band/Ne/

```

$ADFBIN/band << eor
Title Ne matrix 4.2 K

Comment
  Technical
    Hybrid k space integration (3D) (high)
    Reasonable real space integration accuracy
    Definitions of variables
  Features
    Lattice : 3D
    Unit cell : 1 atom
    Basis   : NO+STO w/o core
End

```

```

Kspace 9
Accuracy 4.0

Units
Length Angstrom
End

Define
halflatt=4.43/2
End

Lattice :: FCC
0 halflatt halflatt
halflatt 0 halflatt
halflatt halflatt 0
End

Atoms Ne
0.0 0.0 0.0
End

AtomType Ne
Dirac Ne
3 0
Valence
1S
2S
2P
SubEnd

BasisFunctions
1S 12.45
2S 3.65
2S 1.55
2P 1.45
2P 5.50

3D 2.0
4F 3.0
SubEnd

FitFunctions
3S 2.9000
3S 4.0900
3S 5.7700
3S 8.1400
2S 8.3300
2S 12.5200
2S 18.8100
1S 17.2000
3P 3.1000
3P 4.8000
3P 7.4200
2P 8.4100

```

```

2P 14.1000
3D 2.9000
3D 5.6700
3D 11.1000
4F 3.9500
4F 8.0000
5G 5.0000
SubEnd
End

END INPUT
eor

```

## Atomic energies

*Sample directory:* band/H\_ref/

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

```

## Hydrogen on Pt surface

Sample directory: band/H\_on\_Pt/

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
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 :: layer 1
  -ysh 0.0 -dlay :: layer 2
End

Atoms H
  0.0 0.0 height
End

```

```
...  
END INPUT  
eor
```

## Calculating the atomic forces

*Sample directory:* band/BNForce/

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 zinblende structure (force calculation)  
  
comment  
  Calculate Atomic Forces (energy gradient)  
  Frozen core approximation  
  TZ2P basis  
  A/K -> 5/3  
  2 atoms per unit cell  
end  
  
dependency basis=1e-8  
  
Kspace 3  
Accuracy 5.0  
  
Units  
  Length Angstrom  
End  
  
Define  
  a = 3.60  
End  
  
GRADIENTS  
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  
  0.0 0.0 0.0  
end  
  
Atoms 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 0.019676 0.019676 0.019676
 2 N -0.019677 -0.019677 -0.019677

```

## Optimizing the geometry

*Sample directory:* band/H2BulkGeo/

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 (The example is designed for speed and not for accuracy.)

```

$ADFBIN/band << eor
Title H2 bulk geometry optimization
Comment
  Optimized for speed / Accuracy low
  Basis very small
  Demonstrates the GeoOpt block
  SCF iterations limited to make it faster
End

KSpace 2

Accuracy 3.1

screening
RMadel 9
end

Dependency Basis=1e-8

GeoOpt
Iterations 5
Converge Grad=1e-6
RestartSCF true
End

SCF
  Mixing 0.2
  Iterations 2

```

```
End

Convergence
  Degenerate default
End

DIIS
  NCycleDamp 0
  DiMix 0.5
End

Units
  Angle Radian
End

Define
  aaa=1
End

ATOMS H
  0
  aaa
End

Lattice
  5.0*aaa 0 0
  0 5.0*aaa 0
  0 0 5.0*aaa
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
  :: 4F 3.00
```

```

:: 5G 4.00
SubEnd

End

END INPUT
eor

mv RUNKF H2BulkGeo.runkf

rm Points

```

Note that the RUNKF file is saved. In the next run we use the result file to continue the geometry optimization

```

# ----- second run -----

$ADFBIN/band << eor
Title H2 bulk geometry optimization
Comment
  Restarting the geometry optimization
  Optimized for speed / Accuracy low
  Basis very small
  Demonstrates the GeoOpt block
  SCF iterations limited to make it faster
End

KSpace 2

Accuracy 3.1

screening
RMadel 9
end

Dependency Basis=1e-8

Restart H2BulkGeo.runkf&
GeometryOptimization
end

GeoOpt
Iterations 5
Converge Grad=1e-6
RestartSCF true
End

SCF
Mixing 0.2
:: Iterations 2
End

Convergence
Degenerate default

```

```
End

DIIS
NCycleDamp 0
DiMix 0.5
End

Units
Angle Radian
End

Define
aaa=1
End

ATOMS H
0
aaa
End

Lattice
5.0*aaa 0 0
0 5.0*aaa 0
0 0 5.0*aaa
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
:: 4F 3.00
:: 5G 4.00
SubEnd
```

```
End  
END INPUT  
eor
```

## Nuclear gradient with a MetaGGA functional

*Sample directory:* band/CO\_MetaGGA\_Force/

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  
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  
  
define  
ha=6.60/2  
end  
  
Lattice  
6.0 0 0  
end  
  
atoms C  
0.0  
end  
  
atoms O  
2.20  
end
```

```
BasisDefaults
BasisType DZ
Core Large
end

end input
eor
```

