Volker Eyert

The Augmented Spherical Wave Method

An Extended User Guide

Version 2.6

February 17, 2009

To the memory of my father
and the future of my children Florian and Carolin

Preface

Since its first implementation in the second half of the seventies by Williams, Kübler, and Gelatt at the IBM Research Labs in Yorktown Heights the Augmented Spherical Wave (ASW) program has seen a lot of revisions. Step by step the code was extended and optimized, new functionality was added and even new implementations were started. Yet, they were all more or less based on the original code.

This was not so for a completely new implementation, which I started after having finished my PhD thesis in the group of J. Kübler in Darmstadt. The resulting new package was written completely from scratch. It followed a complete reworking of the ASW method, which is summarized in my recent book published as a Lecture Notes in Physics by Springer [404]. The functionality, usability, and transferability of this package evolved to a stage far beyond that known from most of the previous implementations. To be more specific, the calculation of physical and chemical properties was greatly enhanced and included weighted band structure, densities of states using rotated reference frames, crystal orbital overlap populations and related quantities, just to mention a few. In addition, the search for optimal positions of additional augmentation spheres in larger voids, also know as empty spheres, was made automatic, which extended the field of applications significantly. Finally, the user friendlyness was considerably enhanced by the introduction of the so-called CTRL file, which serves as the one and only input file to all programs.

Nevertheless, this progress was still within the standard ASW method, which is based on the atomic sphere approximation (ASA) and does not allow to calculate accurate total energies. The corresponding coding was termed the 1st generation package and included the versions 1.0 to 1.9.

Only recently I succeeded in developing a new and very fast full-potential ASW method, which allowed for a comparable speed as the standard ASW method. Its implementation is the main achievement of the 2nd generation code ranging from the preliminary version 2.0 to the present versions 2.5 and 2.6.

While the first edition of this user guide addressed the 1st generation version 1.9, the implementation of the full-potential ASW method made a new edition necessary. This is the purpose of the present user guide, which applies to the full-potential versions 2.5 and 2.6 and, in addition, covers new features as, e.g., the implementation of the optical properties and of the LDA+U method. Furthermore, the new versions allow to use the linear tetrahedron method for Brillouin zone integrations.

This user guide addresses all those readers, who want to use the ASW method in practice. In addition to explaining the programs, files, and input parameters, application of the code is explained with several examples, ranging from simple to more complicated ones. Especially new users are strongly encouraged to work through these examples in detail in order to learn about the full functionality of the code and to recognize possible pitfalls.

In writing this new user guide I have switched the layout to that of Springer's Lecture Notes in Physics series. This is just for practical reasons and does not imply that it will be published by Springer.

In implementing the 1st generation standard ASW code as well as developing the full-potential ASW method I have benefited from many discussions with friends and collegues. As in my recent book, I mention especially my friend Jürgen Sticht, who left us very untimely two years ago. His knowledge about code optimization and vectorization eventually influenced many portions of the present code.

The development of the ASW code benefitted a lot from many discussions, helpful advice and support from a lot of people. Without being complete, I particularly appreciate Ole Krogh Andersen, Karl-Heinz Höck, Jürgen Kübler, Samir F. Matar, Thomas Maurer, Alexander Mavromaras, Michael S. Methfessel, Peter Mohn, Peter C. Schmidt, David Singh, Michael Stephan, andras Vernes, and Erich Wimmer.

Potsdam, February 2009 *Volker Eyert*

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Introduction

1.1 Overview

Since its invention in the late seventies the Augmented Spherical Wave (ASW) method has become one of the most widespread methods used for density functional based electronic structure calculations. Its minimal basis set allows for a natural interpretation of materials properties and makes it one of the fastest all-electron methods. The present User Guide addresses practioners who want to apply the ASW method to actual problems but are not or not yet interested in a detailed understanding of the underlying formalism. To those who are I recommend consulting my recent monograph on the ASW method [404].

The original version of the ASW method was developed in the late seventies by A. R. Williams, J. Kübler, and C. D. Gelatt at the IBM research lab in Yorktown Heights [390]. According to the authors, their work was based on the concept of renormalized atom calculations as proposed by Watson, Ehrenreich, Hodges, and Gelatt [129, 160, 376] and inspired by the ideas of the linear methods as presented by O. K. Andersen [11].

In the eighties, the ASW program saw several revisions and extensions mainly done by the Darmstadt group of J. Kübler. These included the development of a version for treating non-collinear spin arrangements [213, 214] as well as the implementation of a first full potential ASW method by myself [106]. In addition, J. Sticht and I put a lot effort in tuning the program to optimal performance especially for vector machines.

Commercializing the code set in by the end of the eighties, when the California based software company BIOSYM (later Materials Science Incorporation, MSI, now Accelrys) started distribution of the standard Darmstadt code.

Nevertheless, the old Darmstadt version still suffered from many drawbacks. Programming was completely done in a rather old fashioned FORTRAN 77 style using e.g. variables and arrays of mixed accuracy. File handling was quite complicated and reading from the input files was done in fixed format. In the startup phase of a calculation several different programs and input files had to be used. All this made the program rather user-unfriendly and error-prone.

In order to overcome these difficulties of the old Darmstadt version, I started a completely new implementation of the code. Programming was done in a clean and systematic style. The source was kept fully self-contained by including standard BLAS or LAPACK routines for the linear algebra problems. Graphics is based to large parts on Gnuplot, which is likewise public domain software. The file handling and the organization of the program was much improved taking away many standard steps from the users responsibility. The interface between the user and the program was completely reshaped and now allows for a very flexible input. Furthermore, a lot more properties can be calculated, which fact facilitates analysis of the electronic properties a lot and make the program exceptional among many other methods. Last not least, the program package has turned out to be very stable and efficient.

Finally, in 2006 I succeeded in implementing a new full potential ASW method, which has already proven to be very fast, having a speed of the same order as the standard ASW method implemented in the versions up to 1.9. At the same time, this new code allows to calculate even elastic properties and phonon frequencies via the frozen phonon approach. The development of the full potential code set in with the preliminary version 2.0. Version 2.2 included the non-spherical parts of the electron densities and the effective potential with the atomic spheres. Finally, version 2.3 was the first true full potential version. The latest versions currently available are 2.5 and 2.6, to which this handbook applies.

This version was originally designed for Unix/Linux machines and most of the commands mentioned below refer to this environment. More information about the ASW method and the program package can be obtained from the ASW homepage,

http://www.physik.uni-augsburg.de/∼eyert/aswhome.shtml

where most of the properties accessible by the programs are discussed and a full list of publications and theses related to the ASW method is given.

Since 1998 a Windows version of the ASW program package including a very clever graphics interface and access to the worlds largest crystallographic database is distributed under the name “Electra” (for “Electronic Structure and Analysis”) by Materials Design Inc., Angel Fire, NM and Materials Design s.a.r.l., Le Mans. See

http://www.materialsdesign.com

for more information.

Any questions, criticisms, and suggestions concerning the ASW program package or this manual are welcome. Please feel free to contact me via email to

eyert@physik.uni-augsburg.de or **volker@eyert.de**

This user guide falls into three parts. Following this introductory chapter the capabilities of the program package are demonstrated by several examples in Chap. 2. Chap. 3 comprises an overview over all programs, shell scripts, and data files coming with the distribution or being created during execution. Finally, a detailed discussion of the main input file of the package, the CTRL file is given in Chap. 4. While the more experienced practioner will use this chapter as a reference, beginners are strongly recommended to work through the examples of Chap. 2 first.

1.2 Physical background

As many other *ab initio* approaches the ASW method is based on the Born-Oppenheimer approximation, which allows to consider the electronic structure independent of the dynamics of the lattice. Furthermore, it makes use of crystalline periodicity and the Bloch theorem built thereon. Finally, the ASW method relies on density functional theory (DFT) as founded by Hohenberg, Kohn, and Sham.

As it stands the ASW program package employs the local density approximation (LDA) coming with DFT. By now, all common parametrizations have been implemented. Alternatively, the generalized gradient approximation (GGA) in all known parametrizations can be used. Quite recently, I implemented the LDA+U method as originally invented by Anisimov, Zaanen, and Andersen [28].

As all other augmentation schemes the ASW method is built upon the muffin-tin approximation (MTA), which approximates the full crystal potential by spherically symmetric potential wells inside the non-overlapping muffin-tin spheres and a constant in the remaining, interstitial region. This situation resembles that of a muffin-tin as it is sketched in Fig. 1.1. Yet, the ASW method, like the LMTO method, is based on a special form of the MTA, namely, the atomic sphere approximation (ASA) as invented by Andersen, which is characterized by the requirement that the sum of all atomic spheres inside the unit cell has the same volume as that cell. Inside the spheres the potential as well as the electron densities (core and valence) are assumed to be spherical symmetric. While this socalled shape approximation of both the MTA and the ASA might seem as too crude an approximation to the full crystal potential the ASA actually is not. This can be readily understood from the fact that the ASA condition creates overlap regions along the bond paths just between two atoms. In these regions the superposition of the two ASA potentials experiences an effective downshift as compared to the potentials of the single spheres and thus mimics the full potential quite well. Indeed, electronic properties calculated using ASA based methods can hardly be distinguished from those growing out of the much more elaborate full potential methods.

However, due to the spherical symmetry and the overlap of the potential wells calculated total energies still lack the accuracy needed e.g. for calculating elastic properties or phonon frequencies. For this reason, I have implemented the new full potential version, which is now available for the first time.

As an all-electron scheme the ASW method fully includes both the core and the valence electrons in the self-consistent field calculations. For this reason, it allows full coverage of the periodic table including transition metal atoms as well as the

Figure 1.1 Muffin-tin.

lanthanides and actinides. The code is applicable to metals, semiconductors and insulators without any restrictions.

Much of the efficiency of the program package stems from the use of a minimal basis set built from atomiclike (s, p, d) orbitals. As a consequence, each atom contributes with nine or 16 basis functions to the secular matrix, which is much less than the ≈ 100 functions usually needed in plane wave based methods. Furthermore, the atomiclike orbitals allow for an easy setup of e.g. partial densities of states and a much more natural interpretation of the results.

Additional speedup of the program results from the fact that the ASW method like the LMTO or LAPW is a socalled linear method. The latter approach as invented by Andersen is based on the observation that the energy dependence of the wave function is rather weak and, hence, may be well approximated by only few terms of a Taylor expansion. Within the ASA only the first two terms are actually needed (the famous ϕ and $\dot{\phi}$ of the LMTO method). As a result, solving for the zeros of the secular matrix reduces to an eigenvalue problem, which is tractable by standard routines, and can thus be done much faster as the complicated root tracing done before.

Finally, as it stands the ASW package allows for non-relativistic as well as scalar-relativistic calculations and it can handle both spin-restricted and spin-polarized calculations, the latter including a special branch for antiferromagnetic order. Much work has been put into the code for accelerating the iterations towards self-consistency.

Last not least, due to the implementeation of the sphere geometry optimization (SGO) algorithm the ASW programs allow for considering closed-packed systems as well as rather open crystal structures. The SGO algorithm performs an automatic sphere packing including the generation of additional augmentation sphere positions and the determination of optimal atomic sphere radii for use with the ASA.

Readers interested in a more detailed account of the ASW method are referred to my book [404].

Over the years more and more physical and chemical properties have become available by the ASW program package. Among them are the following.

- Electronic Properties
  - electronic dispersions $E(\mathbf{k})$ ("band structure")
  - electronic wave functionsWave function $\psi(\mathbf{k}) = \sum_i c_i H_i(\mathbf{k})$ → projected band structure
  - total/partial (site/state projected) densities of states (DOS)
  - Fermi surface
  - electron densities
  - Laplacians of the electron density
  - Bader analysis of the electron density
  - electric field gradients
  - charge densities at the nuclei → isomer shifts
  - core level spectra
- Cohesive and Elastic Properties
  - cohesive energy
  - bulk modulus
  - elastic constants
  - phonon frequencies
- Chemical Bonding
  - total/partial crystal orbital overlap population (COOP), total/partial crystal orbital Hamiltonian population (COHP), total/partial covalence energy (E_{cov})
- Magnetic Properties
  - total and site/state projected magnetic moments
  - magnetic ordering (ferro-, ferri-, antiferromagnetic)
  - magnetic energies
  - spin densities
  - spin densities at the nuclei → hyperfine fields
- Optical Properties

  - plasma frequency
  - optical conductivity
  - dielectric function
  - index of refraction
  - extinction coefficient
  - optical reflectivity
  - optical absorption
  - energy-loss function

- Transport Properties
  - electrical conductivity
  - electrical resistivity
  - thermopower
  - thermoelectric power factor
  - thermoelectric figure of merit
  - thermal conductivity (electronic contribution only)
  - Hall conductivity
  - Hall coefficient

Suggestions for additional properties, which should be implemented are always welcome. Just sent an email to the address given above.

1.3 Programming

At present, the ASW program package consists of $\approx$ 120000 lines of source code, which are organized in a dozen main programs and about 450 subroutines. While the first versions were written in FORTRAN 77, the latest versions have been fully adapted to the Fortran 95 standard. In particular, extensive use of dynamic memory now makes the package much faster and more flexible than before. Moreover, switching to Fortran 95 has enhanced portability of the code considerably.

In setting up prior versions of the program I have much benefitted from *ftnchek*, a public domain syntax checker for Fortran programs. Unfortunetely, *ftnchek* is no longer developed and, in particular, can not be applied to Fortran 95 code.

As it stands the ASW program package is fully self-contained without the need to link any library. Standard linear algebra tasks are handled by use of the LAPACK library. For plotting the calculated data the programs provide interfaces to Gnuplot, RasMol, and XCrysDen, which are all public domain software. As a consequence, commercial libraries are not needed at all.

Finally, the program is fully portable to and has been tested on a large variety of platform and with many compilers including

- IBM RS6000 (XL Fortran 95)
- HP 9000 (Fortran 90)
- CRAY Y-MP, YEL, J90, T90 (CF90)

- SGI (f90)
- SNI S400 (frt), VPP500 (frtpx)
- Sun SPARC (Solaris, f90)
- Convex (ConvexOS, fc -f90)
- Compaq Alpha (Fortran 95)
- Power Mac G5 Mac OS X (G95)
- PC (AMD/Intel) (Lahey/Fujitsu Fortran 95, PGI f90, Absoft Pro Fortran, NAG f95, Intel f95)
- All platforms: G95, GNU Fortran 95

For this reason, installing the package poses no problems and can be done within a few minutes.

Last but not least, in order to facilitate running the programs on larger machines the package includes shell scripts for use with the most common job queuing systems as there are

- IBM's LoadLeveler
- Portable Batch System - PBS
- Sun Grid Engine - SGE

1.4 Installation

Installation of the ASW package proceeds along two different lines. Usually, the executables and shell scripts are sent as a tarball. In this case the following steps have to be performed.

1. Unpack the tarball by typing `gunzip aswbin_2.5.tar.gz` and `tar -xvf aswbin_2.5.tar`, which creates a subdirectory `aswbin_2.5`. This subdirectory contains
   - all the executable (files `mn*.run`, `pl*.run`)
   - all shell scripts (files `mn*.x`, `pl*.x`, `pl*.lx`, and some more)
   - all the information files (README, COPYRIGHT, NEW2.5, HELP, SPCGRP)
2. Include this directory into your PATH settings.
3. As a very first test you may type the command `mnmpr.run`, which generates a one-page output of machine parameters (see Sec. 3.1) and proves the correct functionality of the executables.
4. From within the subdirectory `aswbin_2.5`, invoke the shell script `upshl`, which writes the correct path to all other shell scripts. As a consequence, the shell scripts can be called from any directory and they will call the correct executables.
5. Have fun running the ASW codes!

The alternative route starts from the source code. In this case these files first may have to be extracted from a tarball in a manner similar to the procedure described above. Since the ASW package has been written with portability in mind, installation on various platforms is straightforward. In particular, only few steps are needed, which are also described in the INSTALL file.

1. Unpack the tarball by typing `gunzip aswhp_2.5.tar.gz` and `tar -xvf aswhp_2.5.tar`, which creates a subdirectory `aswhp_2.5`. This subdirectory contains the full distribution.
2. Within the subdirectory `aswhp_2.5` edit the Makefile:
   In the first part of the Makefile several items must be specified:

COMPILER	Machine and/or compiler
ARCH	Machine architecture (for IBM only)
LOCALLIB	Use of local BLAS library (recommended)
APPLICATION	Switch between testing and production runs

   The ASW program package uses several routines from the BLAS and LAPACK libraries. The source codes of these routines are included in the distribution and will be compiled and linked into the executables in case the entry LOCALLIB is left empty. This option makes the ASW package completely self-contained. No additional libraries are necessary to run the programs. Yet, on most machines vendor specific installations of these libraries exist, which are able to make use of machine specifications and thus in many cases are very fast. Hence, whenever a precompiled BLAS or LAPACK library exists, it's use is highly recommended. In this case you should specify LOCALLIB = USE. Recent developments in the field of mathematical libraries have led to the Automatically Tuned Linear Algebra Subroutine (ATLAS) library, which is available also for PC's running under Linux, can be easily installed, and outperforms even some vendor supplied libraries. Alternatively, the GotoBLAS package, which is a BLAS implementation by K. Goto, has proven to be highly efficient. This package can be downloaded from the University of Texas in Austin.
   For the last item, please use APPLICATION = PROD.
   Finally, the installation directory, where the executables and the LaTeX envelope files will be copied, must be given.
3. Edit the file jbout.f:
   Select the settings valid for your machine by (un)commenting the corresponding lines in the source code. Yet, due to the increased portability of Fortran 95, this step can be skipped on most machines.
4. Edit the file dimen.f:
   This module is called by all main programs and contains all the dimension parameters, which control the size of most arrays. In case you have a machine with very small memory you may reduce some of the dimension parameters. However, most arrays are dynamically allocated during execution. For this reason, there is usually no need to reduce these dimensions. In contrast, in case you want to run very big applications, you may need to increase the maximum number of atoms, which by default is 1024.
5. Type `make all`:
   This step, which alternatively can be performed as background procedure by invoking the shell-script `mkall.x`, generates all executables. Due to the many new

features incorporated in the Makefile its execution might require GNU make, which is free software and available from many servers, e.g. www.gnu.org.

6. Type `make install`:
   This copies all executables, shell-scripts and LaTeX envelope files to the directory specified in step 1 above.
7. Have fun running the ASW codes!

In addition to the above steps the following `make` commands are useful.

- `make clean`:
  This command will remove all listing files possibly created by the compiler or by any of the syntax checkers as, e.g. *ftnchek* or *forcheck*. However, it will not affect any of the object files or any of the executables.
- `make realclean`:
  This command will remove all module and objects files as well as all executables in addition to the listing files possibly created by the compiler or by any of the syntax checkers.

1.5 Linking with external software

As it stands, the ASW program package delegates several tasks to specialized software. This holds especially for linear algebra problems and visualization of the results.

The following software can be combined with the ASW package. This means that the Makefile and the programs themselves are perpared to be linked with the software listed below. In particular, the plot routines provide the corresponding interfaces and the programs write data files in the specific formats required by the external viausalization tools. To be specific, crystal structure and Fermi surface data as well as electron densities and related quantities are written in a format, which can be directly used by XCrysDen. Finally, many of the shell script used for plotting include a call to the corresponding external software.

All software included in the following list is public domain software. However, please do not forget referencing the particular software in publications in case you are asked for in order to appreciate the work of those who provide it.

ftnchek

(http://www.dsm.fordham.edu/~ftnchek/)

A most valuable tool during several stages of the development of the ASW package was ftnchek (short for ForTraN CHEcKer), which was developed by Robert

Moniot at Fordham University. ftnchek is a syntax analyzer for FORTRAN 77 programs. In addition, it has a special branch for the construction of calling trees for large program packages.

The Makefile of the ASW program package is prepared for working with ftnchek. However, development of ftnchek never went beyond FORTRAN 77. For this reason, after switching to Fortran 95, I have never used it any more.

BLAS/LAPACK

(http://www.netlib.org/blas/, http://www.netlib.org/lapack/)

BLAS and LAPACK have eveloved as THE standard software for solving linear algebra problems. While basic linear algebra tasks are deferred to the BLAS (Basic Linear Algebra Subroutines), LAPACK provides a number of high level driver routines, which grew out of a combination of its predecessors LINPACK and EISPACK.

However, all BLAS and LAPACK routines needed by the ASW software are already included in the ASW program package. This makes the distribution self-contained and allows to compile the ASW programs without any need to download the source codes of these libraries.

In addition, since LAPACK has become a de facto standard, the library is included in many Linux distributions. Furthermore, most machine dependent and vendor provided libraries as, e.g. ESSL by IBM have adopted the LAPACK calling sequences. Since these libraries are often very efficient it is recommended not to use the BLAS/LAPACK sources coming with the ASW distribution, but to link with the machine libraries.

ATLAS

(http://math-atlas.sourceforge.net/)

The ATLAS (Automatically Tuned Linear Algebra Software) provides a combined effort to supply LAPACK software with optimal tuning for a given machine architecture. To this end, ATLAS performs an extended check of systems resources, the result of which is transferred to the software in terms of, e.g. optimal block sizes of matrices. All this is done completely automatic and leads to a highly optimized LAPACK library for a given machine.

GotoBLAS

(http://www.tacc.utexas.edu/resources/software/)

Some years ago, K. Goto from the University of Texas in Austin provided a new implementation of BLAS/LAPACK, which outperforms the classical software in several cases. This is achieved by a more efficient use of memory mainly.

Gnuplot

(http://www.gnuplot.info/)

This is one of the classical tools for visualization.

XCrysDen

(http://www.xcrysden.org/)

This software was developed by A. Kokalj at the Jozef Stefan Institute in Ljubljana [405]. While the first version was still commercial, the code has been made public domain more recently. According to the website XCrySDen is a crystalline and molecular structure visualisation program, which aims at display of isosurfaces and contours, which can be superimposed on crystalline structures and interactively rotated and manipulated. It can run on most UNIX platforms, without any special hardware requirements.

In the last years, XCrysDen has found much appreciation in the community and on my opinion it is one of the best programs for displaying crystal structures, electron densities and related quantities, and Fermi surfaces.

RasMol

(http://www.rasmol.org/)

Another plot program going together with the ASW package is RasMol, which was developed by Roger A. Sayle. RasMol is used for plotting crystal structures and reads files created by the plot program `plstr.run`. RasMol is also public domain and like Gnuplot it usually comes along with the standard Linux distributions. However, since this software was originally designed to visualize large molecules it is somewhat weak at display periodic systems and does not provide much functionality for crystals.

1.6 Legal matters

Since the ASW program package is also commercially distributed legal matters have to be considered. Most of this is contained in the file COPYRIGHT coming with the distribution, which is printed here for completeness.

```
  **********************************************************************
  ***                     ASW software package                       ***
  **********************************************************************
  ***                         Version 2.6                            ***
  **********************************************************************
  ***                       Copyright notice                         ***
  **********************************************************************
  **********************************************************************

      The ASW software package was written by Volker Eyert.

      In setting up the package the author has benefitted from
      experience gained during stays at the following institutes:

        Institut fuer Festkoerperphysik, TH Darmstadt,
        Hochschulstr. 6, 64289 Darmstadt, Germany
        Institut fuer Physikalische Chemie, TH Darmstadt,
        Petersenstr. 20, 64287 Darmstadt, Germany
        Max-Planck-Institut fuer Festkoerperforschung,
        Heisenbergstr. 1, 70569 Stuttgart, Germany
        Hahn-Meitner-Institut,
        Glienicker Str. 100, 14109 Berlin, Germany
        Institut fuer Physik, Universitaet Augsburg,
        Universitaetsstr. 1, 86135 Augsburg, Germany

  **********************************************************************

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      Copyright (C) 1992-2009 Volker Eyert
  **********************************************************************


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Here and in the following the term "the author" refers to Volker Eyert
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You can contact the author via normal mail to the last of the above
adresses or via email to:
  volker@eyert.de

Here and in the following the term "ASW software package" refers to the
```

```
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  **********************************************************************
```

1.7 Upward compatibility

In general, upward compatibility is guaranteed by the program. It is controlled by the token ASW- in category VERSION of the CTRL file. For this reason, one should be careful in changing this token by hand. After reading the CTRL file the programs perform a complex check of the atomic files. This includes a check of the version of the code, which had written these files.

However, especially the transition from the old ASA-based versions (up to version 1.9) to the full-potential versions (gradually starting from version 2.0) required many changes in the underlying theory. In particular, the electron density and all related quantities now included also the non-spherical contribution inside the atomic spheres. As a consequence, the structure of the atomic files had to be changed completely and I decided to break the upwards compatibility rule. Hence, atomic files generated by programs prior to version 2.0 can no longer be used as input to programs with version 2.0 and higher.

An important issue of upward compatibility regards the interpretation of the atomic coordinates coming with the CTRL file. To be specific, the interpretation of the relative atomic coordinates has been changed in a major revision in version 2.1. Whereas in all program versions prior to this version relative coordinates (for switch CARTP=F) were referred to the primitive translation they are now referred to the translations of the conventional cell, as is usual in crystallography. While this makes the setup much more comfortable it leads to difficulties if old CTRL files are still to be used. For this reason, I have implemented the following rule: If an old CTRL file, i.e. a CTRL file generated by a version prior to version 2.1, is to be used with the atomic positions given in relative coordinates in terms of the primitive translations, then the old version number should be specified with the token ASW-in category VERSION. In other words, whenever the program reads a CTRL file with the version number lower than 2.1, it interpretes the relative coordinates in terms of the primitive translations rather than the translations of the conventional cell.

1.8 Known bugs

So far the following bug is known, which has not yet been removed from the code:

1. The packing program `mnpac.run` was originally designed for the spin-degenerate case only. As a consequence, it produces wrong results if NSPIN=2 is specified in the CTRL file. Please make sure that NSPIN=1 in the CTRL file or that this token is missing at all.

Chapter 2

Execution of the ASW programs: Case studies

In the present chapter we will discuss how the ASW package can be used in an optimal way. In doing so, we will apply the programs to several representative test cases, namely Cu, Si, FeS_2, CrO_2, and Gd.

In passing we mention that the total CPU time for all calculations described in the chapter was about 48,000 sec on an Intel Pentium Mobile with 2.0 GHz.

2.1 A simple case: Cu

Elemental copper has been used as a test case for electronic structure programs since long. This is for several reasons. As we will learn below, the electronic structure of this metal is strongly influenced by three groups of electrons. While the core electrons are tightly bound to the nucleus and, hence, have a very high electron density at the center of the atom but an almost negligible density in the outer region, the wave functions of the $4s$ and $4p$ valence electrons reach far out and spread even into the region of neighbouring atoms. Finally, the $3d$ valence electrons are somewhat intermediate in that they likewise contribute to the overlap with neighbouring atoms, hence, to the metallic bonding but still are rather well localized near the nuclei. Since the $3d$ states of copper are almost filled they contribute only weakly to the Fermi surface, which is therefore formed mostly by the $4s$ and $4p$ states. As a consequence, although the $3d$ states are found well below E_F any changes or errors in the $4sp$–$3d$ overlap strongly affect the Fermi surface. For this reason, copper is regarded as a sensitive test case. Calculated electronic structures for this material were compared to the results of photoemission experiments already in the early 1960's by Burdick [406].

The following calculations proceed in several steps. First we have to set up the CTRL file, which is the only input file for the calculations. All other files needed during the execution of the programs are created automatically and auxiliary files are deleted in case the programs do not need them any more. Once the self-consistent calculation has converged, additional main programs may be invoked to evaluate the band structure, the partial DOS, or the Fermi surface. Finally, the plot programs can be used to visualize the results.

In order to prepare for the calculations, we start creating a directory, where all the files should be stored, by typing

```
mkdir cu
cd cu
mkdir nm
cd nm
```

at the operating systems prompt. This creates a directory named `cu` with a subdirectory named `nm`, where `nm` stands for non-magnetic. This directory will hold all files connected with the particular application. Specifically, it will hold the CTRL file, which is the one and only input file to all ASW programs and has to be generated at the very beginning.

2.1.1 CTRL file

Let us start by listing a minimum CTRL file for Cu, which you may either write from scratch or copy from the example file database. In case you write it yourself remember not to use tabulators. On opening the CTRL file with your favorite editor you will see the following.

```
HEADER  Cu fcc
        data by Landolt-Boernstein
VERSION ASW-2.6
STRUC   ALAT=6.83079 CNTR=F
CLASS   ATOM=CU Z=29
SITE    ATOM=CU POS= 0.0  0.0  0.0
```

Each CTRL file is grouped into categories, which begin with a keyword at the beginning of a line. In the above listing, five categories are identified, namely HEADER, VERSION, STRUC, CLASS, and SITE. Each category comprises additional information, which, except for the first category, is passed to the program by socalled tokens. With the one and only exception being ASW-, these tokens have the form TOKEN=, followed by one or more integer numbers, real numbers, character strings or logical switches (T or F). To be specific, in the present example the category STRUC contains all information about the Bravais lattice in form of the lattice constant, ALAT=6.83079 and the centering type, namely, CNTR=F (face-centered). While this fixes the unit cell of the crystal, information about the geometry inside the unit cell is contained in the category SITE, which gives the positions of all atoms. In the present case, only one atom exists, which is located at the origin. This atom is labelled by ATOM=CU. Finally, the types of all atoms have to be specified. This is done in category CLASS, where each atom via its label is assigned an atomic number. In the present case, there is only one atom with atomic number 29. Note that the label CU could be replaced by anything else. However, the program assumes that labels will not exceed six characters.

Finally, the category HEADER holds space for up to 20 lines of text for user comments. However, note that the first line (the one containing the keyword HEADER) is exceptional as by default its entry is used as a title line for all plots. Last not least, category VERSION specfies the version of the program, which has generated the file or, if you have written the CTRL file from scratch, the version to be used.

While the above CTRL file already allows for a complete calculation a standard CTRL file may look as follows.

```
HEADER  Cu fcc
        data by Landolt-Boernstein
VERSION ASW-2.6
IO      HELP=F SHOW=T VERBOS=30 CLEAN=T
OPTIONS REL=T OVLCHK=T
STRUC   ALAT=6.83079 CNTR=F
CLASS   ATOM=CU Z=29 R=2.6694476 LMXL=2 CONF=4 4 3 4 COORB=0 1 2
                QVAL= 1.0  0.0  10.0  0.0
SITE    ATOM=CU POS= 0.0  0.0  0.0
SYMGRP
ENVEL   EKAP=-0.015
BZSMP   NKBAB=6 BZINT=LTM EMIN=-1.0 EMAX=1.5 NDOS=2500
        NORD=5 WIDTH=0.02 SAVDOS=F SAVCOOP=F SAVFERM=F SAVOPT=F
CHARGE  NETA=2 EETA=-3.0 -5.0 SAVRHO=F
CONTROL START= QUIT= FREE=F NITBND=99 CNVG=1.0D-08 CNVGET=1.0D-08
        NITATM=50 CNVGQA=1.0D-10
MIXING  NMIXB=5 BETAB=0.5 INCBB=T NMIXA=5 BETAA=0.5
SYMLIN  NPAN=5 NPTS=400 ORBWGT=T CARTE=F
        LABEL=W ENDPT= 0.500  0.250  0.750
        LABEL=L ENDPT= 0.500  0.500  0.500
        LABEL=g ENDPT= 0.000  0.000  0.000
        LABEL=X ENDPT= 0.500  0.000  0.500
        LABEL=W ENDPT= 0.500  0.250  0.750
        LABEL=K ENDPT= 0.375  0.375  0.750
PLOT    CARTV=T
        ORIGIN= 0.0  0.0  0.0
        RPLOT1= 1.0  0.0  0.0
        RPLOT2= 0.0  1.0  0.0
        RPLOT3= 0.0  0.0  1.0
        NPDIV1=50 NPDIV2=50 NPDIV3=00
```

It contains a lot more categories and tokens, all of which are discussed in detail in Chap. 4. Here we mention, in particular, the switch to scalar-relativistic calculations, REL=T, the types of orbitals used in the calculations as specified by the maximum angular momentum, LMXL=2, the principal quantum numbers of all orbitals CONF=4 4 3 4, and the respective orbital occupations QVAL=.... In case you are in doubt about the input for these three tokens just omit them. The program will add them for you. Moreover, we have specified the number of **k**-points to be used in the Brillouin zone integration by the token NKBAB=6, which gives the number of **k**-points per inverse Bohr radii along each of the translation vectors of the reciprocal unit cell (see Chap. 4). Finally, the categories SYMLIN and PLOT, respectively, hold information about the lines within the first Brillouin zone to be used for the band structure, and the region in real space used for plotting the crystal structure as well as the electron density and potential.

Note that all entries given in the standard CTRL file above, which go beyond those contained in the minimum CTRL file, reflect the default values. For this reason, they do not need to be specified at all. In this context, two tokens are very helpful. First, by setting HELP=T in category IO and running any of the many programs `mn*.run` (except for `mnmpr.run`) a file named HELP is created, which contains a short description of every token. At the same time, an extended copy of the CTRL file, which includes all possible tokens with their default values, is written to standard output. Alternatively, for HELP=F and VERBOS=40 (or a value greater than that) the program, besides executing its proposed task creates a file named CALL at the very end, which also contains an extended copy of the CTRL file.

2.1.2 Execution of the main programs

Once you have generated the CTRL file, the ASW program for self-consistent field calculations can be started by typing

```
mnscf.run
```

at the operating systems prompt. However, for Unix/Linux systems the distribution offers several useful shell scripts. Here, we just type

```
mnscf.x
```

at the systems prompt to start a job with the output sent to file *outscf*. The program will use about 13 iterations to full convergence. On a standard PC the total execution time will be about one second per interation. After completion, the output file *outscf* contains all the information collected during the iterations. In addition, a file named CU (the naming is due to the token ATOM= in categories CLASS and SITE) has been created, which contains all information specific to the respective atom. These data are needed by the program. For this reason, you should not delete an atomic file or change it by hand. Otherwise the program might have to start from scratch again. All main programs have a complex file checking routine included, which detects the status of all atomic files and after that decides about the action to be taken. In particular, this file check will stop execution in case you intend to start from scratch while converged atomic files are detected.

Once self-consistency has been achieved you are able to calculate the band structure by typing

```
mnbnd.run
```

or, better,

```
mnbnd.x
```

This program uses the information contained in the files CTRL and CU and generates a new file called BNDE, which comprises the eigenvalues for each **k**-point, hence, the band structure. Output is stored in file *outbnd*, calculation of the band structure will take about half a second.

In addition, after having changed SAVDOS=F to SAVDOS=T as well as QUIT= to QUIT=BND and running mnscf.run again, you will obtain a file DOS, which holds all information about the partial densities of states for plotting. The same can be achieved by invoking the shell script

```
mndos.x
```

which does the neccessary changes in the CTRL file (and resets to the original state at the end) and writes output to file *outdos*.

Furthermore, in case the tokens SAVCOOP=F and SAVFERM=F are included in category BZSMP, the same run creates the files COOP and FERM, which hold information about the chemical bonding indicators and the Fermi surface.

The total of the previous calculations can be made automatic by using the shell script mnall.x. On typing

```
mnall.x
```

this shell script performs a self-consistent calculation for NKBAB=6 (this must be set in the CTRL file), then switches to NKBAB=12, and then to NKBAB=18. For each of these **k**-point grids a self-consistent calculation is performed. Note that this saves a lot of execution time as compared to starting from scratch with a **k**-point density of 18. This is due to the “restart” facility of the ASW program mnscf.run. Whenever the file checker in the program detects atomic files, which conform with the general settings of the CTRL file as e.g. the lattice type or the number and types of orbitals, the program is able to use this information as a starting point for further calculations. In particular, once the calculations for NKBAB=6 have converged the subsequent calculation for NKBAB=12 starts from the converged files rather than starting from scratch. As a result, only few iterations will be needed for full convergence at the higher **k**-space grid. Such a stepwise increase of the Brillouin zone density serves the additional purpose that on comparing the results we are able to check convergence of the result with respect to the fineness of the **k**-point grid. The results of all these calculations are stored in the files *outlst6*, *outlst12*, and *outlst18*. Finally, the band structure, the (partial) densities of states, the bonding indicators, and possibly the Fermi surface are calculated.

In order to have a quick check of the progress of a self-consistent calculation just type

```
monic outlst6
```

which will extract the following lines from the output file *outlst6* and write them as a short summary to screen

```
ASW-2.6, program MNSCF started on asterix at Tue, 03 Feb 2009, 18:42:55.
Calculation converged after  13 iteration(s).
                        Start of Iteration   13
```

```
    47 irreducible k-points generated from    1000 ( 10, 10, 10).
           Fermi energy - MTZ =     0.686779 Ryd
 The system is a metal:
           DOS at Fermi energy:     3.862991 1/Ryd
           Gamma * (f.u./cell):     0.669252 mJ/(mole*K**2)
 Mean-square residual:                  0.375303D-24
 Total free atom energies     :  -3304.550572 Ryd
 Total variational energy     :  -3304.868759 Ryd
 Cohesive energy              :      0.318187 Ryd
  qdiff =       0.00000000  <        0.00000001
  ediff =       0.00000000  <        0.00000001
 ASW-2.6, program MNSCF ended on asterix at Tue, 03 Feb 2009, 18:43:07.
```

They include information about the **k**-space grid, the position of the Fermi energy, the DOS at E_F, the (variational) total energy, and the self-consistency level already reached as coded by the entries qdiff and ediff.

As a matter of fact the output files generated during the self-consistent field calculations, i.e. those created by program mnscf.run hold the information of all iterations and thus might be rather large. However, after successful convergence one is usually interested in keeping the results of only the last iteration. In order to remove the information of previous iterations from the output files, you may use the shell script o2log. Just type

o2log *outlst6*

to shrink the file. Alternatively, you may type

o2log all

which will affect all output files with names starting with *outlst*, *outblk*, and *outphn*.

2.1.3 Execution of the plot programs

By now, we are in a position to invoke the plotting routines. To start with, we want to display the crystal structure. This is most easily done by typing

plxcr.x STRX

at the systems prompt. This shell script just invokes XCrysDen, which is a public domain software for the visualization of crystal structures, electron densities, and Fermi surfaces written by T. Kokalj [405]. From within XCrysden the crystal structure visualization can be easily modified and then written to file. The result is shown in Fig. 2.1. While crystal structure visualization using XCrysDen is the best choice, you may alternatively use RasMol. They are invoked via the shell script plstr.x, which enters a self-explaining dialog and leads to a call of one of the above graphics tools.

In a next step, we turn to analyzing the electronic band structure. This is started by typing

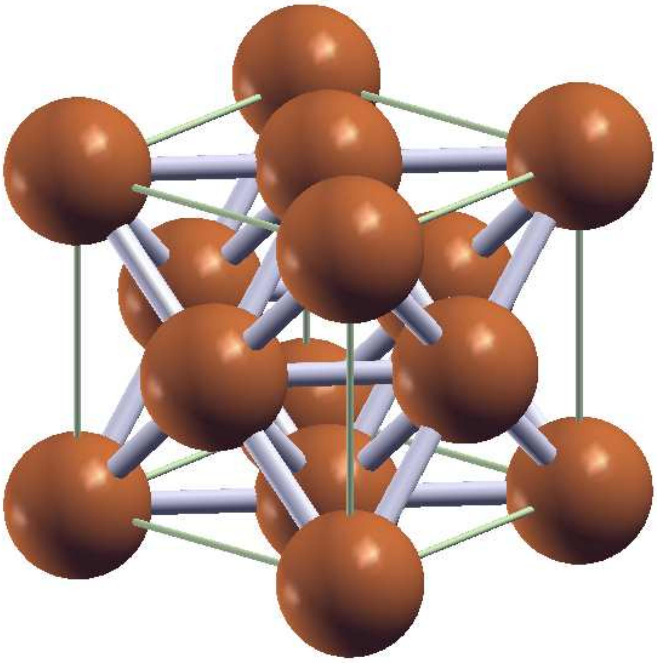

Figure 2.1 Crystal structure of Cu as generated by XCrysden [405].

```
plbnd.run
```

and entering the following dialog.

```
 ASW-2.6, program PLBND started on asterix at Wed, 04 Feb 2009, 10:29:25.

     Copyright (C) 1992-2009 Volker Eyert
     Please see file COPYRIGHT for details

 All input will be echoed to file PLIB.

 Enter terminal type:
 1 = X-Windows (default)
 2 = PC-Screen (vt220-emulation)
 3 = suppress terminal output
/
 Enter output device (default: 1):
 1 = Color postscript
 2 = Postscript
 3 = PDF (not yet supported)
 4 = JPEG (not yet supported)
```

```
 5 = LaTeX
 6 = LaTeX (special)
 7 = HP LaserJet III (PCL5)
 8 = PNG
 9 = GIF
10 = leave decision for later
11 = suppress output to file
/
 Portrait (P), landscape (L) or encapsulated postscript plot (E, default)?
/
 Enter title:
/

 Please wait a moment: I'm reading rest of file BNDE.
 Timing for   39 points out of  398:     0.00000 sec.

 Energies in Rydberg (F) or eV (T, default)?
/
 Energies relative to MTZ (0) or EFermi (F, default)?
/
 Energies connected by lines (T) (default F)?
/

 Ebot =    -9.737937 eV , Etop =    28.185740 eV  relative to EF
 Emin =   -10.000000 eV , Emax =     6.000000 eV  relative to EF
 Enter new Emin, Emax to change these defaults:
/
 task  1, total       :  cpu time:     0.04800 sec

 ASW-2.6, program PLBND ended on asterix at Wed, 04 Feb 2009, 10:29:25.

    Please delete files BNDE BNDV and bnd.ps bnd.tex when finished!!!
```

Here / entered on the programs prompt will keep the default values proposed by the program. All the questions are self-explaining. After this dialog, new files have been created, as there are BND.GNU, BND1, and BOX. By typing gnuplot BND.GNU you will invoke gnuplot and obtain the plot on screen. In addition, a postscript file *bnd.ps* is created, also containing the plot. For Cu the result is shown in Fig. 2.2. As we will discuss in more detail below, the band structure comprises a parabolic band starting at the Γ-point at about -9.74 eV and ending near the W-point at 6 eV. This s-like band hybridizes with the five d-bands, which are visible in the energy interval from -5.5 to -1.5 eV. Note the degeneracies of the d bands especially along the lines Γ-L and Γ-X.

Still the procedure can be simplified by calling the shell script plbnd.x rather than typing plbnd.run. This will run the plot program and invoke Gnuplot automatically. Moreover, the intermediate files BND.GNU, BND1 and BOX will be deleted by the shell script at the very end.

However, user-friendlyness goes even beyond. During execution the plot routine plbnd.run has echoed all your input to a new file called PLIB. By inspecting this file you will find a fully commented echo of all your input. Rename this file to e.g.

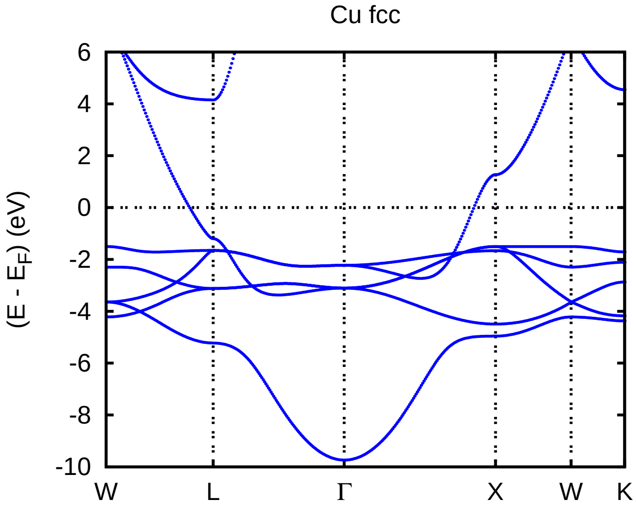

Figure 2.2 Electronic structure of Cu along selected symmetry lines of the first Brillouin zone of the face-centered cubic lattice, see B.1.

PLIBf, type plbnd.x PLIBf, and you obtain the same result as before without having to type anything else. This machinery could now be used to specify e.g. a different energy interval. Just edit file PLIBf and type plbnd.x PLIBf again. Yet, since file PLIB is just a simple echo, you should not change the order of the lines.

Next we are going to plot the partial densities of states. Now typing

```
pldos.x
```

you enter the following dialog.

```
 ASW-2.6, program PLDOS started on asterix at Wed, 04 Feb 2009, 09:52:07.

     Copyright (C) 1992-2009 Volker Eyert
     Please see file COPYRIGHT for details

 All input will be echoed to file PLID.

 Enter terminal type:
 1 = X-Windows (default)
 2 = PC-Screen (vt220-emulation)
 3 = suppress terminal output
/
 Enter output device (default: 1):
 1 = Color postscript
 2 = Postscript
 3 = PDF (not yet supported)
 4 = JPEG (not yet supported)
 5 = LaTeX
 6 = LaTeX (special)
```

```
 7 = HP LaserJet III (PCL5)
 8 = PNG
 9 = GIF
10 = leave decision for later
11 = suppress output to file
/
 Portrait (P), landscape (L) or encapsulated postscript plot (E, default)?
 Enter title:
/

 Please wait a moment: I'm reading rest of file DOS.

 Energies in Rydberg (F) or eV (T, default)?
/
 Energies relative to MTZ (0) or EFermi (F, default)?
/
 Energy axis to the top (F) or right (T, default)?
/
 Plot DOS (F, default) or integrated DOS (T)?
/

 Start setting up curve 1:
 Plot partial (F) or total DOS (T, default)?
F
 For partial DOS: Rotate reference frame for orbitals?
 Enter rotation symbol (Default: E):
/

 Enter orbital(s) to be included:

 Class CU    : atom   1 at      0.000000    0.000000    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
1/

 The following orbitals have been selected:
 Class CU    : atom    1, orbital s

 Enter scaling factor (default 1.0):
/

 Broadening of this curve (T) or not (F, default)?

 Select curve style (default: 1) (A * marks styles already selected):
solid/green      (1)   , dash1/blue       (2)   ,
dash2/red        (3)   , dot/magenta      (4)   ,
dashdot1/cyan    (5)   , dashdot2/yellow  (6)   ,
chaindash1/black (7)   , chaindash2/coral (8)   ,
chaindash3/gray  (9)   ,
/
```

```
 Enter curve label ("/" to suppress)
Cu 4s

 Please wait a moment: I'm working on this curve.
 Set up more curves (T)? Default is F.
T

 Start setting up curve 2:
 Plot partial (F) or total DOS (T, default)?
F
 For partial DOS: Rotate reference frame for orbitals?
 Enter rotation symbol (Default: E):
/

 Enter orbital(s) to be included:

 Class CU    : atom   1 at     0.000000    0.000000    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
-1/

 The following orbitals have been selected:
 Class CU    : atom    1, orbital y
 Class CU    : atom    1, orbital z
 Class CU    : atom    1, orbital x

 Enter scaling factor (default 1.0):
/

 Broadening of this curve (T) or not (F, default)?
/

 Select curve style (default: 2) (A * marks styles already selected):
solid/green      (1) * , dash1/blue       (2)   ,
dash2/red        (3)   , dot/magenta      (4)   ,
dashdot1/cyan    (5)   , dashdot2/yellow  (6)   ,
chaindash1/black (7)   , chaindash2/coral (8)   ,
chaindash3/gray  (9)   ,
/

 Enter curve label ("/" to suppress)
Cu 4p

 Please wait a moment: I'm working on this curve.
 Set up more curves (T)? Default is F.
T

 Start setting up curve 3:
 Plot partial (F) or total DOS (T, default)?
```

```
F
 For partial DOS: Rotate reference frame for orbitals?
 Enter rotation symbol (Default: E):
/

 Enter orbital(s) to be included:

 Class CU    : atom   1 at     0.000000    0.000000    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
5
6
8/

 The following orbitals have been selected:
 Class CU    : atom    1, orbital xy
 Class CU    : atom    1, orbital yz
 Class CU    : atom    1, orbital xz

 Enter scaling factor (default 1.0):
/

 Broadening of this curve (T) or not (F, default)?
/

 Select curve style (default: 3) (A * marks styles already selected):
solid/green      (1) * , dash1/blue       (2) * ,
dash2/red        (3)   , dot/magenta      (4)   ,
dashdot1/cyan    (5)   , dashdot2/yellow  (6)   ,
chaindash1/black (7)   , chaindash2/coral (8)   ,
chaindash3/gray  (9)   ,
/

 Enter curve label ("/" to suppress)
Cu 3d t_{2g}

 Please wait a moment: I'm working on this curve.
 Set up more curves (T)? Default is F.
T

 Start setting up curve 4:
 Plot partial (F) or total DOS (T, default)?
F
 For partial DOS: Rotate reference frame for orbitals?
 Enter rotation symbol (Default: E):
/

 Enter orbital(s) to be included:

 Class CU    : atom   1 at     0.000000    0.000000    0.000000
```

```
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
7
9/

 The following orbitals have been selected:
 Class CU    : atom    1, orbital 3z^2-r^2
 Class CU    : atom    1, orbital x^2-y^2

 Enter scaling factor (default 1.0):
/

 Broadening of this curve (T) or not (F, default)?
/

 Select curve style (default: 4) (A * marks styles already selected):
solid/green      (1) * , dash1/blue       (2) * ,
dash2/red        (3) * , dot/magenta      (4)   ,
dashdot1/cyan    (5)   , dashdot2/yellow  (6)   ,
chaindash1/black (7)   , chaindash2/coral (8)   ,
chaindash3/gray  (9)   ,
/

 Enter curve label ("/" to suppress)
3d e_g

 Please wait a moment: I'm working on this curve.
 Set up more curves (T)? Default is F.
/

 Center of gravity of DOS curve  1 (Spin 1) - EF :    0.4947 eV
 Center of gravity of DOS curve  2 (Spin 1) - EF :    1.9557 eV
 Center of gravity of DOS curve  3 (Spin 1) - EF :   -2.3726 eV
 Center of gravity of DOS curve  4 (Spin 1) - EF :   -2.5612 eV

 Indicate center of gravities (F, default)?
/

 Ebot =    -9.727926 eV , Etop =    11.129600 eV  relative to EF
 Emin =   -10.000000 eV , Emax =     6.000000 eV  relative to EF
 Enter new Emin, Emax to change the default:
/

 DOStop =     4.710970 1/eV
 DOSmax =     5.000000 1/eV
 Enter new DOSmax to change this default:
/
 Enter energetic position of curve labels ("/" to use default):
-4
 task  1, total       :  cpu time:     0.03600 sec
```

```
 ASW-2.6, program PLDOS ended on asterix at Wed, 04 Feb 2009, 09:52:07.

    Please delete files DOS and dos.ps when finished!!!
```

This dialog is much more complex than the one before, since we generated four curves and deviated from the default settings. The resulting plot is shown in Fig. 2.3, where we identify the partial DOS corresponding to the Cu 4s, 4p, and 3d orbitals. The latter have been split into their t_{2g} and e_g components as resulting from the cubic crystal field splitting. In particular, we observe rather small 4s and 4p contributions in the whole energy range. They grow out of the aforementioned parabolic-like band, which leads, in particular, to the square-root behaviour of the 4s partial DOS at low energies. At higher energies, the 3d states set in, which are limited to the energy interval between −5.5 and −1.5 eV but give large contributions.

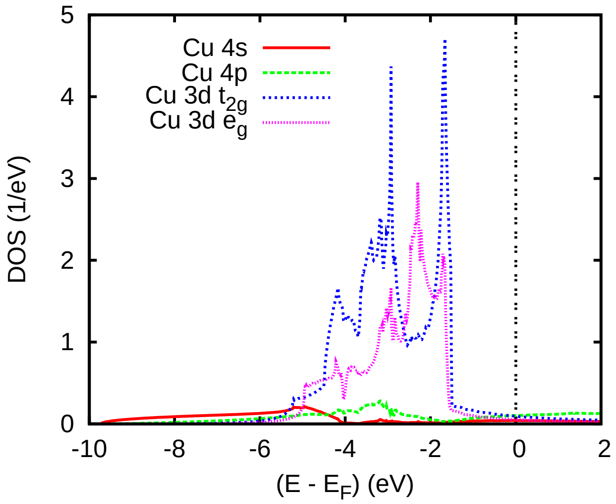

Figure 2.3 Partial densities of states of Cu.

As for the band structure an echo file has been created, which is called PLID. Rename this file to e.g. PLIDf and type `pldos.x` PLIDf in order to reproduce the plot. Of course, this plot routine could be also called without using the shell script, in which case we would have to type `pldos.run` < PLIDf at the systems prompt. Note the Unix/Linux < here, which is already included in the shell script.

2.1.4 Advanced features

So far, we were able to decompose the total DOS into partial densities of states and were thus able to identify orbital contributions in certain energy intervals. However, a corresponding analysis at a **k**-point level would be welcome. Such a tools exists in the ASW program package. In order to use it we enter the CTRL file and change in category SYMLIN the token NPTS=400 to NPTS=200 and ORBWGT=F to ORBWGT=T. It is suggested to first copy the files CTRL and CU to a separate directory and do the changes of the CTRL file there. After having changed the CTRL file as described type mnbnd.x. As before this will produce a file BNDE. In addition, a file named BNDV is generated, which contains all the eigenvectors.

