
**Theoretical Material Science: Electronic structure theory at
the computer**

**Exercise Sheet 9: Electron band structure and density of
states**

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Some rules on expected documentation from this exercise.

The computational exercises are intended as “hands-on” experience with actual, numerical electronic structure theory. Our main goal is to fill some of the basic concepts with life for real systems.

This exercise is intended in parts as a live exercise, with the remainder to be completed as **homework**. The calculations can be performed at the “PC pool” during its opening hours.

Please hand in your solutions to the exercise individually, as you would normally do. What is expected is a record of the basic data that we ask for (e.g., in table form), rough answers to the questions asked (answers can be short, but should be there and should indicate that you understood the meaning of your data), and plots, where required.

For required plots, please use the printer in the PC pool and append them to your exercise materials. As you may know, printed pages usually cost 5 cents per page on that printer. *However*, for the purposes of the exercise, a contingent of free pages has been agreed upon. If you are doing printouts for this class, please mention this to the administrators.

Please note that the page contingent is not gigantic – so be careful and do not print excessively many pages. A few pages at most should be sufficient for the solutions, anyway.

Please hand in all your solutions as usual at the beginning of the exercise in the following week.

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1 Background

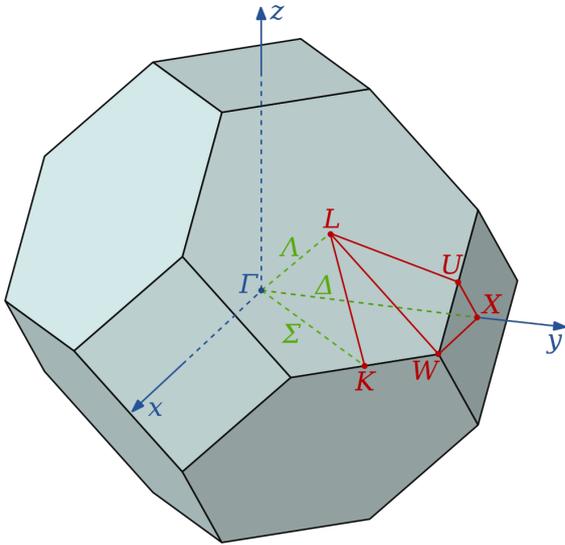


Figure 1: Brillouin zone of the fcc lattice. (taken from Wikipedia)

methodological uncertainty about which exact level of that theory should be employed. In addition, for many years the “band structure” emerging from density functional theory really was the only electronic structure free of empirical parameters that could be calculated to interpret carrier levels, doping, chemical bonding etc. As such, it still has enormous reach in the community as a baseline against which “better” (formally more rigorous) approximations are compared.

As a reminder, Figure 1 shows the Brillouin zone of the fcc lattice and a few high-symmetry directions (the lines between certain high-symmetry k -points). These are the lines along which one typically plots and interprets aspects of the bandstructure $\epsilon_n(\mathbf{k})$. For the present exercise, five points are specifically relevant:

- Γ : Located at $(0,0,0)$ in units of the reciprocal lattice.
- L : Located at $(0.5,0.5,0.5)$ in units of the reciprocal lattice of the primitive fcc cell.
- X : Located at $(0.0,0.5,0.5)$ in units of the reciprocal lattice of the primitive fcc cell.
- W : Located at $(0.25,0.5,0.75)$ in units of the reciprocal lattice of the primitive fcc cell.
- K : Located at $(0.375,0.375,0.75)$ in units of the reciprocal lattice of the primitive fcc cell.

2 Important notes

- This exercise should be performed using exclusively the local-density approximation (LDA) to density-functional theory. Do not choose Hartree-Fock theory by accident.
- Throughout this exercise, use only “light” settings for the species defaults of FHI-aims. This will suffice to demonstrate the principle. In a complete scientific project, one would want to verify the key results with converged “tight” settings, but this is not required here due to the time involved.
- The density of states calculations requested in this exercise can take some time (the Brillouin zone needs to be integrated very accurately for good results). Be sure to refer to the values recommended in this script.