## Frequency run and transition state search

*Sample directory:* band/H2SlabFreqTS/

First run: H<sub>2</sub> slab frequency calculation near minimum. Second run: transition state search, using as restart the results of the first run.

```
$ADFBIN/band << eor
Title H2 slab frequency calculation near minimum
Comment
  Optimized for speed / Accuracy low
  Basis very small
  Demonstrates the frequencies runtime
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 H
:: TS coords
:: 0.408818 -0.059284 0.374229
:: 0.305357 0.059284 -0.374229
:: Local minimum coords:
-0.4 0 0.1
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 transition state

```
$ADFBIN/band << eor
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
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 H2SlabTS.runkf

rm Points
```

# Time dependent DFT

## Time-dependent DFT calculations for bulk silicon

Sample directory: band/Silicon/

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
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
HA/2 HA/2 HA/2
END
...
```

```
END INPUT
eor
```

For Silicon the real and imaginary parts of the dielectric function:  $\epsilon(\omega) = 1 + 4 \text{ Pi Chi}(\omega)$  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.

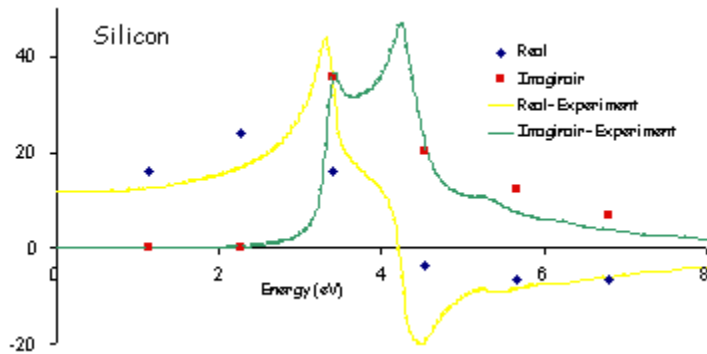
The real and imaginary parts are printed separately. At this frequency, the imaginary part is still zero. Because of the high symmetry of the system, the real part is a constant times the unit matrix except for numerical noise.

```
** 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.



## Time-dependent DFT calculations for bulk helium

Sample directory: band/He\_crystal/

```

$ADFBIN/band << eor
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
0.0 0.0 0.0
HA/2 HA/2 HA/2
END

BasisDefaults
BasisType DZ
End

END INPUT
eor
```

## Time-dependent DFT calculations for bulk diamond

*Sample directory:* band/Diamond/

```
$ADFBIN/band << eor
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
0.0 0.0 0.0
HA/2 HA/2 HA/2
END
```

```

BasisDefaults
BasisType DZ
End

END INPUT
eor

```

## Time-dependent DFT calculations for hydrogen chain

Sample directory: band/H\_chain

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
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
-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

## Time-dependent current DFT calculations for a metal

Sample directory: band/Cu\_resp\_NR\_ALDA/

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
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

```

**k**space 7  
Accuracy 4.0

**RESPONSE**  
**nfreq 2**  
**strtfir 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  
0.0  
End

BasisDefaults  
BasisType DZ  
Core Large  
End

END INPUT  
eor

# ESR

## hyperfine A-tensor

Sample directory: band/TiF3a/

Sample calculation for an ESR A-tensor calculation. The calculation should be spin unrestricted and have the ATENSOR keyword.

```
$ADFBIN/band << eor
Title tif3

comment
end

Kspace 1
Accuracy 5.0

Units
  Length Angstrom
End

Define
  a = 25
  RTIF = 1.78
  RY = RTIF*SQRT(3)/2
End

Unrestricted

ATENSOR
END

Lattice
  a 0.0 0.0
  0.0 a 0.0
  0.0 0.0 a
End

Atoms Ti
  0.0 0.0 0.0
end

Atoms F
  RTIF 0 0
  -RTIF/2 RY 0
  -RTIF/2 -RY 0
end

AtomType Ti
```

```
DIRAC Ti
 7 0
VALENCE
1S
2S
2P
3S
3P
4S
3D 2
SubEnd
BASISFUNCTIONS
 1S 26.300000
 2S 5.600000
 2P 12.000000
 3S 4.650000
 3P 5.400000
 3P 2.300000
 3D 4.950000
 3D 1.040000
 4S 1.900000
 4S 0.800000
 4P 1.200000
 4F 2.300000
SubEnd
FITFUNCTIONS
 1S 52.600000
 2S 58.320000
 2S 39.240000
 3S 38.750000
 3S 27.730000
 4S 26.240000
 4S 19.530000
 4S 14.540000
 5S 13.490000
 5S 10.330000
 5S 7.910000
 6S 7.260000
 6S 5.680000
 6S 4.450000
 6S 3.480000
 7S 3.170000
 7S 2.530000
 7S 2.010000
 7S 1.600000
 2P 38.300000
 3P 25.820000
 4P 17.610000
 5P 12.200000
 5P 7.070000
 6P 4.970000
 6P 3.010000
 7P 2.150000
 3D 28.600000
```

```
4D 19.530000
5D 13.550000
5D 7.860000
6D 5.540000
6D 3.360000
7D 2.400000
4F 13.900000
5F 7.920000
5F 3.800000
6F 2.240000
5G 8.400000
5G 4.390000
5G 2.290000
SubEnd
End

AtomType F
DIRAC F
3 0
VALENCE
1S
2S
2P 5
SubEnd
BASISFUNCTIONS
1S 10.880000
2S 3.240000
2S 0.740000
2P 4.540000
2P 1.240000
3D 2.000000
4F 3.000000
SubEnd
FITFUNCTIONS
1S 21.760000
2S 24.390000
2S 16.560000
2S 11.240000
2S 7.630000
3S 7.600000
3S 5.480000
3S 3.950000
3S 2.850000
3S 2.050000
3S 1.480000
2P 14.400000
2P 7.530000
3P 5.900000
3P 3.420000
3P 1.980000
3D 9.700000
3D 6.160000
3D 3.910000
3D 2.480000
```

```

4F 6.500000
4F 3.750000
5G 4.500000
SubEnd
End

END INPUT
eor