Next you invoke again the plotting shell script plbnd.x and enter the following dialog.

```
 ASW-2.6, program PLBND started on asterix at Wed, 04 Feb 2009, 10:16:03.

     Copyright (C) 1992-2009 Volker Eyert
     Please see file COPYRIGHT for details

 All input will be echoed to file PLIB.

 Enter terminal type:
 1 = X-Windows (default)
 2 = PC-Screen (vt220-emulation)
 3 = suppress terminal output
/
 Enter output device (default: 1):
 1 = Color postscript
 2 = Postscript
 3 = PDF (not yet supported)
 4 = JPEG (not yet supported)
 5 = LaTeX
 6 = LaTeX (special)
 7 = HP LaserJet III (PCL5)
 8 = PNG
 9 = GIF
10 = leave decision for later
11 = suppress output to file
6
 Portrait (P, default) or landscape plot (L)?
/
 Enter title:
&, weighted $ 4s $

 Please wait a moment: I'm reading rest of file BNDE.
 Timing for   39 points out of  398:     0.00000 sec.

 Energies in Rydberg (F) or eV (T, default)?
/
 Energies relative to MTZ (0) or EFermi (F, default)?
/
 Energies connected by lines (T) (default F)?
```

```
/
 Plot orbital character (default F)?
T
 For plotting orbital character: Rotate reference frame for orbitals?
 Enter rotation symbol (E for unity):
/

 Enter orbital(s) to be included:

 Class CU    : atom   1 at     0.000000    0.000000    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2
1

 The following orbitals have been selected:
 Class CU    : atom    1, orbital s

 Ebot =    -9.737937 eV , Etop =    28.185740 eV  relative to EF
 Emin =   -10.000000 eV , Emax =     6.000000 eV  relative to EF
 Enter new Emin, Emax to change these defaults:
/
 Rescale orbital weights (default:   0.4000eV )?
/

 Please wait a moment: I'm working on the weights.
 Timing for   39 points out of  398:     0.00400 sec.

 Enter the horizontal and vertical extension in mm.
 Default: 100.0 x  90.0
/
 task  1, total       :  cpu time:     0.23201 sec

 ASW-2.6, program PLBND ended on asterix at Wed, 04 Feb 2009, 10:16:04.

    Please delete files BNDE BNDV and bnd.tex when finished!!!
```

It differs from the above dialog by asking for

```
Plot orbital character (default f)?
```

and the particular orbital(s) to be included. This section is similar to the plotting of the partial DOS above. The previous dialog will produce a file *bnd.tex*, which can be converted into *bnd.ps* by typing plbnd.lx at the system prompt. The result is shown in Fig. 2.4. In a similar way, orbital weighted band structures for the $4p$, $3dt_{2g}$, and $3de_g$ states can be obtained. They are shown in Figs. 2.5, 2.6, and 2.7. In all these figures we recognize the same band structure as already given in Fig. 2.2. Yet, in Figs. 2.4 to 2.7 to each band at each **k**-point has been appended a bar. The length of each bar is a measure of the contribution of a particular orbital to the respective wavefunction. To be specific, we identify large $4s$ and $4p$ contributions at the bottom as well as at the high energy branches of the parabola starting at

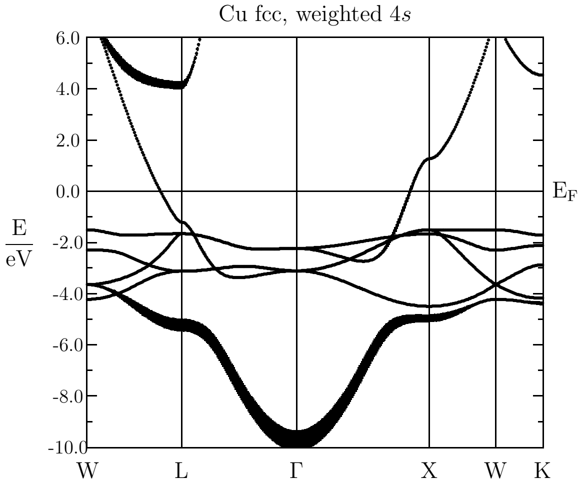

Figure 2.4 Weighted electronic structure of Cu. The width of the bars given for each band indicates the contribution due to the 4s orbital.

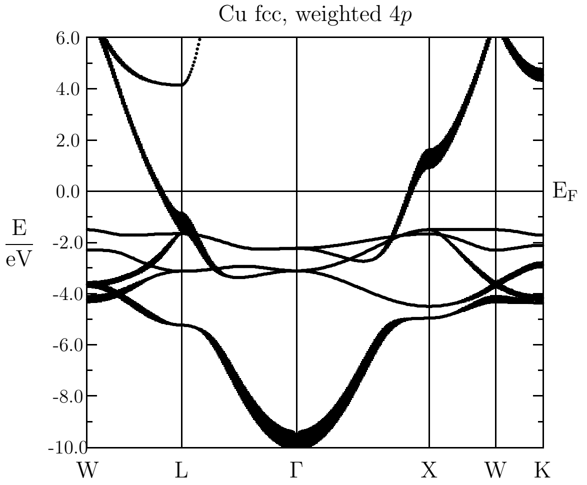

Figure 2.5 Weighted electronic structure of Cu. The width of the bars given for each band indicates the contribution due to the 4p orbitals.

-9.74 eV. In contrast the 3d orbitals dominate in the energy interval from -5.5 to -1.5 eV. These observations thus confirm our arguments put forward in the above discussion of the bare band structure and the partial densities of states. Actually, these orbital weighted band structures are a necessary prerequisite for a complete understanding of the electronic structure. Yet, only few band structure packages offer this analytical tool.

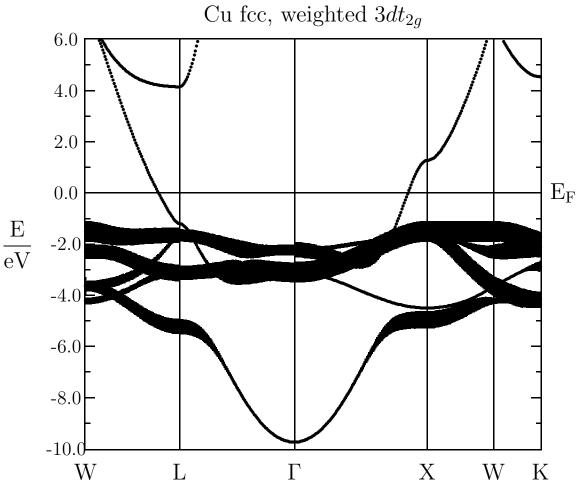

Figure 2.6 Weighted electronic structure of Cu. The width of the bars given for each band indicates the contribution due to the $3dt_{2g}$ orbitals.

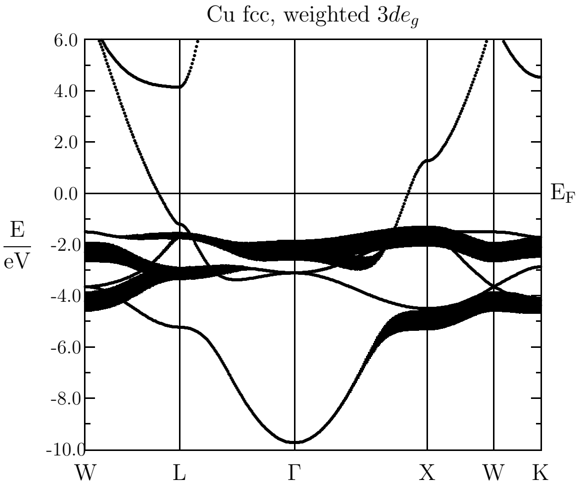

Figure 2.7 Weighted electronic structure of Cu. The width of the bars given for each band indicates the contribution due to the $3de_g$ orbital.

2.1.5 Crystal orbital overlap population

Another feature, which is not standard in modern band structure codes, is the implementation of the crystal orbital overlap populations (COOP). The COOP as originally proposed by Hoffmann allows for an analysis of the chemical bonding [161]. Evaluation of the COOP has been recently implemented in the ASW method [407] (see also Refs. [108]) and was successfully applied to the interpretation of bonding properties of various compounds [108]. In addition to the COOP, Dronskowski and Blöchl proposed the so-called crystal overlap Hamiltonian population (COHP) [95]. More recently, Fähnle and coworkers developed another extension of the COOP, the so-called covalence energy [56], which combines the COOP and the COHP. All three types of binding indicators have been implemented in the ASW package. The calculated covalence energy for Cu is shown in Fig. 2.8. There we observe three curves, which are energy resolved measures of the chemical bonding between the respective orbitals. Negative and positive contributions indicate bonding and antibonding states, respectively. While the $4sp$–$4sp$ bonding is almost negligible, the bonding between $4sp$ and $3d$ states as well as the $3d$–$3d$ bonding is clearly visible. Both are bonding below -2.2 eV and antibonding above. Since the $3d$–$3d$ antibonding behaviour dominates we can conclude that the metallic bonding, hence, crystal stability is carried to a large part by the $4sp$–$3d$ bonding.

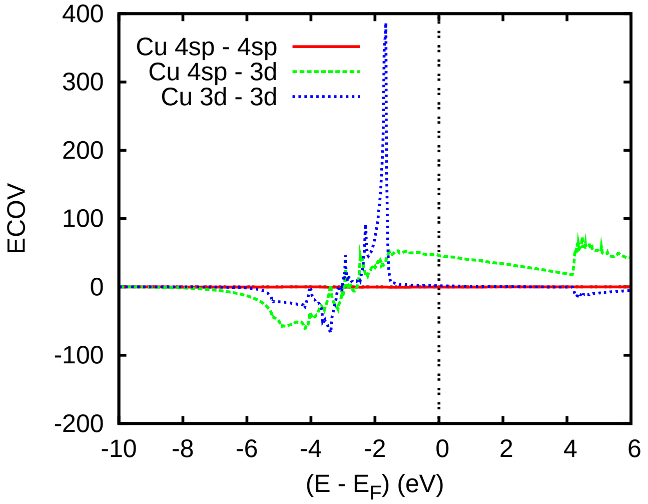

Figure 2.8 Partial covalence energies (E_{cov}) of Cu.

Calculation of the crystal orbital overlap population or else, the covalence energy, is done in the same step as the calculation of the partial DOS. In order to obtain these curves, you have to specify the respective orbitals in the CTRL file. Just add in category CLASS the token COORB=, followed by the angular momenta of the orbitals, you want to be considered. In the present case we have added COORB=0 1 2. Furthermore, we inserted the entry SAVCOOP=F in category BZSMP. Calculation is then invoked by typing `mndos.x` at the systems prompt. Within this shell script the setting SAVCOOP=F is automatically changed. Alternatively, you could specify the tokens COORB= at the very beginning before the self-consistent calculations start and then invoke the shell script `mnall.x`, which likewise includes calculation of the COOP. It generates a new file named COOP. In order to plot the results just type

```
plcop.x
```

and answer the prompts of the program in close accordance with those required by the plotting routine for the DOS. However, note that for each curve a pair of orbitals is required.

2.1.6 Fermi surface

Next we return to the discussion at the beginning of this section and aim at plotting the Fermi surface. This is achieved by invoking the shell script

```
plfrm.x
```

which immediately calls the XCrysDen visualization software mentioned already above. Within XCrysDen different selections can be made and the result stored in several data formats. For the present case the resulting Fermi surface is displayed in Fig. 2.9. According to analysis of the partial densities of states as given in Fig. 2.3 the Fermi surface comprises contributions from the $4s$, $4p$, and $3d$ orbitals.

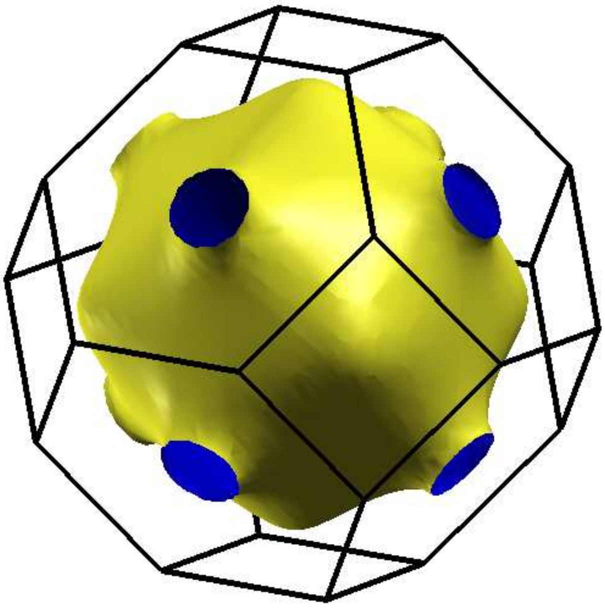

Figure 2.9 Fermi surface of Cu.

Just for completeness and as a demonstration of the generally very good agreement of theory and experiment, we display in Fig. 2.10 the Fermi surface of Cu as

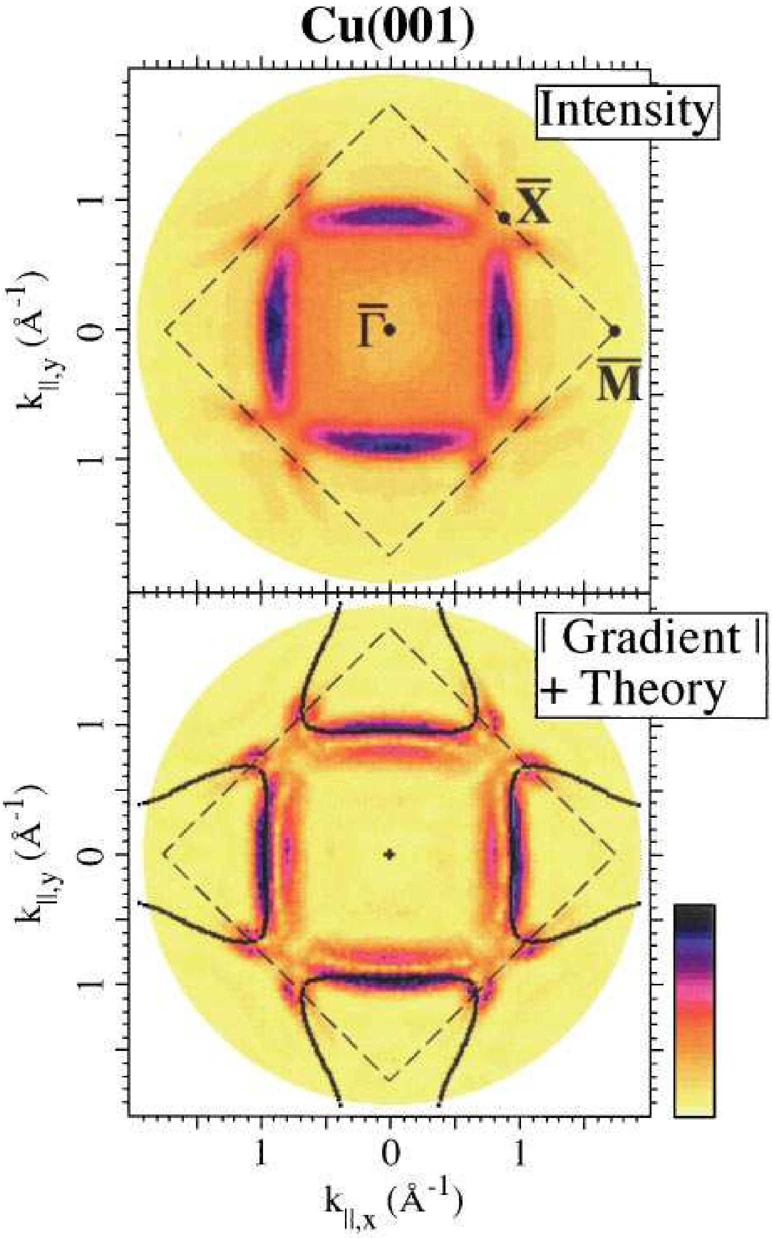

Figure 2.10 Measured and calculated Fermi surfaces of Cu [408].

measured by photoelectron spectroscopy and calculated by an elder version of the ASW method [408].

2.1.7 Electron density and effective potential

The electron densities and the effective potential are calculated by changing SAVRHO=F to SAVRHO=T in category CHARGE as well as setting START=ATM and QUIT=RHO in category CONTROL. Invoking then the program `mnscf.run` will generate a file RHO, which holds both the electron densities (core and valence) and the effective potential. As before, the procedure can be simplified by using a shell script. To be specific, just type

```
mnrho.x
```

which will do all the necessary changes of the CTRL file and run the main program `mnscf.run`.

Plotting the electron density and the effective potential is done by typing

```
plrho.x
```

which leads to the following dialog.

```
 ASW-2.6, program PLRHO started on asterix at Wed, 04 Feb 2009, 11:11:05.

     Copyright (C) 1992-2009 Volker Eyert
     Please see file COPYRIGHT for details

 All input will be echoed to file PLIR.

 Input data files available for plotting: RHO FREE
 Please select (default RHO):
/

 Enter terminal type:
 1 = X-Windows (default)
 2 = PC-Screen (vt220-emulation)
 3 = suppress terminal output
/
 Enter output device (default: 1):
 1 = Color postscript
 2 = Postscript
 3 = PDF (not yet supported)
 4 = JPEG (not yet supported)
 5 = LaTeX
 6 = HP LaserJet III (PCL5)
 7 = PNG
 8 = GIF
 9 = leave decision for later
10 = suppress output to file
/
```

```
 Portrait (P), landscape (L) or encapsulated postscript plot (E, default)?
/
 Enter title:


 Please wait a moment: I’m reading rest of file RHO    .

 Plot density (R, default), neg. Laplacian (L), or potential (V)?
/
 Plot total (0), valence (1, default) or core (2) density?
1

 The plot region is a plane.
 Draw a 3D-surface (T, default) or not (F)?
/
 Enter number of contour lines (default 30):
/

 Please wait a moment: I’m working on the plot.

 The following files can be used for difference plot:
  FREE
 Please select (blank to skip, default):
/

 Difference plot not selected

 rbot =        0.022177 a.u., rtop =       10.989643 a.u.
 rmin =        0.000000 a.u., rmax =       11.400000 a.u.
 Enter new rmin, rmax to change these defaults:
0.0
0.1
 Enter scaling factor (default:   1.0000):
/
 task  1, total       :  cpu time:     0.06800 sec

 ASW-2.6, program PLRHO ended on asterix at Wed, 04 Feb 2009, 11:11:05.

    Please delete files RHO and rho.ps when finished!!!
```

In the present case, it generates the valence electron density on one of the cubic faces as displayed in Fig. 2.11. An interesting alternative arises from the possibility to generate difference electron densities. This is achieved by calling mnrho.x before the self-consistent calculations have started. In this case, a file named FREE is generated, which holds the electron densities and effective potential as arising from overlapping free atoms. The plot routine plrho.run is able to detect both the FREE file and the RHO file and to generate the difference between the overlapping free atoms density and the self-consistent electron density. The result of this procedure is displayed in Fig. 2.12 for the valence electrons.

Finally, we call the plotting shell script plrho.x again and generate the effective potential, which is shown in Fig. 2.13.

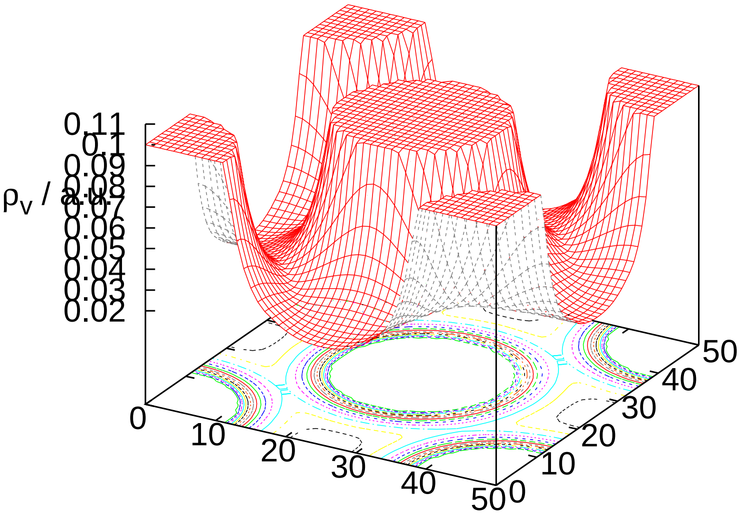

Figure 2.11 Valence electron density of Cu.

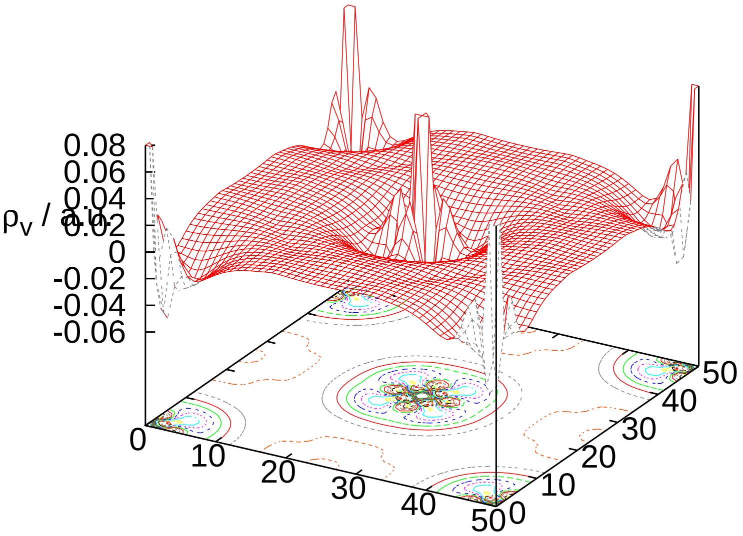

Figure 2.12 Valence electron density difference of Cu.

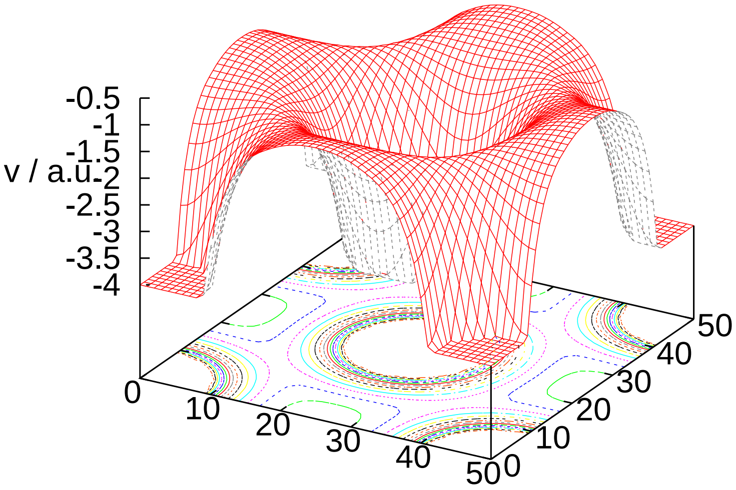

Figure 2.13 Effective potential of Cu.

2.1.8 Bulk modulus

In closing this section we turn to the calculation of the bulk modulus. It is based on a number of self-consistent calculations for different lattice constants. Again this procedure can be made automatic with the help of the shell script `mnblk.x` coming with the ASW distribution. This shell script deletes the atomic files and runs a self-consistent calculation. This process is then repeated for a number of lattice constants by using the shell script `upctr` and changing the token ALAT=. However, note that this shell script has to be adapted to the the actual situation by specifying the correct atomic files to be deleted before each single calculation and setting the relevant lattice constants. Once the shell script has been edited and saved just type

```
mnblk.x
```

After all calculations have finished call the shell script `prblk`, which will extract the cell volumes and total energies from all the output files and write them to a small file called BLK. This file in turn is used by the plotting routine called by the command

```
plblk.x
```

which enters the following simple dialog.

```
 ASW-2.6, program PLBLK started on asterix at Wed, 04 Feb 2009, 12:23:18.

       Copyright (C) 1992-2009 Volker Eyert
       Please see file COPYRIGHT for details

 All input will be echoed to file PLIK.
```

```
 Enter terminal type:
 1 = X-Windows (default)
 2 = PC-Screen (vt220-emulation)
 3 = suppress terminal output
/
 Enter output device (default: 1):
 1 = Color postscript
 2 = Postscript
 3 = PDF (not yet supported)
 4 = JPEG (not yet supported)
 5 = LaTeX
 6 = HP LaserJet III (PCL5)
 7 = PNG
 8 = GIF
 9 = leave decision for later
10 = suppress output to file
/
 Portrait (P), landscape (L) or encapsulated postscript plot (E, default)?
/
 Enter title:

 Energies in Rydberg (F, default) or eV (T)?
/
 Energies relative to the minimum energy (T)? Default is F.
/
 Plot energies vs. volume (F, default) or Wigner-Seitz radius (T)?
/
 Print fit parameters in the plot (T, default)?
/
 Enter relative print position of the parameters ("/" to use default):
/

 Results from parabolic fit:
 Equilibrium WS radius:        2.655461 Bohr radii
 Equilibrium volume:          78.434686 (Bohr radii)**3
 Minimum total energy:     -3304.868543 Ryd
 Bulk modulus:               170.991444 GPa

 Results from 3rd-order Birch-Murnaghan fit:
 Equilibrium WS radius:        2.655044 Bohr radii
 Equilibrium volume:          78.397740 (Bohr radii)**3
 Minimum total energy:     -3304.868540 Ryd
 Bulk modulus:               162.684188 GPa
 Bulk modulus derivative:      6.800347
 task  1, total       :  cpu time:     0.02000 sec

 ASW-2.6, program PLBLK ended on asterix at Wed, 04 Feb 2009, 12:23:18.

    Please delete files BLK and blk.ps when finished!!!
```

The plotting routine performs two different fits to the calculated data, namely, a simple parabolic fit and a third-order Birch-Murnaghan fit [46, 269, 270]. Details can also be found in my book [404]. The results of both fits are printed in the above dialog. In addition, if this has been chosen, they are also displayed in the resulting plot, which is displayed in Fig. 2.14.

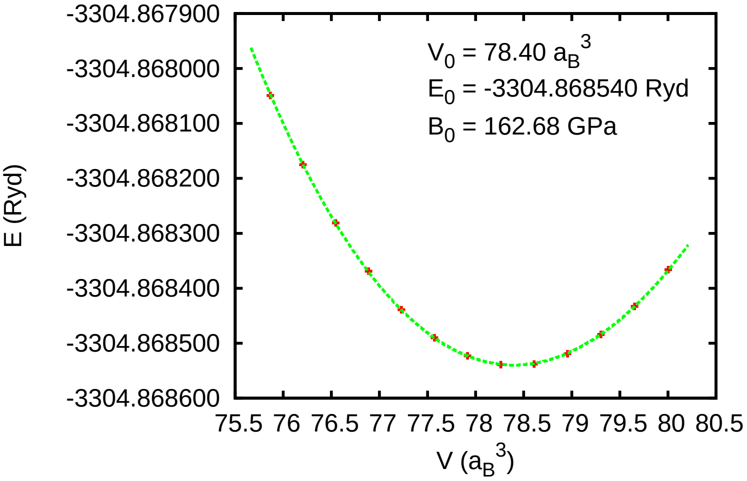

Figure 2.14 Bulk modulus of Cu.

2.2 A semiconductor: Si

Another prominent test case for electronic structure methods and codes is elemental silicon. As well known, silicon is a semiconductor with an indirect optical bandgap of about 1.1 eV, which crystallizes in the diamond structure shown in Fig. 2.15. Of course, interest in this material stems from its huge impact on semiconductor applications during the last decades. Yet, being an elemental system it represents a sufficiently simple test case.

The electronic structure of silicon is dominated by the $3s$ and $3p$ valence states, which also give the largest contributions at the valence band maximum and the conduction band minimum. As compared to the elemental metals, calculations for silicon are confronted with two major challenges. First, the correct representation of the wave function, the electron density and the effective potential within the open diamond crystal structure requires new means. This is due to the fact that such open structures can only be badly filled with the atomic spheres surrounding each atom. Instead, rather large voids remain. However, the above quantities have to be also well respresented within these voids. In a plane wave representation, this is done by introducing a uniform mesh in the unit cell. In contrast, in a method based on

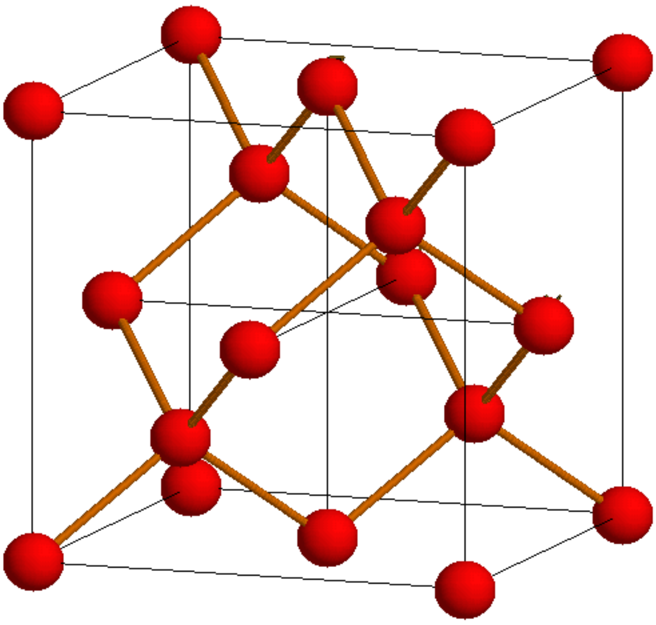

Figure 2.15 Diamond structure of Si.

spherical waves we have to place additional spherical waves in these voids, which are then called interstitial sites. As for the „real“ atoms, these sites are surrounded by atomic spheres. Outside these spheres, Schrödinger's equation for the basis functions is solved analytically, while inside we use a numerical solution, which is augmented to the Hankel and Bessel functions outside. Hence, the setup of the basis functions centered at the interstitial sites is done in complete analogy with the construction at the atomic sites. However, since there are no nuclei located at the interstitial sites, the surrounding spheres are usually called empty spheres, a somewhat misleading terminology. Nevertheless, their placement requires an additional step in the course of the calculations.

The second challenge is much harder to deal with. It is posed by the approximate treatment of the exchange-correlation potential and energy density within the standard local density approximation, which adopts the description of the homogeneous electron gas. As a consequence, while being rather well suited for metals it gives only a limited account of semiconductors and insulators the most obvious signature of the failure being a drastic underestimate of the optical band gap. Even within the generalized gradient approximation the situation is not considerably improved.

Instead, more involved techniques as, e.g. the exact treatment of the exchange interaction are called for, which, however, are very sophisitcaed and not yet implemented in the ASW method.

As in the previous section, our discussion will proceed in several steps. Yet, as just outlined, setup of the CTRL file is more involved due to the inclusion of the empty spheres. Once this has been achieved, the self-consistent calculations are performed and followed by the evaluation of the band structure and partial DOS. In addition, we aim at the optical properties and at calculating phonon frequencies. In doing so, we will also introduce additional plot routines for the visualization.

In order to prepare for the calculations, we start again creating a directory, where all the files should be stored, by typing

```
mkdir si
cd si
mkdir pac
mkdir nm
mkdir nm_phn
cd pac
```

at the operating systems prompt. This creates a directory named `si` with three subdirectories named `pac`, `nm`, and `nm_phn`. Special attention deserves the directory `pac`, to which we turn first.

2.2.1 CTRL file and sphere packing

As well known, the diamond structure shown in Fig. 2.15 is based on a face-centeredcubic lattice with tetrahedrally coordinated atoms located at the positions $(0, 0, 0)$ and $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. This information is reflected by the following CTRL file.

```
HEADER  Si fcc
VERSION ASW-2.6
IO      HELP=F SHOW=T VERBOS=30 CLEAN=T
OPTIONS REL=T OVLCHK=T
STRUC   ALAT=10.2625 CNTR=F
CLASS   ATOM=SI Z=14
SITE    CARTP=T
        ATOM=SI POS= 0.00  0.00  0.00
        ATOM=SI POS= 0.25  0.25  0.25
SYMGRP
ENVEL   EKAP=-0.015
BZSMP   NKBAB=6 BZINT=LTM EMIN=-1.0 EMAX=1.5 NDOS=2500
        NORD=3 WIDTH=0.015 EFTOL=1.0D-04 SAVDOS=F SAVCOOP=F SAVOPT=F
CHARGE  NETA=2 EETA=-3.0 -5.0 SAVRHO=F
CONTROL START= QUIT= FREE=F NITBND=99 CNVG=1.0D-08 CNVGET=1.0D-08
        NITATM=50 CNVGQA=1.0D-10
MIXING  NMIXB=5 BETAB=0.5 INCBB=T NMIXA=5 BETAA=0.5
SYMLIN  NPAN=5 NPTS=400 ORBWGT=F CARTE=F
        LABEL=W ENDPT= 0.500  0.250  0.750
```

```
        LABEL=L ENDPT= 0.500  0.500  0.500
        LABEL=g ENDPT= 0.000  0.000  0.000
        LABEL=X ENDPT= 0.500  0.000  0.500
        LABEL=W ENDPT= 0.500  0.250  0.750
        LABEL=K ENDPT= 0.375  0.375  0.750
PLOT    CARTV=T
        ORIGIN=-0.25 -0.25 -0.25
        RPLOT1= 0.75  0.75  0.00
        RPLOT2= 0.00  0.00  0.75
        RPLOT3= 0.75 -0.75  0.00
        NPDIV1=50 NPDIV2=50 NPDIV3=0
```

Apart from the structural information this CTRL file is very similar to that of Cu as discussed before and thus will not have to be explained in detail. Instead, we refer the reader to Chap. 4 for a full description of the input data entering the CTRL file.

As discussed above, the open diamond structure requires special care as concerns the correct representation of the wave function, the electron density, and the effective potential. This is due to the fact that the construction of the basis functions is still based on the atomic sphere approximation (ASA), where all space is completely filled by (necessarily overlapping) atomic spheres. Of course, for open structures this would lead to too large overlap regions. We recall that the ASA as introduced by Andersen was meant as an approximation to the full crystal potential, which could be well modeled by slightly overlapping potential wells. The validity of this approach has been checked in a lot of cases. However, for open crystal structures the overlap becomes to large and, hence, the approximation to crude. As already outlined above, these problems are solved by inserting so-called empty spheres into the unit cell. Inside these empty spheres, the electronic density and potential can vary and, hence, help modeling the total potential in a much improved way.

In the present situation, displaying the electron density can be rather helpful. As already seen in Sec. 2.1, the electron density is calculated on typing

```
mnrho.x
```

which will do all the necessary changes of the CTRL file and run the main program `mnscf.run` to calculate the densities and potential and store them in files RHO and FREE. Here, we concentrate on the latter, which holds the densities and potential for overlapping free atoms. To be specific, the densities and the potential are constructed by superposing those of free atoms located at the respective crystallographic sites.

As also outlined in Sec. 2.1, the electron densities and the effective potential can be plotted on invoking the corresponding plot routine via

```
plrho.x
```

This generates a plot in the plot space specified by the tokens ORIGIN=, RPLOT1=, RPLOT2=, and RPLOT3=. For the present example, the results are shown in Figs. 2.16 and 2.17 for the valence electron density and the potential, respectively.

As has been argued by Mattheiss, the potential arising from overlapping free atoms resembles the final full crystal potential very much [248]. Hence, it can be

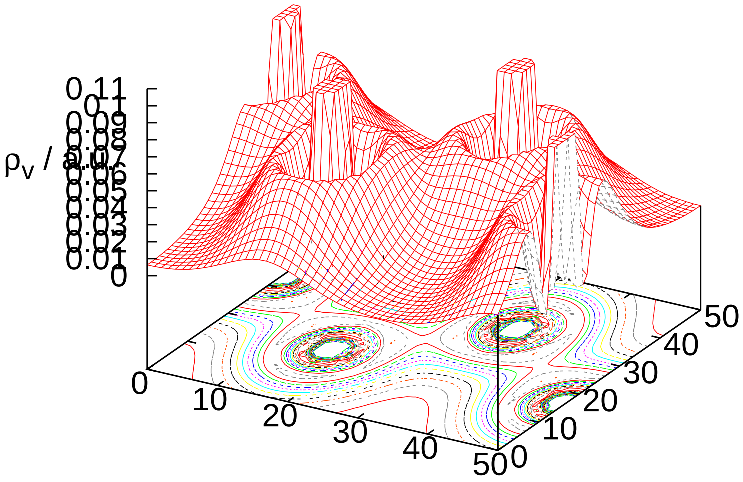

Figure 2.16 Overlapping free atom valence electron density of Si.

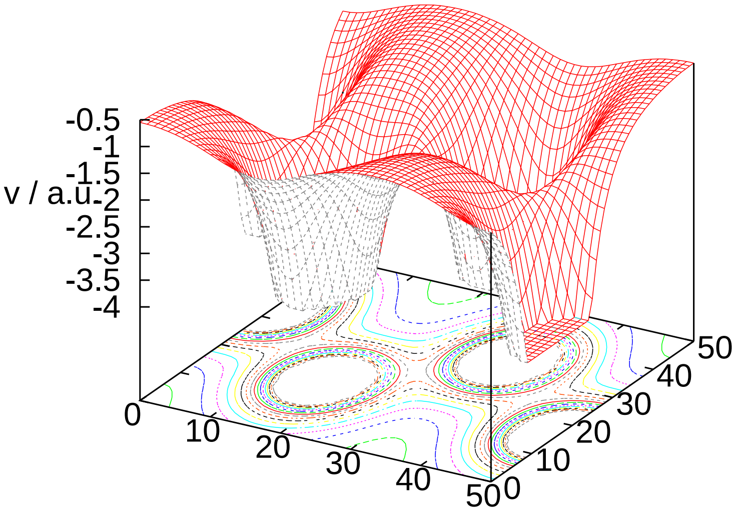

Figure 2.17 Overlapping free atom potential of Si.

well used to locate the position of possible empty spheres and to determine the radii of all spheres. All this is automatically performed in another main program, namely, `mnpac.run`, which is started by typing

```
mnpac.x
```

at the systems prompt. This routine runs the so-called sphere geometry optimization (SGO) algorithm, which consists of several steps. At the very beginning, it scans the overlapping free atom potential along lines connecting the atoms and finds optimal muffin-tin radii, i.e. radii for non-overlapping spheres. These are taken as a guidline for the atomic sphere radii. After that, it starts a search through the unit cell and identifies that position, where the largest possible empty sphere could be placed. Actually, this is done by a genetic algorithm, which is a highly sophisticated method for multi-dimensional optimization [133]. Having found such an empty sphere candidate, the radii of all spheres, including the "physical" spheres and all empty spheres found so far, are blown up until an acceptable overlap is reached. With the resulting atomic sphere radii the overall space filling is checked, and if this is not yet complete, the process is repeated by searching for addtional empty spheres until the ASA condition is obeyed.

After having performed all these steps, the program mnpac.run writes a new version of the CTRL file to file CNEW, which contains all the empty sphere positions as well as atomic sphere radii of all atoms. Recall that the programs never write to file CTRL! Finally, mnpac.run proposes the number of partial waves for the empty spheres. They are included by the tokens LMXL= and CONF=. Of course, the corresponding charges as given by token QVAL= are all zero. The file CNEW looks as follows.

```
HEADER  Si fcc
VERSION ASW-2.6
IO      HELP=F SHOW=T VERBOS=30 CLEAN=T
OPTIONS REL=T OVLCHK=T
STRUC   ALAT=10.2625 CNTR=F
CLASS   ATOM=SI Z=14 R=2.47161370 LMXL=2 CONF=3 3 3 4
                QVAL= 2.0  2.0  0.0  0.0
        ATOM=E1 Z= 0 R=2.57907386 LMXL=2 CONF=1 2 3 4
                QVAL= 0.0  0.0  0.0  0.0
SITE    CARTP=T
        ATOM=SI POS= 0.00  0.00  0.00
        ATOM=SI POS= 0.25  0.25  0.25
        ATOM=E1 POS=-0.25 -0.25 -0.25
        ATOM=E1 POS= 0.00  0.00  0.50
SYMGRP
ENVEL   EKAP=-0.015
BZSMP   NKBAB=6 BZINT=LTM EMIN=-1.0 EMAX=1.5 NDOS=2500
        NORD=3 WIDTH=0.015 SAVDOS=F SAVCOOP=F SAVOPT=F
CHARGE  NETA=2 EETA=-3.0 -5.0 SAVRHO=F
CONTROL START= QUIT= FREE=F NITBND=99 CNVG=1.0D-08 CNVGET=1.0D-08
        NITATM=50 CNVGQA=1.0D-10
MIXING  NMIXB=5 BETAB=0.5 INCBB=T NMIXA=5 BETAA=0.5
SYMLIN  NPAN=5 NPTS=400 ORBWGT=F CARTE=F
        LABEL=W ENDPT= 0.500  0.250  0.750
        LABEL=L ENDPT= 0.500  0.500  0.500
        LABEL=g ENDPT= 0.000  0.000  0.000
        LABEL=X ENDPT= 0.500  0.000  0.500
        LABEL=W ENDPT= 0.500  0.250  0.750
        LABEL=K ENDPT= 0.375  0.375  0.750
PLOT    CARTV=T
```

```
ORIGIN=-0.25 -0.25 -0.25
RPLOT1= 0.75  0.75  0.00
RPLOT2= 0.00  0.00  0.75
RPLOT3= 0.75 -0.75  0.00
NPDIV1=50 NPDIV2=50 NPDIV3=0
```

Obviously, two empty spheres have been added with radii slighty larger than those of the „physical“ spheres. This is due to the fact that empty spheres are allowed to have a slighty larger overlap than the „physical“ spheres as the potential within these spheres is rather flat.

All actions taken by the packing program mnpac.run are recorded in the output file *outpac*, which among other things contains the results of a final overlap check for OVLCHK=T. There the overlap limits are repeated (as a default a linear overlap of 15% is used) and all lines with a linear overlap larger than 10% complemented by one or more exclamation marks. Note that an extra overlap bonus is given to the empty spheres due to the flatness of the potential within these spheres.

2.2.2 Execution of the main programs

With the new CTRL file at hand we are able to perform the set of self-consistent calculations. To this end we copy the CNEW file generated in the subdirectory pac to the CTRL file of subdirectory nm and start the calculations by typing

```
mnscf.x
```

or else

```
mnall.x
```

in case we want to all calculations in one go. After about two minutes the calculations have finished. A first impression of the outcome can be gained via the command

```
monic outlst18
```

which generates the following summary of the output file *outlst18*.

```
ASW-2.6, program MNSCF started on asterix at Wed, 04 Feb 2009, 15:49:59.
Calculation converged after   7 iteration(s).
                     Start of Iteration    7
   220 irreducible k-points generated from    6859 ( 19, 19, 19).
          Fermi energy - MTZ =     0.707668 Ryd.
The system is a semiconductor:
           Indirect band gap =     0.040429 Ryd =     0.550058 eV
Mean-square residual:                  0.122585D-23
Total free atom energies     :  -1155.304982 Ryd
Total variational energy     :  -1156.092086 Ryd
Cohesive energy              :      0.787104 Ryd
 qdiff =       0.00000000  <        0.00000001
 ediff =       0.00000000  <        0.00000001
```

```
ASW-2.6, program MNSCF ended on asterix at Wed, 04 Feb 2009, 15:50:35.
```

According to this summary, silicon is correctly identified as a semiconductor with an indirect optical band gap. However, the band gap is by a factor of two to small, which, as mentioned above, is usual for calculations based on the local density approximation. The evaluation of the band gap results from a rather simple procedure. During the Brillouin zone scan the minimum and maximum energy of each band are calculated together with the corresponding **k**-points. From this the size of the bandgap as well as valence band maximum and conduction band minimum for semiconductors are calculated. Moreover, the Fermi energy is fixed to the midpoint of the gap. Finally, all this information is written to the atomic files and to files BNDE, DOS and COOP.

2.2.3 Execution of the plot programs

By now, we are in a position to invoke the plotting routines. As before, an image of the crystal structure is obtained by either typing

plxcr.x STRX

at the systems prompt and entering XCrysDen or else via

plstr.x

and going through the subsequent dialog, which leads to the visualization tools RasMol.

```
 ASW-2.6, program PLSTR started on asterix at Sun, 08 Feb 2009, 14:33:46.

     Copyright (C) 1992-2009 Volker Eyert
     Please see file COPYRIGHT for details

 All input will be echoed to file PLIS.

 Enter terminal type:
 1 = X-Windows (default)
 2 = PC-Screen (vt220-emulation)
 3 = suppress terminal output
/
 Enter output device (default: 1):
 1 = Color postscript
 2 = Postscript
 3 = GIF
/
 Enter title:

 Use unit cell (F, default) or Wigner-Seitz cell (T)?
/
```

```
 The following colours have been assigned to the classes:
  SI    : red         ,

 Select classes to be assigned a new colour
 (enter blank or "/" when you're done):
/

 By default the bonds will be coloured orange      .
 Enter blank or "/" to accept or select from the following colours:
  red          [r ],  green        [g ],  blue         [b ],  yellow       [y ]
  magenta      [m ],  cyan         [c ],  orange       [o ],  blueviolet   [bv]
  cyanogreen   [cg],  yellowgreen  [yg],  purple       [p ],  cyanoblue    [cb]
  violet       [v ],  pale red     [pr],  pale blue    [pb],  pale green   [pg]
  pale yellow  [py],  pale violet  [pv],  pale cyan    [pc],  black        [bk]
  gray1 (dark) [g1],  gray2        [g2],  gray3        [g3],  gray4        [g4]
  gray5        [g5],  gray6 (lght) [g6],  white        [wh]

 Muffin-tin spheres (M, default), ASA spheres (A), linear radii scaling (R)
 or linear volume scaling (V):
R

 Enter scale factor [  0.100...  1.432] (default:   1.000):
0.6

 The plot space contains    1 unit cell(s).

 Enter strings for rotations. Default strings are:
 rotate x  90
 rotate y  -5
 rotate x  10

 Overwrite or enter "/" when you're done.
/
 task  1, total       :  cpu time:     0.00800 sec

 ASW-2.6, program PLSTR ended on asterix at Sun, 08 Feb 2009, 14:33:46.


    Please delete files STRU and stru.* when finished!!!
```

Note that all your input to the plot routine plstr.run has been echoed to the file PLIS for repeated use.

Next the electronic band structure is plotted using the command

```
plbnd.x
```

and entering the following dialog. Note that for semiconductors and insulators the plotting routines plbnd.run, pldos.run, and plcop.run allow for different choices of the energy zero, which may be the muffin-tin zero, the Fermi energy, the valence band maximum, or the conduction band minimum. The electronic band structure is displayed in Fig. 2.18. Here, a parabolic band starting at the Γ-point at about $-12\,\mathrm{eV}$ and mainly resulting from the $3s$ orbitals is well recognized. In contrast, at

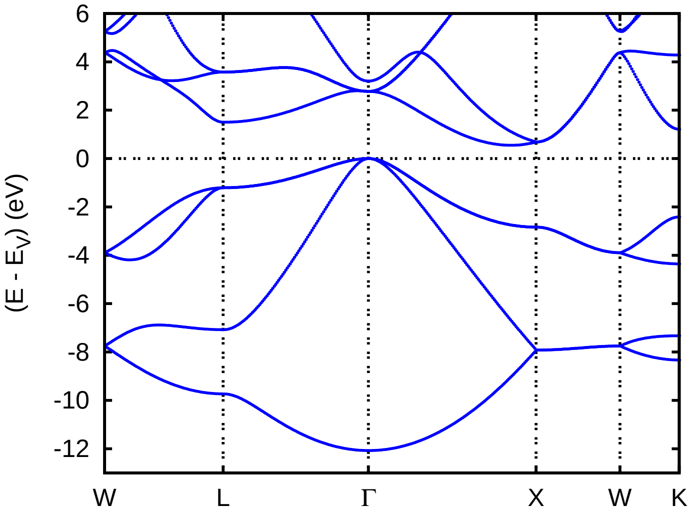

Figure 2.18 Electronic structure of Si along selected symmetry lines of the first Brillouin zone of the face-centered cubic lattice, see B.1.

the valence band maximum a threefold degenerate band is found, which traces back to the $3p$ states.

As before, the partial densities of states are obtained by typing

```
pldos.x
```

and follwoing the subsequent dialog. The result is displayed in Fig. 2.19, where we identify the strong $3s$ and $3p$ contributions at the bottom and the top, respectively, of the valence band.

2.2.4 Electron density and effective potential

As described in Sec. 2.1, the electron densities and the effective potential are obtained by calling the shell script

```
mnrho.x
```

which does all the necessary changes of the CTRL file and runs the main program `mnscf.run`. Subsequently, the electron densities and the effective potential are disiplayed by typing

```
plrho.x
```

and following the dialog. It generates the valence electron density as displayed in Fig. 2.20. Comparing it to the valence electron density arising from overlapping free

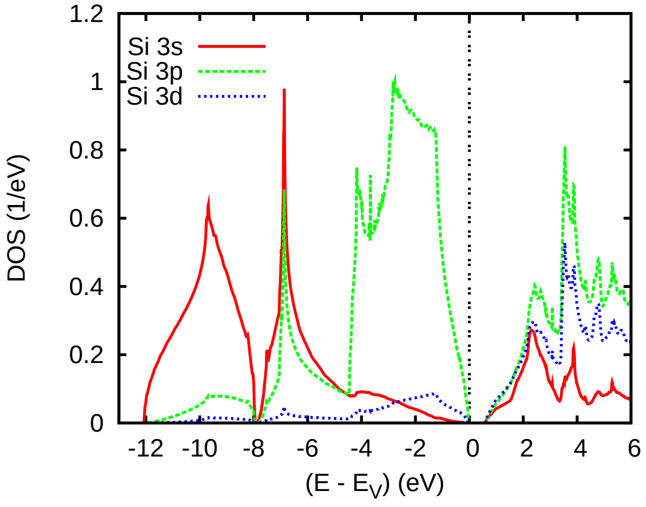

Figure 2.19 Partial densities of states of Si.

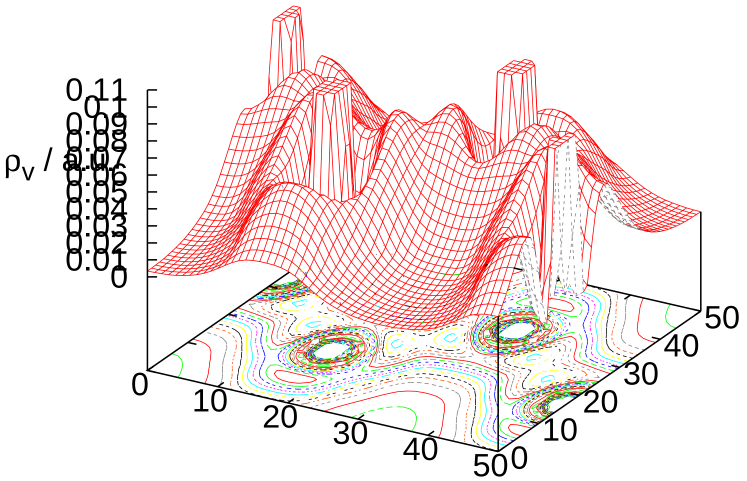

Figure 2.20 Valence electron density of Si.

atoms as shown in Fig. 2.16 we recognize especially the double maxima between the silicon atoms. They can be easily visualized by plotting the difference density, which is generated by calling mnrho.x twice, namely, once before the self-consistent set of calculations and once after completion of these calculations. The first step has been already described above. It generated the file FREE, which stores the electron densities and effective potential as arising from overlapping free atoms. In contrast, after the self-consistent calculations call of mnrho.x writes these quantities to file RHO. The plot routine plrho.run will detect both the FREE file and the RHO file and allows to generate the difference between the overlapping free atoms density and the self-consistent electron density; just follow the dialog. The result of this procedure is displayed in Fig. 2.21 for the valence electrons. As mentioned above, we identifiy the pronounced double maxima between the atoms, which indicate the increased covalent chemical bonding.

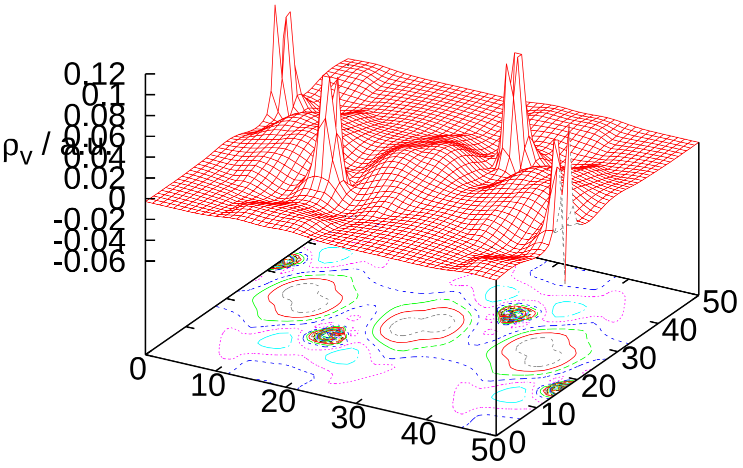

Figure 2.21 Valence electron density difference of Si.

In order to visualize the chemical bonding, solid state chemists have introduced a variety of so-called bonding indicators. Among these are the electron localization function and the negative Laplacian of the electron density. Evaluation of the latter is also implemented in the ASW programs and done along the calculation of the electron density. Visualization is also provided by the plot routine plrho.x; the result is shown in Fig. 2.22. Obviously, the negative Laplacian of the electron density pronounces the fine details of the latter and thus is well suited to visualize covalent bonds.

Finally, we call the plotting shell script plrho.x again and generate the effective potential, which is shown in Fig. 2.23.

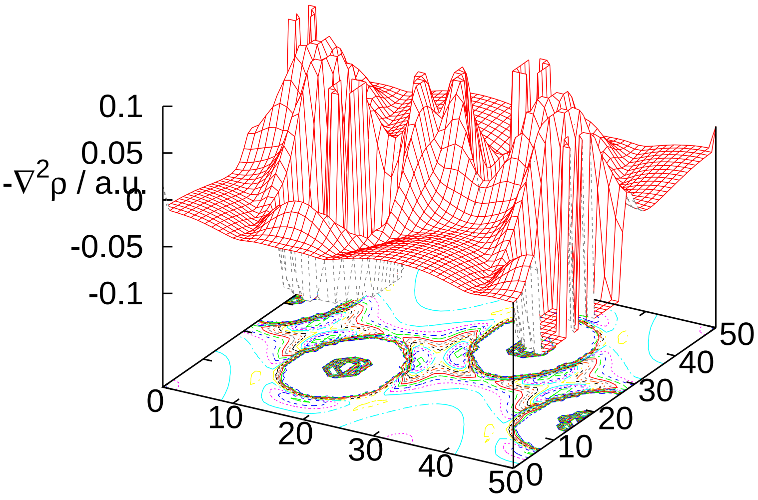

Figure 2.22 Negative Laplacian of Si.

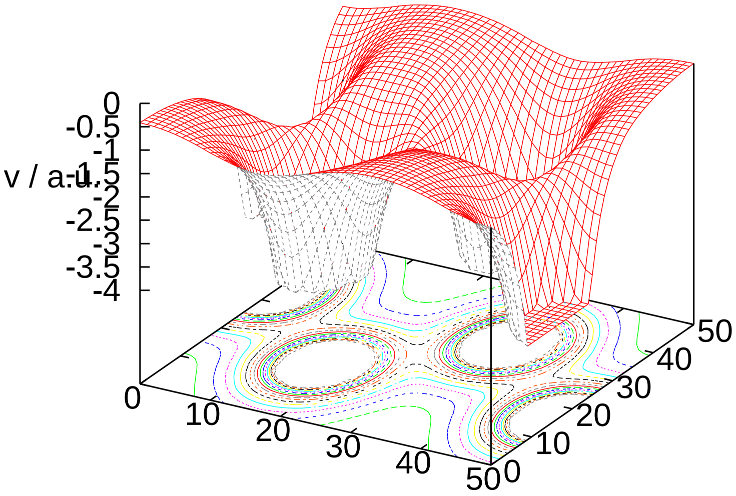

Figure 2.23 Effective potential of Si.