In this exercise, we will use the structure predictions of exercises 18 and 19 as a basis to investigate the electronic structure of three prototypical semiconductors (Si, GaAs, ZnSe) and one metallic phase (fcc Si).

In the present exercise, we will use the eigenvalues calculated in Kohn-Sham density functional theory (DFT-LDA) as an approximation to the actual electronic structure of each semiconductor. We already know from the lecture that, strictly, this “approximation” will be limited in reach. Formally, the Kohn-Sham eigenlevels are nothing more than the Lagrange parameters of the fictitious non-interacting Kohn-Sham system, and we should be using a real many-body theory of quasiparticle levels (e.g., in the GW approximation) instead.

For one thing, however, proper GW calculations are expensive, and there is still some

3 Reminder: FHI-aims at the “PC pool”

As a quick reminder, here is (again) an overview of the most important pieces needed for FHI-aims at the “PC pool”.

- To run the code, create the necessary input files (`control.in` and `geometry.in`) in a working directory of your choice.
- For the present exercise, be sure to use more than one processor to run FHI-aims:

```
mpirun -np 2 aims.scalapack.mpi.x | tee calculation.out
```

As before, although you should not need it, there is a complete manual (pdf) for the FHI-aims code located in `/media/public/TFKP_2012/FHI-aims.pdf`.

4 Exercise 21: Electronic structure in semiconductors

We have learned some of the basics regarding the electronic properties of materials namely, bandstructure and DOS. Besides, in the last exercise sheet, we have computed the cohesive properties of real materials. Without cohesive properties, we would not be able to predict (without empirical parameters) the electronic properties of materials. Now, we are ready to compute the bandstructure and DOS of real materials. In this exercise, we will achieve this goal for semiconductor materials.

4.1 Exercise 21a: Bandstructure and DOS of the diamond phase of Si

To complete this exercise, we require the equilibrium lattice parameter a_0 corresponding to the diamond phase of Si, which was computed in the Exercise Sheet 8. You may use $a_0=5.416$ Å for that purpose. We have already ascertained that a k -space integration grid of density $12\times 12\times 12$ is more than sufficient for accurate calculations of diamond Si.

4.1.1 Calculating the bandstructure and DOS

As usual, it is a good idea to generate a directory

```
mkdir Si_diamond
```

and enter the directory with:

```
cd Si_diamond
```

We recall the geometry input file `geometry.in`:

```
lattice_vector  0.0 <0.5*a0> <0.5*a0>
lattice_vector  <0.5*a0> 0.0 <0.5*a0>
lattice_vector  <0.5*a0> <0.5*a0> 0.0

atom_frac      0.0 0.0 0.0 Si
atom_frac      0.25 0.25 0.25 Si
```

Where a_0 is the equilibrium lattice constant calculated in Exercise Sheet 8. As a check, do not forget to visualize the structure:

```
jmol geometry.in &
```

and (in jmol) use the right mouse button and choose from the menu the category

Symmetry

and then

```
Reload: {444 666 1} .
```

We next recall our computational choices in `control.in` and add further settings related to the calculation of the bandstructure and DOS in FHI-aims:

```
# Physical settings
xc          pw-lda
spin       none

# SCF settings
sc_accuracy_eev  1E-3
sc_accuracy_rho  1E-5
sc_accuracy_etot 1E-6
sc_iter_limit    100

# k-grid settings
k_grid  12 12 12

# Density of states
output dos -30 0 1000 0.1
dos_kgridfactors 5 5 5

# High-symmetry k-points for diamond bandstructure output
output band 0.5 0.5 0.5 0.0 0.0 0.0 50 L Gamma
output band 0.0 0.0 0.0 0.0 0.5 0.5 50 Gamma X
output band 0.0 0.5 0.5 0.25 0.5 0.75 50 X W
output band 0.25 0.5 0.75 0.375 0.375 0.75 50 W K
```

What does this mean?

For the s.c.f. cycle (to converge the electron density, total energy etc.), we have chosen a $12 \times 12 \times 12$ k -space integration grid as established before.