```

## Zeeman g-tensor

*Sample directory:* band/TiF3g/

Sample calculation for an ESR g-tensor calculation. This makes only sense for a relativistic spin orbit calculation.

```

$ADFBIN/band << eor
Title tif3

comment
  1d structure
end

Kspace 1
Accuracy 5.0

Relativistic ZORA SPIN

esr
end

Units
  Length Angstrom
End

Define
  a = 25
  RTIF = 1.78
  RY = RTIF*SQRT(3)/2
End

Lattice
  a
End

Atoms Ti
  0.0 0.0 0.0
end

Atoms F
  0 RTIF 0

```

```

-RY -RTIF/2 0
RY -RTIF/2 0
end

AtomType Ti
DIRAC Ti
7 0
VALENCE
1S
2S
2P
3S
3P
4S
3D 2
SubEnd
BASISFUNCTIONS
1S 26.300000
2S 5.600000
2P 12.000000
3S 4.650000
3P 2.450000
3D 4.950000
3D 1.040000
4S 1.650000
4P 1.200000
SubEnd
FITFUNCTIONS
1S 52.600000
2S 58.320000
2S 39.240000
3S 38.750000
3S 27.730000
4S 26.240000
4S 19.530000
4S 14.540000
5S 13.490000
5S 10.330000
5S 7.910000
6S 7.260000
6S 5.680000
6S 4.450000
6S 3.480000
7S 3.170000
7S 2.530000
7S 2.010000
7S 1.600000
2P 38.300000
3P 25.820000
4P 17.610000
5P 12.200000
5P 7.070000
6P 4.970000
6P 3.010000

```

```
7P 2.150000
3D 28.600000
4D 19.530000
5D 13.550000
5D 7.860000
6D 5.540000
6D 3.360000
7D 2.400000
4F 13.900000
5F 7.920000
5F 3.800000
6F 2.240000
5G 8.400000
5G 4.390000
5G 2.290000
SubEnd
End

AtomType F
DIRAC F
3 0
VALENCE
1S
2S
2P 5
SubEnd
BASISFUNCTIONS
1S 10.880000
2S 3.220000
2P 3.520000
SubEnd
FITFUNCTIONS
1S 21.760000
2S 24.390000
2S 16.560000
2S 11.240000
2S 7.630000
3S 7.600000
3S 5.480000
3S 3.950000
3S 2.850000
3S 2.050000
3S 1.480000
2P 14.400000
2P 7.530000
3P 5.900000
3P 3.420000
3P 1.980000
3D 9.700000
3D 6.160000
3D 3.910000
3D 2.480000
4F 6.500000
4F 3.750000
```

```
5G 4.500000  
SubEnd  
End  
  
END INPUT  
eor
```

# Analysis

## CO absorption on a Cu slab: fragment option and densityplot

Sample directory: band/Frags\_COCu/

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  
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  
End
```

```

Atoms 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
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
End

```

```

Atoms O
  0 0 dist+bond
End

Atoms 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
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
Title Cu slab with CO adsorbed (restart density plot)

Kspace 3
Accuracy 4

Restart COCu.runkf &
DensityPlot
End

Grid
Type Coarse
End

DensityPlot
scf
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
End

Atoms O
  0 0 dist+bond
End

Atoms 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.

## Cu\_slab: 2-dim. Finite temperature and orbital plot

*Sample directory:* band/Cu\_slab/

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 advview.

```
# ----- 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 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 0.0
  0.0 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"

```

## NaCl: ionic fragments

*Sample directory:* band/NaCl\_ionic/

A bulk crystal computation for Sodium Chloride (common salt), starting with charged atoms.

```

$ADFBIN/band << eor
Title NaCl (from charged 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 : Ionic atoms in startup
Note:
  Seems very unstable, highly sensitive to DIIS parameters
  (and simple damping) and well parameters.
End

Accuracy 3.5
Kspace 3

Diris
  NCycleDamp 15
End

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-8
RMax 200.0
VALENCE
1 0
2 0
2 1
3 0 0
SubEnd

BasisFunctions
3S 1.75
3P 1.75
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
RADIAL 2000
RMin 1E-8
RMax 450.0
RWell 150.0
VWell -2.0
VALENCE
1 0
2 0
2 1
3 0
3 1
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

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