2.2.5 Optical spectra

In a next step we turn to the optical properties. Their calculation as based on linear response theory can be routinely performed and is initiated by invoking the corresponding shell script via

```
mnopt.x
```

This does the necessary changes to the CTRL as, e.g. setting SAVOPT=T and runs the main program `mnscf.run`. Insofar it is very similar to the shell script `mndos.x`. However, since the calculation of the optical properties is rather time consuming it is not included in the standard canon of calculations. Once the main program has finished a file OPT has been generated, which is available for plotting using the shell script

```
plopt.x
```

which leads to the following dialog.

```
 ASW-2.6, program PLOPT started on asterix at Sun, 08 Feb 2009, 20:12:10.

     Copyright (C) 1992-2009 Volker Eyert
     Please see file COPYRIGHT for details

 All input will be echoed to file PLIO.

 Enter terminal type:
 1 = X-Windows (default)
 2 = PC-Screen (vt220-emulation)
 3 = suppress terminal output
/
 Enter output device (default: 1):
 1 = Color postscript
 2 = Postscript
 3 = PDF (not yet supported)
 4 = JPEG (not yet supported)
 5 = LaTeX
 6 = LaTeX (special)
 7 = HP LaserJet III (PCL5)
 8 = PNG
 9 = GIF
10 = leave decision for later
11 = suppress output to file
/
 Portrait (P), landscape (L) or encapsulated postscript plot (E, default)?
/
 Enter title:


 Please wait a moment: I'm reading rest of file OPT.
 Energies in Rydberg (F) or eV (T, default)?
/
 Energy axis to the top (F) or right (T, default)?
```

```
/
 Plot OPT (F, default) or integrated OPT (T)?
/

 Start setting up curve 1:
 Select Cartesian components of the tensor (default xx).
/
 Plot optical conductivity (SIG, default), dielectric function (EPS),
 refraction index (RFI), optical reflectivity (REF),
 optical absorption (ABS), electron loss function (ELF)?
/
 Plot absorptive (A, default) or dispersive part (D)?
/
 Plot real (R, default) or imaginary part (I)?
/
 Select from the occ bands of the OPT matrix:
 Plot selected (F) or all occ bands (T, default)?
/
 Select from the unocc bands of the OPT matrix:
 Plot selected (F) or all unocc bands (T, default)?
/

 Include intraband contributions (T) or not (F, default)?
/
 Multiply with energy (F, default)?
/

 Broadening of this curve (T) or not (F, default)?
/

 Select curve style (default: 1) (A * marks styles already selected):
solid/green      (1)   , dash1/blue       (2)   ,
dash2/red        (3)   , dot/magenta      (4)   ,
dashdot1/cyan    (5)   , dashdot2/yellow  (6)   ,
chaindash1/black (7)   , chaindash2/coral (8)   ,
chaindash3/gray  (9)   ,
/

 Enter curve label ("/" to suppress)
Re {/Symbol s}_{a, xx}

 Please wait a moment: I'm working on this curve.
 Set up more curves (T)? Default is F.
T

 Start setting up curve 2:
 Select Cartesian components of the tensor (default xx).
/
 Plot optical conductivity (SIG, default), dielectric function (EPS),
 refraction index (RFI), optical reflectivity (REF),
 optical absorption (ABS), electron loss function (ELF)?
/
 Plot absorptive (A, default) or dispersive part (D)?
D
```

```
 Plot real (R, default) or imaginary part (I)?
I
 Select from the occ bands of the OPT matrix:
 Plot selected (F) or all occ bands (T, default)?
/
 Select from the unocc bands of the OPT matrix:
 Plot selected (F) or all unocc bands (T, default)?
/

 Include intraband contributions (T) or not (F, default)?
/
 Multiply with energy (F, default)?
/

 Broadening of this curve (T) or not (F, default)?
/

 Select curve style (default: 2) (A * marks styles already selected):
solid/green      (1) * , dash1/blue       (2)   ,
dash2/red        (3)   , dot/magenta      (4)   ,
dashdot1/cyan    (5)   , dashdot2/yellow  (6)   ,
chaindash1/black (7)   , chaindash2/coral (8)   ,
chaindash3/gray  (9)   ,
/

 Enter curve label ("/" to suppress)
Im {/Symbol s}_{a, xx}

 Please wait a moment: I'm working on this curve.
 Set up more curves (T)? Default is F.
/

 Ebot =     0.000000 eV , Etop =    34.014231 eV
 Emin =     0.000000 eV , Emax =    35.000000 eV
 Enter new Emin, Emax to change these defaults:

 OPTbot =     -2158.229369 1/eV , OPTtop =      4815.191685 1/eV
 OPTmin =     -2160.000000 1/eV , OPTmax =      4820.000000 1/eV
 Enter new OPTmin, OPTmax to change these defaults:
-2500.0
5000.0
 Enter energetic position of curve labels ("/" to use default):
/
 task  1, total       :  cpu time:     0.45203 sec

 ASW-2.6, program PLOPT ended on asterix at Sun, 08 Feb 2009, 20:12:11.

    Please delete files OPT and opt.ps when finished!!!
```

As a result, we obtain the optical conductivity as displayed in Fig. 2.24. In close analogy, the same plot routine can be used to calculate the dielectric function as displayed in Fig. 2.25, and the complex index of refraction, which is shown in Fig. 2.26.

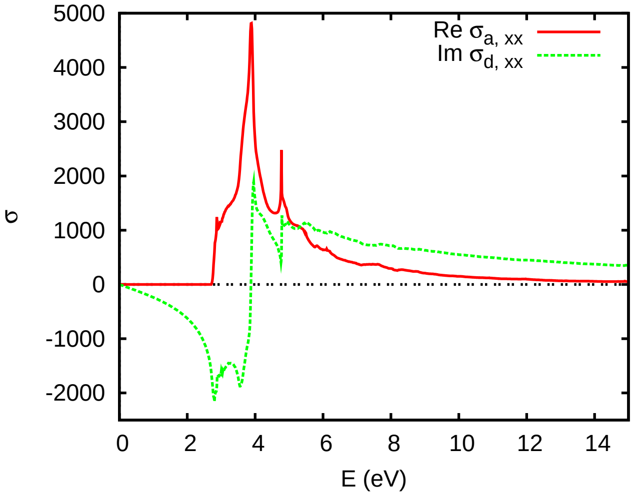

Figure 2.24 Optical conductivity of Si.

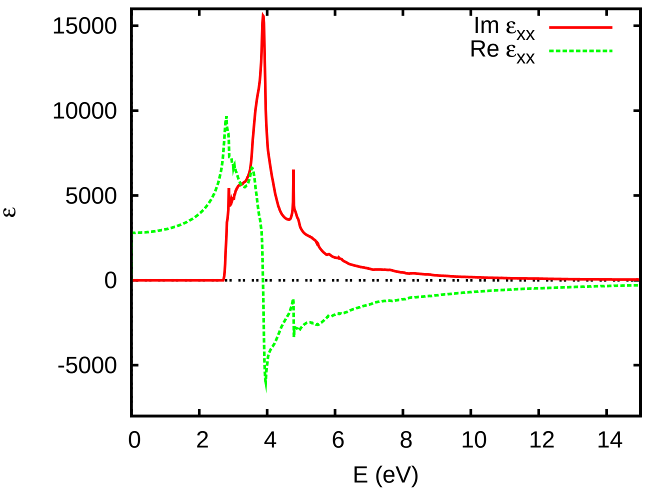

Figure 2.25 Dielectric function of Si.

2.2.6 Phonon frequencies

In closing this section we turn to the calculation of phonon frequencies. This can be achieved via the frozen phonon approach, which is based on evaluation of the total energies for a variety of fixed, hence, frozen atomic positions. Once this approach has been accepted it needs a limited number of self-consistent calculations for different atomic positions. In practice, evaluating a complete phonon spectrum thus requires

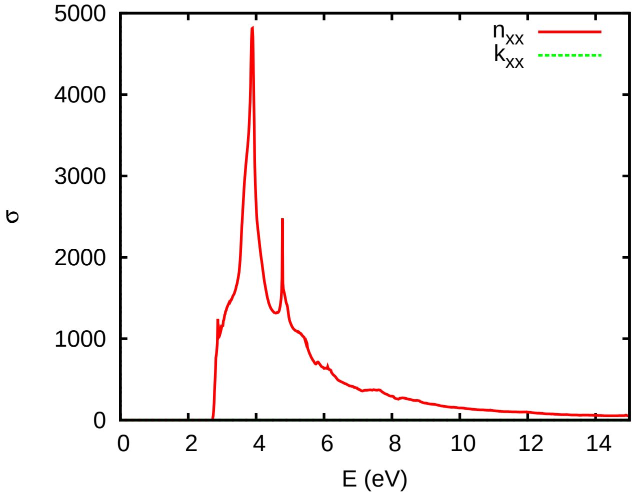

Figure 2.26 Refraction index of Si.

a lot of self-consistent so-called single-point calculations, which may even need a supercell setup for complicated phonon modes. At present, the ASW method is not yet prepared to perform such calculations automatically. Nevertheless, highly accurate phonon frequencies can be calculated with small effort. Usually, for each phonon mode five different atomic positions are needed. This requires a set of five different CTRL files with five different atomic positions. Here, we illustrate the procedure with the LTO Γ-point phonon. It corresponds to a mode, where the two Si atoms of the unit cell move along the bond connecting these atoms. To be specific, we place the Si atoms at the positions ±0.120, ±0.1225, ±0.125, ±0.1275, and ±0.130, and calculate the total energies. Note that the positions of the empty spheres and the atomic sphere radii are not changed during these calculations. The sequence of the calculations can be made automatic with the help of the shell script `mnphn.x` coming with the ASW distribution. This shell script deletes the atomic files, copies one of the five CTRL files (which should be named differently) to the CTRL file, and runs a self-consistent calculation. This process is then repeated five times. Once the shell script has been prepared and saved just type

```
mnphn.x
```

Of course, it is useful to run all these calculations in a separate subdirectory in order not to overwrite the results of the calculations performed for the ground state, which were discussed in the previous subsections. Actually, we mentioned this subdirectory, `nm_phn`, already at the beginning of this section. After all calculations have finished you may find use of the shell script `prphn` helpful, which will extract the atomic positions and the total energies from all the output files and write them to a small file called PHN. However, note that the shell script `prphn` must be adapted to the particular situation. Finally, the file PHN is used by the plotting routine called by the command

```
plphn.x
```

which enters the following simple dialog.

```
 ASW-2.6, program PLPHN started on asterix at Sun, 08 Feb 2009, 14:37:47.

     Copyright (C) 1992-2009 Volker Eyert
     Please see file COPYRIGHT for details

 All input will be echoed to file PLIP.

 Enter terminal type:
 1 = X-Windows (default)
 2 = PC-Screen (vt220-emulation)
 3 = suppress terminal output
/
 Enter output device (default: 1):
 1 = Color postscript
 2 = Postscript
 3 = PDF (not yet supported)
 4 = JPEG (not yet supported)
 5 = LaTeX
 6 = LaTeX (special)
 7 = HP LaserJet III (PCL5)
 8 = PNG
 9 = GIF
10 = leave decision for later
11 = suppress output to file
/
 Portrait (P), landscape (L) or encapsulated postscript plot (E, default)?
/
 Enter title:

 Energies in Rydberg (F, default) or eV (T)?
/
 Energies relative to the minimum energy (T)? Default is F.
/
 Print fit parameters in the plot (T, default)?
/
 Enter relative print position of the parameters ("/" to use default):
/

 Results from polynomial fit:
 Equilibrium position:         0.125000
 Minimum total energy:     -1156.092085 Ryd
 Force constant:             356.953174 Ryd/u**2
 Cubic force constant:     -4181.125308 Ryd/u**3
 task  1, total       :  cpu time:     0.01600 sec

 ASW-2.6, program PLPHN ended on asterix at Sun, 08 Feb 2009, 14:37:47.

    Please delete files PHN and phn.ps when finished!!!
```

The plotting routine performs a 3rd-order polynomial fit to the calculated data. The result of this fit is printed in the above dialog. In addition, if this has been chosen, the fit parameters are also displayed in the resulting plot, which is displayed in Fig. 2.27. Obviously, a stable minimum at the equilibrium position $u_0 = 0.125$ is obtained. This is a success of the full-potential treatment coming with the new ASW method. For comparison we display in Fig. 2.28. the corresponding result obtained from version 2.2, which is still based on the atomic sphere approximation but already includes the nonspherical contributions to the electron densities and the effective potential, hence, the abbreviation ASA$^+$. The difference between both curves is striking and needs no further comments.

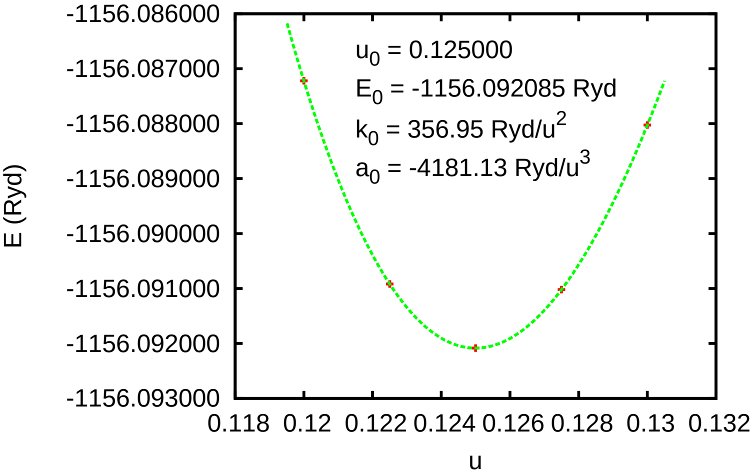

Figure 2.27 Total energy vs. Si position.

Still, we want to evaluate the force constant and the cubic force constant given in the above dialog and in Fig. 2.27. To this end we first have to convert the different values of u to Å. Since the mode moves two atoms along the diagonal of the cube and with a lattice constant of $10.2625 a_B$, we obtain

$$k_0 = 356.9532 \frac{\text{Ryd}}{u^2} = 2.0172 \frac{\text{Ryd}}{\text{Å}^2} = 439.7262 \frac{\text{J}}{\text{m}^2} \ .$$

Combining this with the mass of one Si atom of $M = 28.0855 \times 1.6726231 \times 10^{-27}\,\text{kg}$ we arrive at

$$\frac{k_0}{M} = 9.3606 \times 10^{27} \text{s}^{-2} \ ,$$

which leads to

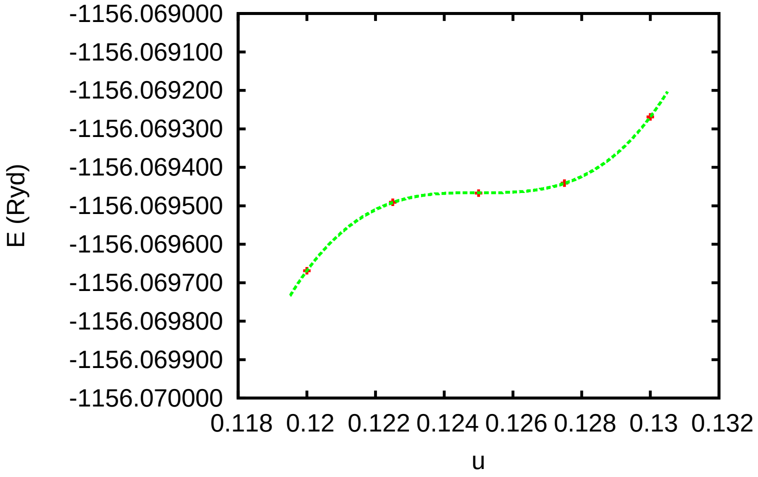

Figure 2.28 Total energy vs. Si position as calculated with an ASA^+ code.

$$\omega = \sqrt{\frac{k_0}{M}} = 9.6750 \times 10^{13}\mathrm{Hz}\ ,$$

hence, a phonon frequency of

$$f = \frac{\omega}{2\pi} = 15.3982 \times 10^{12}\mathrm{Hz}\ .$$

The deviation from the experimental value of 15.53 Hz is less than 1%!

For the cubic force constant calculations proceed along similar lines and we obtain the result

$$a_0 = -4181.1253\frac{\mathrm{Ryd}}{u^3} = -34.1774\frac{\mathrm{eV}}{\mathrm{\AA}^3}\ .$$

In this case the deviation from the experimental value of $-35.1\mathrm{eV}/\mathrm{\AA}^3$ is less than 3%. Note the minus sign in front of the cubic force constant, which is a consequence of the slightly elevated energies for values of u smaller than u_0 and indicates that compression of the bond is energetically more costly than bond elongation.

2.3 A more complicated structure: FeS_2

While the calculations for Cu did not even allow for a coffee break we next turn to a more complicated case with an increased demand of computer resources. To be specific, we turn to the case of iron pyrite, FeS_2, which is the prototype member of a whole class of transition metal disulfides. Background information about this compound is given in Ref. [409].

The work to be described in this section includes the sphere packing, the self-consistent calculations and the optimization of the crystal structure. In order to prepare for the calculations, we start again by creating some directories via

```
mkdir fes2
cd fes2
mkdir pac
mkdir nm
mkdir nm_blk
mkdir nm_opt
cd pac
```

and turn to the setup of the CTRL file and the sphere packing.

2.3.1 CTRL file and sphere packing

The pyrite structure is based on a simple cubic lattice with iron atoms located at the corner of the cell and sulfur pairs aligned along the space diagonal. This information is contained in the following CTRL file.

```
HEADER  FeS2 sc
        data by E. D. Stevens, M. L. DeLucia, and P. Coppens,
        Inorg. Chem. 19, 813 (1980).
VERSION ASW-2.6
IO      HELP=F SHOW=T VERBOS=30 CLEAN=T
OPTIONS REL=T OVLCHK=T
STRUC   ALAT=10.23476
CLASS   ATOM=FE Z=26
        ATOM=S  Z=16
SITE    CARTP=T
        ATOM=FE POS= 0.000000  0.000000  0.000000
        ATOM=FE POS=-0.500000 -0.500000  0.000000
        ATOM=FE POS= 0.000000 -0.500000 -0.500000
        ATOM=FE POS=-0.500000  0.000000 -0.500000
        ATOM=S  POS= 0.384840  0.384840  0.384840
        ATOM=S  POS=-0.384840 -0.384840 -0.384840
        ATOM=S  POS= 0.115160 -0.115160  0.384840
        ATOM=S  POS=-0.115160  0.115160 -0.384840
        ATOM=S  POS= 0.384840  0.115160 -0.115160
        ATOM=S  POS=-0.115160  0.384840  0.115160
        ATOM=S  POS=-0.384840 -0.115160  0.115160
        ATOM=S  POS= 0.115160 -0.384840 -0.115160
SYMGRP  GENPOS=F CARTT=F SGSYM=Pa-3
ENVEL   EKAP=-0.015
BZSMP   NKBAB=6 BZINT=LTM EMIN=-1.0 EMAX=1.5 NDOS=2500
        NORD=3 WIDTH=0.01 SAVDOS=F SAVCOOP=F SAVFERM=F
CHARGE  NETA=2 EETA=-3.0 -5.0 SAVRHO=F
```

```
CONTROL START= QUIT= FREE=F NITBND=99 CNVG=1.0D-08 CNVGET=1.0D-08
        NITATM=50 CNVGQA=1.0D-10
MIXING  NMIXB=5 BETAB=0.5 INCBB=T NMIXA=5 BETAA=0.5
PLOT    CARTV=T
        ORIGIN= 0.5  0.0  0.0
        RPLOT1= 1.0  0.0  0.0
        RPLOT2= 0.0  1.0  0.0
        RPLOT3= 0.0  0.0  1.0
        NPDIV1=50 NPDIV2=50 NPDIV3=0
```

Due to the symmetry of the crystal the simple cubic cell comprises four iron and eight sulfur atoms in total. The crystal structure is shown in Fig. 2.29. In this plot the origin has been shifted by half the cell edge (see token ORIGIN=0.5 0.0 0.0 in category PLOT). As a consequence, one Fe atom is observed in the center of the plot while atoms of the sulfur pair appear in the upper right and lower left corner.

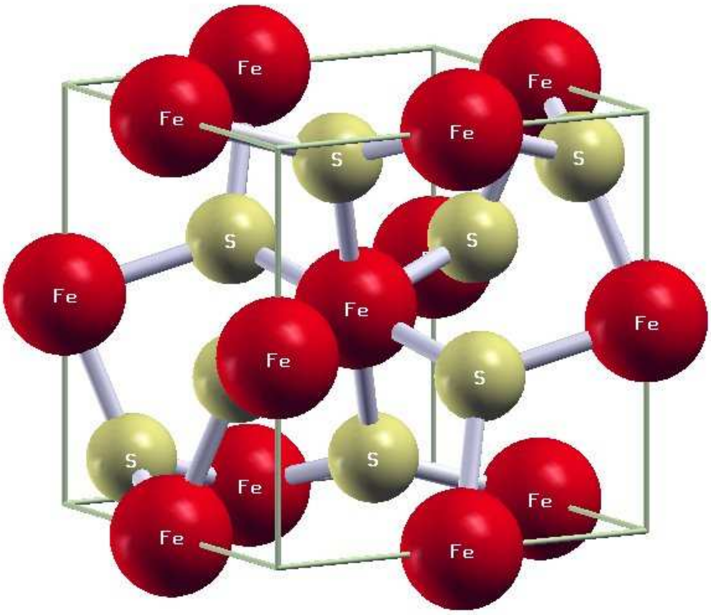

Figure 2.29 Crystal structure of FeS_2. Iron and sulfur atoms are printed in red and yellow, respectively.

The pyrite crystal structure is best described in terms of the NaCl structure with the sublattices occupied by iron atoms and the centers of gravity of sulfur atom pairs, respectively. These sulfur dumb-bells are oriented along the $\langle 111 \rangle$ axes. Being 2.161 Å their bond length is still shorter than the Fe-S distance of 2.265 Å. Whereas the sulfur atoms are tetrahedrally coordinated by one sulfur and three iron atoms the six nearest neighbour sulfur atoms at each iron site form slightly distorted octahedra. The distorted FeS_6 octahedra are interlinked by common corners and, due to the formation of the ⟨111⟩ sulfur pairs, have rotated away from the Cartesian axes by about 23°. For a two dimensional crystal the situation is sketched in Fig. 2.30. Obviously, the formation of the ⟨111⟩ sulfur pairs does not destroy the square planar coordination of the iron atoms. Instead, the squares built by the sulfur atoms just shrink and rotate. Since the orientation of the dumb-bells conforms with the cubic point group the underlying Bravais lattice is no longer face-centered but simple cubic and the unit cell comprises four formula units.

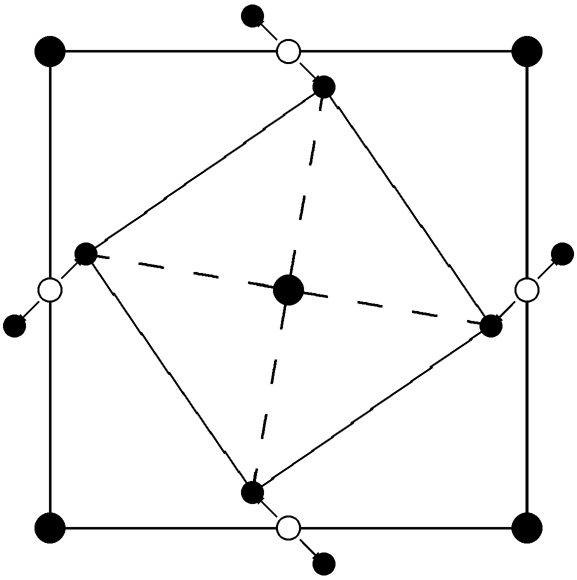

Figure 2.30 Two-dimensional analogue of the pyrite structure. Big and small filled circles designate iron and sulfur atoms, respectively. Small open circles mark the ideal positions of the rocksalt structure.

In the CTRL file listed above we have already included information about the crystal symmetry in category SYMGRP. It contains three tokens, namely, SGSYM=, which specifies the space group of the pyrite structure. A full list of all space groups and the coding of the space group symbols is given in the file SPCGRP coming with the distribution. Alternatively, this file can be generated using the setting HELP=T and running any of the main programs. Instead of the token SGSYM= the token SYMOPS= could be used. With this token, a minimal set of symmetry operation, the socalled generators of the space group, can be specified. The generators are also given in the SPCGRP file. By building all products of these generators the whole space group can be obtained.

The space group information can be used in two different ways. First, for GENPOS=F the program performs a symmetry check using the information about the lattice and the atomic sites. As a result, the full space group information including a list of all allowed symmetry operations is displayed. In addition, this information is compared to the input given in category SYMGRP of the CTRL file. Second, if GENPOS=T is specified, the program proceeds in a different way. In this case the symmetry check of the atomic sites is omitted. Instead, the program generates all atomic sites by applying all space group operations, which arise from the generators, to all atoms given in the CTRL file. For this reason, we would not have to specifiy all atomic sites but only the minimal set of position, i.e. in the present case only one iron and one sulfur atom. This is illustrated in the following listing.

```
HEADER  FeS2 sc
        data by E. D. Stevens, M. L. DeLucia, and P. Coppens,
        Inorg. Chem. 19, 813 (1980).
VERSION ASW-2.6
IO      HELP=F SHOW=T VERBOS=30 CLEAN=T
OPTIONS REL=T OVLCHK=T
STRUC   ALAT=10.23476
CLASS   ATOM=FE Z=26
        ATOM=S  Z=16
SITE    CARTP=T
        ATOM=FE POS= 0.000000  0.000000  0.000000
        ATOM=S  POS= 0.384840  0.384840  0.384840
SYMGRP  GENPOS=T CARTT=F SGSYM=Pa-3
ENVEL   EKAP=-0.015
BZSMP   NKBAB=6 BZINT=LTM EMIN=-1.0 EMAX=1.5 NDOS=2500
        NORD=3 WIDTH=0.01 SAVDOS=F SAVCOOP=F SAVFERM=F
CHARGE  NETA=2 EETA=-3.0 -5.0 SAVRHO=F
CONTROL START= QUIT= FREE=F NITBND=99 CNVG=1.0D-08 CNVGET=1.0D-08
        NITATM=50 CNVGQA=1.0D-10
MIXING  NMIXB=5 BETAB=0.5 INCBB=T NMIXA=5 BETAA=0.5
PLOT    CARTV=T
        ORIGIN= 0.5  0.0  0.0
        RPLOT1= 1.0  0.0  0.0
        RPLOT2= 0.0  1.0  0.0
        RPLOT3= 0.0  0.0  1.0
        NPDIV1=50 NPDIV2=50 NPDIV3=0
```

This representation has the additional advantage that an optimization of the crystal structure, which involves changes of the atomic positions, can be most easily performed.

As is obvious from Fig. 2.29, the pyrite crystal structure as the diamond structure discussed above comprises rather large voids between the atoms. As also discussed in connection to the diamond structure, we thus have to include empty spheres into this structure. Again, this is done automatically by invoking the „packing program“ `mnpac.run` via typing the command

```
mnpac.x
```

at the systems prompt. On successful execution, the program `mnpac.run` writes a new version of the CTRL file to file CNEW, which now contains all the empty sphere positions as well as atomic sphere radii of all atoms. In addition, `mnpac.run` proposes the number of partial waves to be included by the tokens LMXL= and CONF=. We point out again that these two tokens have been set quite conservatively, i.e. LMXL is set to a rather high value and might need an adjustment for the subsequent self-consistent field calculation. We will come back to this issue below. Of course, the corresponding charges as given by token QVAL= are all zero. The file CNEW looks as follows.

```
HEADER  FeS2 sc
        data by E. D. Stevens, M. L. DeLucia, and P. Coppens,
        Inorg. Chem. 19, 813 (1980).
VERSION ASW-2.6
IO      HELP=F SHOW=T VERBOS=30 CLEAN=T
OPTIONS REL=T OVLCHK=T
STRUC   ALAT=10.23476
CLASS   ATOM=FE Z=26 R=2.40019794 LMXL=2 CONF=4 4 3 4
                QVAL= 2.0  0.0  6.0  0.0
        ATOM=S  Z=16 R=2.31735801 LMXL=2 CONF=3 3 3 4
                QVAL= 2.0  4.0  0.0  0.0
        ATOM=E1 Z= 0 R=1.57781865 LMXL=1 CONF=1 2 3
                QVAL= 0.0  0.0  0.0
        ATOM=E2 Z= 0 R=1.42640878 LMXL=1 CONF=1 2 3
                QVAL= 0.0  0.0  0.0
SITE    CARTP=T
        ATOM=FE POS= 0.000000  0.000000  0.000000
        ATOM=FE POS=-0.500000 -0.500000  0.000000
        ATOM=FE POS= 0.000000 -0.500000 -0.500000
        ATOM=FE POS=-0.500000  0.000000 -0.500000
        ATOM=S  POS= 0.384840  0.384840  0.384840
        ATOM=S  POS=-0.384840 -0.384840 -0.384840
        ATOM=S  POS= 0.115160 -0.115160  0.384840
        ATOM=S  POS=-0.115160  0.115160 -0.384840
        ATOM=S  POS= 0.384840  0.115160 -0.115160
        ATOM=S  POS=-0.115160  0.384840  0.115160
        ATOM=S  POS=-0.384840 -0.115160  0.115160
        ATOM=S  POS= 0.115160 -0.384840 -0.115160
        ATOM=E1 POS= 0.305462 -0.194538 -0.305462
        ATOM=E1 POS=-0.305462  0.194538  0.305462
        ATOM=E1 POS=-0.194538 -0.305462  0.305462
        ATOM=E1 POS= 0.194538  0.305462 -0.305462
        ATOM=E1 POS=-0.305462  0.305462 -0.194538
        ATOM=E1 POS= 0.305462 -0.305462  0.194538
        ATOM=E1 POS= 0.194538  0.194538  0.194538
        ATOM=E1 POS=-0.194538 -0.194538 -0.194538
        ATOM=E2 POS=-0.302589  0.062226 -0.134569
        ATOM=E2 POS= 0.302589 -0.062226  0.134569
        ATOM=E2 POS= 0.197411  0.437774  0.134569
        ATOM=E2 POS=-0.197411 -0.437774 -0.134569
        ATOM=E2 POS= 0.302589 -0.437774 -0.365431
        ATOM=E2 POS=-0.302589  0.437774  0.365431
        ATOM=E2 POS= 0.134569  0.197411  0.437774
        ATOM=E2 POS=-0.134569 -0.197411 -0.437774
        ATOM=E2 POS=-0.437774 -0.365431  0.302589
        ATOM=E2 POS= 0.437774  0.365431 -0.302589
        ATOM=E2 POS= 0.437774  0.134569  0.197411
        ATOM=E2 POS=-0.437774 -0.134569 -0.197411
        ATOM=E2 POS= 0.365431 -0.197411 -0.062226
```

```
        ATOM=E2 POS=-0.365431  0.197411  0.062226
        ATOM=E2 POS=-0.197411 -0.062226  0.365431
        ATOM=E2 POS= 0.197411  0.062226 -0.365431
        ATOM=E2 POS=-0.062226  0.365431 -0.197411
        ATOM=E2 POS= 0.062226 -0.365431  0.197411
        ATOM=E2 POS=-0.365431  0.302589 -0.437774
        ATOM=E2 POS= 0.365431 -0.302589  0.437774
        ATOM=E2 POS=-0.134569 -0.302589  0.062226
        ATOM=E2 POS= 0.134569  0.302589 -0.062226
        ATOM=E2 POS= 0.062226 -0.134569 -0.302589
        ATOM=E2 POS=-0.062226  0.134569  0.302589
SYMGRP  GENPOS=T CARTT=F SGSYM=Pa-3
ENVEL   EKAP=-0.015
BZSMP   NKBAB=6 BZINT=LTM EMIN=-1.0 EMAX=1.5 NDOS=2500
        NORD=3 WIDTH=0.01 SAVDOS=F SAVCOOP=F SAVFERM=F
CHARGE  NETA=2 EETA=-3.0 -5.0 SAVRHO=F
CONTROL START= QUIT= FREE=F NITBND=99 CNVG=1.0D-08 CNVGET=1.0D-08
        NITATM=50 CNVGQA=1.0D-10
MIXING  NMIXB=5 BETAB=0.5 INCBB=T NMIXA=5 BETAA=0.5
SYMLIN  NPAN=6 NPTS=400 ORBWGT=F CARTE=F
        LABEL=R ENDPT= 0.5  0.5  0.5
        LABEL=g ENDPT= 0.0  0.0  0.0
        LABEL=X ENDPT= 0.5  0.0  0.0
        LABEL=M ENDPT= 0.5  0.5  0.0
        LABEL=R ENDPT= 0.5  0.5  0.5
        LABEL=X ENDPT= 0.0  0.5  0.0
        LABEL=M ENDPT= 0.5  0.5  0.0
PLOT    CARTV=T
        ORIGIN= 0.5  0.0  0.0
        RPLOT1= 1.0  0.0  0.0
        RPLOT2= 0.0  1.0  0.0
        RPLOT3= 0.0  0.0  1.0
        NPDIV1=50 NPDIV2=50 NPDIV3=0
```

For FeS_2, two types of empty spheres have been added with radii ranging from 1.42 to 1.58 Bohr radii. In total, 32 empty spheres have been inserted into the pyrite structure. Moreover, the program has specified optimal radii for iron and sulfur atoms.

All actions taken by the packing program mnpac.run are recorded in the output file *outpac*, which among other things contains the results of a final overlap check for OVLCHK=T as already mentioned in Sec. 2.2.

2.3.2 Execution of the main programs

Having run the packing program mnpac.run we are able to run the self-consistent field calculation just as in the case for Cu above. To do so, we change to the subdirectory nm and copy file CNEW created in the subdirectory pac to the CTRL file. The set of all self-consistent calculations is then invoked by typing

```
mnall.x
```

at the systems prompt. Already after a few iteration monic outlst6 will tell us that the program found a finite indirect band gap, which qualifies iron pyrite as an semiconductor. Now it is time to browse the input. Going to the end and searching backward for the string “Fermi” will put you on the top of a list containing for each class and partial wave (angular momentum) the amount of charge and the contribution to the density of states at E_F. Of course, for an insulator or semiconductor the second column contains only zeros. Special attention deserves the first column. If compared to the atomic configurations these partial occupations reflect the charge transfer between the orbitals. If summed over all orbitals of an atom they give rise to the deviation from the neutrality of an atom, which is given in an extra list above. For most atoms the occupation of the orbital with highest angular momentum is quite small, below 0.1 electron. This guarantess the convergence of the angular momentum expansions of the wave functions. In case the charge contained in the highest l state is above 0.1 a warning is issued. Values up to 0.13 are still acceptable, otherwise the value given by LMXL= must be increased. In contrast, if the numbers for the two highest l orbitals and their sum is below 0.1 electrons, you might decrease the value set by LMXL= by one. In this context we recall that each orbital included (of course, there are $2l+1$ states for each l) increases the size of the secular matrix and thus leads to an increase of execution time and memory. Since the CPU time scales roughly as the cube of the number of orbitals a reduction of the maximum angular momentum might considerably speed up a calculation. However, such a reduction is allowed only if the above mentioned conditions are fulfilled.

In case you realize during the first iterations that the number of orbitals for a particular atom should be changed you have to stop execution and delete all atomic files (those given by the entries ATOM= in category CLASS). In addition, you must delete the file MIX, which holds information about the progress of the iterations and is deleted automatically once self-consistency has been reached. After that adjust the angular momenta given by the tokens LMXL=. In case you have increased the LMXL= values corresponding entries have to be added to tokens CONF= and QVAL=. However, these latter tokens could likewise be completely erased since the program creates them automatically. Finally, the calculation can be restarted by again typing mnall.x at the systems prompt. The complete set of calculations will take about three quarters of an hour, which is enough for a coffee break!

After completion of all calculations a first impression of the results is obtained on typing

monic *outlst18*

at the system prompt, which prints the following summary to screen.

```
ASW-2.6, program MNSCF started on asterix at Wed, 04 Feb 2009, 20:44:59.
Calculation converged after  10 iteration(s).
                      Start of Iteration   10
    76 irreducible k-points generated from    1331 ( 11, 11, 11).
          Fermi energy - MTZ =     0.823867 Ryd.
The system is a semiconductor:
           Indirect band gap =     0.037749 Ryd =     0.513595 eV
Mean-square residual:                  0.223714D-22
```

```
Total free atom energies      : -16526.992322 Ryd
Total variational energy      : -16532.800042 Ryd
Cohesive energy               :      5.807720 Ryd
 qdiff =       0.00000000  <        0.00000001
 ediff =       0.00000001  <        0.00000001
ASW-2.6, program MNSCF ended on asterix at Wed, 04 Feb 2009, 21:08:13.
```

From this, we identify FeS$_2$ as a semiconductor with an indirect optical band gap of 0.51 eV, which again is much smaller than the experimental value of about 0.9-0.95 eV due to the limitations of the local density approximation.

2.3.3 Execution of the plot programs

Next we turn to the visualization of the result. Typing

`plbnd.x`

and following the dialog we obtain the band structure displayed in Fig. 2.31. Five groups of bands are observed. While two groups are found below -10 eV, a wide group shows up between approx. -7.5 and -2 eV. Just below and above the Fermi energy a rather narrow and a wide group of bands follow. These latter two groups are separated by the optical band gap of 0.51 eV. Note that all energies are referred to the valence band maximum E_V.

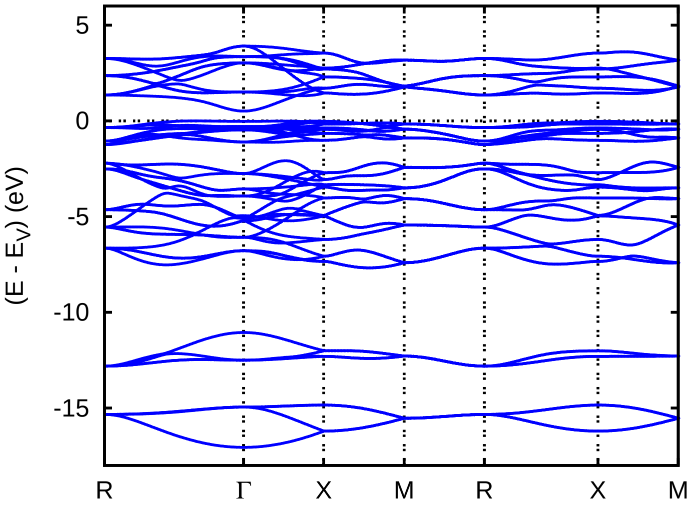

Figure 2.31 Electronic structure of FeS$_2$ along selected symmetry lines of the first Brillouin zone of the simple cubic lattice, see B.1.

The predominant orbital character of these five groups is read off from the partial densities of states as shown in Fig. 2.32. Obviously, the lowest two groups are made exclusively from the semicore-like S 3*s* states, whereas the higher lying states trace back to a mixture of Fe 3*d* and S 3*p* bands. The latter orbitals dominate especially the wider groups between approx. −7.5 and −2 eV as well as between 2.7 and 4.5 eV. In contrast the sharp peak just below E_V is due almost exclusively to the Fe 3*d* states.

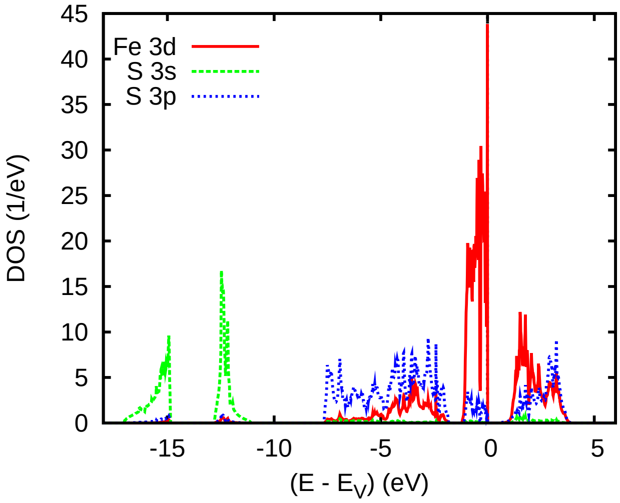

Figure 2.32 Partial densities of states of FeS_2.

The previous analysis of the electronic states can be made more detailed by distinguishing the single *p* and *d* components. For the Fe 3*d* states this is achieved by calling `pldos.x` again and running through the following dialog.

```
 ASW-2.6, program PLDOS started on asterix at Mon, 09 Feb 2009, 12:15:27.

     Copyright (C) 1992-2009 Volker Eyert
     Please see file COPYRIGHT for details

 All input will be echoed to file PLID.

 Enter terminal type:
 1 = X-Windows (default)
 2 = PC-Screen (vt220-emulation)
 3 = suppress terminal output
/
 Enter output device (default: 1):
 1 = Color postscript
 2 = Postscript
 3 = PDF (not yet supported)
```

```
 4 = JPEG (not yet supported)
 5 = LaTeX
 6 = LaTeX (special)
 7 = HP LaserJet III (PCL5)
 8 = PNG
 9 = GIF
10 = leave decision for later
11 = suppress output to file
/
 Portrait (P), landscape (L) or encapsulated postscript plot (E, default)?
/
 Enter title:


 Please wait a moment: I'm reading rest of file DOS.
 Energies in Rydberg (F) or eV (T, default)?
/
 Energies relative to MTZ (0), EVBM (V, default), ECBM (C), or EFermi (F)?
/
 Energy axis to the top (F) or right (T, default)?
/
 Plot DOS (F, default) or integrated DOS (T)?
/

 Start setting up curve 1:
 Plot partial (F) or total DOS (T, default)?
F
 For partial DOS: Rotate reference frame for orbitals?
 Enter rotation symbol (Default: E):
/

 Enter orbital(s) to be included:
 Select from the classes (blank or "/" to complete the list):
  FE      S       E1      E2
FE

 Class FE    : atom   1 at     0.000000    0.000000    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
5
6
8/

 Class FE    : atom   2 at     0.500000    0.500000    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
```

```
/

 Class FE    : atom   3 at     0.000000    0.500000    0.500000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
/

 Class FE    : atom   4 at     0.500000    0.000000    0.500000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
/
 Select from the classes (blank or "/" to complete the list):
  FE      S       E1      E2
/

 The following orbitals have been selected:
 Class FE    : atom    1, orbital xy
 Class FE    : atom    1, orbital yz
 Class FE    : atom    1, orbital xz

 Enter scaling factor (default 1.0):
/

 Broadening of this curve (T) or not (F, default)?
/

 Select curve style (default: 1) (A * marks styles already selected):
solid/green      (1)   , dash1/blue       (2)   ,
dash2/red        (3)   , dot/magenta      (4)   ,
dashdot1/cyan    (5)   , dashdot2/yellow  (6)   ,
chaindash1/black (7)   , chaindash2/coral (8)   ,
chaindash3/gray  (9)   ,
/

 Enter curve label ("/" to suppress)
Fe 3d t_{2g}

 Please wait a moment: I'm working on this curve.
 Set up more curves (T)? Default is F.
T

 Start setting up curve 2:
 Plot partial (F) or total DOS (T, default)?
F
 For partial DOS: Rotate reference frame for orbitals?
 Enter rotation symbol (Default: E):
```

```
/

 Enter orbital(s) to be included:
 Select from the classes (blank or "/" to complete the list):
  FE      S       E1      E2
FE

 Class FE    : atom   1 at     0.000000    0.000000    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
7
9/

 Class FE    : atom   2 at     0.500000    0.500000    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
/

 Class FE    : atom   3 at     0.000000    0.500000    0.500000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
/

 Class FE    : atom   4 at     0.500000    0.000000    0.500000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
/
 Select from the classes (blank or "/" to complete the list):
  FE      S       E1      E2
/

 The following orbitals have been selected:
 Class FE    : atom    1, orbital 3z^2-r^2
 Class FE    : atom    1, orbital x^2-y^2

 Enter scaling factor (default 1.0):
/
```

```
 Broadening of this curve (T) or not (F, default)?
/

 Select curve style (default: 2) (A * marks styles already selected):
solid/green      (1) * , dash1/blue       (2)   ,
dash2/red        (3)   , dot/magenta      (4)   ,
dashdot1/cyan    (5)   , dashdot2/yellow  (6)   ,
chaindash1/black (7)   , chaindash2/coral (8)   ,
chaindash3/gray  (9)   ,
/

 Enter curve label ("/" to suppress)
Fe 3d e_g

 Please wait a moment: I'm working on this curve.
 Set up more curves (T)? Default is F.
/

 Center of gravity of DOS curve  1 (Spin 1) - EV :   -0.0669 eV
 Center of gravity of DOS curve  2 (Spin 1) - EV :   -0.1999 eV

 Indicate center of gravities (F, default)?
/

 Ebot =   -16.729321 eV , Etop =     9.529665 eV  relative to EV
 Emin =   -17.000000 eV , Emax =     6.000000 eV  relative to EV
 Enter new Emin, Emax to change the default:
-9.0
6.0

 DOStop =    10.931710 1/eV
 DOSmax =    20.000000 1/eV
 Enter new DOSmax to change this default:
12.0
 Enter energetic position of curve labels ("/" to use default):
-4.0
 task  1, total       :  cpu time:     0.15601 sec

 ASW-2.6, program PLDOS ended on asterix at Mon, 09 Feb 2009, 12:15:27.

    Please delete files DOS and dos.ps when finished!!!
```

As a result, we obtain the partial densities of states displayed in Fig. 2.33, which separates the Fe 3*d* partial DOS into their t_{2g} and e_g contributions, which in octahedral coordination mediate π and σ type bonding with the respective ligand p orbitals. Yet, the t_{2g} and e_g manifolds obviously are not clearly separated in energy. In contrast, we observe a mixture of both types of states in all group of bands. Of course, this is due to the rotation of the FeS_6 octahedra already discussed in connection with Fig. 2.29. Hence, in order to correctly assign the t_{2g} and e_g orbitals we have to use a rotated reference frame with the Cartesian axes pointing along the Fe-S bonds. With the ASW programs this can be easily achieved. To this end,

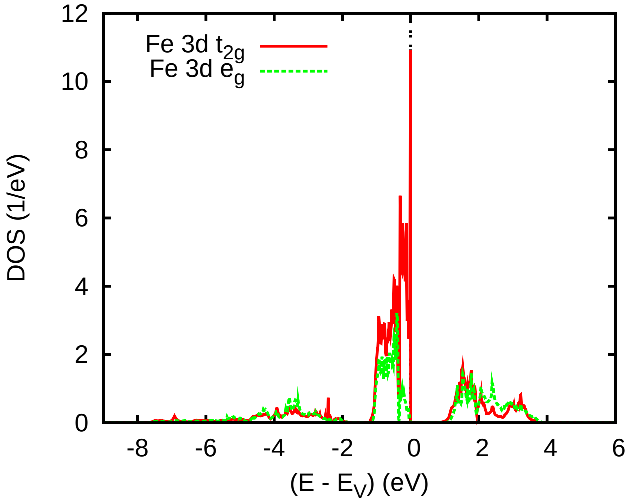

Figure 2.33 Partial Fe $3d$ densities of states of FeS$_2$.

we enter the above dialog again. However, when being asked to enter the rotation symbol, we type

```
R(23)(1,1,0)*R(17)(0,0,1)
```

which describes the rotation of the octahedra away from the Cartesian axes of the underlying cubic lattice. As a result, we obtain the partial DOS shown in Fig. 2.34, which indeed reflect the energetical separation of the t_{2g} and e_g contributions.

The flexibility of the ASW programs to use rotated reference frames is also very helpful for the analysis of the S $3p$ states. Fig. 2.35 shows the partial $3p$ densities of states of two S atoms forming a short bonded pair. Of course, due to the cubic symmetry, all three contributions are identical. However, using a rotated reference frame with the z axis pointing along the bond and the x and y axes being perpendicular to the bond we arrive at a much different picture. The result is displayed in Fig. 2.36, which clearly indicates the strong bonding-antibonding splitting of the σ-bonding orbital pointing along the bond and the weaker splitting of the perpendicular π-bonding orbitals.

Another useful feature is the calculation of orbital weighted band structures, which in the context of the LMTO method, goes under the name „fatband“. Such bands structures can be produced by setting ORBWGT=T in category SYMLIN and running the program `mnbnd.run`. As a result, in addition to the file BNDE a file BNDV is obtained, which holds information about the wave functions. This information can be used to attach to each band at each **k** point a bar, the width of which indicates the contribution of a specified orbital to the respective wave function. The orbital is selected with the help of the plot program `plbnd.run`, which also allows for rotated reference frames. For FeS$_2$, the results are shown in Figs. 2.37

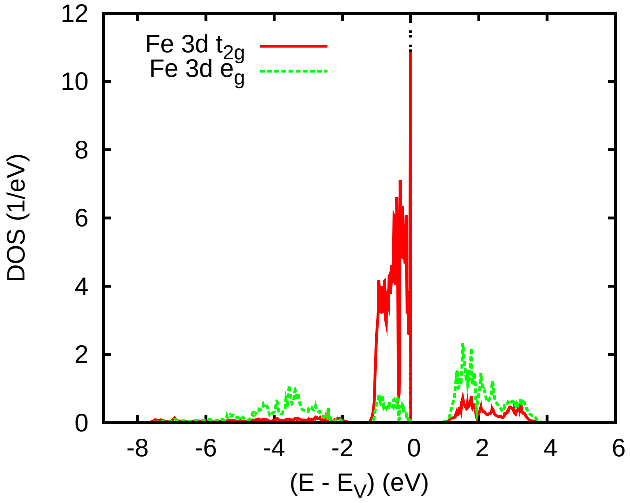

Figure 2.34 Partial Fe 3d densities of states of FeS_2.

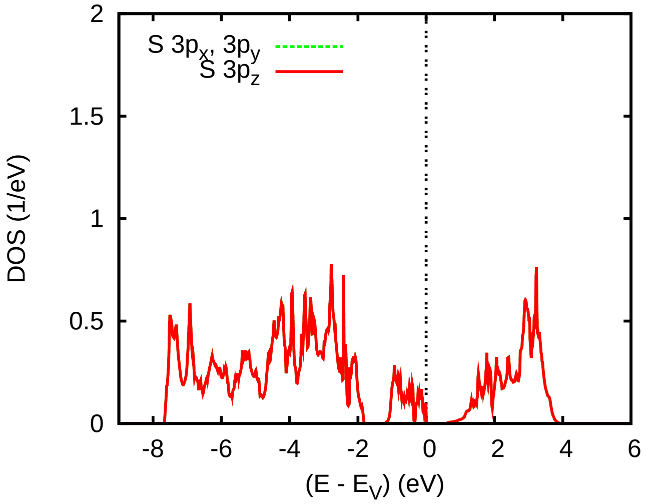

Figure 2.35 Partial S 3p densities of states of FeS_2.

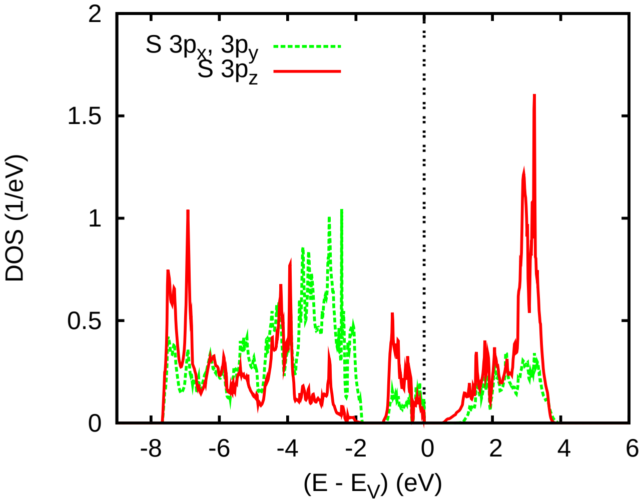

Figure 2.36 Partial S $3p$ densities of states of FeS_2.

and 2.38, which clearly confirm the observation made in the partial DOS, namely

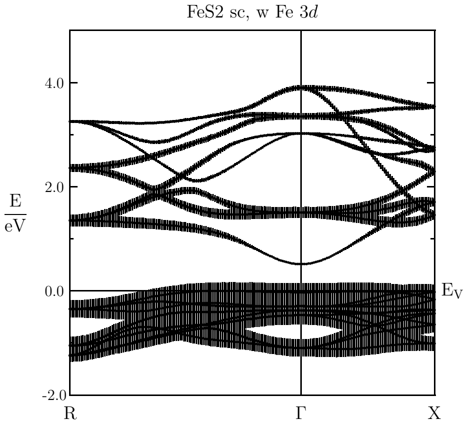

Figure 2.37 Weighted electronic bands of FeS_2. The width of the bars given for each band indicates the contribution due to the Fe $3d$ orbitals.

that the upper valence band as well as the lower half of the conduction band group trace back to the Fe $3d$ states, while the upper half of the conduction band is more S $3p$ like. Yet, the lowest edge of the conduction band near the Γ-point is almost exclusively due to the S $3p$ orbitals and explains the sensitivity of the optical band gap to the bond length within the sulfur pair as found in Ref. [409].

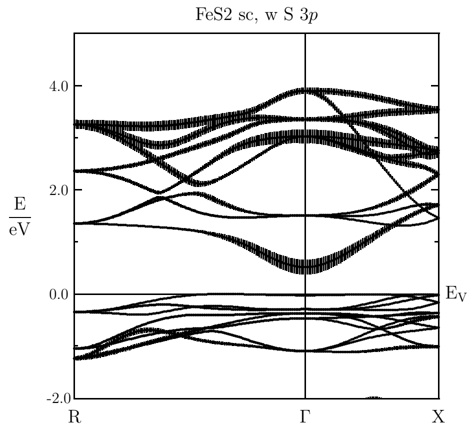

Figure 2.38 Weighted electronic bands of FeS_2. The width of the bars given for each band indicates the contribution due to the S 3*p* orbitals.

2.3.4 Electron densities and potential

We start discussion of the electron densities and the effective potential by calling

```
mnrho.x
```

before the self-consistent calculations start. As outlined previously, this will generate a file FREE, which holds the electron densities and the potential resulting from an assembly of overlapping free atoms in the plot plane defined by the tokens ORIGIN=, RPLOT1=, and RPLOT2=. By typing

```
plrho.x
```

at the systems prompt this file can be used to generate the overlapping free atom potential, which is displayed in Fig. 2.39. where we identify the potential well of the sulfur pair in the middle of the plot. This potential is to be contrasted by the self-consistently calculated potential, which can be accessed by running `mnrho.x` at the very end and going through the plot routine again, this time for file RHO. The result is given in Fig. 2.40. Indeed, both potentials are hard to distinguish. This reflects the observation by Mattheiss mentioned in Sec. 2.2 that the self-consistently calculated electron densities and potential are almost identical to that arising from an overlapping free atom calculation. Of course, the quantities are modified by the formation of the chemical bonds on approaching self-consistency as has been discussed with respect to the valence electron density of Si as displayed in Fig. 2.16 and 2.20. However, as compared to the total valence electron density, these density changes are rather small and, hence, the overlapping free atom quanities serve as a good starting point.