The density of states, however, is a more complex integral over the Brillouin zone:

$$g(\epsilon) \sim \sum_n \int_{\text{BZ}} d^3k \delta[\epsilon - \epsilon_n(\mathbf{k})], \quad (1)$$

where ϵ is the energy we are currently evaluating, and n is the band index.

This expression, however, is nothing which we can evaluate directly in a computation. For one thing, the k space integration grid is discrete. Related, the Dirac δ function will not go over well with a computer. For a finite k -space grid, we compute instead:

$$g(\epsilon) \sim \sum_n \sum_k w[\epsilon - \epsilon_n(\mathbf{k}), \sigma], \quad (2)$$

where the integral has been replaced by a sum over k -points on a grid that span the Brillouin zone. The Dirac δ function has been replaced by a Gaussian broadening function w (width σ) that approximates the Dirac δ , and that “smears out” the discrete eigenlevels at given \mathbf{k} -points to the ϵ values inbetween. Now everything is continuous, and by using a denser k -grid and narrower width σ , we can systematically approach the true expression Eq. (1).

In order to perform a DOS calculation in FHI-aims, the following choices are thus required:

```
output dos <Estart> <Eend> <n_points> <broadening>
dos_kgrid_factors <n1> <n2> <n3>
```

`Estart` and `Eend` are the lower and upper bound of the energy range for which the DOS will be computed. These values should be chosen to enclose the valence electron range reasonably well (−30 eV to 0 eV in the above choice). We compute the DOS for an integer number `n_points` of points, here 1000. Finally, the Gaussian function w has a width (“broadening”) of 0.1 eV.

For the DOS (which is not a single number, but instead spread out over an energy interval), it would turn out that the simple $12 \times 12 \times 12$ grid used for the density and total energy would not yet be enough. What we can do instead is to use a refined k -space integration grid only for the calculation of the DOS. After self-convergence is reached, the DOS is computed using a new k -grid with the dimensions `kn(1)*n1`, `kn(2)*n2`, `kn(3)*n3`, where `kn(i)` are dimensions of the original k -point grid during s.c.f. convergence, made denser by factors `n1`, `n2`, and `n3` for the DOS convergence.

One can thus converge the DOS very well if one has the time. The settings we will use in the present exercise are on the low end of the converged range (but converged for what we need!) in order to save time on the expensive Brillouin zone integral.

To calculate the bandstructure, we have to specify the requested high symmetry points to FHI-aims. This is achieved by the choice:

```
output band <kstart1> <kstart2> <kstart3> <kend1> <kend2> <kend3> <n_points>
<name_start> <name_end>
```

which plots a band from `<kstart1,kstart2,kstart3>` to `<kend1,kend2,kend3>` at `n_points` equally spaced points. The k -vectors are written in relative coordinates of the reciprocal basis vectors. `name_start` corresponds to the name of the starting k -vector and `name_end` corresponds to the name of the ending k -vector.

Finally, we add “light” settings to complete the `control.in` file for Si:

```
> cat /media/public/TFKP_2012/species_defaults/light/14.Si_defaults >>
control.in
```

We can now run the calculation, for example:

```
> mpirun -np 2 aims.scalapack.mpi.x | tee Si_diamond.out
```

4.1.2 Visualizing the bandstructure and the DOS

After a calculation with FHI-aims is performed, some postprocessing is required in order to visualize the bandstructure and DOS. Fortunately, the script `aimsplot.py` will help as long as the `control.in` and `geometry.in` files are in the same directory.

To visualize the bandstructure and the DOS, run the `aimsplot.py` script, `geometry.in` and `control.in` *should be at the same directory*. Simply type:

```
> /media/public/TFKP_2012/bin/aimsplot.py
```

You will see a graphic interface with the bandstructure and the DOS plots. For instance, you can save in different formats to print later.

Note that the energy zero on the plot is chosen as what is written out to be the chemical potential. Since we have a band gap, its location must be somewhere between the valence band maximum and the conduction band minimum, but its exact place is here a purely technical thing, determined by the exact choice of the occupation numbers near the Fermi level.

You are able to answer the questions in the corresponding Exercise Sheet.

- Take a look at the DOS and identify the semiconductor behaviour.