Next we turn to the electron density and, again using `plrho.x` plot the valence electron density, which is displayed in Fig. 2.41. In addition, we show in Fig. 2.42 the

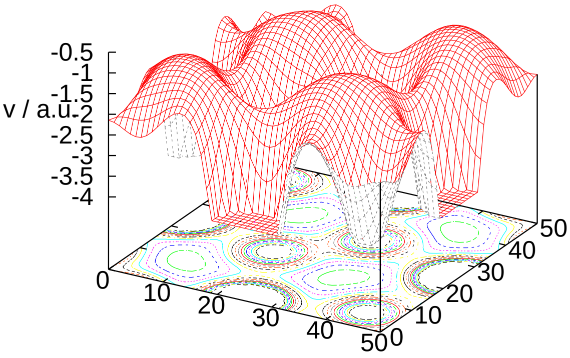

Figure 2.39 Overlapping free atom potential of FeS_2.

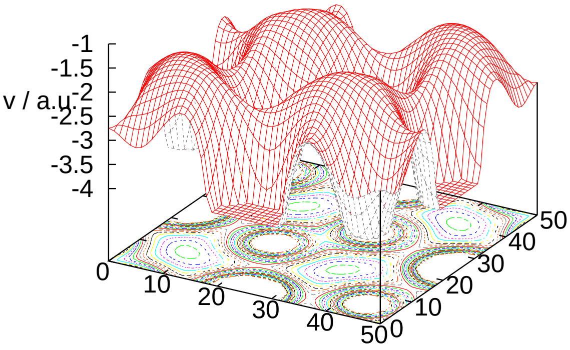

Figure 2.40 Potential of FeS_2.

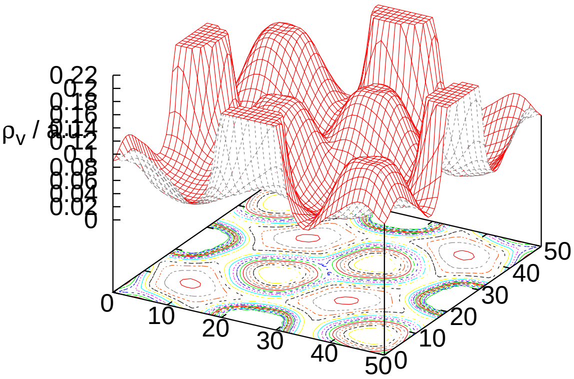

Figure 2.41 Valence electron density of FeS_2.

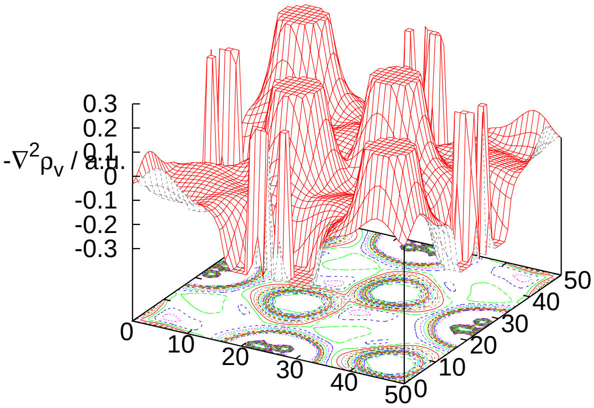

Figure 2.42 Negative Laplacian of the valence electron density of FeS_2.

negative Laplacian, which allows to display more details than the electron density itself.

2.3.5 Structure optimization

In closing this section we turn to full structure optimization for FeS_2. According to the discussion at the begining of this section as well as to the entries in the CTRL file, the pyrite structure depends on two parameters, namely the lattice constant and the sulfur parameter u, which determines the position of the S atoms at (u, u, u) and the symmetry related positions. The subsequent optimization proceeds in two steps.

First, we optimize the lattice constant by calling

```
mnblk.x
```

after having properly prepared both the CTRL file and this shell script along the lines mentioned in Sec. 2.1.8. After successful completion of all calculations, we run the shell script `prblk`, which will extract the cell volumes and total energies from all the output files and write them to a small file called BLK. This file in turn is used by the plot routine called by the command

```
plblk.x
```

and results in the plot given in Fig. 2.43. Here, the dashed line grows out of a third-order Birch-Murnaghan fit [46, 269, 270]. The cell volume corresponds to a lattice constant $a_0 = 10.199 a_B$, which is in good agreement with experimental values. A complete list of published lattice constants is given in Tab. 2.1, which reflects the high quality of the ASW method. This is underlined by a comparison of theoretical and experimental bulk moduli as given in Tab. 2.2,

a_0	method	reference
10.28	NCPP	Zeng and Holzwarth ’94
10.02	FPLO	Opahle *et al.* ’99
10.17	CRYSTAL98	Muscat *et al.* ’02
9.92	CASTEP	Muscat *et al.* ’02
10.20	FPASW	present work
10.23	exp.	Finklea *et al.* ’76
10.22	exp.	Will *et al.* ’84
10.23	exp.	Stevens *et al.* ’91

Table 2.1 Calculated and measured lattice constants of FeS_2.

Next we turn to the internal sulfur parameter. It is optimized following the same procedure as in the frozen phonon calculation for Si in Sec. 2.2. Hence, (after

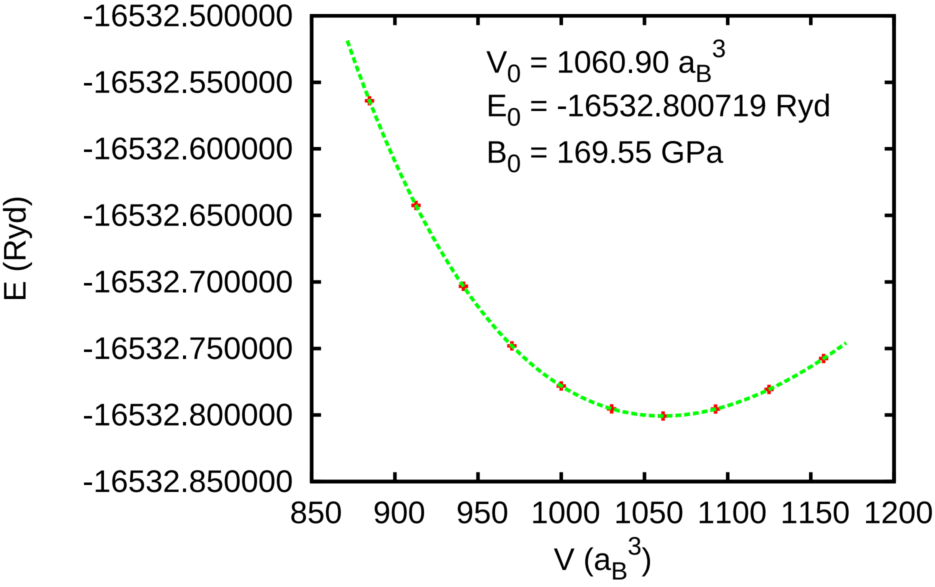

Figure 2.43 Energy vs. volume curve of FeS_2.

B_0	method	reference
187	LMTO	Nguyen-Manh *et al.* ’98
185	FPLO	Opahle *et al.* ’99
209	CRYSTAL98	Muscat *et al.* ’02
208	CASTEP	Muscat *et al.* ’02
170	FPASW	present work
148	exp.	Drickamer *et al.* ’66
118	exp.	Will *et al.* ’84
215	exp.	Chattopadhyay and von Schnering ’85
157	exp.	Fujii *et al.* ’86
143	exp.	Jephcoat and Olson ’87
162	exp.	Ahrens and Jeanloz ’87
145	exp.	Blachnik *et al.* ’98

Table 2.2 Calculated and measured bulk moduli of FeS_2.

changing to subdirectory `mn_opt`) we prepare a set of CTRL files with different sulfur positions (u, u, u), where u varies from 0.376 to 0.386. In addition, we prepare the shell script `mnphn.x` coming with the distribution as described in Sec. 2.2. Running

```
mnphn.x
```

will then produce a set of output files, from which sulfur positions and total enrgies can be extracted and stored in file PHN by the shell script prphn. Finally, the result is plotted by invoking the shell script

```
plphn.x
```

which leads to the results displayed in Fig. 2.44. Again, we contrast the calculated

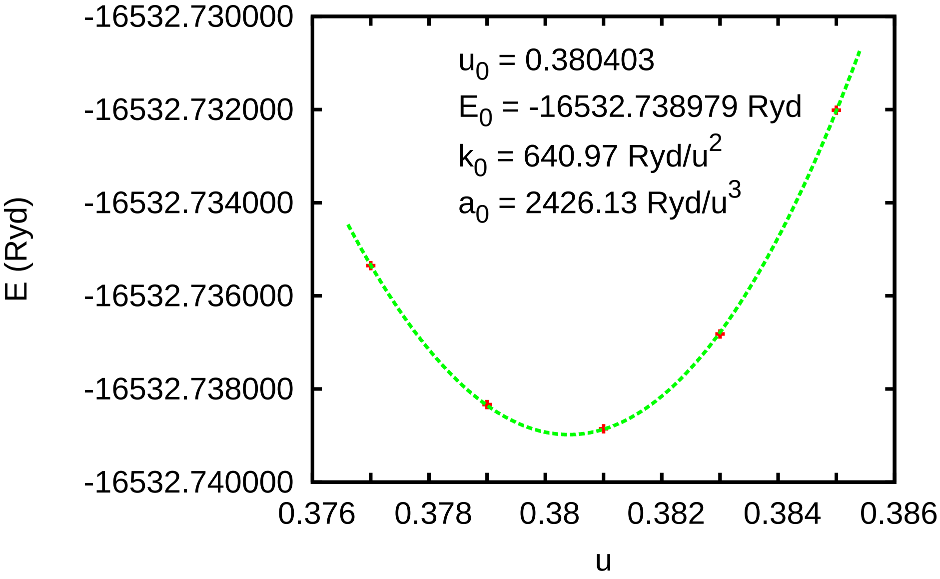

Figure 2.44 Energy vs. sulfur position of FeS$_2$.

u parameter with those growing out of related calculations and experimental values in Tab. 2.3 and again the result gained by the ASW method is not too bad.

Just in order to demonstrate the striking superiority of the full potential description, we complement Fig. 2.44 by Fig. 2.45, which was calculated using version 2.2, which is still based on the ASA but includes the nonspherical contributions to the electron densities and potential. Nevertheless, according to Fig. 2.45, this is not sufficient for the calculation of accurate total energies since the atomic spheres still overlap. Instead, the total energy has to be calculated with nonoverlapping muffin-tin spheres as it is done in the new versions of the ASW code.

u_0	method	reference
0.378	NCPP	Zeng and Holzwarth '94
0.377	FPLO	Opahle *et al.* '99
0.378	CRYSTAL98	Muscat *et al.* '02
0.382	CASTEP	Muscat *et al.* '02
0.380	FPASW	present work
0.386	exp.	Finklea *et al.* '76
0.386	exp.	Will *et al.* '84
0.385	exp.	Stevens *et al.* '91

Table 2.3 Calculated and measured sulfur parameters of FeS_2.

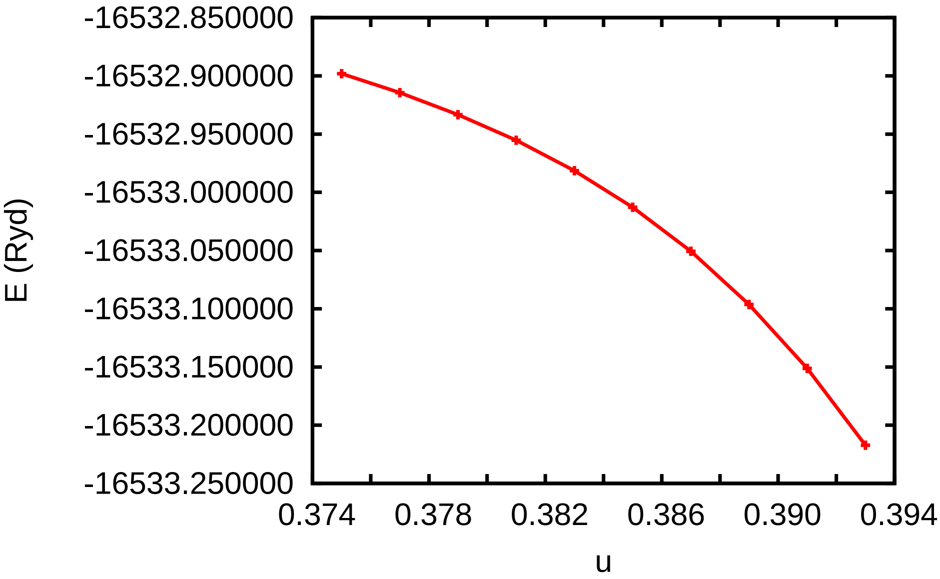

Figure 2.45 Energy vs. sulfur position of FeS_2 as calculated with an ASA^+ code.

2.4 A halfmetallic ferromagnet: CrO_2

Apart from the elemental magnets Fe, Co, Ni, and Gd, chromium dioxide, CrO_2, probably belongs to the most wellknown ferromagnetic metals. Of course, this traces back to its applicability as a material for magnetic recording tapes, which is a consequence of the high Curie point of $T_C = 391K$ well above room temperature.

Additional interest in this compound stems from the fact that in general the transition metal dioxides comprise the largest class of oxides with a similar structure and showing a large variety of physical properties. As is obvious from Tab. 2.4 this diversity shows up mainly in the 3*d* series, which comprises the large-gap

	d^0	d^1	d^2	d^3	d^4	d^5	d^6
3*d*	$\mathrm{TiO_2}$ (S)	$\mathrm{VO_2^*}$ (M–S)	$\mathrm{CrO_2}$ (F–M)	$\mathrm{MnO_2}$ (AF–S)			
4*d*		$\mathrm{NbO_2^*}$ (M–S)	$\mathrm{MoO_2^*}$ (M)	$\mathrm{TcO_2^*}$ (M)	$\mathrm{RuO_2}$ (M)	$\mathrm{RhO_2}$ (M)	
5d		$\mathrm{TaO_2}$ (?)	$\mathrm{WO_2^*}$ (M)	$\mathrm{ReO_2^*}$ (M)	$\mathrm{OsO_2}$ (M)	$\mathrm{IrO_2}$ (M)	$\mathrm{PtO_2^*}$ (M)

* deviations from rutile, M = metal, S = semiconductor
F/AF = ferro-/antiferromagnet

Table 2.4 Properties of transition metal dioxides with rutile-related structure.

semiconductor $\mathrm{TiO_2}$, the metal-insulator system $\mathrm{VO_2}$, the halfmetallic ferromagnet $\mathrm{CrO_2}$, and the antiferromagnetic semiconductor $\mathrm{MnO_2}$ [108]. In contrast, except for $\mathrm{NbO_2}$, which, like $\mathrm{VO_2}$ undergoes a metal-insulator transition accompanied by a structural transition, the 4*d* and 5*d* compounds are neither semiconducting nor magnetic. Nevertheless, there exist several members in each group, which display small but characteristic deviations from the rutile structure [109].

The electronic structure of $\mathrm{CrO_2}$ has been under discussion for a long time. The first calculation performed by Schwarz using the ASW method revealed $\mathrm{CrO_2}$ as a half-metallic ferromagnet, where spin-majority electrons carry metallic conductivity while the spin-minority bands show a gap at the Fermi energy [410]. Subsequent calculations by Matar and coworkers confirmed these findings and revealed the instability of the compound towards antiferromagnetism on slight changes of the crystal structure as might be caused by the fabrication of thin films [411, 412]. Since then several workers have dealt with the material in order to explain the ferromagnetic order.

The rutile structure of $\mathrm{CrO_2}$ is based on a simple tetragonal lattice with space group $P4_2/mnm$ (D_{4h}^{14}, No. 136) and lattice constants $a = 4.4219$Å, $c = 2.9166$Å [413]. The metal atoms are located at the Wyckoff positions (2a): $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and the oxygen atoms occupy the positions (4f): $\pm(u,u,0), \pm(\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2})$ with $u = 0.3024$. The rutile structure is displayed in Fig. 2.46. Alternatively, the structure can be visualized in terms of a body-centered tetragonal lattice formed by the metal atoms, where each metal atom is surrounded by an oxygen octahedron. Octahedra centered at the corners and the center of the cell are rotated by 90° about the tetragonal *c* axis relative to each other. As a consequence, the lattice translational symmetry reduces to simple tetragonal and a unit cell with two for-

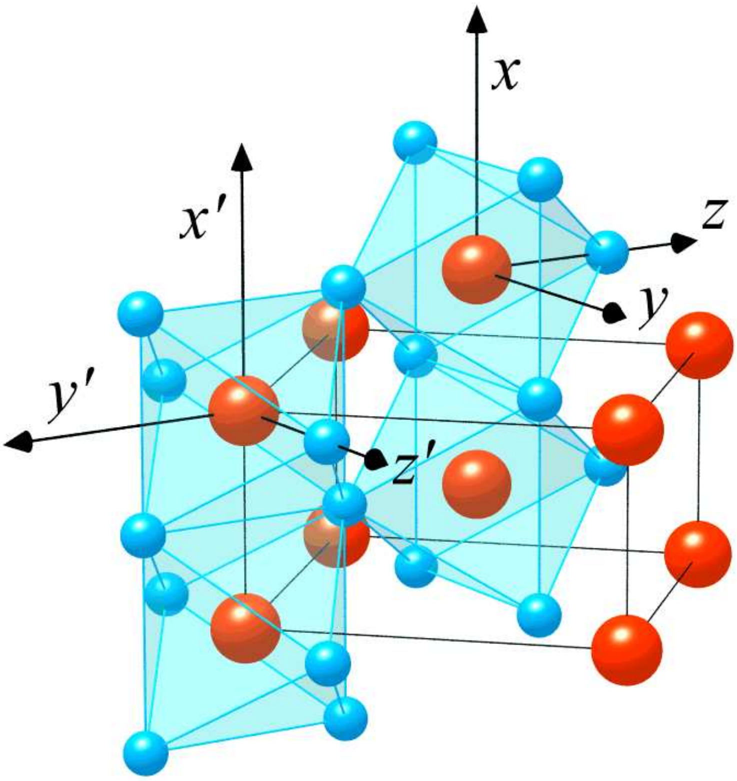

Figure 2.46 The rutile structure. Large and small spheres denote metal and ligand atoms, respectively.

mula units results. Octahedra, which are neighboured along the rutile c axis, share edges whereas the resulting octahedral chains are interlinked via corners. Each octahedron has orthorhombic symmetry although the deviations from tetragonal and even cubic geometry for most compounds are relatively small and still allow for a discussion in terms of the latter. There exist two different metal-oxygen distances, namely, the apical distance, which is between metal and oxygen atoms having the same z value, and the equatorial distance between the metal atom and the four neighbouring ligand atoms with $z = z_{\text{metal}} \pm 1/2$ [108].

As has been already indicated in Fig. 2.46 it is useful to discuss the electronic structure of rutile-type compounds in terms of local coordinate systems centered at each metal site. Note that due to the different orientation of octahedra centered at the corner and the center of the rutile cell, the local z axes point alternately along the [110] and [1$\bar{1}$0] direction. In contrast to the usual adjustment of the x and y axes parallel to the metal-ligand bonds we have rotated these axes by 45° about the local z axes such that they are parallel and perpendicular, respectively, to the rutile c axis.

With the previous choice of local coordinate systems the e_g states resulting from the cubic part of the crystal field splitting of the metal d orbitals comprise the $d_{3z^2-r^2}$ and d_{xy} orbitals whereas the t_{2g} states are made of the $d_{x^2-y^2}$, d_{xz}, and d_{yz} orbitals. While the $d_{x^2-y^2}$ orbitals point along the rutile c and the local y axes, i.e. towards the edges of the basal plane of the octahedron the d_{xz} and d_{yz} orbitals are directed towards the faces.

The calculations to be discussed in the present section proceed in several steps. We start performing spin-degenerate calculations before allowing for spin-polarization. For the latter we distinguish ferromagnetic from antiferromagnetic ordering. In order to prepare for the calculations, we create the corresponding subdirectories by

```
mkdir cro2
cd cro2
mkdir pac
mkdir nm
mkdir fe
mkdir af
cd pac
```

and turn to the setup of the CTRL file and the sphere packing.

2.4.1 CTRL file and sphere packing

The previous information is summarized in the following CTRL file.

```
HEADER  CrO2 rutile
        data by A. A. Bolzan, C. Fong, B. J. Kennedy, C. J. Howard,
        Acta Cryst. B53, 373 (1997).
VERSION ASW-2.6
IO      HELP=F SHOW=T VERBOS=30 CLEAN=T
OPTIONS REL=T OVLCHK=T
STRUC   ALAT=8.35618 CLAT=5.511575 CNTR=P
CLASS   ATOM=CR Z=24 R=2.17957824
        ATOM=O  Z= 8 R=1.86761849
SITE    CARTP=F
        ATOM=CR POS= 0.000000  0.000000  0.000000
        ATOM=CR POS=-0.500000 -0.500000 -0.500000
        ATOM=O  POS= 0.302400  0.302400  0.000000
        ATOM=O  POS=-0.302400 -0.302400  0.000000
        ATOM=O  POS=-0.197600  0.197600 -0.500000
        ATOM=O  POS= 0.197600 -0.197600 -0.500000
SYMGRP
ENVEL   EKAP=-0.015
BZSMP   NKBAB=6 BZINT=LTM EMIN=-1.5 EMAX=1.5 NDOS=3000
        NORD=3 WIDTH=0.01 SAVDOS=F SAVCOOP=F SAVFERM=F
CHARGE  NETA=2 EETA=-3.0 -5.0 SAVRHO=F
CONTROL START= QUIT= FREE=F NITBND=99 CNVG=1.0D-08 CNVGET=1.0D-08
```

```
        NITATM=50 CNVGQA=1.0D-10
MIXING  NMIXB=5 BETAB=0.5 INCBB=T NMIXA=5 BETAA=0.5
SYMLIN  NPAN=7 NPTS=400 CARTE=F
        LABEL=g ENDPT= 0.0  0.0  0.0
        LABEL=M ENDPT= 0.5  0.5  0.0
        LABEL=X ENDPT= 0.0  0.5  0.0
        LABEL=g ENDPT= 0.0  0.0  0.0
        LABEL=Z ENDPT= 0.0  0.0  0.5
        LABEL=A ENDPT= 0.5  0.5  0.5
        LABEL=R ENDPT= 0.0  0.5  0.5
        LABEL=Z ENDPT= 0.0  0.0  0.5
PLOT    CARTV=F
        ORIGIN= 0.0  0.0  0.0
        RPLOT1= 1.0  0.0  0.0
        RPLOT2= 0.0  1.0  0.0
        RPLOT3= 0.0  0.0  1.0
        NPDIV1=50 NPDIV2=50 NPDIV3=0
```

A few new tokens are of special interest here. Scoping with the tetragonal crystal structure we have inserted the token CLAT=, which contains the c lattice constant of the tetragonal cell. Alternatively, we could have specified the ratio c/a of the tetragonal lattice constants using the token CBYA=. In particular for non-cubic crystal structures it is useful to specify the atomic positions in terms of the primitive translations of the conventional cell, which could be non-orthogonal or of unequal length, rather than the Cartesian coordinate system scaled by the lattice constant a. The corresponding switch is covered by the token CARTP=F. As a consequence, the last component of the second chromium site as well as half of the oxygen sites is given by 0.5 rather than 0.32979 ($= \frac{c}{2a}$).

As for iron pyrite the openness of the rutile structure requires to insert empty spheres. Again this is done by executing mnpac.x. It produces file CNEW, which deviates from the above CTRL file by the categories CLASS and SITE updated as follows.

```
CLASS   ATOM=CR Z=24 R=2.16612899 LMXL=2 CONF=4 4 3 4
                QVAL= 1.0  0.0  5.0  0.0
        ATOM=O  Z= 8 R=1.87483912 LMXL=1 CONF=2 2 3
                QVAL= 2.0  4.0  0.0
        ATOM=E1 Z= 0 R=1.65252923 LMXL=1 CONF=1 2 3
                QVAL= 0.0  0.0  0.0
        ATOM=E2 Z= 0 R=1.76771917 LMXL=1 CONF=1 2 3
                QVAL= 0.0  0.0  0.0
        ATOM=E3 Z= 0 R=0.85735960 LMXL=0 CONF=1 2
                QVAL= 0.0  0.0
SITE    CARTP=F
        ATOM=CR POS= 0.000000  0.000000  0.000000
        ATOM=CR POS= 0.500000  0.500000  0.500000
        ATOM=O  POS= 0.302400  0.302400  0.000000
        ATOM=O  POS=-0.302400 -0.302400  0.000000
        ATOM=O  POS=-0.197600  0.197600  0.500000
        ATOM=O  POS= 0.197600 -0.197600  0.500000
        ATOM=E1 POS= 0.500000  0.000000 -0.250000
        ATOM=E1 POS= 0.500000  0.000000  0.250000
```

```
ATOM=E1 POS= 0.000000 -0.500000 -0.250000
ATOM=E1 POS= 0.000000 -0.500000  0.250000
ATOM=E2 POS= 0.318691 -0.318691  0.000000
ATOM=E2 POS=-0.318691  0.318691  0.000000
ATOM=E2 POS=-0.181309 -0.181309 -0.500000
ATOM=E2 POS= 0.181309  0.181309 -0.500000
ATOM=E3 POS= 0.313120 -0.055474  0.000000
ATOM=E3 POS=-0.313120  0.055474  0.000000
ATOM=E3 POS=-0.186880 -0.444526 -0.500000
ATOM=E3 POS= 0.186880  0.444526  0.500000
ATOM=E3 POS= 0.055474 -0.313120  0.000000
ATOM=E3 POS=-0.055474  0.313120  0.000000
ATOM=E3 POS=-0.444526 -0.186880 -0.500000
ATOM=E3 POS= 0.444526  0.186880 -0.500000
```

To be specific, 16 empty spheres of three different types have been added with radii ranging from 0.85 to 1.77 a_B.

2.4.2 Spin-degenerate calculations

With the complete CTRL file at hand we are in a position to perform the self-consistent calculations for non-magnetic CrO_2 by typing

```
mnall.x
```

at the systems prompt. Although it is possible to start with the spin-polarized calculations rightaway, it is recommended to do the calculations for the spin-degenerate case in advance. First, these calculations need about half the execution time since the secular matrix has to be constructed and solved for one spin direction only. Owing to the restart facility of the ASW program `mnscf.run` the subsequent spin-polarized calculations can start away with the converged files of the spin-degenerate calculations rather then starting from scratch. Second, the result for the spin-degenerate case establish a reference, to which the results of the spin-polarized calculation can be compared. In particular, by checking the total energies we are able find out the relative stability of the ferromagnetic state.

After convergence has been achieved `monic outlst18` summarizes the results as follows.

```
ASW-2.6, program MNSCF started on asterix at Thu, 05 Feb 2009, 22:53:46.
Calculation converged after  13 iteration(s).
                      Start of Iteration   13
   396 irreducible k-points generated from    4116 ( 14, 14, 21).
           Fermi energy - MTZ =     0.758139 Ryd
The system is a metal:
           DOS at Fermi energy:   124.457446 1/Ryd
           Gamma * (f.u./cell):    21.561888 mJ/(mole*K**2)
Mean-square residual:                    0.760111D-23
Total free atom energies     :  -4790.190932 Ryd
Total variational energy     :  -4793.995502 Ryd
```

```
 Cohesive energy              :       3.804569 Ryd
  qdiff =        0.00000000  <        0.00000001
  ediff =        0.00000001  <        0.00000001
 ASW-2.6, program MNSCF ended on asterix at Thu, 05 Feb 2009, 23:03:58.
```

In particular, non-magnetic CrO_2 turns out to be a metal with a rather high density of states at E_F. Within the framework of the Stoner theory of magnetism this is interpreted as a precursor of the ferromagnetic order of this material. We display in Fig. 2.47 the electronic states along selected high symmetry lines within the first Brillouin zone of the simple tetragonal lattice, Fig. B.5(a). The corresponding density of states (DOS) is generated with the plot routine pldos.run, which opens the follwoing dialog.

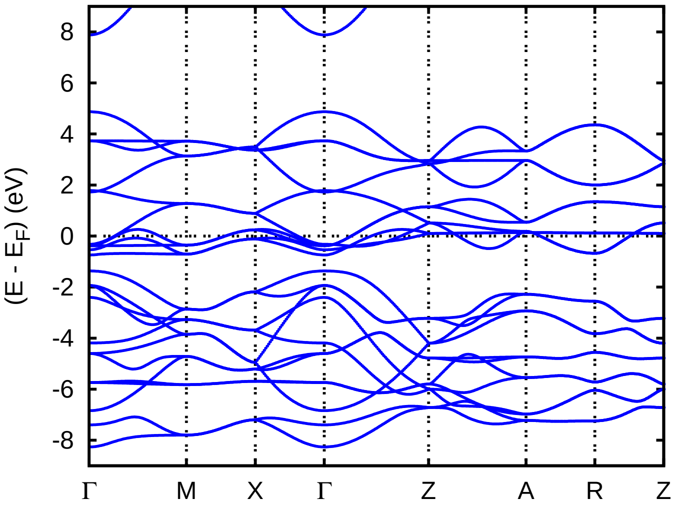

Figure 2.47 Electronic bands of CrO_2 along selected symmetry lines within the first Brillouin zone of the simple tetragonal lattice, Fig. B.5(a).

```
 ASW-2.6, program PLDOS started on asterix at Mon, 09 Feb 2009, 19:46:51.

     Copyright (C) 1992-2009 Volker Eyert
     Please see file COPYRIGHT for details

 All input will be echoed to file PLID.

 Enter terminal type:
 1 = X-Windows (default)
 2 = PC-Screen (vt220-emulation)
 3 = suppress terminal output
/
```

```
 Enter output device (default: 1):
 1 = Color postscript
 2 = Postscript
 3 = PDF (not yet supported)
 4 = JPEG (not yet supported)
 5 = LaTeX
 6 = LaTeX (special)
 7 = HP LaserJet III (PCL5)
 8 = PNG
 9 = GIF
10 = leave decision for later
11 = suppress output to file
/
 Portrait (P), landscape (L) or encapsulated postscript plot (E, default)?
/
 Enter title:


 Please wait a moment: I'm reading rest of file DOS.
 Energies in Rydberg (F) or eV (T, default)?
/
 Energies relative to MTZ (0) or EFermi (F, default)?
/
 Energy axis to the top (F) or right (T, default)?
/
 Plot DOS (F, default) or integrated DOS (T)?
/

 Start setting up curve 1:
 Plot partial (F) or total DOS (T, default)?
F
 For partial DOS: Rotate reference frame for orbitals?
 Enter rotation symbol (Default: E):
R8(-1,-1,0)*R4(1,-1,0)

 Enter orbital(s) to be included:
 Note: notation of the orbitals refers to the rotated reference frame!
 Select from the classes (blank or "/" to complete the list):
  CR      O       E1      E2      E3
CR

 Class CR    : atom   1 at     0.000000    0.000000    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
6
8
9/

 Class CR    : atom   2 at    -0.500000   -0.500000   -0.329790
 Select from the following orbitals:
```

```
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
/
 Select from the classes (blank or "/" to complete the list):
  CR      O       E1      E2      E3
/

 The following orbitals have been selected:
 Class CR    : atom    1, orbital yz
 Class CR    : atom    1, orbital xz
 Class CR    : atom    1, orbital x^2-y^2

 Enter scaling factor (default 1.0):
/

 Broadening of this curve (T) or not (F, default)?
/

 Select curve style (default: 1) (A * marks styles already selected):
solid/green      (1)   , dash1/blue       (2)   ,
dash2/red        (3)   , dot/magenta      (4)   ,
dashdot1/cyan    (5)   , dashdot2/yellow  (6)   ,
chaindash1/black (7)   , chaindash2/coral (8)   ,
chaindash3/gray  (9)   ,
/

 Enter curve label ("/" to suppress)
Cr 3d t_{2g}

 Please wait a moment: I'm working on this curve.
 Set up more curves (T)? Default is F.
T

 Start setting up curve 2:
 Plot partial (F) or total DOS (T, default)?
T
 For partial DOS: Rotate reference frame for orbitals?
 Enter rotation symbol (Default: R8(-1,-1,0)*R4(1,-1,0)):
/

 Enter orbital(s) to be included:
 Note: notation of the orbitals refers to the rotated reference frame!
 Select from the classes (blank or "/" to complete the list):
  CR      O       E1      E2      E3
CR

 Class CR    : atom   1 at     0.000000    0.000000    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
```

```
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
5
7/

 Class CR    : atom   2 at    -0.500000   -0.500000   -0.329790
 Select from the following orbitals:
 0: all         -1: all p       -2: all d       -3: all f
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2     10: 3x^2y-y^3
11: xyz         12: 5yz^2-yr^2  13: 5z^3-3zr^2  14: 5xz^2-xr^2  15: x^2z-y^2z
16: x^3-3xy^2
/
 Select from the classes (blank or "/" to complete the list):
  CR      O       E1      E2      E3
/

 The following orbitals have been selected:
 Class CR    : atom    1, orbital xy
 Class CR    : atom    1, orbital 3z^2-r^2

 Enter scaling factor (default 1.0):
/

 Broadening of this curve (T) or not (F, default)?
/

 Select curve style (default: 2) (A * marks styles already selected):
solid/green      (1) * , dash1/blue       (2)   ,
dash2/red        (3)   , dot/magenta      (4)   ,
dashdot1/cyan    (5)   , dashdot2/yellow  (6)   ,
chaindash1/black (7)   , chaindash2/coral (8)   ,
chaindash3/gray  (9)   ,
/

 Enter curve label ("/" to suppress)
Cr 3d e_g

 Please wait a moment: I'm working on this curve.
 Set up more curves (T)? Default is F.
T

 Start setting up curve 3:
 Plot partial (F) or total DOS (T, default)?
F
 For partial DOS: Rotate reference frame for orbitals?
 Enter rotation symbol (Default: R8(-1,-1,0)*R4(1,-1,0)):
/

 Enter orbital(s) to be included:
 Note: notation of the orbitals refers to the rotated reference frame!
 Select from the classes (blank or "/" to complete the list):
  CR      O       E1      E2      E3
O
```

```
 Class O     : atom   3 at     0.302400    0.302400    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2
-1/

 Class O     : atom   4 at    -0.302400   -0.302400    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2
-1/

 Class O     : atom   5 at    -0.197600    0.197600   -0.329790
 Select from the following orbitals:
 0: all         -1: all p       -2: all d
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2
/

 Class O     : atom   6 at     0.197600   -0.197600   -0.329790
 Select from the following orbitals:
 0: all         -1: all p       -2: all d
 1: s            2: y            3: z            4: x            5: xy
 6: yz           7: 3z^2-r^2     8: xz           9: x^2-y^2
/
 Select from the classes (blank or "/" to complete the list):
  CR      O       E1      E2      E3
/

 The following orbitals have been selected:
 Class O     : atom    3, orbital y
 Class O     : atom    3, orbital z
 Class O     : atom    3, orbital x
 Class O     : atom    4, orbital y
 Class O     : atom    4, orbital z
 Class O     : atom    4, orbital x

 For this choice of orbitals rotation of the reference frame is ignored.

 Enter scaling factor (default 1.0):
/

 Broadening of this curve (T) or not (F, default)?
/

 Select curve style (default: 3) (A * marks styles already selected):
solid/green      (1) * , dash1/blue       (2) * ,
dash2/red        (3)   , dot/magenta      (4)   ,
dashdot1/cyan    (5)   , dashdot2/yellow  (6)   ,
chaindash1/black (7)   , chaindash2/coral (8)   ,
chaindash3/gray  (9)   ,
```

```
/

 Enter curve label ("/" to suppress)
O 2p

 Please wait a moment: I'm working on this curve.
 Set up more curves (T)? Default is F.
/

 Center of gravity of DOS curve  1 (Spin 1) - EF :   -0.3555 eV
 Center of gravity of DOS curve  2 (Spin 1) - EF :    0.2763 eV
 Center of gravity of DOS curve  3 (Spin 1) - EF :   -3.5209 eV

 Indicate center of gravities (F, default)?
/

 Ebot =   -20.192732 eV , Etop =    10.093539 eV  relative to EF
 Emin =   -21.000000 eV , Emax =     6.000000 eV  relative to EF
 Enter new Emin, Emax to change the default:
-9.0
9.0

 DOStop =    10.292535 1/eV
 DOSmax =    20.000000 1/eV
 Enter new DOSmax to change this default:
11.0
 Enter energetic position of curve labels ("/" to use default):
/
 task  1, total       :  cpu time:     0.08800 sec

 ASW-2.6, program PLDOS ended on asterix at Mon, 09 Feb 2009, 19:46:51.

    Please delete files DOS and dos.ps when finished!!!
```

As a result, we obtain partial DOS as given in Fig. 2.48. In Figs. 2.47 and 2.48 four groups of bands are identified. In the energy range from −7.6 to −1.8 eV we observe 12 bands, which trace back mainly to O 2*p* states but have a non-negligible contribution due to the Cr 3*d* states. Bands are most easily counted along the direction X-R where they are twofold degenerate. The next two groups, which extend from −0.8 to 1.7 eV and from 1.7 to 5.2 eV, contain six and four bands, respectively and originate mainly from Cr 3*d* states. Yet, *p*-*d* hybridization causes additional O 2*p* contributions in this energy range. Finally, we observe Cr 4*s* states starting at 8.0 eV.

Crystal field splitting expected from the fact that the metal atoms are located at the centers of slightly distorted CrO_6 octahedra leads to almost perfect energetical separation of the t_{2g} and e_g manifolds of the Cr 3*d* states. Yet, as already mentioned above the standard axes of the local octahedra differ from the Cartesian coodinate system used to specify the primitive translations. For this reason, a transformation of the coordinate system had to be performed before the projected densities of states

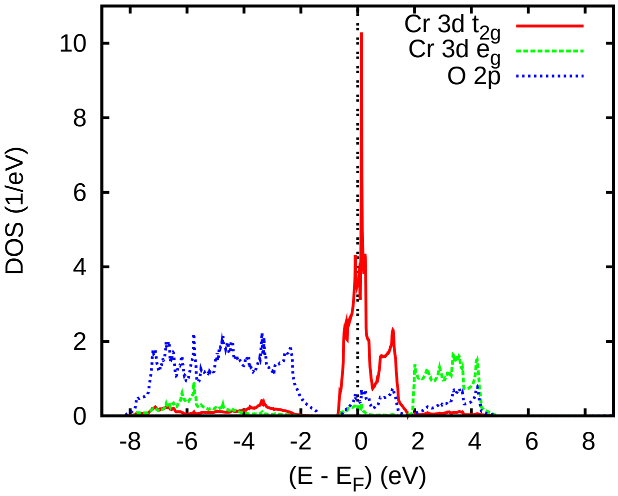

Figure 2.48 Partial densities of states (DOS) of CrO_2 per formula unit. Selection of orbitals is relative to the local rotated reference frame.

could be plotted. This was achieved by specifying the correct rotation matrix in the above dialog, namely

```
R8(-1,-1,0)*R4(1,-1,0)
```

On scanning the dialog you will realize that after the first input of the rotation matrix it is kept as default for the following curves. However, the program detects the selection of all p orbitals for the oxygen partial DOS and notifies the user that the rotation can be ignored in this case.

The single contributions to the partial t_{2g} and e_g DOS are displayed in Fig. 2.49, where again we have included only the single chromium atom at $(0, 0, 0)$ and used the local rotated reference frame. As in Fig. 2.48 the almost perfect energetical separation of the $3d$ t_{2g} and e_g groups of bands is clearly revealed. The former states appear almost exclusively in the energy range from -0.8 to 1.7 eV whereas the e_g states dominate the bands between 1.7 and 5.2 eV. The small but finite t_{2g}-e_g configuration mixing is a measure of octahedral distortions, i.e. the deviation from local cubic symmetry. Contributions of the Cr $3d$ states to the oxygen bands are slightly larger for the e_g states which, forming σ bonds, experience a larger overlap with the O $2p$ states. For the same reason, the bonding-antibonding splitting is larger for the e_g states as compared to the t_{2g} states, which give rise to π bonds.

Chemical bonding is addressed via the COOP or the covalence energy. E_{cov} curves growing out of the plot routine `plcop.run` are displayed in Fig. 2.50. Obviously, bonding within the O $2p$ states hardly contributes. In contrast, metal-ligand overlap is bonding and antibonding in the oxygen and chromium dominated electronic bands, this causing most of the stability of the compound. Finally, metal-metal bonding

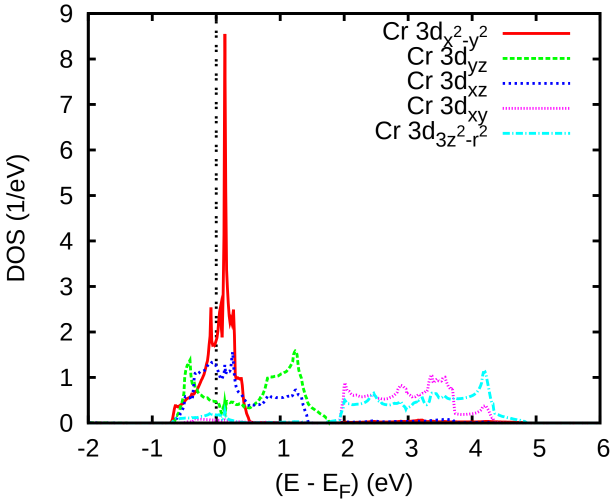

Figure 2.49 Partial Cr $3d$ t_{2g} and e_g densities of states (DOS) of CrO_2. Selection of orbitals is relative to the local rotated reference frame.

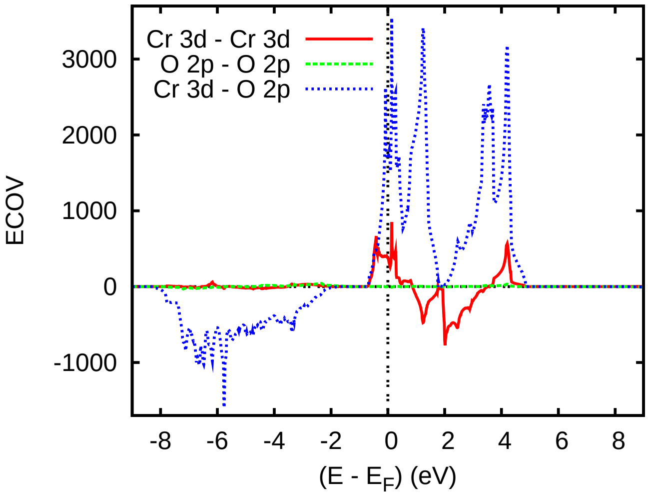

Figure 2.50 Partial covalence energies (E_{cov}) of CrO_2.

appears in the t_{2g} and e_g group of bands, being antibonding and bonding in the respective lower and upper part.

As has turned out in previous work on the neighbouring transition metal dioxides inspection of the weighted band structures is a necessary prerequisite for a deeper understanding of these materials. This holds especially for the chromium $3d$ t_{2g}

levels, which we address separately. For the $d_{x^2-y^2}$ orbital the result is shown in Fig. 2.51. It resulted from calling the plot program plbnd.x and entering the following

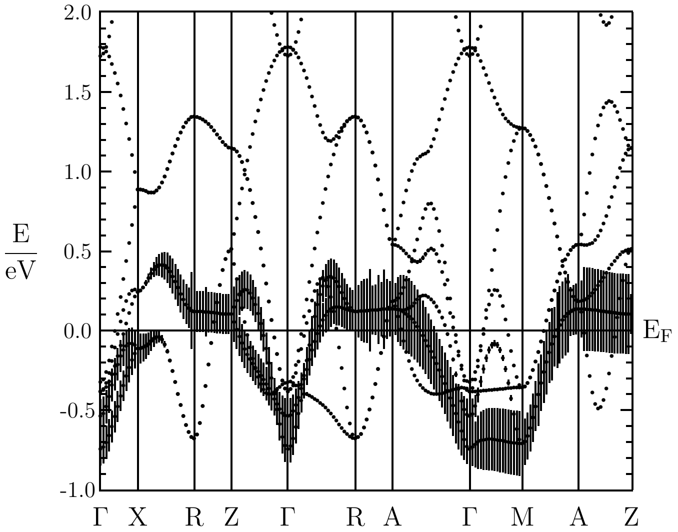

Figure 2.51 Weighted electronic bands of CrO_2. The width of the bars given for each band indicates the contribution due to the $3d_{x^2-y^2}$ orbital of the Cr atom at (0,0,0) relative to the local rotated reference frame.

dialog.

```
 ASW-2.6, program PLBND started on asterix at Mon, 09 Feb 2009, 20:24:16.

     Copyright (C) 1992-2009 Volker Eyert
     Please see file COPYRIGHT for details

 All input will be echoed to file PLIB.

 Enter terminal type:
 1 = X-Windows (default)
 2 = PC-Screen (vt220-emulation)
 3 = suppress terminal output
/
 Enter output device (default: 1):
 1 = Color postscript
 2 = Postscript
 3 = PDF (not yet supported)
 4 = JPEG (not yet supported)
 5 = LaTeX
 6 = LaTeX (special)
 7 = HP LaserJet III (PCL5)
 8 = PNG
 9 = GIF
10 = leave decision for later
```

```
11 = suppress output to file
6
 Portrait (P, default) or landscape plot (L)?
/
 Enter title:


 Please wait a moment: I'm reading rest of file BNDE.
 Timing for   19 points out of  194:     0.00000 sec.

 Energies in Rydberg (F) or eV (T, default)?
/
 Energies relative to MTZ (0) or EFermi (F, default)?
/
 Energies connected by lines (T) (default F)?
/
 Plot orbital character (default F)?
T
 For plotting orbital character: Rotate reference frame for orbitals?
 Enter rotation symbol (E for unity):
R8(-1,-1,0)*R4(1,-1,0)

 Enter orbital(s) to be included:
 Note: notation of the orbitals refers to the rotated reference frame!
 Select from the classes (blank or "/" to complete the list):
  CR      O       E1      E2      E3
CR

 Class CR    : atom   1 at     0.000000    0.000000    0.000000
 Select from the following orbitals:
 0: all         -1: all p       -2: all d
 1: s           2: y            3: z            4: x            5: xy
 6: yz          7: 3z^2-r^2     8: xz           9: x^2-y^2
9/

 Class CR    : atom   2 at    -0.500000   -0.500000   -0.329790
 Select from the following orbitals:
 0: all         -1: all p       -2: all d
 1: s           2: y            3: z            4: x            5: xy
 6: yz          7: 3z^2-r^2     8: xz           9: x^2-y^2
/
 Select from the classes (blank or "/" to complete the list):
  CR      O       E1      E2      E3
/

 The following orbitals have been selected:
 Class CR    : atom    1, orbital x^2-y^2

 Ebot =   -20.225934 eV , Etop =    83.109448 eV  relative to EF
 Emin =   -21.000000 eV , Emax =     6.000000 eV  relative to EF
 Enter new Emin, Emax to change these defaults:
-1.0
2.0
 Rescale orbital weights (default:   0.0750eV )?
```

```
0.3

 Please wait a moment: I'm working on the weights.
 Timing for   19 points out of  194:     0.01200 sec.

 Enter the horizontal and vertical extension in mm.
 Default: 100.0 x  90.0
/
 task  1, total       :  cpu time:     0.25201 sec

 ASW-2.6, program PLBND ended on asterix at Mon, 09 Feb 2009, 20:24:16.

    Please delete files BNDE BNDV and bnd.tex when finished!!!
```

As in Sec. 2.1.4 the orbital to be included has to be specified. Here, the input "9" selects the $d_{x^2-y^2}$ orbital. However, before the rotation matrix has to be given in the same form as for program pldos.run above. Since LaTeX output was requested the plot routine plbnd.run writes to the file *bnd.tex*, from which the postscript file *bnd.ps* is created by invoking the shell script plbnd.lx. The corresponding results for the d_{xz} and d_{yz} orbitals are shown in Figs. 2.52 and 2.53. The following features

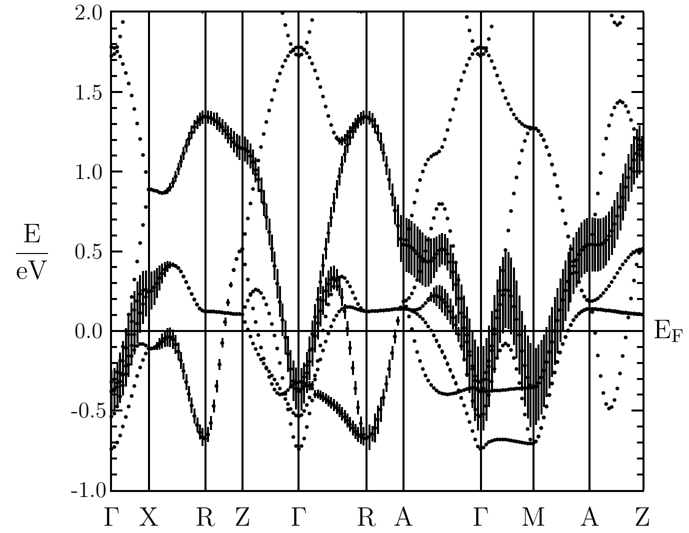

Figure 2.52 Weighted electronic bands of CrO_2. The width of the bars given for each band indicates the contribution due to the $3d_{xz}$ orbital of the Cr atom at (0,0,0) relative to the local rotated reference frame.

are worth mentioning. On relating Fig. 2.51 to the Brillouin zone of the simple tetragonal lattice, Fig. B.5(a) we observe negligible dispersions along all lines within the planes spanned by the either the points *Γ*, X, and M, or else the points Z, R, and A. In contrast, dispersion along all lines connecting these plains is about 0.8 eV.

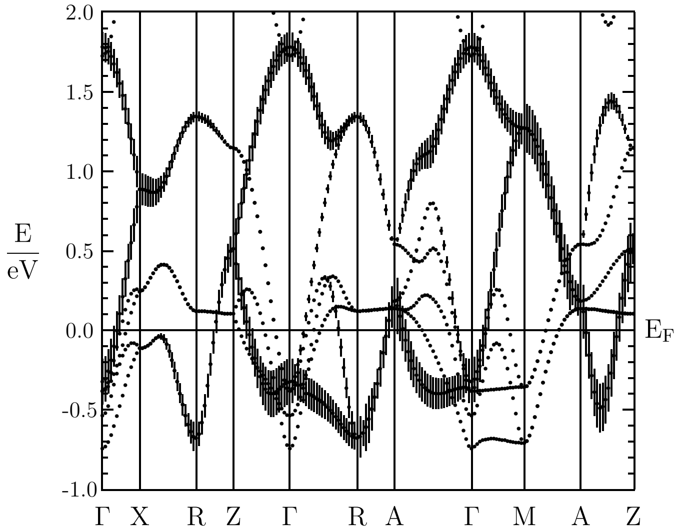

Figure 2.53 Weighted electronic bands of CrO_2. The width of the bars given for each band indicates the contribution due to the $3d_{yz}$ orbital of the Cr atom at (0,0,0) relative to the local rotated reference frame.

Thus one finds a predominantly one-dimensional behaviour. This is different for the bands highlighted in Figs. 2.52 and 2.53, which display dispersions of a similar size along all lines.

2.4.3 Spin-polarized ferromagnetic calculations

Before adapting the CTRL file for the spin-polarized calculations you should copy it to another directory (subdirectory `fe` already created before) in order to preserve the results of the non-magnetic calculations. In order to perform spin-polarized calculations two new tokens have to be added to the new CTRL file. In category OPTIONS the entry NSPIN=2 must be inserted, which tells the program to perform a spin-polarized calculation. Furthermore, each orbital has to be given a starting value for the polarization. Otherwise the calculation would again converge to the spin-degenerate solution. Breaking the spin-symmetry is achieved by adding the token MVAL= for each atomic class in category CLASS followed by the polarization for each orbital. For ferromagnetic CrO_2 the new categroy CLASS looks like the following.

```
CLASS   ATOM=CR Z=24 R=2.16612899 LMXL=2 CONF=4 4 3 4
                QVAL= 1.0  0.0  5.0  0.0  MVAL= 0.0  0.0  2.0  0.0
        ATOM=O  Z= 8 R=1.87483912 LMXL=1 CONF=2 2 3
                QVAL= 2.0  4.0  0.0       MVAL= 0.0  0.0  0.0
        ATOM=E1 Z= 0 R=1.65252923 LMXL=1 CONF=1 2 3
```

```
          QVAL= 0.0  0.0  0.0       MVAL= 0.0  0.0  0.0
     ATOM=E2 Z= 0 R=1.76771917 LMXL=1 CONF=1 2 3
          QVAL= 0.0  0.0  0.0       MVAL= 0.0  0.0  0.0
     ATOM=E3 Z= 0 R=0.85735960 LMXL=0 CONF=1 2
          QVAL= 0.0  0.0            MVAL= 0.0  0.0
```

Once these changes have been made you could type mnall.x as in the spin-degenerate case, Sec. 2.4.2. However, since you have only copied the CTRL file to the new directory the program mnscf.run will start the spin-polarized calculations from scratch. An alternative and very elegant way consists of also copying the atomic files of the converged non-magnetic calculations. Now invoking mnall.x lets the program mnscf.run (which is the first program called from the shell script mnall.x) detect the preconverged files. As already outlined in Sec. 2.1 this will invoke the restart facility of the program. During this startup phase the information from the converged spin-degenerate calculations is combined with the starting values for the magnetic moments per orbital as given in the CTRL file in order to find an optimal starting point for the spin-polarized calculation. As a consequence, very fast iteration to full self-consistency is achieved.

After convergence monic outlst18 summarizes the results as follows.

```
ASW-2.6, program MNSCF started on asterix at Thu, 05 Feb 2009, 23:20:45.
Calculation converged after  14 iteration(s).
                      Start of Iteration   14
   396 irreducible k-points generated from    4116 ( 14, 14, 21).
           Fermi energy - MTZ =     0.739899 Ryd
The system is a magnetic metal and could still be a half-metallic ferromagnet:
           DOS at Fermi energy:    18.932894 1/Ryd
           Gamma * (f.u./cell):     3.280068 mJ/(mole*K**2)
Magnetic moment of unit cell    =     4.000000
Mean-square residual:                   0.681662D-23
Total free atom energies     :  -4790.190932 Ryd
Total variational energy     :  -4794.067509 Ryd
Cohesive energy              :      3.876576 Ryd
 qdiff =       0.00000000  <        0.00000001
 ediff =       0.00000000  <        0.00000001
ASW-2.6, program MNSCF ended on asterix at Thu, 05 Feb 2009, 23:59:01.
```

According to this output a magnetic solution with a magnetic moment of $4.0\mu_B$ per unit cell has indeed been found. Its stability becomes obvious from a comparison of the total energy to that of the non-magnetic solution, the difference being 72 mRyd per formula unit. Worth mentioning is the considerable decrease of the DOS at E_F as compared to the non-magnetic case. The reason is obvious from the band structure, Fig. 2.54, as well as in the corresponding density of states (DOS) as given in Fig. 2.55. While the O $2p$-dominated spin-up and spin-down states still occupy similar energy intervals the Cr $3d$ bands experience spin-splitting of about 2 eV. As a consequence, spin-minority Cr $3d$ states are shifted above the Fermi energy and left unoccupied. In contrast, metallic conductivity is carried alone by the spin-majority states. The classification of CrO_2 as a halfmetallic ferromagnet proposed by Schwarz is thus confirmed.

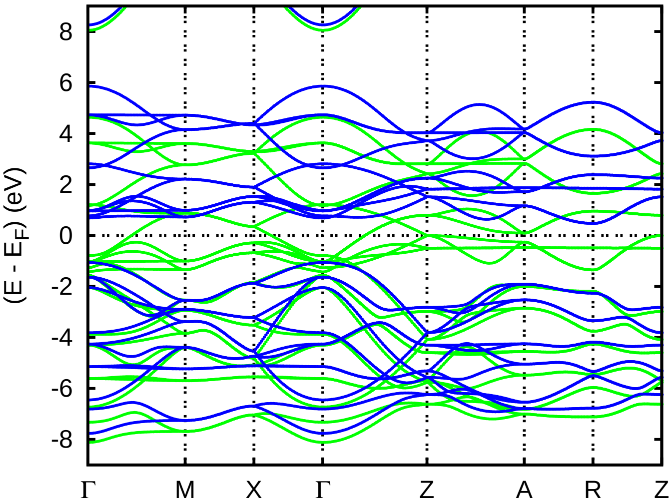

Figure 2.54 Electronic bands of ferromagnetic CrO_2 along selected symmetry lines within the first Brillouin zone of the simple tetragonal lattice, Fig. B.5(a).

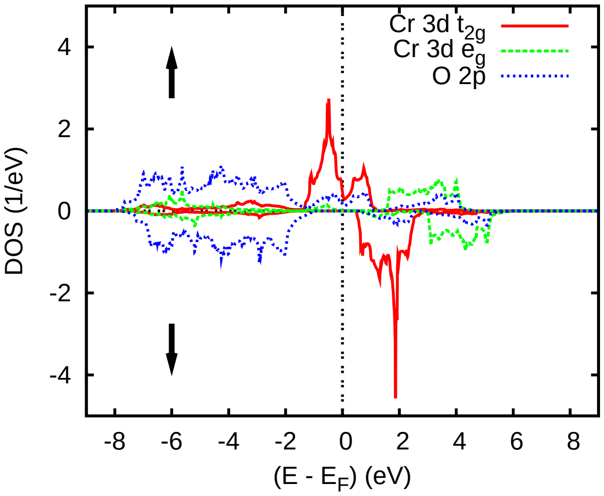

Figure 2.55 Partial densities of states (DOS) of ferromagnetic CrO_2 per formula unit.

As for the spin-degenerate case the partial DOS can be further decomposed into the single d components. The results for the $3d$ t_{2g} and e_g states are shown in Fig. 2.56. Worth mentioning is the up- and downshift of all three spin-up and spin-down partial DOS as compared to the spin-degenerate case, Fig. 2.49, which is responsible for the decrease of the DOS at E_F. In agreement with the Stoner criterion it causes

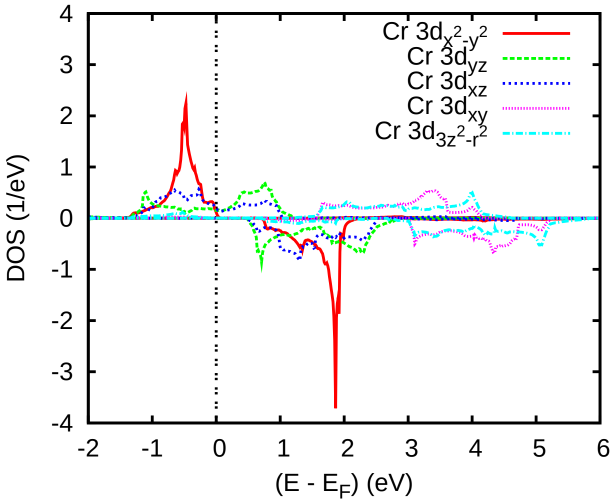

Figure 2.56 Partial Cr $3d$ t_{2g} and e_g DOS of ferromagnetic CrO_2. Selection of orbitals is relative to the local rotated reference frame.

an energy gain especially for the spin-up $d_{x^2-y^2}$-like electrons. In contrast, less energy has to be paid by the spin-down electrons since the sharp peak of the $d_{x^2-y^2}$ partial DOS was above E_F already in the non-magnetic case.

2.4.4 Spin-polarized antiferromagnetic calculations

As already mentioned above CrO_2 shows an instability towards antiferromagnetic order if the lattice constants a and c or the the oxygen parameter u are changed [412]. In the present section we demonstrate how the calculations for an antiferromagnet could be efficiently performed. Again, the CTRL file and the atomic files of the converged spin-polarized calculation for ferromagnetic CrO_2 should be first copied to a different directory. After that two changes have to be made. First, in order to take advantage of the spin-sublattice symmetry coming with antiferromagnetic order, we insert the token AFSYM=T into the category OPTIONS. Second, in order that the program can detect the particular antiferromagnetic order, each atomic site has to desginated as spin-up or spin-down. This is achieved by the tokens SPIN= to be appended to each atomic position in category SITE. The updated category will look like the following.

```
SITE    CARTP=F
        ATOM=CR POS= 0.000000  0.000000  0.000000 SPIN=UP
        ATOM=CR POS= 0.500000  0.500000  0.500000 SPIN=DN
        ATOM=O  POS= 0.302400  0.302400  0.000000 SPIN=UP
```

```
ATOM=O  POS=-0.302400 -0.302400  0.000000 SPIN=UP
ATOM=O  POS=-0.197600  0.197600  0.500000 SPIN=DN
ATOM=O  POS= 0.197600 -0.197600  0.500000 SPIN=DN
ATOM=E1 POS= 0.500000  0.000000 -0.250000 SPIN=DN
ATOM=E1 POS= 0.500000  0.000000  0.250000 SPIN=UP
ATOM=E1 POS= 0.000000 -0.500000 -0.250000 SPIN=DN
ATOM=E1 POS= 0.000000 -0.500000  0.250000 SPIN=UP
ATOM=E2 POS= 0.318691 -0.318691  0.000000 SPIN=UP
ATOM=E2 POS=-0.318691  0.318691  0.000000 SPIN=UP
ATOM=E2 POS=-0.181309 -0.181309 -0.500000 SPIN=DN
ATOM=E2 POS= 0.181309  0.181309 -0.500000 SPIN=DN
ATOM=E3 POS= 0.313120 -0.055474  0.000000 SPIN=UP
ATOM=E3 POS=-0.313120  0.055474  0.000000 SPIN=UP
ATOM=E3 POS=-0.186880 -0.444526 -0.500000 SPIN=DN
ATOM=E3 POS= 0.186880  0.444526  0.500000 SPIN=DN
ATOM=E3 POS= 0.055474 -0.313120  0.000000 SPIN=UP
ATOM=E3 POS=-0.055474  0.313120  0.000000 SPIN=UP
ATOM=E3 POS=-0.444526 -0.186880 -0.500000 SPIN=DN
ATOM=E3 POS= 0.444526  0.186880 -0.500000 SPIN=DN
```

Note that for each class there must be an equal number of SPIN=UP and SPIN=DN entries. Again the self-consistent calculation is started by typing mnall.x at the systems prompt. In case you have forgotten to copy the atomic files of the ferromagnetic calculation the program will start from scratch and, hence, need more iterations. Of course, for antiferromagnetic materials it is *not* not necessary to perform a ferromagnetic calculation first. You could also use the atomic files of a spin-degenerate calculation as a starting point for an antiferromagnetic calculation.

After convergence monic outlst18 summarizes the results as follows.

```
ASW-2.6, program MNSCF started on asterix at Thu, 05 Feb 2009, 23:43:25.
Calculation converged after  18 iteration(s).
                      Start of Iteration   18
   756 irreducible k-points generated from    4116 ( 14, 14, 21).
           Fermi energy - MTZ =     0.732169 Ryd
The system is a magnetic metal and could still be a half-metallic ferromagnet:
           DOS at Fermi energy:    61.416030 1/Ryd
           Gamma * (f.u./cell):    10.640147 mJ/(mole*K**2)
Magnetic moment of UP atoms     =     1.703860
Magnetic moment of unit cell    =     0.000000
Mean-square residual:                   0.552659D-23
Total free atom energies     :  -4790.190932 Ryd
Total variational energy     :  -4794.045025 Ryd
Cohesive energy              :      3.854093 Ryd
 qdiff =       0.00000000  <       0.00000001
 ediff =       0.00000000  <       0.00000001
ASW-2.6, program MNSCF ended on asterix at Fri, 06 Feb 2009, 00:34:18.
```

According to this output a magnetic solution with a magnetic moment of $\approx 1.7\mu_B$ per sublattice has indeed been found. However, while being stable as compared to the spin-degenerate case, its total energy is by 22 mRyd per formula higher as that of the ferromagnetic solution.

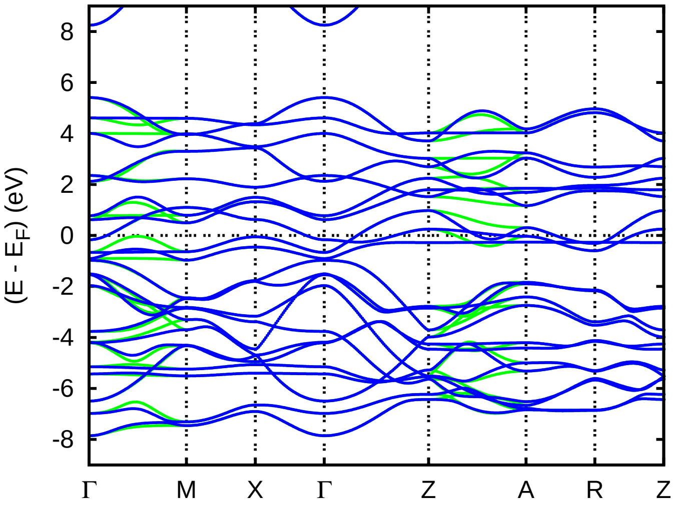

Figure 2.57 Electronic bands of antiferromagnetic CrO_2 along selected symmetry lines within the first Brillouin zone of the simple tetragonal lattice, Fig. B.5(a).

The electronic structure is displayed in Fig. 2.57 and the corresponding partial DOS given in Fig. 2.58. Note the degeneracy of the spin-up and spin-down bands

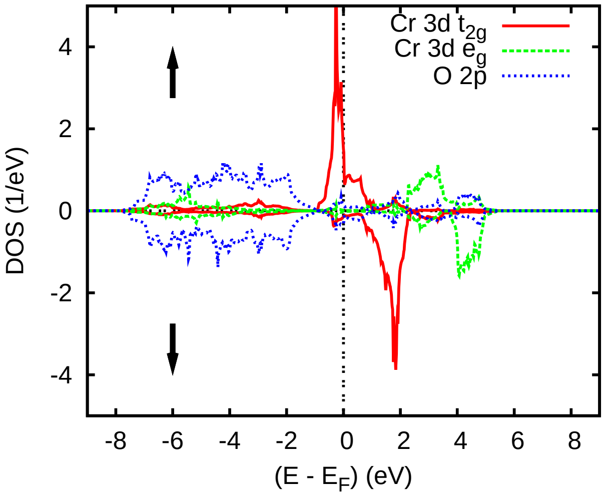

Figure 2.58 Partial DOS of antiferromagnetic CrO_2 per formula unit.

along most of the symmetry lines, which is typical for an antiferromagnet. The splittings along the lines A-Γ, Γ-M, and A-Z are indicative of the reduced symmetry of the antiferromagnetic structure, which calls for a larger irreducible wedge of the first Brillouin zone.

Finally, the partial Cr $3d$ t_{2g} and e_g DOS are shown in Fig. 2.59, where again the rotated reference frame was used. In contrast to the ferromagnetic case, energetical downshift of the spin-up states is much less. As a consequence the $d_{x^2-y^2}$ peak appears near the Fermi energy and contributes to the rather large DOS at E_F. Furthermore, it is responsible for the increase in total energy as compared to ferromagnetic CrO_2.

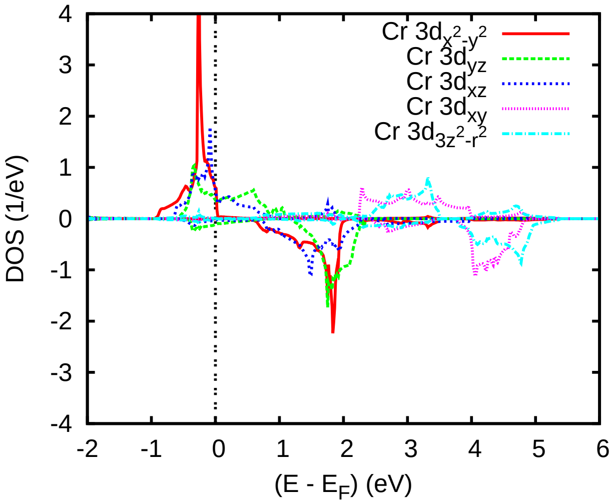

Figure 2.59 Partial Cr $3d$ t_{2g} and e_g DOS of antiferromagnetic CrO_2. Selection of orbitals is relative to the local rotated reference frame.

2.5 A ferromagnetic metal: Gd

As already mentioned at the beginning of Sec. 2.5, gadolinium is the fourth elemental ferromagnet besides the iron, cobalt, and nickel. Since the Curie temperature of this metal of $T_C = 299K$ is too low for many applications, Gd is much less known than the $3d$ systems. Nevertheless, it has aroused a lot of interest due to the dominant influence of the $4f$ electrons, which are responsible for the formation of the magnetic moments and enhance the influence of electronic correlations considerably. In the present section, we will discuss the role of the electronic correlations for the electronic and magnetic properties and learn about means to deal with them.

In the same manner as for CrO_2 we start with a set of spin-degenerate calculations before turning to spin-polarization. Again, we consider both ferromagnetic and antiferromagnetic ordering. In doing so, we will be faced with the limitations of the local density approximation and thus in a third step turn to the inclusion of electronic correlations within the framework of the LDA+U method. In order to prepare for the calculations, we create the corresponding subdirectories by

```
mkdir gd
cd gd
mkdir pac
mkdir nm
mkdir fe
mkdir af
mkdir feu
mkdir afu
cd pac
```

and turn to the setup of the CTRL file and the sphere packing.

2.5.1 CTRL file and sphere packing

As usual we start listing the CTRL file.

```
HEADER  Gd hcp
VERSION ASW-2.6
IO      HELP=F SHOW=T VERBOS=30 CLEAN=T
OPTIONS REL=T OVLCHK=T
STRUC   ALAT=6.85782 CLAT=10.95194 GAMMA=120.0
CLASS   ATOM=GD Z=64 R=3.7620545 LMXL=3 CONF=6 6 5 4 5
                QVAL= 2.0  0.0  1.0  7.0  0.0
SITE    CARTP=F
        ATOM=GD POS= 0.000000  0.000000  0.000000
        ATOM=GD POS= 0.333333 -0.333333 -0.500000
SYMGRP
ENVEL   EKAP=-0.015
BZSMP   NKBAB=6 BZINT=LTM EMIN=-1.5 EMAX=1.5 NDOS=3000
        NORD=3 WIDTH=0.01 SAVDOS=F SAVCOOP=F SAVFERM=F
CHARGE  NETA=2 EETA=-3.0 -5.0 SAVRHO=F
CONTROL START= QUIT= FREE=F NITBND=50 CNVG=1.0D-08 CNVGET=1.0D-08
        NITATM=50 CNVGQA=1.0D-10
MIXING  NMIXB=5 BETAB=0.5 INCBB=T NMIXA=5 BETAA=0.5
SYMLIN  NPAN=7 NPTS=400 ORBWGT=F CARTE=F
        LABEL=g ENDPT= 0.000000  0.000000  0.000000
        LABEL=M ENDPT= 0.166667  0.166667 -0.333333
        LABEL=K ENDPT= 0.000000  0.333333 -0.333333
        LABEL=g ENDPT= 0.000000  0.000000  0.000000
        LABEL=A ENDPT= 0.500000  0.500000  0.500000
        LABEL=L ENDPT= 0.666667  0.666667  0.166667
        LABEL=H ENDPT= 0.500000  0.833333  0.166667
```

```
        LABEL=A ENDPT= 0.500000  0.500000  0.500000
PLOT    CARTV=F
        ORIGIN= 0.65 0.35 0.0
        RPLOT1=-1.0  1.0  0.0
        RPLOT2= 0.0  0.0  1.0
        RPLOT3= 1.0  1.0  0.0
        NPDIV1=50 NPDIV2=50 NPDIV3=0
PLOT    CARTV=F
        ORIGIN= 0.0  0.0  0.0
        RPLOT1= 1.0  0.0  0.0
        RPLOT2= 0.0  1.0  0.0
        RPLOT3= 0.0  0.0  1.0
        NPDIV1=50 NPDIV2=50 NPDIV3=0
```

A few tokens are of interest here. In category STRUC and so far not used token enters, namely GAMMA=, which reflects the 120° angle between the basal plane primitive translations of the hexagonal lattice adopted by Gd. In addition, as for the tetragonal lattice of CrO_2, we specified the c lattice constant by the token CLAT=. Finally, note the entries in category SYMLIN=, where we have specified the end points usually applied for the hexagonal lattice. Whenever you are in doubt about the specification of the end points remove this category from the CTRL file and the programs will propose a standard setting for the particular lattice.

As before, we start running the packing routine mnpac.x, which returns the message that all volume can be filled without empty spheres and with a linear overlap of only 11%. Of course, this is a consequence of the hexagonal close packed structure.

2.5.2 Spin-degenerate calculations

We are thus able to start with the spin-degenerate set of calculatons rightaway by entering

```
mnall.x
```

at the systems prompt. As already mentioned, we prefer starting with the non-magnetic case in order to have a reference at hand. Moreover, we will benefit from the restart facility of the ASW program mnscf.run.

After convergence has been achieved the command monic outlst18 collects the most important results.

```
 ASW-2.6, program MNSCF started on asterix at Thu, 05 Feb 2009, 13:03:41.
 Calculation converged after  25 iteration(s).
                      Start of Iteration   25
    240 irreducible k-points generated from    3610 ( 19, 19, 10).
            Fermi energy - MTZ =     0.457108 Ryd
 The system is a metal:
            DOS at Fermi energy:  1256.643248 1/Ryd
            Gamma * (f.u./cell):   217.709763 mJ/(mole*K**2)
 Mean-square residual:                   0.229578D-22
 Total free atom energies     : -45054.284175 Ryd
```

```
Total variational energy      : -45055.309795 Ryd
Cohesive energy               :      1.025620 Ryd
 qdiff =       0.00000000  <        0.00000001
 ediff =       0.00000000  <        0.00000001
ASW-2.6, program MNSCF ended on asterix at Thu, 05 Feb 2009, 13:06:10.
```

As a matter of fact, non-magnetic Gd is a metal with a huge density of states at E_F. Hence, from Stoner theory we would expect ferromagnetic ordering. We display in Fig. 2.60 the electronic states along selected high symmetry lines within the first Brillouin zone of the hexagonal lattice, Fig. B.4. The corresponding density of states (DOS) is given in Fig. 2.61. From Figs. 2.60 and 2.61 the interpretation of the results is rather simple. While the electronic states are dominated by the sharp $4f$ peak at E_F, the d states show a rather large dispersion eveolving from a parabolic band at the Γ point.

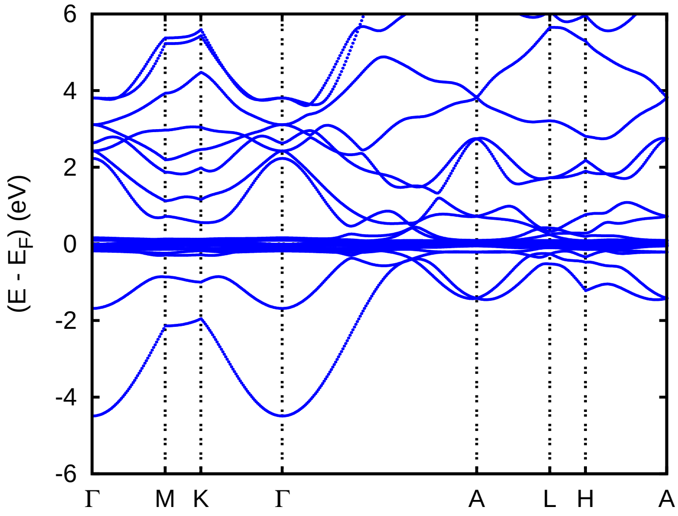

Figure 2.60 Electronic bands of Gd along selected symmetry lines within the first Brillouin zone of the hexagonal lattice, Fig. B.4.

2.5.3 Spin-polarized calculations

Turning to the spin-polarized calculations we begin copying the CTRL file as well as the atomic file GD to the subdirectories `fe` and `af` for use as a starting point. Still, a few things have to be changed in the CTRL files. First, in category OPTIONS the entry NSPIN=2 must be inserted, which tells the program to perform a spin-

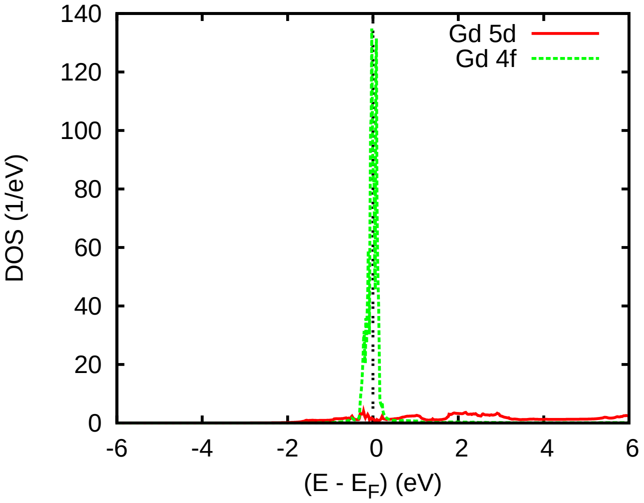

Figure 2.61 Partial densities of states (DOS) of Gd.

polarized calculation. Furthermore, each orbital has to be given a starting value for the polarization as has been already discussed in Sec. 2.4.3. After that, for magnetic Gd the updated categroy CLASS looks as follows.

```
CLASS   ATOM=GD Z=64 R=3.7620545 LMXL=3 CONF=6 6 5 4 5
                QVAL= 2.0  0.0  1.0  7.0  0.0
                MVAL= 0.0  0.0  0.0  7.0  0.0
```

For antiferromagnetic ordering two more tokens have to be added. First, in category OPTIONS the token AFSYM=T has to be included. This token lets the program take account of the sublattice symmetry of the system, which enforces identical magnitude of the local magnetic moments of different sublattices. Of course, one could equally well treat antiferromagnetic systems as a ferrimagnet with just two types of magnetic ions with spin-up and spin-down moments. However, enforcing the sublattice symmetry helps a lot with respect to accuracy and speed of the calculations. In addition to token AFSYM=, we have to assign each atom to one of the two sublattice by adding the token SPIN= to each position in category SITE. As a consequence, the category SITE assumes the following form.

```
SITE    CARTP=F
        ATOM=GD POS= 0.000000  0.000000  0.000000 SPIN=UP
        ATOM=GD POS= 0.333333 -0.333333 -0.500000 SPIN=DN
```

After these preparations we start the self-consistent calculations by issuing the command `mnall.x` in both subdirectories `fe` and `af`. After a coffee break we may collect the results typing `monic outlst18`. For the ferromagnetic case we get the following listing

```
ASW-2.6, program MNSCF started on asterix at Thu, 05 Feb 2009, 13:12:18.
Calculation converged after  14 iteration(s).
                      Start of Iteration   14
   240 irreducible k-points generated from    3610 ( 19, 19, 10).
           Fermi energy - MTZ =     0.470940 Ryd
The system is a magnetic metal and could still be a half-metallic ferromagnet:
           DOS at Fermi energy:    46.385583 1/Ryd
           Gamma * (f.u./cell):     8.036166 mJ/(mole*K**2)
Magnetic moment of unit cell    =    15.242495
Mean-square residual:                    0.462870D-23
Total free atom energies     : -45054.284175 Ryd
Total variational energy     : -45056.338110 Ryd
Cohesive energy              :      2.053936 Ryd
 qdiff =       0.00000000  <        0.00000001
 ediff =       0.00000001  <        0.00000001
ASW-2.6, program MNSCF ended on asterix at Thu, 05 Feb 2009, 13:17:40.
```

According to this output a magnetic solution with a magnetic moment of $15.2\mu_B$ per unit cell is obtained with a total energy lowering of 1028 mRyd as compared to the spin-degenerate case. At the same time, we observe a considerable spin splitting of the $4f$ states of about 4.5 eV in the band structure, Fig. 2.62, as well as in the corresponding density of states (DOS) given in Fig. 2.63.

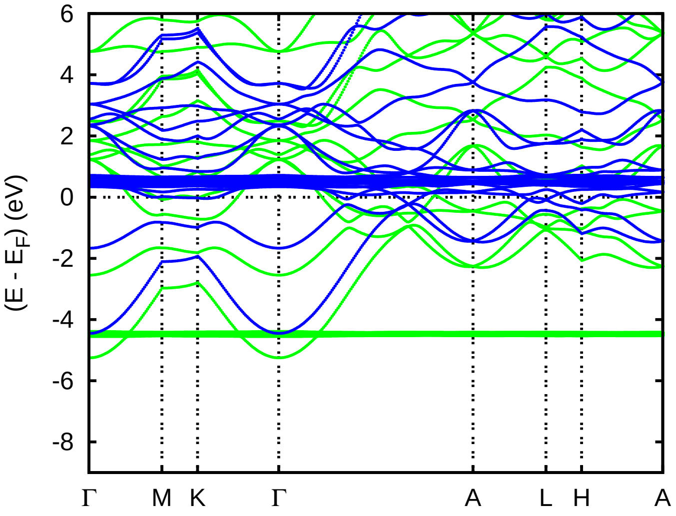

Figure 2.62 Electronic bands of ferromagnetic Gd along selected symmetry lines within the first Brillouin zone of the hexagonal lattice, Fig. B.4.

While the electronic bands and partial DOS look quite similar for the antiferromagnetic situation, the total energy as obtained by typing `monic outlst18` holds a surprise.

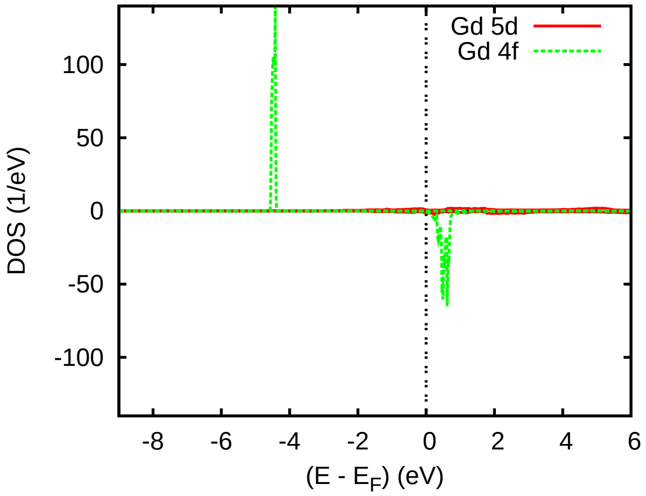

Figure 2.63 Partial densities of states (DOS) of ferromagnetic Gd.

```
ASW-2.6, program MNSCF started on asterix at Thu, 05 Feb 2009, 13:14:34.
Calculation converged after  14 iteration(s).
                      Start of Iteration   14
   240 irreducible k-points generated from    3610 ( 19, 19, 10).
           Fermi energy - MTZ =     0.471016 Ryd
The system is a magnetic metal:
           DOS at Fermi energy:    42.067504 1/Ryd
           Gamma * (f.u./cell):     7.288072 mJ/(mole*K**2)
Magnetic moment of UP atoms     =     7.366000
Magnetic moment of unit cell    =     0.000000
Mean-square residual:                   0.774390D-24
Total free atom energies     : -45054.284175 Ryd
Total variational energy     : -45056.341314 Ryd
Cohesive energy              :      2.057140 Ryd
 qdiff =       0.00000000  <        0.00000001
 ediff =       0.00000000  <        0.00000001
ASW-2.6, program MNSCF ended on asterix at Thu, 05 Feb 2009, 13:19:00.
```

According to the output, antiferromagnetically ordered gadoliniom is still more stable than the ferromagnet by 3.2 mRyd. This is in striking contrast to experiment and can be traced back to the limitations of the local density approximation.

2.5.4 Spin-polarized LDA+U calculations

The problem can be solved by including electronic correlations beyond the local density approximation. In this context, the LDA+U approach invented by Anisimov, Zaanen, and Andersen provides a rather simple but efficient method. While omitting the physical background here, which is very well documented in the literature, we turn to the practicalities. To be specific, in the present context three more tokens have to be included. They are included in the following listing of the CTRL file.

```
HEADER  Gd hcp
VERSION ASW-2.6
IO      HELP=F SHOW=T VERBOS=30 CLEAN=T
OPTIONS REL=T NSPIN=2 OVLCHK=T LDA+U=FLL
STRUC   ALAT=6.85782 CLAT=10.95194 GAMMA=120.0
CLASS   ATOM=GD Z=64 R=3.7620545 LMXL=3 CONF=6 6 5 4 5
                QVAL= 2.0  0.0  1.0  7.0  0.0
                MVAL= 0.0  0.0  0.0  7.0  0.0
                UVAL= 0.0  0.0  0.0  0.5  0.0
                JVAL= 0.0  0.0  0.0  0.05 0.0
SITE    CARTP=F
        ATOM=GD POS= 0.000000  0.000000  0.000000
        ATOM=GD POS= 0.333333 -0.333333 -0.500000
SYMGRP
ENVEL   EKAP=-0.015
BZSMP   NKBAB=6 BZINT=LTM EMIN=-1.5 EMAX=1.5 NDOS=3000
        NORD=3 WIDTH=0.01 SAVDOS=F SAVCOOP=F SAVFERM=F
CHARGE  NETA=2 EETA=-3.0 -5.0 SAVRHO=F
CONTROL START= QUIT= FREE=F NITBND=50 CNVG=1.0D-08 CNVGET=1.0D-08
        NITATM=50 CNVGQA=1.0D-10
MIXING  NMIXB=5 BETAB=0.5 INCBB=T NMIXA=5 BETAA=0.5
SYMLIN  NPAN=7 NPTS=400 ORBWGT=F CARTE=F
        LABEL=g ENDPT= 0.000000  0.000000  0.000000
        LABEL=M ENDPT= 0.166667  0.166667 -0.333333
        LABEL=K ENDPT= 0.000000  0.333333 -0.333333
        LABEL=g ENDPT= 0.000000  0.000000  0.000000
        LABEL=A ENDPT= 0.500000  0.500000  0.500000
        LABEL=L ENDPT= 0.666667  0.666667  0.166667
        LABEL=H ENDPT= 0.500000  0.833333  0.166667
        LABEL=A ENDPT= 0.500000  0.500000  0.500000
PLOT    CARTV=F
        ORIGIN= 0.0  0.0  0.0
        RPLOT1= 1.0  0.0  0.0
        RPLOT2= 0.0  1.0  0.0
        RPLOT3= 0.0  0.0  1.0
        NPDIV1=50 NPDIV2=50 NPDIV3=0
```

First, tokens UVAL= and JVAL= in category CLASS specify the parameters U and J coming with the LDA+U approach. Here, we may specify these parameters for each atom and for each orbital separately. However, in most cases, only a single orbital will be selected. Note that the values for U and J must be given in Rydberg.

Second, a new token LDA+U= enters category OPTIONS. Possible entries are LDA+U=FLL, AMF, and DFT, which specify three different ways of dealing with the so-called double counting terms. Actually, for systems, which are only weakly correlated, the choice of the double-counting correction can be rather sensitive to the results. However, for strongly correlated systems as Gd the fully localized limit (FLL) is a good choice.

Having included these specifications in the CTRL files for both the ferromagnetic and antiferromagnetic situation (after having copyied them to the subdirectories `feu` and `afu` and after having also copied the file GD to these directories) we start the standard canon of calculations again, which allows us to take another coffee break.

After successful completion of the calculations the results are summarized in the listings

```
ASW-2.6, program MNSCF started on asterix at Thu, 05 Feb 2009, 13:38:56.
Calculation converged after  13 iteration(s).
                      Start of Iteration   13
   240 irreducible k-points generated from    3610 ( 19, 19, 10).
           Fermi energy - MTZ =     0.472938 Ryd
The system is a magnetic metal:
           DOS at Fermi energy:    25.238563 1/Ryd
           Gamma * (f.u./cell):     4.372507 mJ/(mole*K**2)
Magnetic moment of unit cell    =    15.670950
Mean-square residual:                   0.161670D-22
Total free atom energies     : -45054.284175 Ryd
Total variational energy     : -45056.340574 Ryd
Cohesive energy              :      2.056400 Ryd
 qdiff =       0.00000000  <        0.00000001
 ediff =       0.00000001  <        0.00000001
ASW-2.6, program MNSCF ended on asterix at Thu, 05 Feb 2009, 13:46:38.
```

for the ferromagnet and

```
ASW-2.6, program MNSCF started on asterix at Thu, 05 Feb 2009, 13:40:24.
Calculation converged after  12 iteration(s).
                      Start of Iteration   12
   240 irreducible k-points generated from    3610 ( 19, 19, 10).
           Fermi energy - MTZ =     0.471700 Ryd
The system is a magnetic metal and could still be a half-metallic ferromagnet:
           DOS at Fermi energy:    36.055204 1/Ryd
           Gamma * (f.u./cell):     6.246459 mJ/(mole*K**2)
Magnetic moment of UP atoms     =     7.502246
Magnetic moment of unit cell    =     0.000000
Mean-square residual:                   0.248595D-22
Total free atom energies     : -45054.284175 Ryd
Total variational energy     : -45056.323725 Ryd
Cohesive energy              :      2.039550 Ryd
 qdiff =       0.00000000  <        0.00000001
 ediff =       0.00000000  <        0.00000001
ASW-2.6, program MNSCF ended on asterix at Thu, 05 Feb 2009, 13:47:08.
```

for the antiferromagnet. Obviously, the order of the total energies is reversed and we obtain a ferromegnatic ground state in agreement with experiment. At the same time, the magnetic moment per cell has slightly increased. Striking changes are also observed in the band structure as shown in Fig. 2.64, as well as in the corresponding

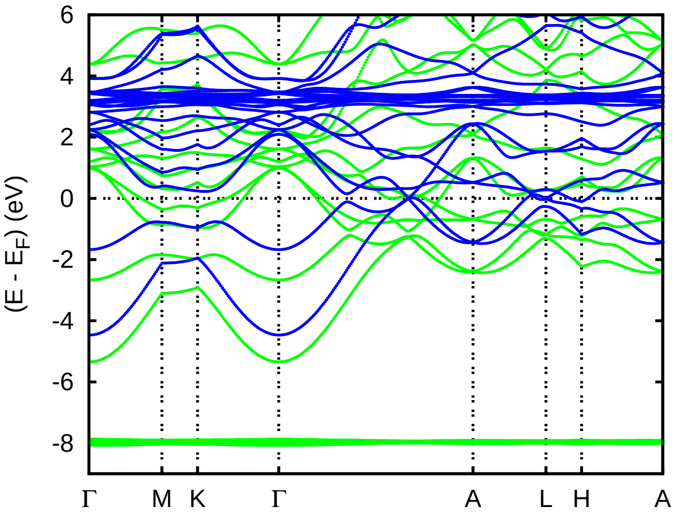

Figure 2.64 Electronic bands of ferromagnetic Gd along selected symmetry lines within the first Brillouin zone of the hexagonal lattice, Fig. B.4 as growing out of an LDA+U calculation.

density of states (DOS) given in Fig. 2.65. Obviously, the exchange splitting has

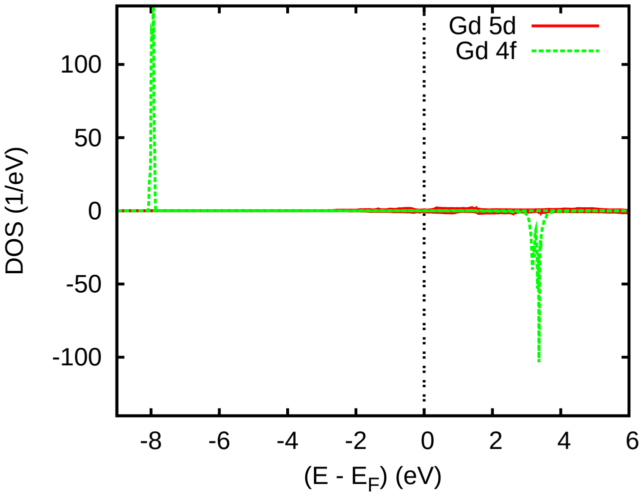

Figure 2.65 Partial densities of states (DOS) of ferromagnetic Gd as growing out of an LDA+U calculation.

considerably increased to a value of about 11.5 eV due to the localizing nature of the LDA+U approach. Again, this is in much better agreement with experimental data from photoemission studies.

Chapter 3

Organization of the ASW program package

In the present chapter an overview is given over all files coming with the distribution or being generated during the execution of the programs. This includes mainly four groups. While the calculations are performed by one of the main programs, the plot programs serve the purpose of visualizing the results. Work of both steps is made easier by a number of shell scripts. Finally, a list of all files, which are either included in the distribution or else created by one of the programs, is given.

3.1 Main programs and shell scripts

In the present section all main programs of the ASW distribution are discussed. In contrast to the plot programs presented in the following section, all main programs (with the exception of mnmpr.run) start reading the CTRL file.

As has been already outlined in Sec. 2.1, the ASW program package includes both the executables (with ending ".run") and corresponding shell scripts (with ending ".x"). The latter call the executables and specify the respective output files. In addition, the shell scripts provide commands for the most common job queuing systems as IBM's LoadLeveler (LoadL), and the public domain packages Portable Batch System (PBS) and Sun's Grid Engine (SGE) (support for the Network Queuing System (NQS) and the Distributed Queuing System (DQS) is also included but these systems do not seem to be used any more). Finally, some of the shell scripts include appropriate modifications of the CTRL file. A fully commented example shell script is contained in the file mnhlp.x, which should be consulted for more information. In the following discussion we will use the names program, executable and shell script synonymously.

3.1.1 mnmpr.run, mnmpr.x

While all main programs calculate the parameters of the actual machine at the very beginning, this program prints them out and stops. The output usually looks like file MACHi coming with the distribution.

```
ASW-2.6, program MNMPR started on asterix at Thu, 15 Jan 2009, 11:47:11.

    Copyright (C) 1992-2009 Volker Eyert
    Please see file COPYRIGHT for details

Machine-specific parameters affecting floating-point arithmethic:

ibase:          2                (base of the machine)
it:            53                (number of (base) digits in the mantissa)
xeps:      2.22044604925031D-16   (= min, such that 1.0 + xeps > 1.0)
xepsn:     1.11022302462516D-16   (= min, such that 1.0 - xepsn < 1.0)
minexp:     -1021                (min exponent before (gradual) underflow)
xzer:      2.22507385850720-308   (underflow threshold = base**(minexp-1))
xmin:      2.22507385850720-308   (safe min, 1/xmin does not overflow)
maxexp:      1024                (largest exponent before overflow)
xinf:      1.79769313486232+308   (overflow threshold = base**maxexp*(1-xepsn))
irnd:           1                (= 0/1 for chopping/rounding in addition)

task  1, total       :  cpu time:     0.00400 sec

ASW-2.6, program MNMPR ended on asterix at Thu, 15 Jan 2009, 11:47:11.
```

This toy program mainly serves the purpose of checking the compiler and machine capabilities.

3.1.2 mnhlp.x

In order to summarize the way most of the shell scripts work I have created this file, which is a fully commented version of the shell script mnmpr.x.

```
#!/bin/sh
########################################################################
#
#     Command file mnhlp.x for queuing a batch job executing an
#     ASW program. This file serves as a commented example file
#     for all the other shell-scripts.
#     The script is prepared for use with the LoadLeveler (LoadL),
#     the Network Queuing System (NQS), the Portable Batch System
#     (PBS), the Distributed Queuing System (DQS), and Sun's Grid
#     Engine (SGE).
#     Please adapt to your own environment and needs.
#
#     Version ASW-2.6 15.01.2009 Volker Eyert
#     Copyright (C) 1992-2009 Volker Eyert
```

```
#     Please see file COPYRIGHT for details.
########################################################################
#
#
#     LoadLeveler specifications:
#
# Specify job queue:
# @ class        = veryshort
#
# Specify system and hardware requirements:
# @ requirements = (OpSys == {"AIX42" "||" "AIX43"}) && (Feature == "pwr3")
#
# Specify requirements for parallel execution:
#   job_type     = parallel
#   requirements = (Adapter == "hps_user")
#   min_processors =  1
#   max_processors = 14
# @ resources = ConsumableCpus(1) ConsumableMemory(80)
#
# Specify executable (done explicitly here; see below):
#   executable   =
#
# Specify stdin, stdout and stderr:
# @ input        = /dev/null
# @ output       = job.$(Cluster).$(Process).out
# @ error        = job.$(Cluster).$(Process).err
#
# Mark job not-restartable:
# @ restart      = no
#
# Suppress any notification:
# @ notification = never
#
# Finally queue the job:
# @ queue
#
########################################################################
#
#
#     Network Queuing System (NQS) specifications:
#
# Specify job queue:
#QSUB -q high_prio
#
# Specify CPU-time and memory:
#QSUB -lT 600
#QSUB -lM 256MB
#
# Specify start from the current working directory:
if [ $QSUB_WORKDIR ]; then cd $QSUB_WORKDIR; fi
#
# Specify stdout and stderr:
#QSUB -o job.out
#QSUB -e job.err
```

```
#
# Specify shell:
#QSUB -s /bin/bash
#
# Mark the job not-restartable:
#QSUB -nr
#
# Require mailing at job starting and ending time:
# QSUB -mb
# QSUB -me
#
########################################################################
#
#
#     Portable Batch System (PBS) specifications:
#
# Specify job queue:
#PBS -q dft
#
# Specify system and hardware requirements:
# PBS -l resc = "(arch=='solaris')||(arch='irix')"
#
# Specify requirements for parallel execution:
#PBS -l nodes=1
#
# Specify CPU-time and memory:
# PBS -l cput=168:00:00
#PBS -l mem=256MB
#
# Specify start from the current working directory:
if [ $PBS_O_WORKDIR ]; then cd $PBS_O_WORKDIR; fi
#
# Specify stdout and stderr:
#PBS -o job.out
#PBS -e job.err
#
# Specify the shell:
#PBS -S /bin/bash
#
# Export all environmental variables:
#PBS -V
#
# Mark the job not-restartable:
#PBS -rn
#
# Suppress any notification:
#PBS -m n
#
########################################################################
#
#
#     Distributed Queuing System (DQS) and Sun's Grid Engine (SGE)
#     specifications:
#
```

```
# Specify job queue:
# $ -q local_queue
#
# Specify CPU-time and memory:
# $ -l qty.eq.1,runtime.ge.600,memory.ge.256
#$ -l s_rt=10:0:0,h_vmem=1800M
#
# Specify start from the current working directory:
#$ -cwd
#
# Specify stdout and stderr:
#$ -o job.out
#$ -e job.err
#
# Specify the shell:
#$ -S /bin/bash
#
# Export all environmental variables:
#$ -V
#
# Mark the job not-restartable:
#$ -r n
#
# Suppress any notification:
#$ -m n
#$
#
########################################################################
#
BINDIR=$HOME/asw/aswhp
#
$BINDIR/upctr "HELP=F" "HELP=T" &&
#
$BINDIR/mnsym.run > outhlp
#
$BINDIR/upctr "HELP=T" "HELP=F" &&
exit
#
########################################################################
```

You may have a look at this prototypical shell script before adapting any of the other scripts.

3.1.3 mnsym.run, mnsym.x

This program reads in the CTRL file, performs a basic check of the input parameters and creates the lattice vectors. In addition, it performs a symmetry check of the crystal structure. Alternatively, depending in token GENPOS=, it builds the full unit cell from a minimal set of atomic positions and the space group information. The latter can be specified in the CTRL file alternatively by the space group symbol, the space group number or the symmetry generators. In both cases the result is printed to file outsym and a file CBAK is created, which contains an updated version of the CTRL file. Finally, the program scales the atomic sphere radii in case this is requested, and checks the overlap of the atomic spheres. The result is printed to file *outsym*, which apart from the result of the symmetry check lists the overlap limits, the positions and radii of all atomic spheres. In addition, a full list of pairs of atoms, their distance, and their overlap is given together with exclamation marks pointing to large overlaps. The number of entries in the list can be controlled by the tokens VERBOS= and DISTL=. With the default setting VERBOS=30 only pairs with a nonvanishing overlap are included. The just sketched evaluations are also performed by all other main programs except for mnmpr.run.

3.1.4 mnpac.run, mnpac.x

In order to invoke the sphere packing using the sphere geometry optimization algorithm you have to call this program. In a first part free atoms are superposed in order to generate the potential along lines connecting all atoms. From this information the muffin-tin radii of the physical atoms can be evaluated. In a second step, the muffin-tin radii are blown up until the overlap limits specified by tokens OBYDMX= and OBYRMX= are reached. If space filling as fixed by token FILLING= can not yet be achieved, a search for the largest possible empty sphere sets in. Once this has been found again all spheres are blown up until the maximum space filling compatible with the overlap limits is reached. This process is repeated until full space filling has been achieved. However, see the description of all tokens in category PACK for more detailed information.

WARNING: As it stands this program was designed for the spin-degenerate case only. So, please make sure that NSPIN=1 (or this token is missing at all) in the CTRL file.

3.1.5 mnstr.x

This special variant of shell script mnpac.x likewise calls the packing program but stops after the determination of the muffin-tin radii according from the superposition of the free atom electron densities and effective potentials. The latter usually goes under the name Mattheiss construction. The result as contained in file STRU can be used for plotting the crystal structure with the plot program plstr.run (or plstr.x).

3.1.6 mnscf.run, mnscf.x

This is the most comprehensive of all programs. After reading the CTRL file it performs the self-consistent calculations until full convergence or the maximum iteration count as specified by token NITBND= has been reached. In this course, the program calculates density matrices, which could be used to calculate partial charges and magnetic moments, electron densities, densities of states and the total energy. The program naturally falls into two parts.

In a band part, calculated intraatomic matrix elements are used to set up the secular matrix. From solving the corresponding eigenvalue problem eigenvalues and eigenvectors are obtained and the respective contributions added to the electron density and the partial densities of states. This process is repeated for all **k**-points in the irreducible wedge of the first Brillouin zone. The band part usually takes more than 95% of the execution time of the program. Note that during this time no files are read or written. Hence, if you want to stop the program for whatever reason without loosing the atomic files you should do it during the band part.

In the real space part, the local density matrices provided by the band part are used to calculate the intraatomic wave functions and from these the intraatomic electron densities. Within the notions of density functional theory and the local density approximation the latter give rise to the effective potential and total energy. Finally, the potential enters a radial Schrödinger equation leading to new intraatomic wave functions and matrix elements for use in the band part. Note that during the real space calculations the atomic files are accessed several times. Stopping the program in this step thus might cause a loss of files.

3.1.7 mnbnd.run, mnbnd.x

Another quantity of interest after full convergence has been achieved is the band structure. It is calculated by employing the shell script `mnbnd.x`, which scans the **k**-space path defined by tokens ENDPT= and calculated eigenvalues, the $E(\mathbf{k})$. The result is written to file BNDE. In addition, if ORBWGT=T has been specified, eigenvectors, i.e. wave functions are calculated for latter plotting of orbital weighted band structures as shown in Figs. 2.3 to 2.6 and 2.34. The result is written to file BNDV. Note that this file might be very large up to some hundreds of MByte. In case you want to calculate orbital weighted band structures check the output file *outbnd* and search for the line beginning with

```
 File BNDV will need approx.
```

which gives a good estimate of the disk space needed.

3.1.8 mndos.x

During normal execution of program mnscf.run only l-resolved partial densities are usually calculated. This saves both execution time and memory. Once the iterations have converged, the shell script mndos.x will call the program mnscf.run once more. If present, before running the program the tokens SAVDOS=F, SAVCOOP=F, and SAVFERM=F will be changed to SAVDOS=T, SAVCOOP=T, and SAVFERM=T, respectively. In case you use BZINT=SMS instead of the preferred BZINT=LTM, the former is set to BZINT=HPS. In addition, NKBAB=6 is changed to NKBAB=18 or NKABC=6 is changed to NKABC=30. After the band part has been finished and the partial DOS and COOPs as well as the Fermi surface information are written to files DOS, COOP, and FERM the program stops and the above changes of the CTRL file are reset to their original values.

3.1.9 mnopt.x

Once self-consistency has been achieved, the shell script mnopt.x may be used to call the program mnscf.run again after having changed the token SAVOPT=F to SAVOPT=T, if present. In addition, NKBAB=6 is changed to NKBAB=12. During execution, only the band part is performed and at the very end the optical conductivity is calculated. After the band part has been finished and the optical functions have been written to file OPT the program stops and the above changes of the CTRL file are reset to their original values.

3.1.10 mnrho.x

This shell script executes only part of the real space calculations by first changing SAVRHO=F to SAVRHO=T (if present) and invoking the program mnscf.run in order to evaluate the electron densities, their negative Laplacians, and the effective potential on a real space grid. The latter is specified by the origin of the plot space and up to three plot vectors as well as their divisions. This is done by the tokens ORIGIN=, RPLOT1=, RPLOT2=, and RPLOT3= as well as NPDIV1=, NPDIV2=, and NPDIV3. E.g., for generating a line plot, set NPDIV2=0 and NPDIV3=0. The result of these calculations is written to file RHO and can be plotted using plrho.run or plrho.x.

3.1.11 mnall.x

Most of the aforementioned calculations can be made automatic by employing the shell script mnall.x, which calls the program mnscf.run successively for an increasing number of **k**-points ranging from NKBAB=6 to NKBAB=18. After this it includes the calculations already covered by the shell scripts mnbnd.x and mndos.x. For compounds with larger unit cells or for semiconductors and insulators it may be useful to copy the shell script mnall.x to the actual directory and delete the lines

```
$BINDIR/upctr "NKBAB=12" "NKBAB=18" &&
$BINDIR/mnscf.run > outlst18 &&
```

In this case the self-consistent calculations will stop after the iterations for NKBAB=12 have converged.

3.1.12 mnscl.run, mnscl.x

Whenever it is necessary to perform a supercell calculation this utility program does the supercell setup. In the CTRL file an additional category SUPCELL must be given, which otherwise looks identical to category STRUC but holds the information about the lattice of the supercell. In addition, token EQUIV=F can be used to copy existing atomic files to equivalent files of atoms located in different regions of the new supercell. Token PSHIFT= will introduce an overall shift of all atoms and, finally, token QSWAVE= holds a spin wave vector of a possible collinear antiferromagnetic structure imposed on the supercell.

3.1.13 upctr

This shell script allows to update the CTRL file. Just type e.g. `upctr ALAT=6.83079 ALAT=6.89979` to shrink the lattice constant of Cu by 1% or `upctr QUIT= QUIT=BND` to enforce a program stop after the band part. Actually, the script upctr is contained in many other of the above listed shell scripts.

3.1.14 monic

This utility shell script has been created to **MONI**tor the progress of the **C**onvergence of the calculations towards self-consistency by extracting selected results from the output. The shell script is listed here.

```
#!/bin/sh
##########################################################################
```

```
#
#     Shell-script monic MONItores the progress of the Convergence
#     of the ASW calculations towards self-consistency.
#
#     Version ASW-2.6 15.01.2009 Volker Eyert
#     Copyright (C) 1994-2009 Volker Eyert
#     Please see file COPYRIGHT for details.
########################################################################
#
#
if [ $1 -a -r $1 ]
then
   echo " "
   grep "started on"                      $1
   grep "converged after"                 $1 | tail -1
   grep "Start of Iteration"              $1 | tail -1
   grep "irreducible k-points"            $1 | tail -1
   grep "Fermi energy - MTZ"              $1 | tail -1
   grep "The system is a"                 $1 | tail -1
   grep "band gap"                        $1 | tail -1
   grep "DOS at Fermi energy:"            $1 | grep "1/Ryd" | tail -1
   grep "Sommerfeld coeff"                $1 | tail -1
   grep "Gamma"                           $1 | tail -1
   grep "Magnetic moment of UP atoms"     $1 | tail -1
   grep "Magnetic moment of unit cell"    $1 | tail -1
   grep "Unit cell deviates"              $1 | tail -1
   grep "square"                          $1 | tail -1
   grep "Madelung energy:"                $1 | tail -1
   grep "Zeeman energy:"                  $1 | tail -1
   grep "Total 3pV:"                      $1 | tail -1
   grep "Total free atom energies"        $1 | tail -1
#   grep "Total virial energy"             $1 | tail -1
   grep "Total variational energy"        $1 | tail -1
   grep "Cohesive energy"                 $1 | tail -1
   grep "qdiff ="                         $1 | tail -1
   grep "ediff ="                         $1 | tail -1
   grep "ended on"                        $1
   echo " "
else
   echo
   echo usage:  monic filename
   echo
fi
#
########################################################################
```

Typing e.g. monic outlst18 will generate the following about a 20 lines on screen (see Sec. 2.1.2) including information about the **k**-space grid, the position of the Fermi energy, the DOS at E_F, the total magnetic moment, the (variational) total energy, and the self-consistency level already reached as coded by the entries qdiff and ediff.

3.1.15 o2log

This utility shell script has turned out very useful in contracting the output files generated during the self-consistent field calculations executed by program `mnscf.run`. In particular, with this shell script, output generated by intermediate iterations is removed from the output files and only the portion of the most recent iteration is kept. Invoking `o2log all` will apply this procedure to all files with names beginning with `outlst`, `outblk`, or `outphn`.

3.2 Plot programs and shell scripts

The plot programs coming with the distribution are distinguished from the main programs in that they do are completely independent of the CTRL file but start from files created by one of the main programs.

As for the main program there exist both executables (with ending ".run") and corresponding shell scripts (with ending ".x"), which latter call the executables and include an automatic call of the respective plot program as Gnuplot, RasMol or XCrysDen. In addition, intermediate files are deleted at the end. Whenever these files are needed e.g. for exchange with other plot porgams one should employ the executable rather than the shell script. Again, we will use the names program, executable and shell script synonymously in the following discussion.

As an extra service to the user all specifications of the plot as entered during the dialog are echoed to a file PLIx, where x=B, D, C, K, O, P, R, S, or T depending on the plot program. After the name of this file has been changed it can be edited and used for new plots by typing e.g. `mnbnd.run < PLIBnew` or `mnbnd.x PLIBnew`.

Another feature common to all plot programs concerns the title of the plot. On invoking any of the plot programs one is asked for specifying the title. Entering a "/" here will make the program use the title given by the first line of the CTRL file. In addition, if you type `& arbitrary text` the title will be constructed from the first line of the CTRL file complemented by the "arbitrary text".

3.2.1 plstr.run, plstr.x

This program starts from file STRU, which holds atomic positions and radii of all atoms within the plot region specified by tokens ORIGIN= and RPLOTn= and prepares for later use of RasMol. During the dialog colours and sizes of the atomic spheres as well as the plot perspective can be specified. By default the muffin-tin radii are used for plotting. Nevertheless, the radii may still be scaled. Each class of atoms is given a default colour which also may be changed while running `plstr.run`. The shell script `plstr.x`, after running `plstr.run`, automatically invokes RasMol. In case you want to print out the 3D plot please specify the command „`write ps` *stru.ps*“ from within RasMol in order to create a postscript file *stru.ps* of the image.

3.2.2 plbnd.run, plbnd.x

This program allows for plotting of the (weighted) band structure. It start from file BNDE containing the $E(\mathbf{k})$ for all bands and, if token ORBWGT=T has been specified, from file BNDV, which holds the corresponding eigenvectors. These data are prepared for later plotting with either Gnuplot or LaTeX. In the latter case the shell script `plbnd.lx` has to be used in addition. During the dialog invoked by calling `plbnd.x` among other things the energy scale and reference as well as the energy window must be specified. An example has been given in Sec. 2.1.3.

If output should be prepared for Gnuplot the program usually creates a file *bnd.ps*, which holds a postscript copy of the plot. A particular nice feature arises from specifying writing to a LaTeX file. This will produce a file *bnd.tex*. Next you have to invoke the shell script `plbnd.lx` (see below), which will run LaTeX on a file named *plbnd.tex*, into which *bnd.tex* is included via LaTeX's input command. As a result, in case the band structure is not too complicated, hence, file *bnd.tex* is not too large, a final file *bnd.ps* is created. This LaTeX option is particularly suited for plotting weighted band structures.

In the latter situation another important feature comes in. First, you are asked to specify the orbitals to be included. Actually, the program plots for each **k**-point and band the projection of a particular orbital onto the full wave function. Furthermore, the program allows to specify the coordinate system, within which the orbitals are selected. This is particularly useful, when the crystal field split d orbitals of a transition metal atom are to be considered as in the prvious examples of FeS_2 or CrO_2. for this reason the plot routine asks for a rotation matrix, which can be given in the same form as the symmetry matrices in token SYMOPS of the CTRL file. See Chap. 4 for more details and examples. Alternatively, the string characterizing the rotation can be written to a file named ROTS. In that case just enter "f" in the dialog.

3.2.3 pldos.run, pldos.x

The plot program `pldos.x` enables plotting of the total and partial densities of states (DOS). Both the DOS itself and the integrated DOS can be displayed. Input is read from file DOS. Intermediate files are prepared for both Gnuplot and LaTeX. However, for the DOS, Gnuplot produces a nicer output, usually contained in the postscript file *dos.ps*.

During the dialog the user is asked for the energy window, scale, and reference. In addition, for each curve the orbitals to be included and a scaling factor must be specified. Finally, the curve can be broadened by folding with a Gaussian, a Lorentzian, the Fermi function, or a combination of these. This is useful especially for a comparison with experimental results. While for Gaussian broadening a constant width can be specified, the Lorentzian broadening allows for an energy dependent width of the form $w_L = w_{L0} + w_{L1}(E - E_F)^2$. Such an energy dependent broadening is useful for comparison to experiments where lifetime effects might play a role.

As for the band structure plots, a rotation matrix can be specified for each curve in order to make the program refer the orbitals to a rotated coordinate system. While in prior versions, the use of local coordinate systems in the plot routines was restricted to rotations with angle equal to one digit integer divisions of the full circle, this restriction has been removed in the later versions. As a consequence, rotations may be specified as „RiA“ as before, where A is the axis and i is a one digit integer division of the full circle. In addition, the respective plot programs accepts the notation „R(ii)A“, where „ii“ must be an integer specifying the angle in degrees, i.e. it can be any integer between -360 and +360. The assumption of integer angles should be sufficient for most cases.

For magnetic systems, there is a choice for each curvei. The program can display the contribution from only one spin or from both spins as well as their sum and difference, respectively. Finally, the total number of curves generated by the program is limited to nine.

3.2.4 plcop.run, plcop.x

This program must be used for plotting the total and partial crystal orbital overlap population (COOP). Again, also the integrated quantities can be plotted. Input is read from file COOP. If Gnuplot is specified for output usually a file *coop.ps*. The dialog proceeds in much the same way as for `pldos.x`. However, note that for each curve *two* orbitals have to given.

3.2.5 plopt.run, plopt.x

This program allows to plot the optical properties as the optical conductivity, dielectric function, index of refraction, extinction coefficient, optical reflectivity, optical absorption, and the energy-loss function. In addition to the interband contributions, the calculated plasma frequency can be used to include the intraband terms.

Input is read from file OPT and output is generated for use with Gnuplot, which by default writes to a postscript file *opt.ps*.

3.2.6 *pltrp.run, pltrp.x*

This program allows to plot the transport and thermoelectric properties. Their evaluation is performed within Boltzmann transport theory. Calculations include the electrical conductivity and resistivity, the thermopower, the power factor, the electrothermal figure of merit, the thermal conductivity, as well as the Hall conductivity and coefficient. The calculation of these properties is initiated by setting the new token, SAVTRP=T and running mnscf.run. The calculations work with all Brillouin zone integration schemes. However, use of BZINT=HPS should be avoided due to the strong oscillations near the band edges, which leads to wrong results especially for the thermopower and related quantities of doped semiconductors. This is essentially due to the fact that the thermopower is based on an energy integration in a narrow range around the Fermi energy, which is then most affected by the oscisllations. Plotting is done with a new routine, pltrp.run, which behave much like the other plotting routines. Input is echoed to the file PLIT. The plotting routine also allows to take into account the effect of doping within a rigid band scheme.

Input is read from file TRAP and output is generated for use with Gnuplot, which by default writes to a postscript file *trap.ps*.

3.2.7 *plfre.run, plfre.x*

This program starts from file FREE, which holds the overlapping free atom charge densities and potential within the plot region specified by tokens ORIGIN= and RPLOTn=. It prepares for later use of Gnuplot. During the dialog you can choose between a contour or 3D plot. In addition, plot of the core charge density, valence charge density or both or else the potential can be specified.

3.2.8 *plbnd.lx, pldos.lx, plcop.lx, plopt.lx, pltrp.lx*

These shell script include files bnd.tex, dos.tex, coop.tex, opt.tex, and trap.tex into the LaTeX envelope files plbnd.tex, pldos.tex, plcop.tex, plopt.tex, and pltrp.tex, respectively, and run LaTeX as well as dvips. As a result, postscript files bnd.ps, dos.ps, coop.ps, opt.ps, and trap.ps, respectively, are obtained.

3.2.9 *plbnd.tex, pldos.tex, plcop.tex, plopt.tex, pltrp.tex*

These are LaTeX envelope files used to include bnd.tex, dos.tex, coop.tex, opt.tex, and trap.tex, respectively, and to produce postscript files of the band structure, DOS, COOP, optical and transport properties.

3.3 Installation shell scripts

3.3.1 Makefile

This is the makefile of the ASW program package for compiling and linking the source and object files in a Unix/Linux environment. Typing `make all` will automatically create all executables and typing `make install` will install them in a prespecified directory. A full description of this process has already been given in Sec. 1.4.

3.3.2 mkall.x

The compiling and linking step can be performed as a background job by invoking the shell script `mkall.x`.

3.3.3 upshl

This shell script updates the specification of the directory, where the executables are installed, in all shell scripts listed in Secs. 3.1 and 3.2. It is automatically called during the `make install` process.

3.4 General purpose files

Input data as well as data created by the ASW programs are spread over a large number of files. Yet, exchange of the user with the programs is limited essentially to a single file, i.e. the CTRL file. All other files serve the purpose of holding specific information about the distribution or are meant for information exchange between different programs. Neither of these latter files has to be changed by the user. Anyway, in the following list a short description is given for all files.

3.4.1 README

The README comprises a shortcut version of this user guide. Actually, the present manuscript has its roots in the README file. It contains very brief information about the distribution, installation and execution of the programs as well as some remarks about external software to be used with the ASW program package.

3.4.2 INSTALL

A concise description of the installation process is provided by this file.

3.4.3 COPYRIGHT

The COPYRIGHT file covers all the copyright information concerning the ASW program package. It is printed in Sec. 1.6 and should be read by any user at the very beginning.

3.4.4 LICENCE

The LICENCE file contains a single line indicating the expiration date for the present licence.

3.5 CTRL files

Input data as well as data created by the ASW programs are spread over a large number of files. Yet, exchange of the user with the programs is limited essentially to a single file, i.e. the CTRL file. All other files serve the purpose of holding specific information about the distribution or are meant for information exchange between different programs. Neither of these latter files has to be changed by the user. Anyway, in the following list a short description is given for all files.

3.5.1 CTRL

The CTRL file is the one and only input file to the main programs. It

- is fully free format and thus allows for a flexible setup,
- is subdivided in sections (categories) each containing
- a set of catchwords (tokens),
- has many options,
- many useful defaults.

The CTRL file contains information about

- the crystal structure,
- the constituent atoms,

- the symmetry lines,
- settings for input/output,
- parameters for sphere packing,
- Brillouin zone sampling,
- iteration acceleration,
- and convergence criteria.

All files following in the present list are automatically created and deleted by the programs. A complete description of the CTRL file and all its categories and tokens is given in Chap. 4.

3.5.2 CBAK

All the main programs except for `mnmpr.run` write an updated copy of the CTRL file to file CBAK unless a different name is specified by token WRITE= in category IO.

3.5.3 CALL

If the verbosity is set to 40 or a higher values this file is written by all the main programs except for `mnmpr.run`. As the file CBAK it holds an updated copy of the CTRL. However, in contrast to CBAK it contains all categories and tokens irrespective of their appearance in the CTRL file.

3.5.4 CNEW

The packing program `mnpac.run` writes a new CTRL file named CNEW (remember: file CTRL is never written to), which includes possibly created empty sphere positions as well as the radii of all spheres. Before proceeding with the self-consistent calculations you must rename the file CNEW to CTRL.

3.6 Information files

Input data as well as data created by the ASW programs are spread over a large number of files. Yet, exchange of the user with the programs is limited essentially to a single file, i.e. the CTRL file. All other files serve the purpose of holding specific information about the distribution or are meant for information exchange between different programs. Neither of these latter files has to be changed by the user. Anyway, in the following list a short description is given for all files.

3.6.1 HELP

A first overview over the capabilities of the ASW program package can be best obtained by creating the HELP file. In case this is missing in the distribution it can be most easily obtained by writing the line

IO HELP=T

to the CTRL and running any of the ASW main programs (those starting with "mn"). This will generate the HELP file listed here.

```
HELP-file for ASW-2.6


category HEADER
  title

category VERSION
  token ASW- of cast double
        Version/release of program which has written CTRL

category IO
  token HELP= of cast logical
        Switch to print HELP file
  token SHOW= of cast logical
        Switch to echo CTRL file to output
  token VERBOS= of cast integer
        Verbosity level for printing of output
  token CLEAN= of cast logical
        Switch to shrink atomic files after convergence
  token WRITE= of cast character
        Name of file to which a copy of CTRL file is written
  token EXTENS= of cast character
        Default extension for all files besides CTRL file

category OPTIONS
  token REL= of cast logical
        Switch to scalar-relativistic mode
  token LSCPL= of cast logical
        Switch to turn on LS-coupling
  token NSPIN= of cast integer
        Number of spin-channels
  token AFSYM= of cast logical
        Switch to use antiferromagnetic symmetry if present
  token BEXT= of cast double
        External magnetic field (in z-direction)
  token XCPAR= of cast character
        String for XC-parametrization
```

```
  token GGA= of cast character
        String for GGA-parametrization
  token LDA+U= of cast character
        String for LDA+U-flavor
  token OVLCHK= of cast logical
        Switch to perform overlap check
  token DISTL= of cast double
        Maximum distance between atoms in the neighbour list
  token CCOR= of cast logical
        Switch to use combined correction to the ASA
  token CORDRD= of cast logical
        Switch to frozen-core calculations

category STRUC (mandatory)
  token UNITS= of cast character
        Units to be used in STRUC and SUPCELL
  token ALAT= of cast double (mandatory)
        Lattice constant A in UNITS
  token PLAT= of cast double and length 9 (mandatory)    --- OR:
        Primitive translations in units of A
  [
  token SLAT= of cast character
        String for Bravais lattice (obsolete)
  token BLAT= of cast double    --- OR:
        Lattice constant B in UNITS
  token BBYA= of cast double
        Ratio of the lattice constants B/A
  token CLAT= of cast double    --- OR:
        Lattice constant C in UNITS
  token CBYA= of cast double
        Ratio of the lattice constants C/A
  token ALPHA= of cast double
        Angle alpha
  token BETA= of cast double
        Angle beta
  token GAMMA= of cast double
        Angle gamma
  ]
  token CNTR= of cast character
        Centering type of the Bravais lattice
  token ADJLAT= of cast logical
        Switch to allow for adjusting the lattice

category CLASS (mandatory)
  token NCLASS= of cast integer
        Number of different atoms (classes)
  token ATOM= of cast character (mandatory)
        Class labels
  token Z= of cast integer (mandatory)
        Atomic numbers
  token R= of cast double    --- OR:
        Atomic sphere radii in atomic units
  token R/RA= of cast double
        Atomic sphere radii in arbitrary units (obsolete)
```

```
  token LMXL= of cast integer
        Maximum angular momentum including the lower waves
  token LMXI= of cast integer
        Maximum angular momentum including intermediate waves
  token CONF= of cast integer and length 4
        Principal quantum numbers for all orbitals
  token COORB= of cast integer
        Orbitals to be included in the COOP
  token QVAL= of cast double and length 4
        Valence charges for starting from scratch
  token MVAL= of cast double and length 4
        Valence moments for starting spinpolarized calculations
  token UVAL= of cast double and length 4
        Screened Coulomb parameters U for all orbitals
  token JVAL= of cast double and length 4
        Screened Stoner parameters J for all orbitals

category SITE (mandatory)
  token NBAS= of cast integer
        Number of atoms
  token CARTP= of cast logical
        Switch to treat atomic positions as Cartesian
  token CHOUT= of cast logical
        Switch to change interpretation of atomic positions
  token ADJPOS= of cast logical
        Switch to allow for adjusting the atomic positions
  token ATOM= of cast character (mandatory)
        Class labels
  token POS= of cast double and length 3 (mandatory)
        Positions of basis atoms
  token SPIN= of cast character
        String characterizing the spin direction

category SYMGRP
  token GENPOS= of cast logical
        Switch to complete atomic basis by use of symmetry
  token CARTR= of cast logical
        Switch to treat rotation axes as Cartesian
  token CARTT= of cast logical
        Switch to treat fractional translations as Cartesian
  token ORIGIN= of cast integer
        Origin choice
  token SGSYM= of cast character    --- OR:
        Space group symbol
  token SGNUM= of cast integer    --- OR:
        Space group number
  token SYMOPS= of cast character and length 48
        Strings for space group generators

category PACK
  token FILLNG= of cast double
        Filling factor for atomic sphere volumes
  token OBYDMX= of cast double
        Maximum allowed overlap/distance
```

```
  token OBYRMX= of cast double
        Maximum allowed overlap/radius
  token ESBONS= of cast double
        Empty sphere bonus to be added to OBYDMX and OBYRMX
  token NCEMAX= of cast integer
        Maximum number of allowed empty sphere classes
  token RADMIN= of cast double
        Minimum muffin-tin radius for empty spheres
  token RADMAX= of cast double
        Maximum atomic sphere radius for empty spheres
  token RADACC= of cast double
        Accuracy required for sphere radii
  token POSACC= of cast double
        Accuracy required for empty sphere positions

category ENVEL
  token NKAP= of cast integer
        Number of envelope function energies
  token EKAP= of cast double
        Array of envelope function energies
  token EWPAR= of cast double
        Ewald parameter without volume scaling
  token EWTOL= of cast double
        Precision sought for Ewald sums

category BZSMP
  token NKBAB= of cast integer    --- OR:
        Spacing of k-points for Brillouin zone integration
  token NKABC= of cast integer and length 3
        Numbers of k-points for Brillouin zone integration
  token BZINT= of cast character
        String for Brillouin-zone integration scheme
  token EMIN= of cast double
        Minimum energy for DOS calculation
  token EMAX= of cast double
        Maximum energy for DOS calculation
  token NDOS= of cast integer
        Number of division of the interval EMIN-EMAX
 ... if BZINT=HPS the following two tokens are needed:
  token NORD= of cast integer
        Order of approximant in high-precision BZ sampling
  token WIDTH= of cast double
        Broadening in high-precision BZ sampling
  token SAVDOS= of cast logical
        Switch to save calculated partial DOSs
  token SAVCOOP= of cast logical
        Switch to save calculated COOPs
  token CTYPE= of cast character
        String for type of COOP calculation
  token MSPLIT= of cast logical
        Switch to calculate m-splitted COOPs
  token TEMPFD= of cast double
        Temperature for Fermi-Dirac folding
  token SAVFERM= of cast logical
```

```
        Switch to save Fermi surface data
  token SAVOPT= of cast logical
        Switch to save calculated partial optical spectra

category CHARGE
  token NETA= of cast integer
        Number of charge density envelope function energies
  token EETA= of cast double and length 2
        Array of charge density envelope function energies
  token SAVRHO= of cast logical
        Switch to save calculated charge density
  token SAVELF= of cast logical
        Switch to save calculated electron localisation funct.
  token CHARWIN= of cast logical
        Switch to narrow down the charge density energy window
  token EMINC= of cast double
        Minimum energy for charge density calculation
  token EMAXC= of cast double
        Maximum energy for charge density calculation

category CONTROL
  token START= of cast character
        String controlling program starting point
  token QUIT= of cast character
        String controlling program end point
  token FREE= of cast logical
        Switch to free atom calculations / free electron bands
  token NITBND= of cast integer
        Maximum number of band iterations
  token CNVG= of cast double
        Convergence tolerance for zero moments
  token CNVGET= of cast double
        Convergence tolerance for total energy
  token NITATM= of cast integer
        Maximum number of intraatomic iterations
  token CNVGQA= of cast double
        Convergence tolerance for atomic charges

category MIXING
  token NMIXB= of cast integer
        Number of previous iterations used in band mixing
  token BETAB= of cast double
        Mixing parameter for band mixing
  token INCBB= of cast logical
        Switch to increase band mixing parameter
  token NMIXA= of cast integer
        Number of previous iterations used in atom mixing
  token BETAA= of cast double
        Mixing parameter for atom mixing

category SUPCELL
  token ALAT= of cast double
        Supercell lattice constant A in UNITS
  token PLAT= of cast double and length 9    --- OR:
```

```
        Supercell primitive translations in units of A
   [
   token SLAT= of cast character
         String for supercell Bravais lattice (obsolete)
   token BLAT= of cast double    --- OR:
         Supercell lattice constant B in UNITS
   token BBYA= of cast double
         Ratio of the supercell lattice constants B/A
   token CLAT= of cast double    --- OR:
         Supercell lattice constant C in UNITS
   token CBYA= of cast double
         Ratio of the supercell lattice constants C/A
   token ALPHA= of cast double
         Angle alpha
   token BETA= of cast double
         Angle beta
   token GAMMA= of cast double
         Angle gamma
   ]
   token CNTR= of cast character
         Centering type of the supercell Bravais lattice
   token EQUIV= of cast logical
         Switch to keep subcells equivalent
   token CARTS= of cast logical
         Switch to treat position shift vector as Cartesian
   token PSHIFT= of cast double and length 3
         Shift vector for the supercell atomic positions
   token CARTQ= of cast logical
         Switch to treat spin wave vector as Cartesian
   token QSWAVE= of cast double and length 3
         Spin wave vector of (collinear) antiferromagnets

 category SYMLIN
   token NPAN= of cast integer
         Number of symmetry lines (panels)
   token NPTS= of cast integer
         Maximum total number of points
   token ORBWGT= of cast logical
         Switch to calculate orbital weights
   token SPATH= of cast logical
         Switch to use spherical pathways
   token EKPV0= of cast double
         Photoelectron kinetic energy plus inner potential
   token CPNORM= of cast double and length 3
         Cleavage plane normal vector
   token CARTN= of cast logical
         Switch to treat normal vector as Cartesian
   token CARTE= of cast logical
         Switch to treat endpoints as Cartesian
   token LABEL= of cast character
         Labels of endpoints
   token ENDPT= of cast double and length 3
         Endpoints of symmetry lines
```

```
category PLOT
  token CARTV= of cast logical
        Switch to treat plot vectors as Cartesian
  token ORIGIN= of cast double and length 3
        Origin of plot space
  token RPLOT1= of cast double and length 3
        Plot vector specifying plot space
  token RPLOT2= of cast double and length 3
        Plot vector specifying plot space
  token RPLOT3= of cast double and length 3
        Plot vector specifying plot space
  token NPDIV1= of cast integer
        Number of divisions of plot space
  token NPDIV2= of cast integer
        Number of divisions of plot space
  token NPDIV3= of cast integer
        Number of divisions of plot space
```

In addition, an output file is generated, which includes a full CTRL file, where all categories and tokens are given with their default values. This output looks like

```
 ASW-2.6, program MNSCF started on asterix at Tue, 10 Feb 2009, 14:42:00.

     Copyright (C) 1992-2009 Volker Eyert
     Please see file COPYRIGHT for details


 Write information to file HELP for HELP=T:

 SHOW=T lists default values for optional input.

 Echo CTRL file for SHOW=T:
HEADER  Cu fcc
        data by Landolt-Boernstein
VERSION ASW-2.6
IO      HELP=T SHOW=T VERBOS=30 CLEAN=T WRITE=CBAK EXTENS=
OPTIONS REL=T LSCPL=F NSPIN=1 AFSYM=F BEXT=0.0 XCPAR= GGA= LDA+U=FLL OVLCHK=T
        DISTL=3.0 CCOR=T CORDRD=F
STRUC   UNITS=BOHR ALAT=6.83079 PLAT= 0.0  0.0  0.0
                                      0.0  0.0  0.0
                                      0.0  0.0  0.0
        SLAT= BLAT=6.83079 BBYA=1.0 CLAT=6.83079 CBYA=1.0 ALPHA=90.0 BETA=90.0
        GAMMA=90.0 CNTR=F ADJLAT=F
CLASS   NCLASS=1
        ATOM=CU Z=29 R=2.6694476 R/RA=1.0 LMXL=2 LMXI=3 CONF=4 4 3 4
        COORB=0 1 2
                QVAL= 1.0  0.0  10.0  0.0  MVAL= 0.0  0.0  0.0  0.0
                UVAL= 0.0  0.0  0.0  0.0   JVAL= 0.0  0.0  0.0  0.0
SITE    NBAS=1 CARTP=T CHOUT=F ADJPOS=T
        ATOM=CU POS= 0.0  0.0  0.0 SPIN=UP
SYMGRP  GENPOS=F CARTR=T CARTT=F ORIGIN=1 SGSYM=Ia-3d SGNUM=230 SYMOPS=
PACK    FILLNG=1.0 OBYDMX=0.15 OBYRMX=0.4 ESBONS=0.05 NCEMAX=1024 RADMIN=0.5
```

```
        RADMAX=5.0 RADACC=1.0D-02 POSACC=1.0D-12
ENVEL   NKAP=1 EKAP=-0.015 EWPAR=2.54950976 EWTOL=1.0D-10
BZSMP   NKBAB=6 NKABC=0 0 0 BZINT=LTM EMIN=-1.0 EMAX=1.5 NDOS=2500
        NORD=5 WIDTH=0.02 SAVDOS=F SAVCOOP=F CTYPE=ECOV MSPLIT=F TEMPFD=300.0
        SAVFERM=F SAVOPT=F SAVTRAP=F
CHARGE  NETA=2 EETA=-3.0 -5.0 SAVRHO=F SAVELF=F CHARWIN=F EMINC=-100.0
        EMAXC=100.0
CONTROL START= QUIT= FREE=F NITBND=99 CNVG=1.0D-08 CNVGET=1.0D-08
        NITATM=50 CNVGQA=1.0D-10
MIXING  NMIXB=5 BETAB=0.5 INCBB=T NMIXA=5 BETAA=0.5
SUPCELL ALAT=6.83079 PLAT= 0.0  0.0  0.0
                           0.0  0.0  0.0
                           0.0  0.0  0.0
        SLAT= BLAT=6.83079 BBYA=1.0 CLAT=6.83079 CBYA=1.0 ALPHA=90.0 BETA=90.0
        GAMMA=90.0 CNTR=P EQUIV=T CARTS=T PSHIFT= 0.0  0.0  0.0 CARTQ=T
        QSWAVE= 0.0  0.0  0.0
SYMLIN  NPAN=5 NPTS=400 ORBWGT=T SPATH=F EKPV0=0.0 CPNORM= 0.0  0.0  0.0
        CARTN=T CARTE=F
        LABEL=W ENDPT= 0.500  0.250  0.750
        LABEL=L ENDPT= 0.500  0.500  0.500
        LABEL=g ENDPT= 0.000  0.000  0.000
        LABEL=X ENDPT= 0.500  0.000  0.500
        LABEL=W ENDPT= 0.500  0.250  0.750
        LABEL=K ENDPT= 0.375  0.375  0.750
PLOT    CARTV=T
        ORIGIN= 0.0  0.0  0.0
        RPLOT1= 1.0  0.0  0.0
        RPLOT2= 0.0  1.0  0.0
        RPLOT3= 0.0  0.0  1.0
        NPDIV1=50 NPDIV2=50 NPDIV3=0
 task  3, I/O         :  cpu time:     0.02800 sec

 Execution stopping for HELP=T.

 ASW-2.6, program MNSCF ended on asterix at Tue, 10 Feb 2009, 14:42:00.
```

3.6.2 SPCGRP

This file is written along with the HELP file. The SPCGRP file contains a list of all 230 space groups, which for each entry gives the Bravais lattice, the numbers of the point and space group, respectively, the space group symbol in the Hermann-Mauguin notation, and the generators of the space group. The SPCGRP file is listed below.

```
 SPCGRP-file for ASW-2.6


 Lat PG  SG O SG-Symbol  Generators

 tri  1   1   P1         E
```

```
tri  2   2   P-1        I
 sm  3   3   P2         R2Y
 sm  3   3   P121       R2Y
 sm  3   4   P2_1       R2Y:T(0,1/2,0)
 sm  3   4   P12_11     R2Y:T(0,1/2,0)
 cm  3   5   C2         R2Y
 cm  3   5   A2         R2Y
 cm  3   5   I2         R2Y
 cm  3   5   C121       R2Y
 cm  3   5   A121       R2Y
 cm  3   5   I121       R2Y
 sm  4   6   Pm         MY
 sm  4   6   P1m1       MY
 sm  4   7   Pc         MY:T(0,0,1/2)
 sm  4   7   Pa         MY:T(1/2,0,0)
 sm  4   7   Pn         MY:T(1/2,0,1/2)
 sm  4   7   P1c1       MY:T(0,0,1/2)
 sm  4   7   P1a1       MY:T(1/2,0,0)
 sm  4   7   P1n1       MY:T(1/2,0,1/2)
 cm  4   8   Cm         MY
 cm  4   8   Am         MY
 cm  4   8   Im         MY
 cm  4   8   C1m1       MY
 cm  4   8   A1m1       MY
 cm  4   8   I1m1       MY
 cm  4   9   Cc         MY:T(0,0,1/2)
 cm  4   9   Cn         MY:T(1/2,0,1/2)
 cm  4   9   Aa         MY:T(1/2,0,0)
 cm  4   9   An         MY:T(1/2,1/2,0)
 cm  4   9   Ia         MY:T(1/2,0,0)
 cm  4   9   Ic         MY:T(0,0,1/2)
 cm  4   9   C1c1       MY:T(0,0,1/2)
 cm  4   9   C1n1       MY:T(1/2,0,1/2)
 cm  4   9   A1a1       MY:T(1/2,0,0)
 cm  4   9   A1n1       MY:T(1/2,1/2,0)
 cm  4   9   I1a1       MY:T(1/2,0,0)
 cm  4   9   I1c1       MY:T(0,0,1/2)
 sm  5  10   P2/m       I MY
 sm  5  10   P12/m1     I MY
 sm  5  11   P2_1/m     I MY:T(0,1/2,0)
 sm  5  11   P12_1/m1   I MY:T(0,1/2,0)
 cm  5  12   C2/m       I MY
 cm  5  12   A2/m       I MY
 cm  5  12   I2/m       I MY
 cm  5  12   C12/m1     I MY
 cm  5  12   A12/m1     I MY
 cm  5  12   I12/m1     I MY
 sm  5  13   P2/c       I MY:T(0,0,1/2)
 sm  5  13   P2/a       I MY:T(1/2,0,0)
 sm  5  13   P2/n       I MY:T(1/2,0,1/2)
 sm  5  13   P12/c1     I MY:T(0,0,1/2)
 sm  5  13   P12/a1     I MY:T(1/2,0,0)
 sm  5  13   P12/n1     I MY:T(1/2,0,1/2)
 sm  5  14   P2_1/c     I MY:T(0,1/2,1/2)
```

```
 sm  5  14  P2_1/a     I MY:T(1/2,1/2,0)
 sm  5  14  P2_1/n     I MY:T(1/2,1/2,1/2)
 sm  5  14  P12_1/c1   I MY:T(0,1/2,1/2)
 sm  5  14  P12_1/a1   I MY:T(1/2,1/2,0)
 sm  5  14  P12_1/n1   I MY:T(1/2,1/2,1/2)
 cm  5  15  C2/c       I MY:T(0,0,1/2)
 cm  5  15  C2/n       I MY:T(1/2,0,1/2)
 cm  5  15  A2/a       I MY:T(1/2,0,0)
 cm  5  15  A2/n       I MY:T(1/2,1/2,0)
 cm  5  15  I2/a       I MY:T(1/2,0,0)
 cm  5  15  I2/c       I MY:T(0,0,1/2)
 cm  5  15  C12/c1     I MY:T(0,0,1/2)
 cm  5  15  C12/n1     I MY:T(1/2,0,1/2)
 cm  5  15  A12/a1     I MY:T(1/2,0,0)
 cm  5  15  A12/n1     I MY:T(1/2,1/2,0)
 cm  5  15  I12/a1     I MY:T(1/2,0,0)
 cm  5  15  I12/c1     I MY:T(0,0,1/2)
 so  6  16  P222       R2X R2Y
 so  6  17  P222_1     R2X R2Y:T(0,0,1/2)
 so  6  17  P22_12     R2X R2Y:T(0,1/2,0)
 so  6  17  P2_122     R2X:T(1/2,0,0) R2Y
 so  6  18  P22_12_1   R2X R2Y:T(0,1/2,1/2)
 so  6  18  P2_122_1   R2X:T(1/2,0,1/2) R2Y
 so  6  18  P2_12_12   R2X:T(1/2,1/2,0) R2Y:T(1/2,1/2,0)
 so  6  19  P2_12_12_1 R2X:T(1/2,1/2,0) R2Y:T(0,1/2,1/2)
sco  6  20  C222_1     R2X R2Y:T(0,0,1/2)
sco  6  20  A2_122     R2X:T(1/2,0,0) R2Y
sco  6  20  B22_12     R2X R2Y:T(0,1/2,0)
sco  6  21  C222       R2X R2Y
sco  6  21  A222       R2X R2Y
sco  6  21  B222       R2X R2Y
fco  6  22  F222       R2X R2Y
bco  6  23  I222       R2X R2Y
bco  6  24  I2_12_12_1 R2X:T(0,0,1/2) R2Y:T(1/2,0,0)
 so  7  25  Pmm2       MX MY
 so  7  25  Pm2m       MX MZ
 so  7  25  P2mm       MY MZ
 so  7  26  Pmc2_1     MX MY:T(0,0,1/2)
 so  7  26  Pcm2_1     MX:T(0,0,1/2) MY
 so  7  26  Pm2_1b     MX MZ:T(0,1/2,0)
 so  7  26  Pb2_1m     MX:T(0,1/2,0) MZ
 so  7  26  P2_1ma     MY MZ:T(1/2,0,0)
 so  7  26  P2_1am     MY:T(1/2,0,0) MZ
 so  7  27  Pcc2       MX:T(0,0,1/2) MY:T(0,0,1/2)
 so  7  27  Pb2b       MX:T(0,1/2,0) MZ:T(0,1/2,0)
 so  7  27  P2aa       MY:T(1/2,0,0) MZ:T(1/2,0,0)
 so  7  28  Pma2       MX:T(1/2,0,0) MY:T(1/2,0,0)
 so  7  28  Pbm2       MX:T(0,1/2,0) MY:T(0,1/2,0)
 so  7  28  Pm2a       MX:T(1/2,0,0) MZ:T(1/2,0,0)
 so  7  28  Pc2m       MX:T(0,0,1/2) MZ:T(0,0,1/2)
 so  7  28  P2mb       MY:T(0,1/2,0) MZ:T(0,1/2,0)
 so  7  28  P2cm       MY:T(0,0,1/2) MZ:T(0,0,1/2)
 so  7  29  Pca2_1     MX:T(1/2,0,1/2) MY:T(1/2,0,0)
 so  7  29  Pbc2_1     MX:T(0,1/2,0) MY:T(0,1/2,1/2)
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 so  7  29  Pb2_1a     MX:T(1/2,1/2,0) MZ:T(1/2,0,0)
 so  7  29  Pc2_1b     MX:T(0,0,1/2) MZ:T(0,1/2,1/2)
 so  7  29  P2_1ab     MY:T(1/2,1/2,0) MZ:T(0,1/2,0)
 so  7  29  P2_1ca     MY:T(0,0,1/2) MZ:T(1/2,0,1/2)
 so  7  30  Pnc2       MX:T(0,1/2,1/2) MY:T(0,1/2,1/2)
 so  7  30  Pcn2       MX:T(1/2,0,1/2) MY:T(1/2,0,1/2)
 so  7  30  Pn2b       MX:T(0,1/2,1/2) MZ:T(0,1/2,1/2)
 so  7  30  Pb2n       MX:T(1/2,1/2,0) MZ:T(1/2,1/2,0)
 so  7  30  P2an       MY:T(1/2,1/2,0) MZ:T(1/2,1/2,0)
 so  7  30  P2na       MY:T(1/2,0,1/2) MZ:T(1/2,0,1/2)
 so  7  31  Pmn2_1     MX MY:T(1/2,0,1/2)
 so  7  31  Pnm2_1     MX:T(0,1/2,1/2) MY
 so  7  31  Pn2_1m     MX:T(0,1/2,1/2) MZ
 so  7  31  Pm2_1n     MX MZ:T(1/2,1/2,0)
 so  7  31  P2_1mn     MY MZ:T(1/2,1/2,0)
 so  7  31  P2_1nm     MY:T(1/2,0,1/2) MZ
 so  7  32  Pba2       MX:T(1/2,1/2,0) MY:T(1/2,1/2,0)
 so  7  32  Pc2a       MX:T(1/2,0,1/2) MZ:T(1/2,0,1/2)
 so  7  32  P2cb       MY:T(0,1/2,1/2) MZ:T(0,1/2,1/2)
 so  7  33  Pna2_1     MX:T(1/2,1/2,1/2) MY:T(1/2,1/2,0)
 so  7  33  Pbn2_1     MX:T(1/2,1/2,0) MY:T(1/2,1/2,1/2)
 so  7  33  Pc2_1n     MX:T(1/2,0,1/2) MZ:T(1/2,1/2,1/2)
 so  7  33  Pn2_1a     MX:T(1/2,1/2,1/2) MZ:T(1/2,0,1/2)
 so  7  33  P2_1nb     MY:T(1/2,1/2,1/2) MZ:T(0,1/2,1/2)
 so  7  33  P2_1cn     MY:T(0,1/2,1/2) MZ:T(1/2,1/2,1/2)
 so  7  34  Pnn2       MX:T(1/2,1/2,1/2) MY:T(1/2,1/2,1/2)
 so  7  34  Pn2n       MX:T(1/2,1/2,1/2) MZ:T(1/2,1/2,1/2)
 so  7  34  P2nn       MY:T(1/2,1/2,1/2) MZ:T(1/2,1/2,1/2)
sco  7  35  Cmm2       MX MY
sco  7  35  Bm2m       MX MZ
sco  7  35  A2mm       MY MZ
sco  7  36  Cmc2_1     MX MY:T(0,0,1/2)
sco  7  36  Ccm2_1     MX:T(0,0,1/2) MY
sco  7  36  Bb2_1m     MX:T(0,1/2,0) MZ
sco  7  36  Bm2_1b     MX MZ:T(0,1/2,0)
sco  7  36  A2_1ma     MY MZ:T(1/2,0,0)
sco  7  36  A2_1am     MY:T(1/2,0,0) MZ
sco  7  37  Ccc2       MX:T(0,0,1/2) MY:T(0,0,1/2)
sco  7  37  Bb2b       MX:T(0,1/2,0) MZ:T(0,1/2,0)
sco  7  37  A2aa       MY:T(1/2,0,0) MZ:T(1/2,0,0)
sco  7  38  Amm2       MX MY
sco  7  38  Bmm2       MX MY
sco  7  38  Am2m       MX MZ
sco  7  38  Cm2m       MX MZ
sco  7  38  B2mm       MY MZ
sco  7  38  C2mm       MY MZ
sco  7  39  Abm2       MX:T(0,1/2,0) MY:T(0,1/2,0)
sco  7  39  Bma2       MX:T(1/2,0,0) MY:T(1/2,0,0)
sco  7  39  Cm2a       MX:T(1/2,0,0) MZ:T(1/2,0,0)
sco  7  39  Ac2m       MX:T(0,1/2,0) MZ:T(0,1/2,0)
sco  7  39  B2cm       MY:T(1/2,0,0) MZ:T(1/2,0,0)
sco  7  39  C2mb       MY:T(1/2,0,0) MZ:T(1/2,0,0)
sco  7  40  Ama2       MX:T(1/2,0,0) MY:T(1/2,0,0)
sco  7  40  Bbm2       MX:T(0,1/2,0) MY:T(0,1/2,0)
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sco  7  40   Cc2m      MX:T(0,0,1/2) MZ:T(0,0,1/2)
sco  7  40   Am2a      MX:T(1/2,0,0) MZ:T(1/2,0,0)
sco  7  40   B2mb      MY:T(0,1/2,0) MZ:T(0,1/2,0)
sco  7  40   C2cm      MY:T(0,0,1/2) MZ:T(0,0,1/2)
sco  7  41   Aba2      MX:T(1/2,1/2,0) MY:T(1/2,1/2,0)
sco  7  41   Bba2      MX:T(1/2,1/2,0) MY:T(1/2,1/2,0)
sco  7  41   Cc2a      MX:T(1/2,0,1/2) MZ:T(1/2,0,1/2)
sco  7  41   Ac2a      MX:T(1/2,1/2,0) MZ:T(1/2,1/2,0)
sco  7  41   B2cb      MY:T(1/2,1/2,0) MZ:T(1/2,1/2,0)
sco  7  41   C2cb      MY:T(1/2,0,1/2) MZ:T(1/2,0,1/2)
fco  7  42   Fmm2      MX MY
fco  7  42   Fm2m      MX MZ
fco  7  42   F2mm      MY MZ
fco  7  43   Fdd2      MX:T(1/4,1/4,1/4) MY:T(1/4,1/4,1/4)
fco  7  43   Fd2d      MX:T(1/4,1/4,1/4) MZ:T(1/4,1/4,1/4)
fco  7  43   F2dd      MY:T(1/4,1/4,1/4) MZ:T(1/4,1/4,1/4)
bco  7  44   Imm2      MX MY
bco  7  44   Im2m      MX MZ
bco  7  44   I2mm      MY MZ
bco  7  45   Iba2      MX:T(0,0,1/2) MY:T(0,0,1/2)
bco  7  45   Ic2a      MX:T(0,1/2,0) MZ:T(0,1/2,0)
bco  7  45   I2cb      MY:T(1/2,0,0) MZ:T(1/2,0,0)
bco  7  46   Ima2      MX:T(1/2,0,0) MY:T(1/2,0,0)
bco  7  46   Ibm2      MX:T(0,1/2,0) MY:T(0,1/2,0)
bco  7  46   Ic2m      MX:T(0,0,1/2) MZ:T(0,0,1/2)
bco  7  46   Im2a      MX:T(1/2,0,0) MZ:T(1/2,0,0)
bco  7  46   I2mb      MY:T(0,1/2,0) MZ:T(0,1/2,0)
bco  7  46   I2cm      MY:T(0,0,1/2) MZ:T(0,0,1/2)
 so  8  47   Pmmm       I MX MY
 so  8  48 1 Pnnn       I:T(1/2,1/2,1/2) MX:T(1/2,1/2,1/2) MY:T(1/2,1/2,1/2)
 so  8  48 2 Pnnn       I MX:T(0,1/2,1/2) MY:T(1/2,0,1/2)
 so  8  49   Pccm       I MX:T(0,0,1/2) MY:T(0,0,1/2)
 so  8  49   Pmaa       I MX MY:T(1/2,0,0)
 so  8  49   Pbmb       I MX:T(0,1/2,0) MY
 so  8  50 1 Pban       I:T(1/2,1/2,0) MX:T(1/2,1/2,0) MY:T(1/2,1/2,0)
 so  8  50 2 Pban       I MX:T(0,1/2,0) MY:T(1/2,0,0)
 so  8  50 1 Pncb       I:T(0,1/2,1/2) MX:T(0,1/2,1/2) MY:T(0,1/2,1/2)
 so  8  50 2 Pncb       I MX:T(0,1/2,1/2) MY:T(0,0,1/2)
 so  8  50 1 Pcna       I:T(1/2,0,1/2) MX:T(1/2,0,1/2) MY:T(1/2,0,1/2)
 so  8  50 2 Pcna       I MX:T(0,0,1/2) MY:T(1/2,0,1/2)
 so  8  51   Pmma       I MX:T(1/2,0,0) MY
 so  8  51   Pmmb       I MX MY:T(0,1/2,0)
 so  8  51   Pbmm       I MX:T(0,1/2,0) MY:T(0,1/2,0)
 so  8  51   Pcmm       I MX:T(0,0,1/2) MY
 so  8  51   Pmcm       I MX MY:T(0,0,1/2)
 so  8  51   Pmam       I MX:T(1/2,0,0) MY:T(1/2,0,0)
 so  8  52   Pnna       I MX:T(0,1/2,1/2) MY:T(1/2,1/2,1/2)
 so  8  52   Pnnb       I MX:T(1/2,1/2,1/2) MY:T(1/2,0,1/2)
 so  8  52   Pbnn       I MX:T(0,1/2,0) MY:T(1/2,0,1/2)
 so  8  52   Pcnn       I MX:T(0,0,1/2) MY:T(1/2,1/2,1/2)
 so  8  52   Pncn       I MX:T(1/2,1/2,1/2) MY:T(0,0,1/2)
 so  8  52   Pnan       I MX:T(0,1/2,1/2) MY:T(1/2,0,0)
 so  8  53   Pmna       I MX MY:T(1/2,0,1/2)
 so  8  53   Pnmb       I MX:T(0,1/2,1/2) MY
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 so  8  53   Pbmn       I MX:T(1/2,1/2,0) MY
 so  8  53   Pcnm       I MX:T(1/2,0,1/2) MY:T(1/2,0,1/2)
 so  8  53   Pncm       I MX:T(0,1/2,1/2) MY:T(0,1/2,1/2)
 so  8  53   Pman       I MX MY:T(1/2,1/2,0)
 so  8  54   Pcca       I MX:T(1/2,0,1/2) MY:T(0,0,1/2)
 so  8  54   Pccb       I MX:T(0,0,1/2) MY:T(0,1/2,1/2)
 so  8  54   Pbaa       I MX:T(0,1/2,0) MY:T(1/2,1/2,0)
 so  8  54   Pcaa       I MX:T(0,0,1/2) MY:T(1/2,0,0)
 so  8  54   Pbcb       I MX:T(0,1/2,0) MY:T(0,0,1/2)
 so  8  54   Pbab       I MX:T(1/2,1/2,0) MY:T(1/2,0,0)
 so  8  55   Pbam       I MX:T(1/2,1/2,0) MY:T(1/2,1/2,0)
 so  8  55   Pmcb       I MX MY:T(0,1/2,1/2)
 so  8  55   Pcma       I MX:T(1/2,0,1/2) MY
 so  8  56   Pccn       I MX:T(1/2,0,1/2) MY:T(0,1/2,1/2)
 so  8  56   Pnaa       I MX:T(0,1/2,1/2) MY:T(1/2,1/2,0)
 so  8  56   Pbnb       I MX:T(1/2,1/2,0) MY:T(1/2,0,1/2)
 so  8  57   Pbcm       I MX:T(0,1/2,0) MY:T(0,1/2,1/2)
 so  8  57   Pcam       I MX:T(1/2,0,1/2) MY:T(1/2,0,0)
 so  8  57   Pmca       I MX:T(1/2,0,0) MY:T(0,0,1/2)
 so  8  57   Pmab       I MX:T(1/2,0,0) MY:T(1/2,1/2,0)
 so  8  57   Pbma       I MX:T(1/2,1/2,0) MY:T(0,1/2,0)
 so  8  57   Pcmb       I MX:T(0,0,1/2) MY:T(0,1/2,0)
 so  8  58   Pnnm       I MX:T(1/2,1/2,1/2) MY:T(1/2,1/2,1/2)
 so  8  58   Pmnn       I MX MY:T(1/2,1/2,1/2)
 so  8  58   Pnmn       I MX:T(1/2,1/2,1/2) MY
 so  8  59 1 Pmmn       I:T(1/2,1/2,0) MX MY
 so  8  59 2 Pmmn       I MX:T(1/2,0,0) MY:T(0,1/2,0)
 so  8  59 1 Pmnm       I:T(1/2,0,1/2) MX MY:T(1/2,0,1/2)
 so  8  59 2 Pmnm       I MX:T(1/2,0,0) MY:T(1/2,0,1/2)
 so  8  59 1 Pnmm       I:T(0,1/2,1/2) MX:T(0,1/2,1/2) MY
 so  8  59 2 Pnmm       I MX:T(0,1/2,1/2) MY:T(0,1/2,0)
 so  8  60   Pbcn       I MX:T(1/2,1/2,0) MY:T(0,0,1/2)
 so  8  60   Pcan       I MX:T(0,0,1/2) MY:T(1/2,1/2,0)
 so  8  60   Pnca       I MX:T(1/2,1/2,1/2) MY:T(0,1/2,1/2)
 so  8  60   Pnab       I MX:T(1/2,1/2,1/2) MY:T(1/2,0,0)
 so  8  60   Pbna       I MX:T(0,1/2,0) MY:T(1/2,1/2,1/2)
 so  8  60   Pcnb       I MX:T(1/2,0,1/2) MY:T(1/2,1/2,1/2)
 so  8  61   Pbca       I MX:T(1/2,1/2,0) MY:T(0,1/2,1/2)
 so  8  61   Pcab       I MX:T(1/2,0,1/2) MY:T(1/2,1/2,0)
 so  8  62   Pnma       I MX:T(1/2,1/2,1/2) MY:T(0,1/2,0)
 so  8  62   Pmnb       I MX:T(1/2,0,0) MY:T(1/2,1/2,1/2)
 so  8  62   Pbnm       I MX:T(1/2,1/2,0) MY:T(1/2,1/2,1/2)
 so  8  62   Pcmn       I MX:T(1/2,0,1/2) MY:T(0,1/2,0)
 so  8  62   Pmcn       I MX:T(1/2,0,0) MY:T(0,1/2,1/2)
 so  8  62   Pnam       I MX:T(1/2,1/2,1/2) MY:T(1/2,1/2,0)
sco  8  63   Cmcm       I MX MY:T(0,0,1/2)
sco  8  63   Ccmm       I MX:T(0,0,1/2) MY
sco  8  63   Amma       I MX:T(1/2,0,0) MY
sco  8  63   Amam       I MX:T(1/2,0,0) MY:T(1/2,0,0)
sco  8  63   Bbmm       I MX:T(0,1/2,0) MY:T(0,1/2,0)
sco  8  63   Bmmb       I MX MY:T(0,1/2,0)
sco  8  64   Cmca       I MX MY:T(1/2,0,1/2)
sco  8  64   Ccmb       I MX:T(1/2,0,1/2) MY
sco  8  64   Abma       I MX:T(1/2,1/2,0) MY
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sco  8  64   Acam       I MX:T(1/2,1/2,0) MY:T(1/2,1/2,0)
sco  8  64   Bbcm       I MX:T(1/2,1/2,0) MY:T(1/2,1/2,0)
sco  8  64   Bmab       I MX MY:T(1/2,1/2,0)
sco  8  65   Cmmm       I MX MY
sco  8  65   Ammm       I MX MY
sco  8  65   Bmmm       I MX MY
sco  8  66   Cccm       I MX:T(0,0,1/2) MY:T(0,0,1/2)
sco  8  66   Amaa       I MX MY:T(1/2,0,0)
sco  8  66   Bbmb       I MX:T(0,1/2,0) MY
sco  8  67   Cmma       I MX MY:T(1/2,0,0)
sco  8  67   Cmmb       I MX:T(1/2,0,0) MY
sco  8  67   Abmm       I MX:T(0,1/2,0) MY
sco  8  67   Acmm       I MX:T(0,1/2,0) MY:T(0,1/2,0)
sco  8  67   Bmcm       I MX:T(1/2,0,0) MY:T(1/2,0,0)
sco  8  67   Bmam       I MX MY:T(1/2,0,0)
sco  8  68 1 Ccca       I:T(1/2,0,1/2) MX:T(1/2,0,1/2) MY:T(1/2,0,1/2)
sco  8  68 2 Ccca       I MX:T(1/2,0,1/2) MY:T(0,0,1/2)
sco  8  68 1 Cccb       I:T(1/2,0,1/2) MX:T(1/2,0,1/2) MY:T(1/2,0,1/2)
sco  8  68 2 Cccb       I MX:T(0,0,1/2) MY:T(1/2,0,1/2)
sco  8  68 1 Abaa       I:T(1/2,1/2,0) MX:T(1/2,1/2,0) MY:T(1/2,1/2,0)
sco  8  68 2 Abaa       I MX:T(0,1/2,0) MY:T(1/2,1/2,0)
sco  8  68 1 Acaa       I:T(1/2,1/2,0) MX:T(1/2,1/2,0) MY:T(1/2,1/2,0)
sco  8  68 2 Acaa       I MX:T(0,1/2,0) MY:T(1/2,0,0)
sco  8  68 1 Bbcb       I:T(1/2,1/2,0) MX:T(1/2,1/2,0) MY:T(1/2,1/2,0)
sco  8  68 2 Bbcb       I MX:T(0,1/2,0) MY:T(1/2,0,0)
sco  8  68 1 Bbab       I:T(1/2,1/2,0) MX:T(1/2,1/2,0) MY:T(1/2,1/2,0)
sco  8  68 2 Bbab       I MX:T(1/2,1/2,0) MY:T(1/2,0,0)
fco  8  69   Fmmm       I MX MY
fco  8  70 1 Fddd       I:T(1/4,1/4,1/4) MX:T(1/4,1/4,1/4) MY:T(1/4,1/4,1/4)
fco  8  70 2 Fddd       I MX:T(0,1/4,1/4) MY:T(1/4,0,1/4)
bco  8  71   Immm       I MX MY
bco  8  72   Ibam       I MX:T(0,0,1/2) MY:T(0,0,1/2)
bco  8  72   Imcb       I MX MY:T(1/2,0,0)
bco  8  72   Icma       I MX:T(0,1/2,0) MY
bco  8  73   Ibca       I MX:T(0,0,1/2) MY:T(1/2,0,0)
bco  8  73   Icab       I MX:T(0,1/2,0) MY:T(0,0,1/2)
bco  8  74   Imma       I MX MY:T(0,1/2,0)
bco  8  74   Immb       I MX:T(1/2,0,0) MY
bco  8  74   Ibmm       I MX:T(0,0,1/2) MY
bco  8  74   Icmm       I MX:T(0,1/2,0) MY:T(0,1/2,0)
bco  8  74   Imcm       I MX:T(1/2,0,0) MY:T(1/2,0,0)
bco  8  74   Imam       I MX MY:T(0,0,1/2)
 st  9  75   P4         R4Z
 st  9  76   P4_1       R4Z:T(0,0,1/4)
 st  9  77   P4_2       R4Z:T(0,0,1/2)
 st  9  78   P4_3       R4Z:T(0,0,-1/4)
 ct  9  79   I4         R4Z
 ct  9  80   I4_1       R4Z:T(1/2,0,-1/4)
 st 10  81   P-4        S4Z
 ct 10  82   I-4        S4Z
 st 11  83   P4/m       I R4Z
 st 11  84   P4_2/m     I R4Z:T(0,0,1/2)
 st 11  85 1 P4/n       I:T(1/2,1/2,0) R4Z:T(1/2,1/2,0)
 st 11  85 2 P4/n       I R4Z:T(1/2,0,0)
```

```
st 11  86 1 P4_2/n     I:T(1/2,1/2,1/2) R4Z:T(1/2,1/2,1/2)
st 11  86 2 P4_2/n     I R4Z:T(0,1/2,1/2)
ct 11  87   I4/m       I R4Z
ct 11  88 1 I4_1/a     I:T(1/2,0,-1/4) R4Z:T(1/2,0,-1/4)
ct 11  88 2 I4_1/a     I R4Z:T(-1/4,1/4,1/4)
st 12  89   P422       R4Z R2X
st 12  90   P42_12     R4Z:T(1/2,1/2,0) R2X:T(1/2,1/2,0)
st 12  91   P4_122     R4Z:T(0,0,1/4) R2X:T(0,0,1/2)
st 12  92   P4_12_12   R4Z:T(1/2,1/2,1/4) R2X:T(1/2,1/2,-1/4)
st 12  93   P4_222     R4Z:T(0,0,1/2) R2X
st 12  94   P4_22_12   R4Z:T(1/2,1/2,1/2) R2X:T(1/2,1/2,1/2)
st 12  95   P4_322     R4Z:T(0,0,-1/4) R2X:T(0,0,1/2)
st 12  96   P4_32_12   R4Z:T(1/2,1/2,-1/4) R2X:T(1/2,1/2,1/4)
ct 12  97   I422       R4Z R2X
ct 12  98   I4_122     R4Z:T(1/2,0,-1/4) R2X:T(1/2,0,-1/4)
st 13  99   P4mm       R4Z MX
st 13 100   P4bm       R4Z MX:T(1/2,1/2,0)
st 13 101   P4_2cm     R4Z:T(0,0,1/2) MX:T(0,0,1/2)
st 13 102   P4_2nm     R4Z:T(1/2,1/2,1/2) MX:T(1/2,1/2,1/2)
st 13 103   P4cc       R4Z MX:T(0,0,1/2)
st 13 104   P4nc       R4Z MX:T(1/2,1/2,1/2)
st 13 105   P4_2mc     R4Z:T(0,0,1/2) MX
st 13 106   P4_2bc     R4Z:T(0,0,1/2) MX:T(1/2,1/2,0)
ct 13 107   I4mm       R4Z MX
ct 13 108   I4cm       R4Z MX:T(0,0,1/2)
ct 13 109   I4_1md     R4Z:T(1/2,0,-1/4) MX
ct 13 110   I4_1cd     R4Z:T(1/2,0,-1/4) MX:T(0,0,1/2)
st 14 111   P-42m      S4Z R2X
st 14 112   P-42c      S4Z R2X:T(0,0,1/2)
st 14 113   P-42_1m    S4Z R2X:T(1/2,1/2,0)
st 14 114   P-42_1c    S4Z R2X:T(1/2,1/2,1/2)
st 14 115   P-4m2      S4Z MX
st 14 116   P-4c2      S4Z MX:T(0,0,1/2)
st 14 117   P-4b2      S4Z MX:T(1/2,1/2,0)
st 14 118   P-4n2      S4Z MX:T(1/2,1/2,1/2)
ct 14 119   I-4m2      S4Z MX
ct 14 120   I-4c2      S4Z MX:T(0,0,1/2)
ct 14 121   I-42m      S4Z R2X
ct 14 122   I-42d      S4Z R2X:T(1/2,0,-1/4)
st 15 123   P4/mmm     I R4Z MX
st 15 124   P4/mcc     I R4Z MX:T(0,0,1/2)
st 15 125 1 P4/nbm     I:T(1/2,1/2,0) R4Z MX:T(1/2,1/2,0)
st 15 125 2 P4/nbm     I R4Z:T(1/2,0,0) MX:T(0,1/2,0)
st 15 126 1 P4/nnc     I:T(1/2,1/2,1/2) R4Z MX:T(1/2,1/2,1/2)
st 15 126 2 P4/nnc     I R4Z:T(1/2,0,0) MX:T(0,1/2,1/2)
st 15 127   P4/mbm     I R4Z MX:T(1/2,1/2,0)
st 15 128   P4/mnc     I R4Z MX:T(1/2,1/2,1/2)
st 15 129 1 P4/nmm     I:T(1/2,1/2,0) R4Z:T(1/2,1/2,0) MX
st 15 129 2 P4/nmm     I R4Z:T(1/2,0,0) MX:T(1/2,0,0)
st 15 130 1 P4/ncc     I:T(1/2,1/2,0) R4Z:T(1/2,1/2,0) MX:T(0,0,1/2)
st 15 130 2 P4/ncc     I R4Z:T(1/2,0,0) MX:T(1/2,0,1/2)
st 15 131   P4_2/mmc   I R4Z:T(0,0,1/2) MX
st 15 132   P4_2/mcm   I R4Z:T(0,0,1/2) MX:T(0,0,1/2)
st 15 133 1 P4_2/nbc   I:T(1/2,1/2,1/2) R4Z:T(1/2,1/2,1/2) MX:T(1/2,1/2,0)
```

```
 st 15 133 2 P4_2/nbc   I R4Z:T(1/2,0,1/2) MX:T(0,1/2,0)
 st 15 134 1 P4_2/nnm   I:T(1/2,1/2,1/2) R4Z:T(1/2,1/2,1/2) MX:T(1/2,1/2,1/2)
 st 15 134 2 P4_2/nnm   I R4Z:T(1/2,0,1/2) MX:T(0,1/2,1/2)
 st 15 135   P4_2/mbc   I R4Z:T(0,0,1/2) MX:T(1/2,1/2,0)
 st 15 136   P4_2/mnm   I R4Z:T(1/2,1/2,1/2) MX:T(1/2,1/2,1/2)
 st 15 137 1 P4_2/nmc   I:T(1/2,1/2,1/2) R4Z:T(1/2,1/2,1/2) MX
 st 15 137 2 P4_2/nmc   I R4Z:T(1/2,0,1/2) MX:T(1/2,0,0)
 st 15 138 1 P4_2/ncm   I:T(1/2,1/2,1/2) R4Z:T(1/2,1/2,1/2) MX:T(0,0,1/2)
 st 15 138 2 P4_2/ncm   I R4Z:T(1/2,0,1/2) MX:T(1/2,0,1/2)
 ct 15 139   I4/mmm     I R4Z MX
 ct 15 140   I4/mcm     I R4Z MX:T(0,0,1/2)
 ct 15 141 1 I4_1/amd   I:T(1/2,0,-1/4) R4Z:T(1/2,0,-1/4) MX
 ct 15 141 2 I4_1/amd   I R4Z:T(1/4,-1/4,1/4) MX
 ct 15 142 1 I4_1/acd   I:T(1/2,0,-1/4) R4Z:T(1/2,0,-1/4) MX:T(0,0,1/2)
 ct 15 142 2 I4_1/acd   I R4Z:T(1/4,-1/4,1/4) MX:T(0,0,1/2)
hex 16 143   P3         R3Z
hex 16 143   P311       R3Z
hex 16 144   P3_1       R3Z:T(0,0,1/3)
hex 16 144   P3_111     R3Z:T(0,0,1/3)
hex 16 145   P3_2       R3Z:T(0,0,-1/3)
hex 16 145   P3_211     R3Z:T(0,0,-1/3)
rho 16 146   R3         R3Z
rho 16 146   P31        R3Z
hex 17 147   P-3        I R3Z
hex 17 147   P-311      I R3Z
rho 17 148   R-3        I R3Z
rho 17 148   P-31       I R3Z
hex 18 149   P312       R3Z R2X
hex 18 150   P321       R3Z R2Y
hex 18 151   P3_112     R3Z:T(0,0,1/3) R2X
hex 18 152   P3_121     R3Z:T(0,0,1/3) R2Y:T(0,0,1/3)
hex 18 153   P3_212     R3Z:T(0,0,-1/3) R2X
hex 18 154   P3_221     R3Z:T(0,0,-1/3) R2Y:T(0,0,-1/3)
rho 18 155   R32        R3Z R2Y
rho 18 155   P32        R3Z R2Y
hex 19 156   P3m1       R3Z MY
hex 19 157   P31m       R3Z MX
hex 19 158   P3c1       R3Z MY:T(0,0,1/2)
hex 19 159   P31c       R3Z MX:T(0,0,1/2)
rho 19 160   R3m        R3Z MY
rho 19 160   P3m        R3Z MY
rho 19 161   R3c        R3Z MY:T(0,0,1/2)
rho 19 161   P3c        R3Z MY:T(1/2,1/2,1/2)
hex 20 162   P-31m      I R3Z MX
hex 20 163   P-31c      I R3Z MX:T(0,0,1/2)
hex 20 164   P-3m1      I R3Z MY
hex 20 165   P-3c1      I R3Z MY:T(0,0,1/2)
rho 20 166   R-3m       I R3Z MY
rho 20 166   P-3m       I R3Z MY
rho 20 167   R-3c       I R3Z MY:T(0,0,1/2)
rho 20 167   P-3c       I R3Z MY:T(1/2,1/2,1/2)
hex 21 168   P6         R6Z
hex 21 169   P6_1       R6Z:T(0,0,1/6)
hex 21 170   P6_5       R6Z:T(0,0,-1/6)
```

```
hex 21 171   P6_2       R6Z:T(0,0,1/3)
hex 21 172   P6_4       R6Z:T(0,0,-1/3)
hex 21 173   P6_3       R6Z:T(0,0,1/2)
hex 22 174   P-6        S6Z
hex 23 175   P6/m       I R6Z
hex 23 176   P6_3/m     I R6Z:T(0,0,1/2)
hex 24 177   P622       R6Z R2X
hex 24 178   P6_122     R6Z:T(0,0,1/6) R2X:T(0,0,1/6)
hex 24 179   P6_522     R6Z:T(0,0,-1/6) R2X:T(0,0,-1/6)
hex 24 180   P6_222     R6Z:T(0,0,1/3) R2X:T(0,0,1/3)
hex 24 181   P6_422     R6Z:T(0,0,-1/3) R2X:T(0,0,-1/3)
hex 24 182   P6_322     R6Z:T(0,0,1/2) R2X:T(0,0,1/2)
hex 25 183   P6mm       R6Z MX
hex 25 184   P6cc       R6Z MX:T(0,0,1/2)
hex 25 185   P6_3cm     R6Z:T(0,0,1/2) MX
hex 25 186   P6_3mc     R6Z:T(0,0,1/2) MX:T(0,0,1/2)
hex 26 187   P-6m2      S6Z MY
hex 26 188   P-6c2      S6Z:T(0,0,1/2) MY:T(0,0,1/2)
hex 26 189   P-62m      S6Z MX
hex 26 190   P-62c      S6Z:T(0,0,1/2) MX:T(0,0,1/2)
hex 27 191   P6/mmm     I R6Z MX
hex 27 192   P6/mcc     I R6Z MX:T(0,0,1/2)
hex 27 193   P6_3/mcm   I R6Z:T(0,0,1/2) MX
hex 27 194   P6_3/mmc   I R6Z:T(0,0,1/2) MX:T(0,0,1/2)
 sc 28 195   P23        R3D R2X
fcc 28 196   F23        R3D R2X
bcc 28 197   I23        R3D R2X
 sc 28 198   P2_13      R3D R2X:T(1/2,1/2,0)
bcc 28 199   I2_13      R3D R2X:T(0,0,1/2)
 sc 29 200   Pm-3       I R3D MX
 sc 29 201 1 Pn-3       I:T(1/2,1/2,1/2) R3D MX:T(1/2,1/2,1/2)
 sc 29 201 2 Pn-3       I R3D MX:T(0,1/2,1/2)
fcc 29 202   Fm-3       I R3D MX
fcc 29 203 1 Fd-3       I:T(1/4,1/4,1/4) R3D MX:T(1/4,1/4,1/4)
fcc 29 203 2 Fd-3       I R3D MX:T(0,1/4,1/4)
bcc 29 204   Im-3       I R3D MX
 sc 29 205   Pa-3       I R3D MX:T(1/2,1/2,0)
bcc 29 206   Ia-3       I R3D MX:T(0,0,1/2)
 sc 30 207   P432       R4X R3D
 sc 30 208   P4_232     R4X:T(1/2,1/2,1/2) R3D
fcc 30 209   F432       R4X R3D
fcc 30 210   F4_132     R4X:T(1/4,1/4,1/4) R3D
bcc 30 211   I432       R4X R3D
 sc 30 212   P4_332     R4X:T(-1/4,-1/4,1/4) R3D
 sc 30 213   P4_132     R4X:T(1/4,1/4,-1/4) R3D
bcc 30 214   I4_132     R4X:T(1/4,1/4,-1/4) R3D
 sc 31 215   P-43m      S4X R3D
fcc 31 216   F-43m      S4X R3D
bcc 31 217   I-43m      S4X R3D
 sc 31 218   P-43n      S4X:T(1/2,1/2,1/2) R3D
fcc 31 219   F-43c      S4X:T(1/2,1/2,1/2) R3D
bcc 31 220   I-43d      S4X:T(1/4,1/4,-1/4) R3D
 sc 32 221   Pm-3m      I R4X R3D
 sc 32 222 1 Pn-3n      I:T(1/2,1/2,1/2) R4X R3D
```

```
  sc 32 222 2 Pn-3n      I R4X:T(0,1/2,0) R3D
  sc 32 223   Pm-3n      I R4X:T(1/2,1/2,1/2) R3D
  sc 32 224 1 Pn-3m      I:T(1/2,1/2,1/2) R4X:T(1/2,1/2,1/2) R3D
  sc 32 224 2 Pn-3m      I R4X:T(1/2,0,1/2) R3D
 fcc 32 225   Fm-3m      I R4X R3D
 fcc 32 226   Fm-3c      I R4X:T(1/2,1/2,1/2) R3D
 fcc 32 227 1 Fd-3m      I:T(1/4,1/4,1/4) R4X:T(1/4,1/4,1/4) R3D
 fcc 32 227 2 Fd-3m      I R4X:T(1/4,0,1/4) R3D
 fcc 32 228 1 Fd-3c      I:T(-1/4,-1/4,-1/4) R4X:T(1/4,1/4,1/4) R3D
 fcc 32 228 2 Fd-3c      I R4X:T(1/4,1/2,1/4) R3D
 bcc 32 229   Im-3m      I R4X R3D
 bcc 32 230   Ia-3d      I R4X:T(1/4,1/4,-1/4) R3D
```

```
 Bravais lattices:
   tri  triclinic                       sm  simple monoclinic
    cm  centered monoclinic             so  simple orthorhombic
   sco  base-centered orthorhombic     bco  body-centered orthorhombic
   fco  face-centered orthorhombic      st  simple tetragonal
    ct  centered tetragonal            rho  rhombohedral
   hex  hexagonal                       sc  simple cubic
   bcc  body-centered cubic            fcc  face-centered cubic
```

```
 Point group symbols:
  # Symb    # Symb    # Symb    # Symb    # Symb    # Symb    # Symb    # Symb
  1 1       2 -1      3 2       4 m       5 2/m     6 222     7 mm2     8 mmm
  9 4      10 -4     11 4/m    12 422    13 4mm    14 -42m   15 4/mmm  16 3
 17 -3     18 32     19 3m     20 -3m    21 6      22 -6     23 6/m    24 622
 25 6mm    26 -62m   27 6/mmm  28 23     29 m-3    30 432    31 -432   32 m-3m
```

3.7 Data files

Input data as well as data created by the ASW programs are spread over a large number of files. Yet, exchange of the user with the programs is limited essentially to a single file, i.e. the CTRL file. All other files serve the purpose of holding specific information about the distribution or are meant for information exchange between different programs. Neither of these latter files has to be changed by the user. Anyway, in the following list a short description is given for all files.

3.7.1 The atomic files

Like most other files the atomic files are created automatically by the main program mnscf.run according to the entries ATOM= in categories CLASS and SITE of the CTRL file.

Each atomic file contains all information about the atom at hand. Similar to the CTRL file it falls in eight categories named GEN, LDMT, ESJH, MOPT, VMTA, VLOC, RLOC, and CORE. They comprise the following data.

GEN	Atomic number, angular momenta, valence state configuration, indicators for spin-polarized and relativistic calculations, information about the intraatomic radial mesh, core state orbitals, net atomic charge, Madelung potential, muffin-tin zero, and total energy contributions.
LDMT	Local density matrices as arising from the band calculation.
ESJH	Hankel and Bessel energies and integrals for use in the intraatomic integrals entering the secular matrix.
MOPT	Intraatomic optical matrix elements.
VMTA	Spherical symmetric intraatomic single-particle potential.
VLOC	Intraatomic full potential.
RLOC	Intraatomic full valence electron density.
CORE	Core state energies and spherical symmetric intraatomic core electron charge density.

An example atomic file looks like.

```
GEN:  CU                                                  written by ASW-2.6
 Z= 29  LMXL=2  LMXI=3  CONF= 4 4 3 4  NSPIN=1  REL=T
 RMAX=  2.669448    NR= 541  AR=  0.20000000D-01  BR=  0.544565163250D-04
  RMT=  2.367581  NRMT= 535
 NCORE= 5  LCORE= 0 0 0 1 1  QCORE= 18
 RHOV0=  0.1093061994D+03
 NKAP=1  EKAP=   -0.015000
  VMTZ= -0.101593247946D+01
 VRMAX= -0.101593247946D+01
  EVBM=  0.114473077936D+01  ECBM=  0.515675388697D+00
 EFMIN=  0.200000000000D+00 EFMAX=  0.120000000000D+01
 EFERM=  0.681989411882D+00
 ETFAT= -0.330455057198D+04 ETVAR= -0.330486846445D+04
LDMT:  CU
 WLLCC=  0.6864836706D+00  0.1523417630D-23  0.2757268709D-24 -0.2767936098D-25
         0.1449338654D-18 -0.8122190416D-18  0.5788441776D-18 -0.1416149700D-18
         0.1012977311D-17  0.0000000000D+00  0.0000000000D+00  0.0000000000D+00
         ...
         ...
         ...
 WLLCA=  0.2702275600D-01  0.4885379417D-26  0.0000000000D+00 -0.1954151767D-25
         0.4379444365D-18 -0.1298097441D-17 -0.5963111949D-18 -0.5638172905D-18
```

```
         0.2394279798D-18  0.0000000000D+00  0.0000000000D+00  0.0000000000D+00
         ...
         ...
         ...
 WLLAA=  0.2768160943D-01 -0.7908889916D-25 -0.2171968297D-25  0.1228003504D-25
         0.7497342241D-19 -0.1895172744D-18  0.7678466682D-19 -0.1312662766D-18
         0.1812971300D-18  0.3937420436D-26 -0.1003773840D-24  0.4368433128D-25
         ...
         ...
         ...
ESJH:  CU
 N L S          EHAN              EBES              SHAN              SBES
 4 0 1  0.4443301305D+00 -0.6969317074D-01  0.6484687281D+00  0.5921039036D+01
 4 1 1  0.1332828649D+01 -0.9136422052D-01  0.1704680720D+00  0.3102146828D+01
 3 2 1  0.4790057314D+00 -0.3618341076D+00  0.3531087671D+01  0.8458719099D+00
 4 3 1  0.4174489094D+01 -0.1191803276D+00  0.1012729572D+01  0.7191640791D-01
   VHH=  0.9341213354D-02 -0.7375579101D-10 -0.7375579354D-10 -0.1391813866D-07
        -0.3886705205D-08 -0.3886704598D-08 -0.3886709952D-08 -0.3886705255D-08
        -0.3886702972D-08 -0.3461399420D-07 -0.3461399434D-07 -0.3461399448D-07
         ...
         ...
         ...
   VHJ=  0.3310617248D-01 -0.2002889994D-09 -0.2002890054D-09 -0.4644303321D-07
        -0.1026790881D-07 -0.1026790637D-07 -0.1026792824D-07 -0.1026790900D-07
        -0.1026790013D-07 -0.9630564904D-07 -0.9630564952D-07 -0.9630565000D-07
         ...
         ...
         ...
   VJJ=  0.1167285622D+00 -0.6451192721D-09 -0.6451192782D-09 -0.2364898375D-06
        -0.6440567415D-08 -0.6440559472D-08 -0.6440628425D-08 -0.6440567963D-08
        -0.6440541109D-08 -0.1431478215D-07 -0.1431478233D-07 -0.1431478252D-07
         ...
         ...
         ...
MOPT:  CU
   MHH=  0.0000000000D+00 -0.6507614309D-01  0.0000000000D+00  0.0000000000D+00
         0.3235736296D+00  0.0000000000D+00  0.3937543036D+00  0.0000000000D+00
         0.0000000000D+00 -0.2454696177D+00  0.0000000000D+00 -0.2979002690D+01
         0.0000000000D+00  0.0000000000D+00  0.3301748000D+01  0.0000000000D+00
   MHJ=  0.0000000000D+00  0.9557802382D-01  0.0000000000D+00  0.0000000000D+00
         0.2135106097D+01  0.0000000000D+00  0.1862979714D+01  0.0000000000D+00
         0.0000000000D+00  0.5727075033D+00  0.0000000000D+00 -0.5419268947D+00
         0.0000000000D+00  0.0000000000D+00  0.6053496286D+00  0.0000000000D+00
   MJH=  0.0000000000D+00 -0.4038246046D+00  0.0000000000D+00  0.0000000000D+00
         0.8784526829D+00  0.0000000000D+00 -0.1146460821D+00  0.0000000000D+00
         0.0000000000D+00 -0.8698565251D+00  0.0000000000D+00 -0.4041095516D+00
         0.0000000000D+00  0.0000000000D+00  0.1538889316D+01  0.0000000000D+00
   MJJ=  0.0000000000D+00  0.1451750170D+00  0.0000000000D+00  0.0000000000D+00
         0.6378431349D+01  0.0000000000D+00  0.4516010729D+00  0.0000000000D+00
         0.0000000000D+00  0.2616322297D+01  0.0000000000D+00 -0.6231920666D-01
         0.0000000000D+00  0.0000000000D+00  0.6839972983D+00  0.0000000000D+00
VMTA:  CU
 NSPIN=1  RMAX=  2.669448  NR= 541  AR=  0.02000000  BR=  0.544565163250D-04
  2.157039581415D+02  2.163036514691D+02  2.169282902168D+02  2.172948467082D+02
```

```
2.175555310144D+02  2.177597897297D+02  2.179281747599D+02  2.180718055997D+02
2.181973599295D+02  2.183091431584D+02  2.184100915493D+02  2.185022968519D+02
...
...
...
2.540183818359D+01  2.492023067790D+01  2.444560720037D+01  2.397778672220D+01
2.351641175972D+01  2.306106447621D+01  2.261134947117D+01  2.216689282712D+01
2.172734163502D+01
```

A rather complex file check routine is invoked at the beginning of most of the main programs. During this check data from each atomic file is read in and compared to the information gained from previous reading of the CTRL file. Whenever inconsistencies arise the program will issue a message and respond adequately. For instance, if the lattice constant is changed in the CTRL file, the program will identify the inconsistency of the sphere radii. In the following, the radii will be automatically adjusted and the program enforces an intraatomic restart calculation in order to update the intraatomic integrals for the secular matrix. In contrast, if the program detects converged files but the CTRL files would require a start from scratch by the setting START=REN the program stops in order not to overwrite the atomic files. Finally, if a spin-polarized calculation finds converged spin-degenerate files, starting values for the intraatomic magnetic moments are imposed and the program enters a restart calculation. Please see Sec. 2.3 and Chap. 4 for more detailed information.

3.7.2 FREE

The information about the overlapping free atom charge densities and potentials as created by program `mnfre.run` go into this file. It is a formatted file, hence, it is written in ASCII.

3.7.3 STRU

This formatted file is written by all main programs. It contains the positions and covalent radii of all atoms for later plotting with RasMol. All atoms within the plot region specified in the CTRL file are included. However, in case this was not given or not properly specified the unit cell is used instead.

3.7.4 STRX

This formatted file is written by all main programs. It contains the positions of all atoms. The file is written in XCrysDen's xsf format and, hence, can be directly used by XCrysDen. Just invoke „`xcrysden –xsf` STRX“ or use the shell script `plxcr.x`.

3.7.5 BNDE

The formatted file BNDE contains the band structure $E(\mathbf{k})$ as calculated as calculated by program `mnbnd.run`.

3.7.6 BNDV

If required according to token ORBWGT=T the eigenvectors are written to the unformatted file BNDV by program `mnbnd.run`.

3.7.7 DOS

The unformatted file DOS is written by program `mnscf.run` if token SAVDOS=T is set. It contains the partial DOS for later plotting.

3.7.8 COOP

For SAVCOOP=T and the respective settings COORB= program `mnscf.run` creates an unformatted file COOP, which holds all information about the partial crystal orbital overlap populations (COOP), the crystal orbital Hamiltonian population (COHP) or the covalence energy (E_{cov}).

3.7.9 OPT

The unformatted file OPT is written by program `mnscf.run` if token SAVOPT=T is set. It contains the different contributions to the optical conductivity for later plotting.

3.7.10 TRAP

The unformatted file TRAP is written by program mnscf.run if token SAVTRAP=T is set. It contains the transport distribution and the related so-called Hall-distribution for later plotting of the transport properties.

3.7.11 FERM

The formatted file FERM is written by program mnscf.run if the system is a metal and if token SAVFERM=T is set. It holds information about all bands straddling the Fermi energy, which are stored on a regular mesh. The file is in XCrysDen's bxsf format. Once the FERM file has been generated the Fermi surface can be plotted by the command „xcrysden –bxsf FERM“ or use of the shell script plfrm.x.

3.7.12 RHO

This formatted file contains the electronic density (core and valence), their negative Laplacians, and the effective potential. Depending on the dimensionality of the plot region as specified in the CTRL file these data can be plotted using Gnuplot or XCrysDen.

3.7.13 Output files

Naming of the output files is completely free. However, if you are using the shell scripts mn***.x output is written to file *out****, where the last three letters indicate the type of the program. In contrast, shell script mnall.x writes output files *outlstnn*, where by default *nn* ranges from 6 to 18 according to the **k**-space grid.

3.8 Temporary files

Input data as well as data created by the ASW programs are spread over a large number of files. Yet, exchange of the user with the programs is limited essentially to a single file, i.e. the CTRL file. All other files serve the purpose of holding specific information about the distribution or are meant for information exchange between different programs. Neither of these latter files has to be changed by the user. Anyway, in the following list a short description is given for all files.

3.8.1 EIGE, EIGV, EIGVC, EIGVO

In case the linear tetrahedron method is chosen for the Brillouin zone integrations these unformatted files are used to temporarily store the eigenvalues and eigenvectors resulting from the band calculations. Once the Brillouin zone integration is finished these files are automatically deleted.

3.8.2 MIX

This file holds all information about the previous and the present band iterations to be used during the self-consistency cycle. It is automatically created by program mnscf.run and, after convergence has been achieved, it is deleted. However, in case you stop the program and restart after a change of orbitals as described in Sec. 2.3.2, this file must be deleted. Note that MIX is an unformatted file.

3.9 Plot files

3.9.1 PLI*

The input to all the plot routines is echoed to the so-called plot information files, which are named PLIx, where x depends on the plot routine used. The following naming assignments exist.

- plstr.run ↔ PLIS
- plbnd.run ↔ PLIB
- pldos.run ↔ PLID
- plcop.run ↔ PLIC
- plopt.run ↔ PLIO
- pltrp.run ↔ PLIT
- plrho.run ↔ PLIR
- plblk.run ↔ PLIK
- plphn.run ↔ PLIP

These files are formatted files and can be edited, all entries are self-explaining. As an example, we give the file PLIB as generated by the plot routine for the band structure.

```
 1                          / Terminal type
 1                          / Output device
E                           / Portrait (P), landscape (L) or EPS (E, default)?
Cu fcc
T                           / Rydberg (F) or eV (T, default)?
F                           / E-MTZ (0) or E-EF (F, default)?
```

```
F                            / Lines (T) (default F)?
F                            / Orbital character (default F)?
      -10.000000
        6.000000             / Emin, Emax
```

The appealing feature of these plot information files is that they can be used as input to a subsequent run of the same plot routine. To be specific, the command „plbnd.run < PLIB“ or, in case you prefer the shell scripts, „plbnd.x PLIB“ (there is no „<“ in this case) will generate the same plot as before without the need to respond to the prompts of the plot routine directly. Hence, if you want to display the band structure, e.g. in a different energy window, you just have to change the corresponding entry in the PLIB file and run the plot routine again. This is extremely helpful especially for the plot routines for the densities of states, the crystal orbital overlap population, the optical or the transport properties since in these cases several curves can be included in one plot and the input can be much more complex.

However, two points should be noted. First, since the plot routines overwrite the plot information files, i.e. the file PLIB in the above example, you should rename this file in order to have it conserved during the run. Second, while editing a plot information file you should keep in mind that any change may force the plot routine to request other or more information from the user. For example, if you use the routine plrho.run for plotting the electron density rather than the potential it will ask additionally for the type of electron density (valence, core, or both).

3.9.2 ROTS

This formatted file can be used to store a character string characterizing a rotation to be used in plots of the weighted band structure or the partial DOS. The rotation is given in the same notation as the generators specified by token SYMOPS= of the CTRL file. See Chap. 4 for more details and examples.

3.9.3 LaTeX files

The LaTeX files bnd.tex, dos.tex, coop.tex, opt.tex, and trap.tex are created by the plot programs plbnd.run, pldos.run, plcop.run, plopt.run, and pltrp.run, respectively, if LaTeX output has been specified in the dialog.

3.9.4 Postscript files

The postscript files bnd.ps, dos.ps, coop.ps, opt.ps, trap.ps, and rho.ps are usually created by the plot programs `plbnd.run`, `pldos.run`, `plcop.run`, `plopt.run`, `pltrp.run`, and `plrho.run`, respectively, if Gnuplot postscript output has been specified in the dialog.

Chapter 4

The main input file: CTRL

In this chapter we describe the structure and content of the CTRL file, which is the main input file for the ASW package and, hence, the only interface between the user and the main programs. Besides information on the crystal structure and the atoms making the crystal it contains also more technical parameters controlling the execution. The CTRL file is fully free format, i.e. users do not have to obey any format specification. Yet, the file must not contain any tabulators (TABs).

It is important to notice that the CTRL file is exclusively used as an *input* file to the programs. None of the programs writes to this file at all. Only some shell scripts, like "upctr", are allowed to manipulate the CTRL file (see below). As a consequence, the CTRL file will never be destroyed even if you interrupt the program during execution or if your computer system crashes. Whenever the program creates new data as e.g. empty sphere positions, atomic radii, or a supercell, it generates a new CTRL file called CNEW. In addition, most of the programs write an updated copy of CTRL to the file specified by the token WRITE=, which, by default, is CBAK. Finally, if the verbosity is increased, a file CALL is written, which comprises all possible tokens and their default values, if not set otherwise in the CTRL file.

The CTRL file is grouped into categories each starting in the first column of the file. Each category contains tokens specifying a portion of the input: e.g. in order to specify the lattice constant you just write ALAT=6.76 somewhere in the category STRUC. A complete list of all categories and tokens is supplied in the file HELP, which is printed in Sec. 3.6. It is included as a separate file in the ASW package, but could be generated running any of the main programs with HELP=T specified in category IO of the CTRL file.

At present, the ASW program package interprets 142 tokens grouped in 17 different categories. However, actually only entries in the three categories STRUC, CLASS, and SITE must be mandatorily specified by the user. For all other tokens meaningful and well tested default values exist. For this reason, only very few information is actually needed to successfully run the ASW program. Information required from the user includes the crystal's Bravais lattice, the type of atoms in the crystal (their atomic numbers), and the positions of these species within the unit cell of the crystal. The respective categories and tokens are indicated as mandatory below.

Once the program is started, it automatically creates the atomic files, which have the names specified by token ATOM= in category CLASS. There is only one file for each atom. In addition, the program creates a file for the mixing (file MIX); this file is deleted once self-consistency has been reached. Furthermore, in case the linear tetrahedron method is chosen for the Brillouin zone integration, the program creates and deletes the unformatted files EIGE, EIGV, EIGVC, and EIGVO, which hold information about the eigenvalues and eigenvectors. Finally, the files DOS, COOP, OPT, TRAP (all unformatted), and FERM (formatted) are created and written to in case SAVDOS=T, SAVCOOP=T, SAVOPT=T, SAVTRAP=T and SAVFERM=T, respectively, are specified in category BZSMP.

A short version of the following explicit description is given in the HELP file, which comes with the distribution but can be easily created by specifying HELP=T in category OPTIONS and running any of the ASW main programs. For this purpose, you may just construct a minimal CTRL file like

```
VERSION ASW-2.6
IO      HELP=T
```

and run any ASW program.

4.1 Category HEADER

This category is meant to hold a short description of the calculation. At present, this category is limited to 20 lines. Formally, the first line is treated differently from the following lines as it is interpreted as a title, which, by default, is appended to most plots. For this reason, I recommend to specify only a short title in the first line and to put longer comments into the following lines. Usually, I include references to important previous work on this compound in these lines.

4.2 Category VERSION

This category contains information about the version of the ASW package.

4.2.1 Token ASW- (cast real)

This token specifies the version and release number of the ASW program, which has been used to create the CTRL file or which you are intending to use, in case you have created the CTRL file by hand. The version and release number consists of two one-digit numbers separated by a dot. For the present version the default is ASW-2.6. This token is useful if you want to use a CTRL file written by an elder version/release, where some tokens had been in other categories as they are in version 2.6. By specifying the correct version you can take advantage of the upward compatibility of the package.

4.3 Category IO

This category contains specifications about which and how much information the programs should write to output as well as to the atomic files.

4.3.1 Token HELP= (cast logical)

This logical switch allows to print out the HELP file as listed in Sec. 3.6, which comprises a short hand version of this chapter. Default is HELP=F. To create the HELP file, set HELP=T and run any of the main programs (those starting with "mn"). To be specific, create a minimal CTRL file containing the lines

```
VERSION ASW-2.6
IO      HELP=T
```

and write "mnscf.x" at the operating system's prompt. In addition to the HELP file the program produces an output file (called outscf), which mainly contains a full CTRL file comprising all categories and tokens with their default values.

4.3.2 Token SHOW= (cast logical)

If set to true, this token makes the program echo the CTRL file to the output. This mode is highly recommended since then the input for the calculation is well documented and can be checked lateron. In addition, as an extra bonus, whenever you have lost the CTRL file you may easily recover it just by cutting the respective portion out of the output. For these reasons, the default is SHOW=T.

4.3.3 Token VERBOS= (cast integer)

Here you can specify a verbosity level for printing the output. The following verbosity levels are at present in use:

verbosity ≥ 0 : nearly nothing is printed,
≥ 10 : very terse,
≥ 20 : terse,
≥ 30 : normal,
≥ 40 : verbose,
≥ 50 : very verbose,
≥ 60 : higher verbosity,
≥ 80 : highest verbosity,

≥ 100 : low-level debugging,
≥ 110 : intermediate-level debugging,
≥ 120 : high-level debugging.

The default is VERBOS=30. In normal operation, you should not go beyond VERBOS=50. In particular, for VERBOS=80, the Hamiltonian matrix and related matrices are written to the output file, which, hence, will become extremely large.

4.3.4 Token CLEAN= (cast logical)

Like the CTRL file the atomic files are organized in a collection of eight categories named GEN, LDMT, ESJH, MOPT, VMTA, VLOC, RLOC, CORE. The first five of these comprise, respectively, general information about the atom at hand, the local density matrices, the partial Hankel and Bessel energies and integrals, the optical matrix elements, and the spherical part of the effective single-particle potential. The last three, and by far most extensive, groups contain the full effective single-particle potential as well as the self-consistent full valence and core electron densities.

Since, within the full-potential ASW method, the latter three entities can be generated from the local density matrices and the spherical part of the effective single-particle potential, they can be removed from the atomic files, once a calculation has been iterated to self-consistency. The token CLEAN=, which by default is CLEAN=T, makes the program delete the full single-particle potential and the electron densities, i.e. the categories VLOC, RLOC, and CORE, from the atomic files and thus allows for much reduced storage needs. Yet, see token CORDRD= below for exceptions.

4.3.5 Token WRITE= (cast character)

Here you can specify the name of an updated backup version of the CTRL file, which will be written just before completion. The default is WRITE=CBAK.

4.3.6 Token EXTENS= (cast character)

Using this token you may specify a standard extension appended to all file names created by the program as e.g. ".dat" or ".DAT". This is meant to conform with WINDOWS or VAX file name conventions. The default is empty, hence, all file names come without an extension.

4.4 Category OPTIONS

The following tokens can be used to specify details of the calculations.

4.4.1 Token REL= (cast logical)

This token allows to switch between non-relativistic and scalar-relativistic mode. The default is REL=T (scalar-relativistic).

4.4.2 Token LSCPL= (cast logical)

In future versions this token will enable for including the LS-coupling, which, however, is not yet implemented.

4.4.3 Token NSPIN= (cast integer)

Here you can specify the number of spin-channels. The default is NSPIN=1.

4.4.4 Token AFSYM= (cast logical)

In spin-polarized calculations, this token allows to use „spin-sublattice“ symmetry, which preserves the electronic states on going from one sublattice to the other and at the same time changing spins. This symmetry allows to perform the band calculation for one spin only and to extract the other spins results from the first ones. When AFSYM=T is specified, in addition, for each atom the „direction“ of spin has to be specified with the help of token SPIN= (see below). A more detailed description of how to perform spin-polarized calculations has been given in Secs. 2.4 and 2.5.

4.4.5 Token BEXT= (cast double)

This token comprises an external magnetic field (in z-direction). The default value is BEXT=0.0. Note that use of finite magnetic fields has not yet been fully tested.

4.4.6 Token XCPAR= (cast character)

Since version ASW-1.7, token XCPAR= enables specification of different LDA schemes. Actually, almost all known parametrizations are included now. The desired LDA parametrization is specified in the form XCPAR=P-S, where

P denotes the parametrization by

KSG: Kohn, Sham, and Gaspar (exchange only) [123,194]
GLW: Gunnarsson, Lundqvist, and Wilkins [146]
JMW: Janak, Moruzzi, and Williams [169]
VBH: von Barth and Hedin [37]
MJW: Moruzzi, Janak, and Williams [267]
PZ: Perdew and Zunger [297]
VWN: Vosko, Wilk, and Nusair [370]
PW: Perdew and Wang [296]

and
S denotes the spin interpolation by

GLW: Gunnarsson, Lundqvist, and Wilkins [146]
VBH: von Barth and Hedin [37]
VWN: Vosko, Wilk, and Nusair [370]
PW: Perdew and Wang [296]

Note that while the default was XCPAR=MJW-VBH in all versions up to ASW-1.6, it is now set to the more accurate XCPAR=VWN-VWN.

4.4.7 Token GGA= (cast character)

Since version ASW-1.8, a new token, GGA= has been included, which allows specification of different schemes of the generalized gradient approximation (GGA). Possible GGA parametrizations are GGA=G where

G denotes the parametrization by

PW86	Perdew and Wang 1986 (GGA-I) [295]
PW:	Perdew and Wang 1991 (GGA-II) [227, 289, 293]
EV:	Engel and Vosko 1993 [100]
PBE:	Perdew, Burke, and Ernzerhof 1996 [290, 292]
ZY	Zhang and Yang 1998 [401]
WC	Wu and Cohen 2006 [398]

The default is GGA= , which means to use none of these schemes.

4.4.8 Token LDA+U= (cast character)

Version 2.4 was the first version to allow for LDA+U calculations by specifying by the token LDA+U= one of three schemes. They differ by the double-counting terms introduced to avoid the double counting of electronic interactions within the LDA and the Hubbard model. Possible specifications are LDA+U=D where

D denotes the parametrization by

AMF:	around mean field proposed by Anisimov, Zaanen, and Andersen 1991 [28]
FLL:	fully localized limit proposed by Anisimov, Solovyev, Korotin, Czyzyk, and Sawatzky 1993 [27]
DFT:	interpolation scheme proposed by Petukhov, Mazin, Chioncel, and Liechtenstein 2003 [299]

The default is LDA+U= , which means that the LDA+U scheme is not used.

4.4.9 Token OVLCHK= (cast logical)

In elder versions of the standard ASW method (and also the LMTO method) slight ambiguities came in by bad settings of the atomic sphere radii. Most of such inaccuracies come from too large overlap of the spheres. In particular for the ASW method, the situation has much improved by the invention of the sphere geometry optimization (SGO) algorthim, which allows to automatically evaluate the radii. However, it is still recommended to check the radii for too large overlap. This overlap check is invoked by the token OVLCHK=, which, by default, is OVLCHK=T. In this case a list of atom pairs is generated, which, for each pair, holds the vector between the respective atomic sites, their distance, the sum of the radii, the linear overlap of the atomic spheres as well as the overlap scaled to the distance and the radii. Finally, each line may contain up to three exclamation marks indicating that the overlap scaled to the distance exceed 10%, 20%, and 30%, respectively.

4.4.10 Token DISTL= (cast double)

With this token a maximum distance between atoms can be specified (in atomic units). Atom pairs with distance below this value will be included in the above mentioned list printed to the output. The default value is 3.0.

4.4.11 Token CCOR= (cast logical)

This switch enforces use of the socalled combined correction to the ASA. Actually, the term combined correction is more related to the LMTO method since most early calculations were done with the pure ASA. For this reason, calculations employing the combined corrections earned an extra bonus. In contrast, in the ASW method these corrections to the ASA were included from the very beginning and, hence, calculations without the combined corrections actually were never done. Hence, the default is CCOR=T.

Since switching off the combined correction does not make sense in a full-potential code this token will most likely be removed in future versions.

4.4.12 Token CORDRD= (cast logical)

For some instances asi, e.g., calculation of rather small energy differences, it might be necessary to freeze the core state during the self-consistency cycle. This is allowed for by setting CORDRD=T. Yet, the default is CORDRD=F.

Note that in case of frozen core calculations the last of the above mentioned categories contained in the atomic files, i.e. the category CORE must not be deleted from the file after successful convergence. As a consequence, for CORDRD=T specifying CLEAN=T will remove only the categories VLOC and RLOC from the atomic files, but will preserve the category CORE.

4.5 Category STRUC (mandatory)

This category holds all the information about the Bravais lattice. Of course, its presence is necessary for any calculation.

4.5.1 Token UNITS= (cast character)

Here you can choose the units to be used for the following tokens, which may be atomic units (UNITS=BOHR, default) or Angstroems (UNITS=ANGS). Note that this choice also affects all input in category SUPCELL (see below).

4.5.2 Token ALAT= (mandatory; cast double)

This token contains the lattice constant in the units specified by token UNITS=. The default is ALAT=0.0. As a consequence, if the lattice constant is not given a finite value the program aborts.

Actually, the tokens ALAT= and PLAT= below are complementary in that each of them can be scaled by a factor if the number(s) coming with the respective other token are scaled by the inverse. An equivalent statement holds for the tokens BBYA= and CBYA=, also given below. As a consequence, you may regard the input given by ALAT= as a length scale for the whole crystal used for the primitive translations.

4.5.3 Token PLAT= (mandatory; cast double; length 9)

Information about the Bravais lattice is covered by this token, which contains the three primitive translations $\mathbf{a}_i,\ i = 1, 2, 3$ in units of the lattice constant as specified by token ALAT=. All nine components must be given in the order $\mathbf{a}_{1x}$, $\mathbf{a}_{1y}$, $\mathbf{a}_{1z}$, $\mathbf{a}_{2x}$, $\mathbf{a}_{2y}$, $\mathbf{a}_{2z}$, $\mathbf{a}_{3x}$, $\mathbf{a}_{3y}$, $\mathbf{a}_{3z}$.

4.5.4 Token SLAT= (cast character; marked obsolete)

As an alternative to explicitly specifying the primitive translations by PLAT= you may use the following five tokens together with the token BETA=, which rely on default lattice vectors coded in the ASW package.

However, note that the token SLAT= is marked obsolete and the token CNTR= together with the tokens for the lattice constants and the angles should be used instead.

Token SLAT= indicates a string for the Bravais lattice. Possible values are

SC: simple cubic
BCC: body-centered cubic
FCC: face-centered cubic
ST: simple tetragonal
BCT: body-centered tetragonal
SO: simple orthorhombic
SCO: base-centered orthorhombic
BCO: body-centered orthorhombic
FCO: face-centered orthorhombic
SM: simple monoclinic
SCM: base-centered monoclinic
TRI: trigonal
HEX: hexagonal

Note that the primitive translations coming with these specifications correspond to the definitions of Bradley and Cracknell, which in some instances deviate from the definitions commonly used. For this reason, you are strongly urged to check the primitive translations, which are printed to output at the beginning of the programs execution.

4.5.5 Token BLAT= (cast double)

For the other lattice constants coming with non-cubic and non-trigonal systems there exist two different ways of specification. Token BLAT= gives the lattice constant B explicitly in the units specified by token UNITS=. As for ALAT=, the default is BLAT=0.0.

4.5.6 Token BBYA= (cast double)

Alternatively, the lattice constant B can be specified by the token BBYA=, which fixes the ratio of the lattice constants BLAT and ALAT. As for BLAT= above the default is BBYA=0.0.

4.5.7 Token CLAT= (cast double)

Token CLAT= gives the lattice constant C explicitly in the units specified by token UNITS=. As for ALAT=, the default is CLAT=0.0.

4.5.8 Token CBYA= (cast double)

Alternatively, the token CBYA= allows to specify the lattice constant C in terms of the ratio of the lattice constants CLAT and ALAT. The default is CBYA=0.0.

4.5.9 Token ALPHA= (cast double)

With this token the angle between the second and third lattice vectors is specificed. The default value is ALPHA=90.0.

4.5.10 Token BETA= (cast double)

With this token the angle between the first and third lattice vectors is specificed. The default value is BETA=90.0.

4.5.11 Token GAMMA= (cast double)

With this token the angle between the first and second lattice vectors is specificed. The default value is GAMMA=90.0.

4.5.12 Token CNTR= (cast character)

With this token one of the following seven centering types of the Bravais lattice can be selected.

P	primitive
C	face-centered on the a,b-plane
B	face-centered on the c,a-plane
A	face-centered on the b,c-plane
I	body-centered

F	face-centered
R	rhombohedral

The default value is CNTR=P.

4.5.13 Token ADJLAT= (cast logical)

If set to ADJLAT=T this switch allows the program to adjust the lattice vectors to the optimal choice. The default is ADJLAT=F.

4.6 Category CLASS (mandatory)

Once the Bravais lattice has been specified the information about the crystal structure is completed by giving the positions of the atoms within the unit cell as well as the species of atoms, which hold these sites. While the present category comprises all information about the atomic species, the atomic sites will be given in the following section of the CTRL file.

4.6.1 Token NCLASS= (cast integer)

The number of different atoms, which we call classes of atoms, can be specified in two different ways. The most comfortable and standard procdure consists of letting the programs count the number of ATOM= entries just below.

However, in the course of calculations it might be useful to exclude some of the classes listed below from consideration by the program. This can be most easily accomplished by shifting the corresponding ATOM= entries to the end of this category and reducing the number of classes, which are taken into account by the programs by setting NCLASS= to the reduced number of classes.

To summarize, if a number of classes is specified by a NCLASS=n entry the program tries to reads as many classes. Any subsequent ATOM= entries are ignored. On the other hand, if the are less ATOM= entries than specified by NCLASS=n, the program will warn for the missing classes and stop.

4.6.2 Token ATOM= (mandatory; cast character)

Here you must label each of the classes. In the course of the calculations these labels are used to name the atomic files. My personal preference is to label classes by their names given in the periodic table extended by a roman number, whenever different classes with the same atomic number exist.

4.6.3 Token Z= (mandatory; cast integer)

This entry holds the atomic number. Note that the minimum input for each atom consists of giving a name by ATOM= and specifying the atomic number by Z=. All other input given in this category can be derived from these two tokens.

4.6.4 Token R= (cast double)

The atomic sphere radii can be specified in two different ways. In case you want to give absolute values, use this token. The default is R=0.0.

4.6.5 Token R/RA= (cast double; marked obsolete)

As an alternative to the previous token relative atomic sphere radii may be chosen. In this case the radii will be scaled to the ASA-condition unless you specify a value for FILLNG= (see below) different from one. The default value is R/RA=1.0. Note that this token is marked obsolete. Instead, the token FILLNG should be used.

4.6.6 Token LMXL= (cast integer)

This token specifies for each atom the maximum angular momentum for the lower partial waves, which are taken into account in the secular matrix. In practice, the lower partial waves include the valence states of interest for that particular atom. The default values are derived from the atomic number Z as given by the previous token.

4.6.7 Token LMXI= (cast integer)

In addition, for each atom a maximum angular momentum for the intermediate waves is needed. These waves are used for expanding the Hankel envelope functions at neighbouring sites in Bessel envelope functions. As a default, the input for the lower wave maximum angular momentum plus one is used.

For small empty spheres, which carry a very small amount of charge already in their lower partial wave, it might be useful to set the maximum l value for the intermediate waves to that for the lower waves. To the contrary, only rare situations exist, where l_{int} should be set to $l_{low} + 2$.

4.6.8 Token CONF= (cast integer; length 4)

While the previous two tokens specify the maximum number of partial waves per atoms, the principal quantum numbers for all these orbitals must be given here. Again, the default values are taken from a small database in accordance with the above input for the atomic number.

4.6.9 Token COORB= (cast integer)

With this token you can select the orbitals, which you want ot be included in the calculation as well as presentation of the crystal orbital overlap population (COOP), the crystal orbital Hamiltonian population (COHP) or the covalence energy (E_{cov}). The input consists just of the angular momenta of the desired orbital, i.e. for including p and d states you write COORB=1 2. As a default, no orbitals will be included.

4.6.10 Token QVAL= (cast double; length 5)

This token holds the valence charges for each atom, which will be needed if a calculation starts from scratch. As for the previous tokens, this input can be uniquely derived from the atomic number.

4.6.11 Token MVAL= (cast double; length 5)

Here you can give starting values for the magnetic moments of the valence states to be used for starting a spinpolarized calculation. These moments arise as the difference of the spin up and spin down partial charges. Reasonable default values for each atom are proposed by the program.

4.6.12 Token UVAL= (cast double; length 5)

This token specifies the U-values for each orbital as needed for LDA+U calculations. The default values are 0.0.

4.6.13 Token JVAL= (cast double; length 5)

This token specifies the J-values for each orbital as needed for LDA+U calculations. The default values are 0.0.

4.7 Category SITE (mandatory)

Finally, the structural information is completed by specifying the atomic sites in this category.

4.7.1 Token NBAS= (cast integer)

This token allows to specify the total number of atomic sites irrespective of the atomic species (class). However, note that this token needs not to be given since the number of sites is counted by the program as the number of POS= entries (see below). Otherwise for token NBAS= the same holds as was already said for token NCLASS= above.

4.7.2 Token CARTP= (cast logical)

This switch specifies whether the following entries for the atomic positions are interpreted as Cartesian coordinates (CARTP=T) or as relative components in terms of the translations of the conventional unit cell (CARTP=F). The default value is CARTP=T.

4.7.3 Token CHOUT= (cast logical)

Sometimes it is useful to change the representation of the atomic positions from Cartesian coordinates to relative components or vice versa. By setting CHOUT=T you may enforce that the respective other representation is written to the backup copy of the CTRL file (see token WRITE= above). To be specific, if the atomic positions are given in Cartesian coordinates (CARTP=T) and CHOUT=T is given, the copy of CTRL written at the end will contain the atomic positions as given in terms of the primitive translations. At the same time, these tokens are changed to CARTP=F and CHOUT=F. The default is CHOUT=F.

4.7.4 Token ADJPOS= (cast logical)

If set to ADJPOS=T this switch allows the program to adjust the atomic positions. The default is ADJPOS=F.

4.7.5 Token ATOM= (mandatory; cast character)

Before entering the atomic positions you must for each site give the class label in order to attach entries in categories CLASS and SITE to each other. Hence, the present token must match one of the ATOM= entries given in category CLASS.

4.7.6 Token POS= (mandatory; cast double; length 3)

Here you must specify the atomic position in the representation selected by the above token CARTP=.

4.7.7 Token SPIN= (cast character)

In case of antiferromagnetic order the site information may be complemented with information about the sublattice (spin up or down), the respective atom belongs to. This can be done by setting SPIN=UP or SPIN=DN for each atom. Obviously, the number of UP and DN entries must be equal for each class. Note that these entries are used only if AFSYM=T is given in category OPTIONS.

4.8 Category SYMGRP

Information about the analysis and use of space group symmetry underlying the crystal structure is supplied by this category. There exist essentially two modes. Either the symmetry of the crystal may be analyzed from the above information about the atomic classes and sites. This is the default. However, for large systems it may be useful to enter only a minimal set of atomic sites and to set up the remaining sites from the given symmetry operations. Finally, in case that both the complete set of atomic sites and the generators for all symmetry operations are given both are checked for consistency.

4.8.1 Token GENPOS= (cast logical)

This switch indicates that the basis set of atomic positions is completed by using the minimal set of positions given in category SITE and the following generators of the full group of symmetry operations. The default is GENPOS=F.

4.8.2 Token CARTR= (cast logical)

This switch specifies whether the entries for the rotation axes are interpreted as Cartesian coordinates (CARTR=T) or as relative components in terms of the primitive translations (CARTR=F). The default value is CARTR=T.

4.8.3 Token CARTT= (cast logical)

This switch specifies whether the entries for the fractional translations are interpreted as Cartesian coordinates (CARTT=T) or as relative components in terms of the primitive translations (CARTT=F). The default value is CARTT=T.

4.8.4 Token ORIGIN= (cast integer)

This token can be used to choose one of possibly two different choices for the origin of the space group of the crystal. The default values is ORIGIN=1.

4.8.5 Token SGSYM= (cast character)

With this token the space group of the crystal is specified by the respective Hermann-Mauguin symbol as listed in file SPCGRP. The default is SGSYM=, i.e. the space group symbol is not set.

4.8.6 Token SGNUM= (cast integer)

With this token the space group of the crystal is specified by the respective space group number as listed in file SPCGRP. The default is SGNUM=0, i.e. the space group number is not set.

4.8.7 Token SYMOPS= (cast character; length 48)

Here you may specify generators for the full group of the symmetry operations. These generators are most easily coded by using the following short hand notation: ’E’ and ’I’ denote unity operation and inversion, while ’R’, ’S’ and ’M’ are short for proper and improper rotation, respectively and reflection. Finally ’:T’ stands for a fractional translation following any of the just mentioned operations. ’R’ must be followed by an integer denoting the angle of rotation in terms of the number of divisions of the full circle. In particular, this number may be ’2’, ’3’, ’4’, or ’6’. Moreover, ’Ri’, ’M’ and ’:T’ must be followed by a vector ’(a,b,c)’ specifying the rotation axis, the vector perpendicular to the mirror plane and the translation vector, respectively. The components a, b, and c of the vectors must be real numbers, exceptions being the abbreviations ’C’ and ’S’ for 0.5 and 0.5*sqrt(3), respectively, and ’0’, ’1’, ’1/2’, ’1/3’, ’1/4’, and ’1/6’. In addition, the following short hand notations exist. While ’D’ is short for the diagonal, i.e. the vector (1,1,1), ’X’, ’Y’, and ’Z’ abbreviate the vectors (1,0,0), (0,1,0), and (0,0,1). The following examples will help understanding this notation.

R6(1,0,0)	a positive rotation by 60° about the x-axis,
R6(-1,0,0)	a positive rotation by 60° about the $-x$-axis, i.e. a negative rotation by 60° about the x-axis,
R6(C,S,0)	a positive rotation by 60° about the axis (0.5,0.8660,0),
R3D	a positive rotation by 120° about the (1,1,1)-axis,
R4(1,1,0):T(0,0,0.5)	a positive rotation by 90° about the (1,1,0)-axis followed by a translation by the vector (0,0,0.5),
MX	a reflection about the plane spanned by the y- and z-axis, which transforms x to $-x$,
I	the inversion.

Specifically, the operations R4X, MX, and R3D are sufficient to generate all 48 elements of the full cubic group.

Finally, all the aforementioned operations may be combined by *, where A*B is converted to mat(A)*mat(B), i.e. the operations are applied from right to left. Note the originally 4x4-character of all operations when combining them.

4.9 Category PACK

This category summarizes all the options used by the sphere geometry optimization (SGO) algorithm. In the atomic sphere approximation (ASA), space is divided into spheres centered at the atomic sites. These spheres are required to fill space completely in order that the region between the spheres, the socalled interstitial region, vanishes. However, there exist crystal structures, where the aforementioned condition would lead to rather large overlaps of the atomic spheres. In that case, usually socalled empty spheres are included, which model the crystal potential in such large voids. The SGO algorithm automatically finds optimal empty spheres positions and the best radii of all, physical and empty spheres.

4.9.1 Token FILLNG= (cast double)

This token specifies the fraction of space, which eventually must be filled by the atomic spheres. The default is FILLNG=1.0. The special settings FILLNG=0.0 and FILLNG=-1.0 enforce scaling of the sphere radii to those of touching spheres and the use of the radii given in the CTRL file, respectively.

4.9.2 Token OBYDMX= (cast double)

Maximum allowed overlap for any pair of spheres scaled to the distance between the sphere centers. A good value is OBYDMX=0.15, which is the default. For some systems, it might be necessary to go beyond this value in order to achieve complete space filling. However, you should not go beyond OBYDMX=0.2.

4.9.3 Token OBYRMX= (cast double)

Maximum allowed overlap for any pair of spheres scaled to the radii of the respective spheres. The default value is OBYRMX=0.4 but OBYRMX=0.5 is still acceptable. This token is important for systems containing large differences in sphere radii, where, hence, small spheres might be swallowed by large spheres if, e.g., touching spheres are blown up to space filling.

4.9.4 Token ESBONS= (cast double)

Since the empty spheres are included in order to mimic the full crystal potential in large voids between the physcial spheres the potential within these spheres is rather flat. For that reason, empty spheres can have a larger overlap with the neighbouring spheres. ESBONS= specifies this extra bonus to be to OBYDMX and OBYRMX. The default is ESBONS=0.05 and the actual value should not exceed ESBONS=0.1

4.9.5 Token NCEMAX= (cast integer)

This token fixes the maximum number of empty sphere classes sought for by the program. If space filling can not be achieved with less empty spheres the program issues a warning saying that the result of the sphere packing might depend on this parameter. The default value is 256.

4.9.6 Token RADMIN= (cast double)

This token gives the minimum muffin-tin radius for an empty sphere. Once the SGO algorithm subsequently identifies two possible empty spheres candidates with muffin-tin radii smaller than RADMIN the packing routine stops. The default value is RADMIN=0.5, which hardly has to be changed.

4.9.7 Token RADMAX= (cast double)

The token RADMAX= fixes the maximum atomic sphere radius for an empty sphere. This setting has two opposing consequences. A large radius for an empty sphere might be prohibitive since higher and higher partial waves (angular momenta) would be needed to properly describe the electronic wave function within such a large sphere. To the contrary, if the maximum radius is set to a rather small value, it might be difficult to fill space by spheres if large voids exist in the crystal structure. The default value is RADMAX=5.0, which is quite high in order not to limit the sphere size. For most crystal structures you will not need to change this value. Yet, in case you obtain large empty spheres, you might try RADMAX=3.0 or even RADMAX=2.5.

4.9.8 Token RADACC= (cast double)

Here you can specify the accuracy required for the sphere radii. The default value of RADACC=0.02 hardly needs a change.

4.9.9 Token POSACC= (cast double)

This token gives the accuracy required for the empty sphere positions. As before, the default value of POSACC=0.003 usually is sufficient.

4.10 Category ENVEL

In the ASW method the basis functions for the subsequent variational procedure are constructed by starting out from analytically known solutions of Schrödinger's equation with a constant potential. These are either plane waves or spherical waves. In the ASW method, only the latter are used in the form of spherical Hankel functions. Within the atomic spheres, these spherical waves are replaced, or "augmented", by numerical solutions of the radial Schrödinger equation with the spherical part of the actual potential. These numerical solutions are subject to the conditions of regularity at the respective origin and continuous and differentiable matching of the envelope functions at the respective sphere radius. The situation is sketched in Fig. 4.1 for two augmented spherical waves centered at two different sites A and B.

The present category specifies the analytical solutions outside the atomic spheres, which are the socalled envelope functions. The region outside the spheres is called the interstitial region. The tokens in this category usually need not be changed from their default value. Hence, in most cases you can ignore this category at all.

4.10.1 Token NKAP= (cast integer)

Here the number of envelope functions, i.e. the number of analytical solutions outside the atomic spheres per atom and angular momentum are fixed. The maximum value is 3, the default is NKAP=1.

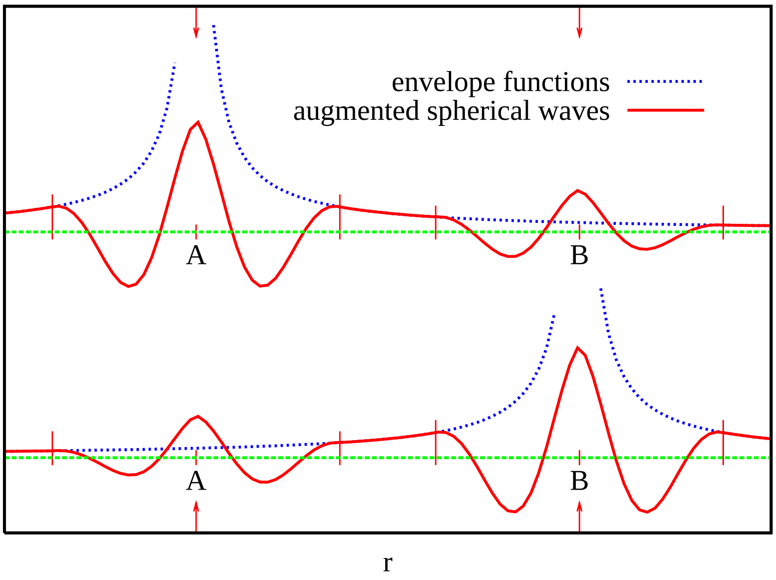


Figure 4.1 Augmented spherical waves centered at two different sites A and B. The envelope functions and the full augmented spherical waves are given in red and blue, respectively.

4.10.2 Token EKAP= (cast double)

EKAP= is used to specify the energies of the solutions of Schrödinger's equation in the interstitial region. The default value for the (first) solution is EKAP=-0.015, which is the classical ASW value.

4.10.3 Token EWPAR= (cast double)

The Ewald parameter is used to calculate lattice sums of spherical Hankel functions located at lattice sites. Following the seminal method first proposed by Ewald the resulting lattice sums are cut into two, one being performed in real space, while the other is performed in recirpocal space. The cutoff radius for these two sums is called the Ewald parameter. The default value is EWPAR=2.44949.

4.10.4 Token EWTOL= (cast double)

Using the token EWTOL you can specify the precision sought for the convergence of the above mentioned lattice sums. The default is EWTOL=1.0D-10.

4.11 Category BZSMP

The category BZSMP holds all information related to the Brillouin zone sampling.

4.11.1 Token NKBAB= (cast integer)

This new token allows to specify the spacing of the **k**-points used for the Brillouin zone integration in terms of the number of **k**-points per inverse Bohr radii. It guarantees a uniform distribution of **k**-points in the Brillouin zone. In particular, the **k**-points are distributed according to the lengths of the reciprocal space vectors.

The default setting for this token is NKBAB=6. In most cases it is useful to start from this value and, after convergence, to switch to NKBAB=12 and, finally to NKBAB=18. This way the dependence of the results on the fineness of the **k**-space grid could be checked.

For metals, going up to NKBAB=18 suffices in almost all cases, except for the nearly free electron metals like Al and Na. In contrast, for semiconductors and insulators much lower values as e.g. NKBAB=8 are sufficient. However, note that these values also depend on the scheme for the Brillouin zone integration.

4.11.2 Token NKABC= (cast integer; length 3)

Alternatively, this token can be used to specify the numbers of mesh points to be taken along each of the reciprocal space primitive translations. As such it determines the **k**-space grid used for the Brillouin zone integrations. For examples, with NKABC=6 6 6, the Brillouin zone is divided into 216 microcells. A special notation has been invented for this token, which makes life much easier. Whenever one of the three numbers is set to 0 in the CTRL file, it is interpreted by the programs as being identical to the preceding number. To be specific, the following interpretations can be used

NKABC=6 0 0 ≡ NKABC=6 6 6
NKABC=6 8 0 ≡ NKABC=6 8 8
NKABC=6 0 8 ≡ NKABC=6 6 8

This feature enables fast switching to a finer grid after a calculation with a coarse grid has converged. The default setting for this token is NKABC=8 0 0. However, in most cases it is best to start from NKABC=6 0 0. After convergence, one should switch to NKABC=8 0 0, then 12, 16, 20, and 30. This way the dependence of the results on the fineness of the **k**-space grid could be checked.

For metals, going up to NKABC=30 0 0 suffices in almost all cases, except for the nearly free electron metals like Al and Na. In contrast, for semiconductors and insulators much lower values as e.g. NKABC=16 0 0 are enough. The same holds for rather large unit cells comprising e.g. 30 or more atoms. Since these unit cells have smaller Brillouin zones going up to NKABC=16 0 0 will also suffice. Of course, these numbers are only rough estimates the particular choice being more or less a matter of the desired accuracy.

4.11.3 Token BZINT= (cast character)

The token BZINT= allows to choose the scheme used for the Brillouin zone integration. At present, it can be BZINT=SMS (simple sampling), BZINT=HPS (high-precision sampling), or BZINT=LTM (linear tetrahedron method), which is the default. Details on these schemes can be found in my book on the ASW method [404].

The simple-sampling scheme uses a simple histogram technique. Due to its statistical nature the calculated densities of states look rather noisy. This becomes most obvious from the densities of states of sodium, which calculated as an example. In Fig. 4.2 we display the density of states of Na as calculated using the simple-sampling method with $30 \times 30 \times 30$ **k**-points. While the square-root behaviour typical for free-electron like metals is still visible the result clearly reflects the statistical nature of the simple-sampling scheme. The noise produced by this procedure could be suppressed only with a very huge number of **k**-points. As a consequence, the simple-sampling method is rather inefficient. Nevertheless, note that for the calculation of integrated densities of states the statistical errors average out to a large extent this leading to reasonable results.

A considerable improvement can be achieved by using the high-precision sampling method as proposed by Methfessel and Paxton [258]. The result is shown in Fig. 4.3. It displays the density of states of Na as calculated using the high-precision sampling method with the same number of **k**-points as used for the generation of Fig. 4.2. Obviously, the statistical nature has been completely abandoned. However, there are still some oscillations in the curve especially at higher energies. In addition, the smoothing coming with the truncation of the series causes distinct deviations from the square-root behaviour at the lower band edge.

Finally, the superiority of the linear tetrahedron method is clearly revealed by Fig. 4.4, which displays the density of states of Na as calculated using the linear tetrahedron method with the same number of **k**-points as used in Figs. 4.2 and 4.3. Again, we observe considerable progress. While the high-precision sampling method was able to suppress the statistical noise of the simple sampling method,

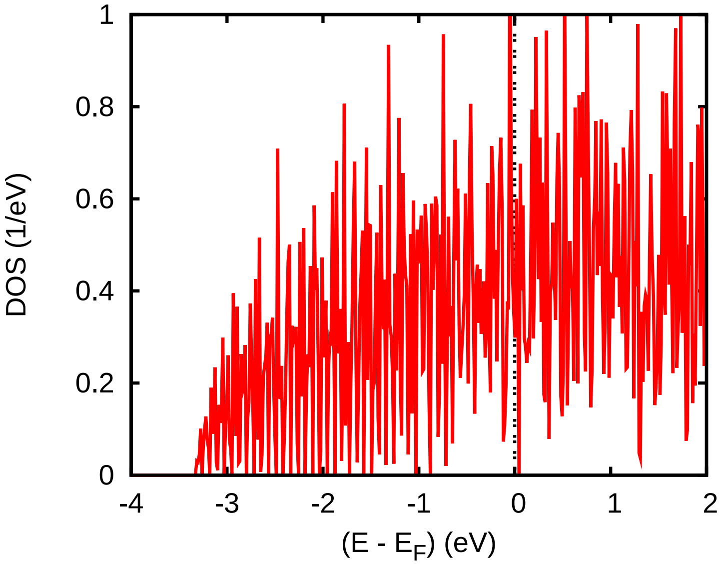


Figure 4.2 Density of states of Na as calculated with the simple-sampling method with 30×30×30 **k**-points.

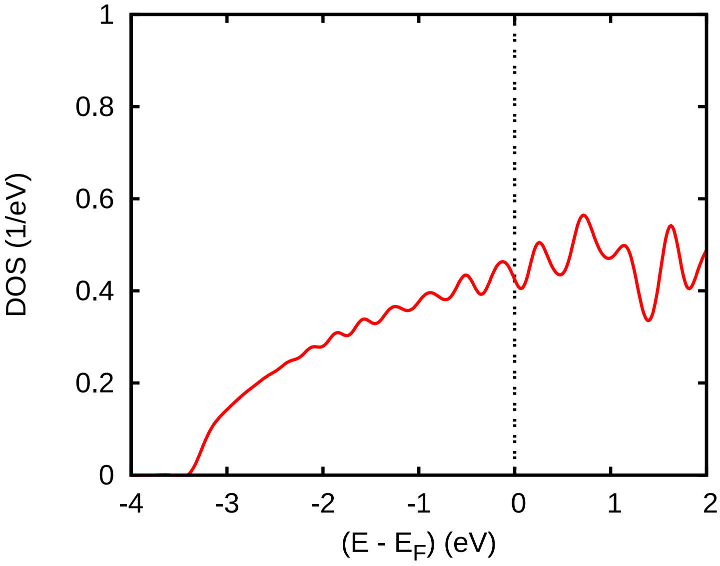


Figure 4.3 Density of states of Na as calculated with the high-precision sampling method with 30 × 30 × 30 **k**-points.

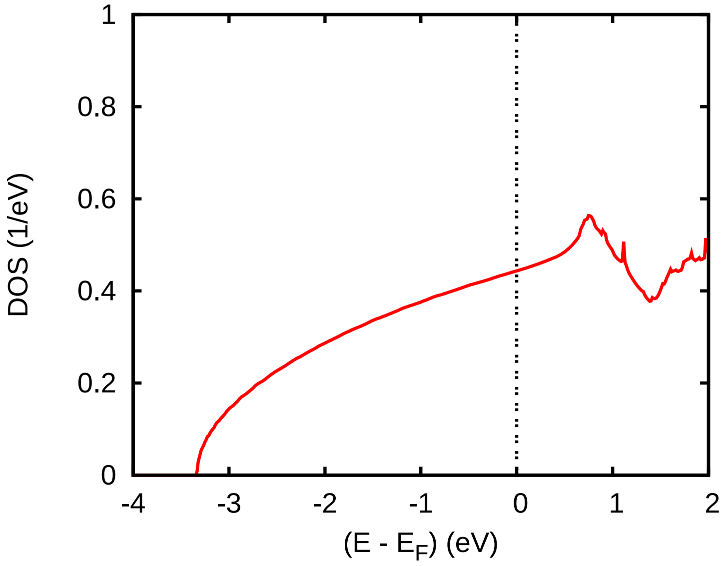


Figure 4.4 Density of states of Na as calculated with the linear tetrahedron method with 30 × 30 × 30 **k**-points.

both the broadening and the oscillations observed in Fig. 4.3 have now vanished. From this example it should be obvious that the linear tetrahedron method is highly recommended. With the same number of **k**-points a much higher qualitiy of the results can be achieved.

Nevertheless, the DOS given in Fig. 4.4 still displays some tiny spikes at energies beyond the maximum of the curve, which might be indicative of numerical instabilities. However, such spikes are well knwon to be an artifact of the linear tetrahedron method. In contrast, the numerical stability of the method can be easily proven by a calculation using an extremely high number of **k** points. Indeed, the result of a calculation using $100 \times 100 \times 100$ **k** points as shown in Fig. 4.5 clearly confirms the stability and superiority of the linear tetrahedron method, which is thus the method of choice.

4.11.4 Token EMIN= (cast double)

The tokens EMIN= and EMAX= fix the energy interval used for the calculation of the (partial) densities of states. Note that this interval is used not only for visualization purposes but also during the iterations towards self-consistency, where the integrated DOS is needed for calculating the electronic charge density. For this

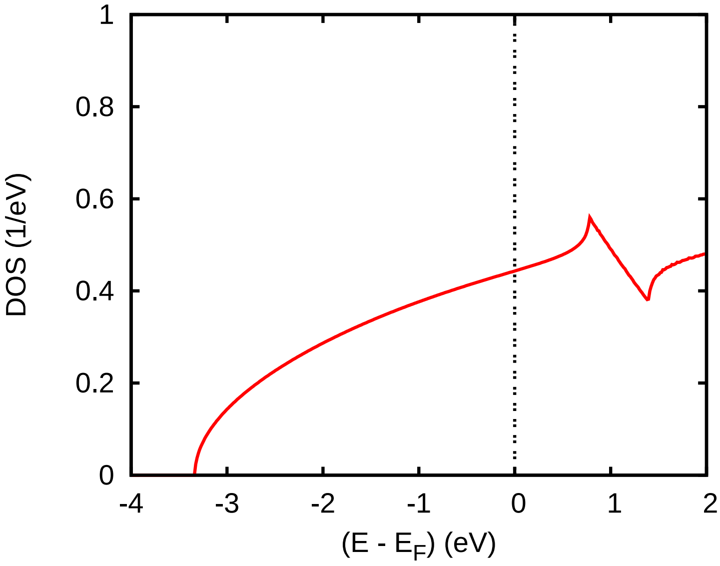


Figure 4.5 Density of states of Na as calculated with the linear tetrahedron method with 100 × 100 × 100 **k**-points.

reason EMIN and EMAX must be below the lowest valence band and higher than the Fermi energy, respectively. The default value is EMIN=-2.0 (Ryd).

4.11.5 Token EMAX= (cast double)

Token EMAX= fixes the upper bound of the interval used for the densities of states calculation. It must be above the Fermi energy. The default value is EMAX=1.0 (Ryd).

4.11.6 Token NDOS= (cast integer)

Token NDOS= gives the number of divisions of the [EMIN:EMAX]. Choosing a small value will result in inaccuracies of the calculated densities of states. However, a too high value will produce some statistical noise in the simple-sampling scheme. A good choice is NDOS=nnnn, where nnnn is the width of the energy interval [EMIN:EMAX] in Ryd divided by 1 mRyd. The default is NDOS=3000.

4.11.7 Token NORD= (cast integer)

In case that BZINT=HPS has been specified the following two tokens are needed:

Token NORD= fixes the order of the approximant in the high-precision Brillouin zome scheme of Methfessel and Paxton. While low values might cause inaccuracies, high values might lead to too sharp structures. A good choice is NORD=3, which is the default.

4.11.8 Token WIDTH= (cast double)

This token specifies the internal broadening used for the high-precision Brillouin zome scheme. The default value is WIDTH=0.01 (Ryd).

4.11.9 Token SAVDOS= (cast logical)

Since the calculation of the partial (m-resolved) densities of states (DOS) requires additional CPU time, token SAVDOS= has been implemented to switch of calculation of all partial DOS during iteration towards self-consistency. For this reason the default is SAVDOS=F. Once full self-consistency is achieved you can choose SAVDOS=T and calculate the partial densities of states for plotting in one additional calculation. It is advantageous to switch from BZINT=SMS to BZINT=HPS in this case, too.

4.11.10 Token SAVCOOP= (cast logical)

The meaning of this token is equivalent to that of the previous one. During the iterations, SAVCOOP=F should be used in order to suppress calculation of the crystal orbital overlap populations (COOP), the crystal orbital Hamiltonian population (COHP) or the covalence energy ($\mathrm{E}_{\mathrm{cov}}$) at all. Only in the additional run after self-consistency has been reached, SAVCOOP=T should be used. Note that the latter choice is only effective if the orbitals to be included have been specified by tokens COORB= in category CLASS.

4.11.11 Token CTYPE= (cast character)

The token CTYPE= allows to choose the scheme used to describe chemical bonding. At present, it can be either CTYPE=COOP for the crystal orbital overlap population introduced by Hoffmann [161], CTYPE=COHP for the crystal orbital Hamilton population as proposed by Dronskowski and Blöchl [95], and CTYPE=ECOV for the covalence energy put forward by Fähnle and coworkers [45, 55, 56].

4.11.12 Token MSPLIT= (cast logical)

This token allows to calculated m-resolved COOP's. However, this feature has not been fully tested and, in addition, requires additional CPU time and memory. For these reasons, the default is MSPLIT=F.

4.11.13 Token TEMPFD= (cast double)

With this token you can specify the temperature (in Kelvin) entering the Fermi-Dirac distribution function, which will be used for folding with the calculated density of states. This allows to evaluate the position of the chemical potential from the condition that at the given temperature the numbers of excited holes and electrons must be identical. In a second step these numbers are resolved in contributions from atoms and angular momenta, i.e. the partial numbers of excited holes and electrons are calculated. This helps to quickly identify the relevant optical transitions. The default is TEMPFD=300 (K).

4.11.14 Token SAVFERM= (cast logical)

With this switch the program is advised to write out information about the Fermi surface for metals, which can be plotted using the XCrysDen software [405]. The default value is SAVFERM=F, which should be used during the self-consistent calculations. Once full self-consistency is achieved you can choose SAVFERM=T.

4.11.15 Token SAVOPT= (cast logical)

Version 2.4 was the first one, which allowed to calculate the optical conductivity [404]. This includes both the real and imaginary as well as both the absorptive and dispersive parts. As a consequence, no additional Kramers-Kronig transformation is needed. This token can be used to invoke calculation of the optical conductivity. The default value is SAVOPT=F, which should be used during the self-consistent calculations. Once full self-consistency is achieved you may choose SAVOPT=T. Note that calculation of the optical conductivity is rather time consuming.

4.11.16 Token SAVTRAP= (cast logical)

From version 2.6 on, also the calculation of transport properties as based on Boltzmann theory is implemented. This includes calculation of the electric conductivity, the electronic part of the thermal conductivity, thermopower, the Hall conductivity, and derived quantities [404]. The default value is SAVTRAP=F, which should be used during the self-consistent calculations. Once full self-consistency is achieved you may choose SAVTRAP=T. Calculation of the transport quantities is somewhat time consuming but the computational demands are considerably lower as for the optical properties.

4.12 Category CHARGE

4.12.1 Token NETA= (cast integer)

The number of functions per atom and angular momentum to be used to represent the interstitial electron density is fixed to two and cannot be changed on input. For this reason, this token is a dummy.

4.12.2 Token EETA= (cast double; length 2)

EETA= is used to specify the energies of the functions used to represent the interstitial electron density. The default values are EETA=-3.0 -5.0, which are still under consideration. In case you experience instabilities during the iteration process as signaled especially by a negative value for the Fermi energy you should try out switching to more negative values.

4.12.3 Token SAVRHO= (cast logical)

With this switch you may invoke calculation of the electron densities (core and valence), their negative Laplacian, and the effective potential. The default value is SAVRHO=F, which should be kept during the self-consistent calculations.

4.12.4 Token SAVELF= (cast logical)

In future versions, this switch may be used to invoke calculation of the electron localization function and related functions. The default value is SAVELF=F, which should be kept during the self-consistent calculations.

4.12.5 Token CHARWIN= (cast logical)

In future versions, this switch will allow to print the electron densities resulting from electronic states of only a small energy window as specified by the following two tokens. The default value is CHARWIN=F.

4.12.6 Token EMINC= (cast double)

In future versions, the tokens EMINC= and EMAXC= fix the energy interval used for the calculation of the electron densities. The default value is EMINC=-100.0 (Ryd).

4.12.7 Token EMAXC= (cast double)

In future versions, token EMAXC= fixes the upper energy limit used for the calculation of the electron densities. The default value is EMAXC=100.0 (Ryd).

4.13 Category CONTROL

4.13.1 Token START= (cast character)

The tokens START= and QUIT= can be used to control the sequence of all calculations performed during execution especially of program mnscf.run. In general, ASW calculations towards self-consistency are subdivided into two parts. In one part, starting from integrals of the partial waves, the program sets up as well as diagonalizes the secular matrix for every **k**-point and supplies the local density matrices. This part is called the band calculation.

In the other part, the local density matrices are used to calculate electron densities, and, using the notions of density functional theory, the potential. The latter in turn allows evaluation of the integrals for use in the secular matrix. This part is called the atomic part. At the start of the program, overlapping atomic electron densities are used to boot the execution.

In general, four different starting points of the programs execution can be distinguished, which may be selected by token START= but, of course, also depend on the information gained in previous executions.

START=REN	Execution starts from scratch. The program performs a renormalized atom calculation using the charges as specified by QVAL= and magnetic moments as given by MVAL=, respectively. In contrast, if FREE=T has been given, a free atom calculation is performed using a sphere radius of 20 Bohr radii.
START=RST	In this case the program does a restart calculation, where the local density matrices and the spherically symmetric potentials inside the atomic spheres are used to initiate all the atomic calculations. The latter eventually lead to the matrix elements entering the secular matrix.
START=ATM	The program invokes one (or more) full band iterations starting with the intraatomic calculations, i.e. starting from the local density matrices and the spherically symmetric potentials inside the atomic spheres in the same manner as for the restart calculations.
START=BND	This is the default. The program invokes one or more full band iterations starting with the Brillouin zone sampling.

In case START= has not been specified the default START=BND will be used. Furthermore the program will look up the atomic files and check them if present. Depending on the outcome of this check the program will then decide automatically where to start. In addition, if START= has been specified, this setting is compared to the content of the atomic files and the program might opt for a different starting point. If, for instance, the atomic sphere radii have been changed in the CTRL-file and, hence, are no longer in agreement with those given in the atomic files the program will automatically invoke a restart calculation. The same happens when a change from a non-spinpolarized to a spinpolarized calculation has been detected. Another case to be mentioned is the situation where START=REN is specified and converged atomic files exist. In this case the program stops in order to prevent the converged atomic files from being overwritten.

4.13.2 Token QUIT= (cast character)

Token START= is complemented by token QUIT=, which allows to stop execution prior to the end of the calculation normally performed by the program. To be specific, at present the following entries could be used.

QUIT=OVL	Any of the main programs stops after having performed the symmetry analysis and the overlap check for the atomic spheres.
QUIT=STR	Program mnpac.run stops after the radii of non-overlapping muffin-tin spheres have been determined from the overlapping free atom potential as arising within the so-called Mattheiss construction.
QUIT=REN	Program mnscf.run stops after having finished a free atom calculation.
QUIT=ATM	Program mnscf.run stops after having finished the intraatomic atom calculations for the first time.
QUIT=BND	Program mnscf.run stops after having finished the band calculations for the first time but before entering the atomic part of the calculations. This setting is particularly useful for calculating the partial densities of states in a single run after self-consistency has been achieved.
QUIT=RHO	Program mnscf.run stops after having calculated the electron density and related quantities on the mesh given in the CTRL file. This setting is useful for invoking the rather time-consuming calculation of the electron density and related quantities once self-consistency has been achieved.

4.13.3 Token FREE= (cast logical)

This token has two different meanings. The default is FREE=F. First, if program mnscf.run is called with FREE=T is performs a free atom calculation for all atoms in the unit cell. Second, if used with program mnbnd.run, FREE=T enforces calculation of the free electron bands.

4.13.4 Token NITBND= (cast integer)

This token fixes the maximum number of iterations to be executed by the program. The default value is NITBND=99. This token is useful if only a limited amount of CPU time is available. A good estimate for the total execution time can be evaluated as follows. For most applications, the band part of the calculations takes about 95%

of the total execution time. Once the band calculation, i.e. the loop over all **k**-points has started, the program checks the CPU time per **k**-point and, on adding the CPU time needed for the previous atomic calculations, prints out the CPU time estimate for one iteration.

4.13.5 Token CNVG= (cast double)

With this token the desired accuracy of the calculation is fixed. Once this value has achieved, the self-consistency cycle stops. In particular, CNVG= is the accuracy for the root mean square difference of the intraatomic charge density resulting from the previous and the present iteration. The default value is CNVG=1.0D-8, which is *very* accurate. You might well switch to CNVG=1.0D-6 without loosing to much. However, note that going from 10^{-6} to 10^{-8} usually requires only very few iterations and, hence, can be achieved at a very low cost.

4.13.6 Token CNVGET= (cast double)

This token specifies the desired accuracy for the total energy. Whenever the difference between the total energies of the previous and the present iteration is below this value, and the condition set by CNVG= is fulfilled, the self-consistency cycle is stopped. The default is CNVGET=1.0D-8 (Ryd), which again is *very* accurate.

4.13.7 Token NITATM= (cast integer)

Actually, there exist two different self-consistency cycles within the ASW main program mnscf.run. The *outer* cycle, also called the band iteration, is the usual one, which aims at making the whole electronic density, the effective potential, the Hamiltonian matrix etc. self-consistent. In addition, there are intratomic calculations, which are invoked to make a starting electron density from that of overlapping free atoms. In contrast to token NITBND= the above token NITATM= specifies the number of these startup intraatomic iterations. The default value is NITATM=50, which hardly needs a change.

4.13.8 Token CNVGQA= (cast double)

This token fixes the desired accuracy of the intraatomic calculations. Once this value has achieved, the intraatomic self-consistency cycle stops. In particular, CN-

VGQA= is the accuracy for the root mean square difference of the intraatomic electron density resulting from the previous and the present intraatomic iteration. The default value is CNVG=1.0D-10, which is *very* accurate. However, due to the very low execution time of the intraatomic calculations, this value is well justified and needs no changes.

4.14 Category MIXING

This category can be used to influence the iteration towards self-consistency. Actually, there exist two different self-consistency loops. One, which is called the band iteration, affects the calculation of local density matrices once the Brillouin zone sampling has been finished. The other, intraatomic self-consistency loop is performed for each atom as part of the intraatomic calculations at startup time of the calculation in order to construct a starting electron density from those of overlapping free atoms. All this is explained in more detail in my review as well as my book on the ASW method [110, 404].

Both types of iterations are accelerated by using the extended Anderson mixing, which superseeds both the elder versions of the Anderson mixing and the Broyden update [107]. The extended Anderson mixing is controlled by two parameters, namely the number of previous iterations to be mixed in and the mixing parameter β.

The values proposed for all tokens in this categories have been thoroughly tested in a huge number of applications. They hardly need a change. However, whenever convergence is rather slow, you might reduce the β value used for the band iterations to BETAB=0.3 and switch off the automatic increase of β by setting INCBB=F.

4.14.1 Token NMIXB= (cast integer)

This token holds the number of previous band iterations to be used for the band mixing. The maximum value is 8, the default is NMIXB=5.

4.14.2 Token BETAB= (cast double)

Here you can specify the mixing parameter to be used for the band mixing. The default is BETAB=0.5.

4.14.3 Token INCBB= (cast logical)

With INCBB=T this switch allows to increase the β value used for the band iterations, hence, to speedup these iterations once the self-consistency loop has stabilized.

4.14.4 Token NMIXA= (cast integer)

This token holds the number of previous intraatomic iterations to be used for the atomic mixing. The default is NMIXA=5.

4.14.5 Token BETAA= (cast double)

Here you can specify the mixing parameter to be used for the intraatomic mixing. The default is BETAA=0.5.

4.15 Category SUPCELL

4.15.1 Token ALAT= (cast double)

This token contains the supercell lattice constant in the units specified by token UNITS=. Default is ALAT=0.0.

4.15.2 Token PLAT= (cast double; length 9)

Information about the Bravais lattice is covered by this token, which contains the three supercell primitive translations $\mathbf{a}_i,\ i = 1, 2, 3$ in units of the lattice constant. All nine components must be given in the order $\mathbf{a}_{1x}$, $\mathbf{a}_{1y}$, $\mathbf{a}_{1z}$, $\mathbf{a}_{2x}$, $\mathbf{a}_{2y}$, $\mathbf{a}_{2z}$, $\mathbf{a}_{3x}$, $\mathbf{a}_{3y}$, $\mathbf{a}_{3z}$.

4.15.3 Token SLAT= (cast character; marked obsolete)

As an alternative to explicitly specifying the supercell primitive translations by PLAT= you may use the following six tokens, which rely on default lattice vectors coded in the ASW package. First of all, token SLAT= indicates a string for the Bravais lattice. Possible values are

SC: simple cubic
BCC: body-centered cubic
FCC: face-centered cubic
ST: simple tetragonal
BCT: body-centered tetragonal
SO: simple orthorhombic
SCO: base-centered orthorhombic
BCO: body-centered orthorhombic
FCO: face-centered orthorhombic
SM: simple monoclinic
SCM: base-centered monoclinic
TRI: trigonal
HEX: hexagonal

Note, however, that the primitive translations coming with these specifications correspond to the definitions of Bradley and Cracknell, which in some instances deviate from the definitions commonly used. For this reason, you are strongly urged to check the primitive translations, which are printed to output at the beginning of the programs execution. Note that the token SLAT= is marked obsolete. Instead the token CNTR= should be used.

4.15.4 Token BLAT= (cast double)

For the other lattice constants coming with non-cubic and non-trigonal systems there exist two different ways of specification. Token BLAT= gives the lattice constant B explicitly in the units specified by token UNITS=. As for ALAT=, the default is BLAT=0.0.

4.15.5 Token BBYA= (cast double)

Alternatively, the lattice constant B can be specified by the token BBYA=, which fixes the ratio of the lattice constants BLAT and ALAT. As for BLAT= above the default is BBYA=0.0.

4.15.6 Token CLAT= (cast double)

Token CLAT= gives the lattice constant C explicitly in the units specified by token UNITS=. As for ALAT=, the default is CLAT=0.0.

4.15.7 Token CBYA= (cast double)

Alternatively, the token CBYA= allows to specify the lattice constant C in terms of the ratio of the lattice constants CLAT and ALAT. The default is CBYA=0.0.

4.15.8 Token ALPHA= (cast double)

With this token the angle between the second and third supercell lattice vectors is specificed. The default value is ALPHA=90.0.

4.15.9 Token BETA= (cast double)

With this token the angle between the first and third supercell lattice vectors is specificed. The default value is BETA=90.0.

4.15.10 Token GAMMA= (cast double)

With this token the angle between the first and second supercell lattice vectors is specificed. The default value is GAMMA=90.0.

4.15.11 Token CNTR= (cast character)

With this token one of the following seven centering types of the supercell Bravais lattice can be specified.

P	primitive
C	face-centered on the a,b-plane
B	face-centered on the c,a-plane
A	face-centered on the b,c-plane
I	body-centered

F	face-centered
R	rhombohedral

The default values if CNTR=P.

4.15.12 Token EQUIV= (cast logical)

This switch requires that after construction of the supercell atoms located at the equivalent positions in different subcells still belong to the same class even if they are not related by a symmetry operation of the supercell. The default is EQUIV=T.

4.15.13 Token CARTS= (cast logical)

This switch specifies whether the following entries for the shift vector are interpreted as Cartesian coordinates (CARTS=T) or as relative components in terms of the primitive translations (CARTS=F). The default value is CARTS=T.

4.15.14 Token PSHIFT= (cast double; length 3)

This token holds a shift vector, which is added to all atomic positions after a supercell has been constructed. Note, however, that in order to avoid confusion this token is interpreted only by routine mnscl.run. The default is PSHIFT= 0.0 0.0 0.0.

4.15.15 Token CARTQ= (cast logical)

This switch specifies whether the following entries for the spin wave vector are interpreted as Cartesian coordinates (CARTQ=T) or as relative components in terms of the primitive translations (CARTQ=F). The default value is CARTQ=T.

4.15.16 Token QSWAVE= (cast double; length 3)

With this token you may specify a spin wave vector for a (collinear) antiferromagnetic structure to be imprinted on the supercell. The simplest case is that of doubling the unit cell and treating the two subcells as the spin up and spin down sublattice. The spin wave vector must be given in units of 2π divided by the supercell lattice constant a; its default is QSWAVE= 0.0 0.0 0.0.

4.16 Category SYMLIN

This category comprises all the information needed for plotting the band structure. Note that the program contains a full database of high-symmetry points for all crystal lattices and all centering types. As a consequence, whenever, the entries for the high-symmetry points are left empty, they will be taken from the database.

4.16.1 Token NPAN= (cast integer)

This token holds the number of panels, which is the number of different symmetry lines in the Brillouin zone, along which the band structure is represented. The default is NPAN=0. However, note that for this token the same as for tokens NCLASS= and NBAS= holds. The number of symmetry lines will be calculated from the following entries, but token NPAN= can be used to hide additional entries from the program.

4.16.2 Token NPTS= (cast integer)

Here you can give the maximum number of points to be used for the band structure plot. The actual number will be calculated by the program and usually will be slightly less than the input given by this token. The default is NPTS=400. However, in case you choose to calculate orbital projected band structures (see below), you should use NPTS=200.

4.16.3 Token ORBWGT= (cast logical)

This switch allows to plot orbital projected band structures. If ORBWGT=T is selected the program will print out the eigenvectors for each **k** point in addition to the eigenvalues. This allows to evaluate the contribution from each orbital of the basis set to the wave function at each **k** point and for each band, which may be represented as the width of a bar attached to each $E(\mathbf{k})$ in the plot. The default is ORBWGT=F.

4.16.4 Token SPATH= (cast logical)

This switch allows to use spherical pathways for plotting the band structure. For SPATH=T the **k**-space path will be one the surface of a sphere with radius $\sqrt{E_{kin}+V_0}$, where E_{kin} is the kinetic energy of an electron leaving the crystal in a photoemission experiment and V_0 denotes the so-called inner potential. The path is further specified by the cleavage plane normal vector, which allows to distinguish the parallel and perpendicular (to the surface) components of the **k**-vector. While the former is given by

$$\sqrt{\frac{\hbar^2}{2m}}\mathbf{k}_{in,\parallel} = \sqrt{\frac{\hbar^2}{2m}}\mathbf{k}_{out,\parallel} = \sqrt{E_{kin}}\sin(\vartheta)$$

the latter can be calculated from

$$\sqrt{\frac{\hbar^2}{2m}}\mathbf{k}_{in,\perp} = \sqrt{E_{kin}+V_0-\frac{\hbar^2}{2m}\mathbf{k}^2_{in,\parallel}} = \sqrt{E_{kin}\cos^2(\vartheta)+V_0}$$

The default is SPATH=F.

4.16.5 Token EKPV0= (cast double)

With this token the value of $\sqrt{E_{kin}+V_0}$, i.e. the radius of the sphere in **k**-space is specified. The default value is EKPV0=0.0.

4.16.6 Token CPNORM= (cast double; length 3)

With this token the cleavage plane is specified, which allows to distinguish the parallel and perpendicular (to the surface) components of the **k**-vector. By default, all components of the cleavage plane normal vector are set to zero.

4.16.7 Token CARTN= (cast logical)

This switch specifies whether the entry for the cleavage plane normal vector is interpreted as Cartesian coordinates (CARTN=T) or as relative components in terms of the primitive translations (CARTN=F). The default value is CARTN=T.

4.16.8 Token CARTE= (cast logical)

This switch specifies whether the following entries for the end points of the symmetry lines are interpreted as Cartesian coordinates (CARTE=T) or as relative components in terms of the primitive translations (CARTE=F). The default value is CARTE=T.

4.16.9 Token LABEL= (cast character)

There exists standard notation for labelling the high symmetry points of the first Brillouin zone. These labels are usually appended to the band structure plots.

4.16.10 Token ENDPT= (cast double; length 3)

This token holds the end points of the symmetry lines, along which the band structure should be plotted.

4.17 Category PLOT

The last category contains information to be used for 3D plots of e.g. the crystal structure, the charge density or the potential. This comprises a set of vectors confining the plot space (a line, a plane or a volume) as well as the divisions along these vectors.

4.17.1 Token CARTV= (cast logical)

This switch specifies whether the following entries for the plot vectors are interpreted as Cartesian coordinates (CARTV=T) or as relative components in terms of the primitive translations (CARTV=F). The default value is CARTV=T.

4.17.2 Token ORIGIN= (cast double; length 3)

This token is useful, if the origin of the plotting volume deviates from the origin of the unit cell as specified by token PLAT= in category STRUC. Default is ORIGIN= 0.0 0.0 0.0.

4.17.3 Token RPLOT1= (cast double; length 3)

First plot vector specifying the plot space. Default is RPLOT1= 0.0 0.0 0.0.

4.17.4 Token RPLOT2= (cast double; length 3)

Second plot vector specifying the plot space. Default is RPLOT2= 0.0 0.0 0.0.

4.17.5 Token RPLOT3= (cast double; length 3)

Third plot vector specifying the plot space. Default is RPLOT3= 0.0 0.0 0.0.

4.17.6 Token NPDIV1= (cast integer)

Number of divisions along the first plot vector. Default is NPDIV1=50.

4.17.7 Token NPDIV2= (cast integer)

Number of divisions along the first plot vector. Default is NPDIV2=50.

4.17.8 Token NPDIV3= (cast integer)

Number of divisions along the first plot vector. Default is NPDIV3=50.

Appendix A
The ASW database

Over the years many people using the ASW method have contributed to what is now called the ASW database. It consists of a large number of CTRL files for various elemental systems and compounds. The complete list of files, which have been used for calculations with one of the 2nd generation versions, is given below.

```
 CTRL files in the ASW-2.5 database:
 (status as of 14.01.2009: 256 entries)

CTRL_Ag                 CTRL_CrCl3trgaf    CTRL_LaNi9Ge4:Cu3          CTRL_Sc3MnC4
CTRL_AgAlO2             CTRL_CrF3              CTRL_LaNi9Si4                    CTRL_Sc3NiC4
CTRL_AgGaO2             CTRL_CrF3af        CTRL_Li                              CTRL_Sc3OsC4bco
CTRL_AgI      CTRL_CrI3              CTRL_LiCoO2            CTRL_Sc3OsC4cm
CTRL_AgInO2             CTRL_CrI3af        CTRL_LiCrO2                CTRL_Sc3RuC4bco
CTRL_AgScO2             CTRL_CrO2              CTRL_LiF                         CTRL_Sc3RuC4cm
CTRL_Al                 CTRL_CrO2af        CTRL_LiH                             CTRL_Si
CTRL_Al2O3alp           CTRL_CrO2fe        CTRL_LiRh2O4               CTRL_Sm
CTRL_AlP      CTRL_Cs                CTRL_Lu                          CTRL_SmS
CTRL_Ar                 CTRL_CsI               CTRL_Mg                          CTRL_Sn
CTRL_Au                 CTRL_Cu                CTRL_MgCO3             CTRL_SnO2
CTRL_Ba                 CTRL_Cu3VO4        CTRL_MgO                             CTRL_SnS
CTRL_BaHfO3             CTRL_Cu4               CTRL_Mn                          CTRL_SnS2-18R
CTRL_BaNiO2             CTRL_Cu8               CTRL_Mn3Ga             CTRL_SnS2-2H
CTRL_BaNiO3             CTRL_CuAlO2        CTRL_Mn3Gafi               CTRL_SnSe2-18R
CTRL_BaO      CTRL_CuCrO2        CTRL_Mn3Sn                 CTRL_SnSe2-2H
CTRL_Be                 CTRL_CuFeO2        CTRL_MnO                             CTRL_Sr
CTRL_Be2C     CTRL_CuFeO2-2H     CTRL_MnOrh                 CTRL_Sr3P2O8:Eu
CTRL_[BEDT-TTF]2I3  CTRL_CuFeO2mon     CTRL_Mo                        CTRL_SrAu3In3
CTRL_BeO      CTRL_CuFeO2monfi   CTRL_MoO2fcc               CTRL_SrBPO5
CTRL_Bi2Pd3S2bcc    CTRL_CuGaO2        CTRL_MoO2mon                   CTRL_SrBPO5:Eu
CTRL_Bi2Pd3S2cm     CTRL_CuInO2        CTRL_MoO3            CTRL_SrCuO2
CTRL_Bi2Pd3Se2          CTRL_CuInS2        CTRL_Na                              CTRL_SrO
CTRL_BN                 CTRL_CuRhO2        CTRL_NaxCoO2so002          CTRL_SrTiO3
CTRL_C                  CTRL_Dy                CTRL_NaxCoO2so010      CTRL_Ta
CTRL_C3N4beta           CTRL_Er                CTRL_NaxCoO2so080      CTRL_Tb
CTRL_C60      CTRL_Es                CTRL_NaxCoO2so109      CTRL_Tc
CTRL_Ca                 CTRL_EuO               CTRL_NaxCoO2so128      CTRL_Th
CTRL_Ca3Au3In           CTRL_EuS               CTRL_NaxCoO2so223      CTRL_Ti
```

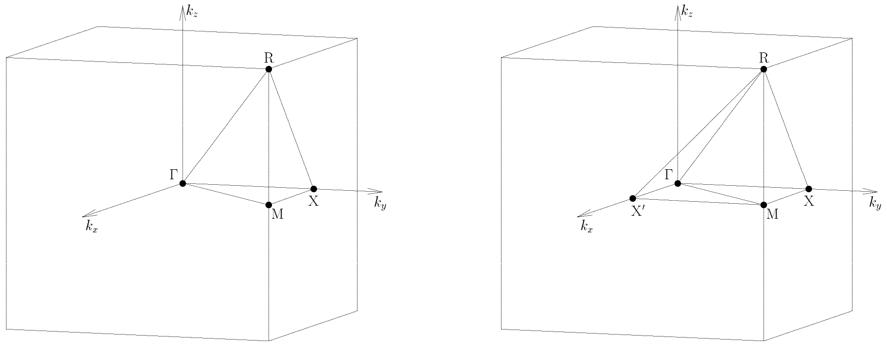
```
CTRL_Ca3Ru2O7ht     CTRL_Fe          CTRL_NaxCoO2so300      CTRL_Ti2O3ht
CTRL_Ca3Ru2O7lt     CTRL_Fe2         CTRL_NaxCoO2so450      CTRL_Ti2O3rt
CTRL_CaCu3Ru4O12    CTRL_Fe4         CTRL_Nb                          CTRL_TiB
CTRL_CaNiN              CTRL_Fe8               CTRL_NbO                         CTRL_TiO
CTRL_CaO      CTRL_FeC24S2N6     CTRL_NbSe2-2H              CTRL_TiO2ant
CTRL_CaTe2O5            CTRL_FeS2              CTRL_Nd                          CTRL_TiO2rut
CTRL_Cd                 CTRL_Ga2O3             CTRL_Ne                          CTRL_TiSi2fco
CTRL_CdCr2S4            CTRL_GaN               CTRL_[NH2CH2COOH]2*HNO3          CTRL_TiSi2sco
CTRL_CdS      CTRL_GaP               CTRL_Ni                          CTRL_TiTe2
CTRL_Ce                 CTRL_Gd                CTRL_Ni2MnGa           CTRL_Tl
CTRL_Ce2RuZn4           CTRL_GdN               CTRL_NiS                         CTRL_TlI
CTRL_CeNi9Ge4           CTRL_GdS               CTRL_NiSisc            CTRL_Tm
CTRL_CeNi9Ge4:Cu1   CTRL_Ge          CTRL_NiSiso            CTRL_U
CTRL_CeNi9Ge4:Cu2   CTRL_H           CTRL_Os                          CTRL_UB2
CTRL_CeNi9Ge4:Cu3   CTRL_He          CTRL_OsS2              CTRL_UB4
CTRL_CeNi9Si4           CTRL_Hf                CTRL_Pb                          CTRL_UB6
CTRL_CeRhSn             CTRL_Hg                CTRL_Pd                          CTRL_UO2
CTRL_CeRuSn             CTRL_Ho                CTRL_PdCoO2            CTRL_V
CTRL_CH3ReO3            CTRL_In                CTRL_Pr                          CTRL_VH
CTRL_CN2      CTRL_In2O3             CTRL_PrRuSn            CTRL_VO
CTRL_Co2MnGe            CTRL_In2VO5        CTRL_Pt                              CTRL_W
CTRL_Co2O3hs            CTRL_In2VO5af      CTRL_PtCoO2                CTRL_Xe
CTRL_Co2O3ls            CTRL_InP               CTRL_Pu                          CTRL_Y
CTRL_Co3In2S2           CTRL_Ir                CTRL_Rb                          CTRL_Yb
CTRL_CoO      CTRL_IrO2rut       CTRL_Re                              CTRL_YB6
CTRL_CP2      CTRL_K                 CTRL_Rh                          CTRL_YF3
CTRL_Cr                 CTRL_KB6               CTRL_RhO2              CTRL_YFe2
CTRL_Cr2F5              CTRL_Kr                CTRL_Ru                          CTRL_Zn
CTRL_CrBr3              CTRL_La                CTRL_RuC                         CTRL_ZnCr2Se4
CTRL_CrBr3af            CTRL_LaBaCo2O55    CTRL_RuS2                  CTRL_ZnO
CTRL_CrCl2              CTRL_LaCoO3        CTRL_Sc                              CTRL_ZnS
CTRL_CrCl2af            CTRL_LaMnO3so      CTRL_Sc3C4                 CTRL_ZnV2O4ht
CTRL_CrCl3              CTRL_LaNi9Ge4      CTRL_Sc3CoC4               CTRL_ZnV2O4lt
CTRL_CrCl3af            CTRL_LaNi9Ge4:Cu1  CTRL_Sc3FeC4               CTRL_Zr
CTRL_CrCl3trg           CTRL_LaNi9Ge4:Cu2  CTRL_Sc3FeC4af             CTRL_ZrFe2
```

In addition, there exist a lot of CTRL files, which are still in the format used by the 1st generation version and have not yet been transformed. However, they would be fully compatible with the 2nd generation programs.

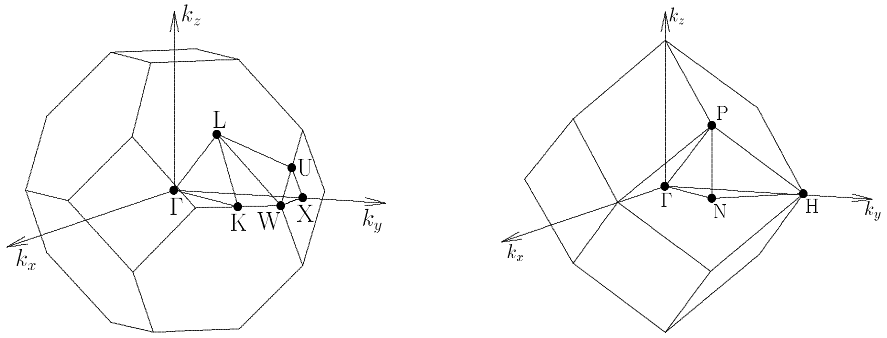
Whenever you want to perform a calculation for one of the systems already in the database just copy the CTRL file. However, please read the README file contained in the database before. In turn, I do welcome any new CTRL file.

Appendix B
Brillouin zones

This Appendix displays the Brillouin zones of some lattices.

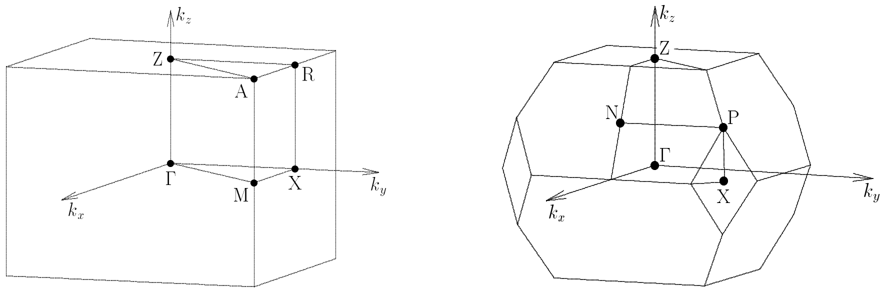


(a) simple cubic (b) T_h^6 structure



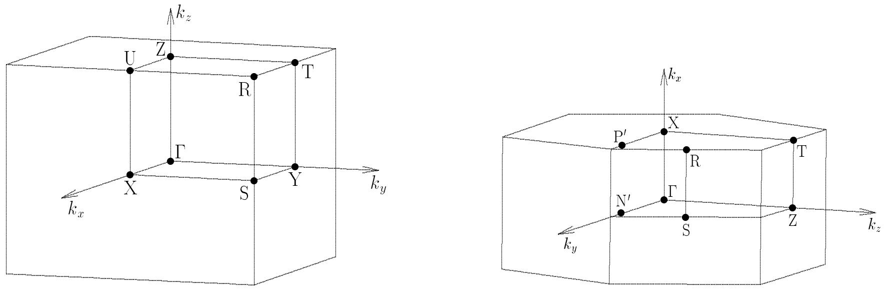
(c) face-centered cubic (d) body-centered cubic

Figure B.1 Brillouin zones of cubic lattices.



(a) simple tetragonal (b) centered tetragonal

Figure B.2 Brillouin zones of tetragonal lattices.



(a) simple orthorhombic (b) base-centered orthorhombic

Figure B.3 Brillouin zones of orthorhombic lattices.

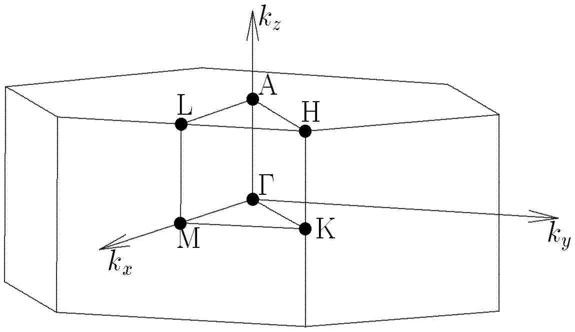
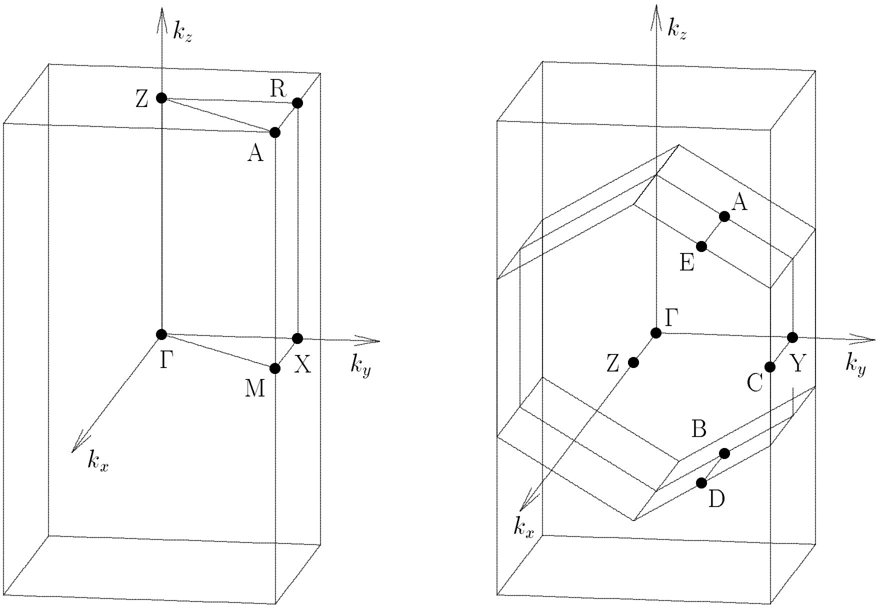


Figure B.4 Brillouin zones of hexagonal lattice.



(a) simple tetragonal (b) simple monoclinic

Figure B.5 Brillouin zones of rutile and related structures.

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