- Search for the maximum of the valence band (VB) and the minimum of the conduction band (CB) in the bandstructure and identify if you are dealing with either direct or indirect bandgap semiconductor. Mark your findings in the plot.
- By inspecting the location and occupation numbers of the “highest occupied” and “lowest unoccupied” levels in the final s.c.f. iteration, extract the LDA bandgap value, compare it with the experimental value of 1.17 eV, and comment on it.

Of course, as in previous exercise, you may also want to rely on the written output of FHI-aims. For each band, the band gap along that k -space direction is given.

4.2 Exercise 21b: Bandstructure and DOS of GaAs and ZnSe

Both materials crystallize in the zincblende structure. They are semiconductors with practical applications. As before, we require the equilibrium lattice parameter a_0 of both materials computed in the Exercise Sheet 8. Due to computational time use a k -space integration grid of density $8 \times 8 \times 8$.

4.2.1 Calculating the bandstructure and DOS of GaAs and ZnSe

In the case of GaAs, generate a directory

```
mkdir GaAs
```

and enter the directory with:

```
cd GaAs
```

Repeat the same procedure for ZnSe.

The geometry input file `geometry.in` for the zincblende structure is:

```
lattice_vector  0.0 <0.5*a0> <0.5*a0>
lattice_vector  <0.5*a0> 0.0 <0.5*a0>
lattice_vector  <0.5*a0> <0.5*a0> 0.0

atom_frac      0.0 0.0 0.0 Ga
atom_frac      0.25 0.25 0.25 As
```

Again, a_0 are the equilibrium lattice parameters calculated in Exercise Sheet 8. You may use $a_0=5.624$ Å for GaAs and $a_0=5.588$ Å for ZnSe.

Note: The `geometry.in` file is also valid for ZnSe if you specify Zn and Se instead of Ga and As, and use the corresponding lattice constant a_0 .

You can visualize the structure:

```
jmol geometry.in &
```

and (in jmol) use the right mouse button and choose from the menu the category

Symmetry

and then

```
Reload: {444 666 1} .
```

We next recall our computational choices in `control.in` and add the settings related to the calculation of the bandstructure and DOS in FHI-aims as given above:

```

# Physical settings
xc          pw-lda
spin        none
relativistic atomic_zora scalar

# SCF settings
sc_accuracy_eev 1E-3
sc_accuracy_rho 1E-5
sc_accuracy_etot 1E-6
sc_iter_limit 100

# k-grid settings
k_grid 8 8 8

# Density of states
output dos -30 0 1000 0.1
dos_kgrid_factors 5 5 5

# High-symmetry k-points for diamond (and zincblende) bandstructure output
output band 0.5 0.5 0.5 0.0 0.0 0.0 50 L Gamma
output band 0.0 0.0 0.0 0.0 0.5 0.5 50 Gamma X
output band 0.0 0.5 0.5 0.25 0.5 0.75 50 X W
output band 0.25 0.5 0.75 0.375 0.375 0.75 50 W K

```

Here, we have chosen the LDA, as well as a $8 \times 8 \times 8$ k -space integration grid.

We are dealing with heavy elements. This means that the core electrons feel relativistic effects and FHI-aims will force you to choose an appropriate treatment of these effects. That is the reason to add the choice `relativistic atomic_zora scalar`, which, in brief, invokes a simple so-called “scalar relativistic” approximation to deal with relativistic effects.

As before we have used the choices

```
output dos <Estart> <Eend> <n_points> <broadening>
```

```
dos_kgrid_factors <n1> <n2> <n3>
```

to calculate the DOS and the choice:

```
output band <kstart1> <kstart2> <kstart3> <kend1> <kend2> <kend3> <n_points>
<name.start> <name.end>
```

to calculate the bandstructure along the high symmetry points as mentioned in the exercise sheet.

Note: The `control.in` file is also valid for ZnSe.

Finally, we add “light” settings to complete the necessary settings in the `control.in` file for GaAs:

```
> cat /media/public/TFKP_2012/species_defaults/light/31_Ga_default >> control.in
> cat /media/public/TFKP_2012/species_defaults/light/33_As_default >> control.in
```

Note: In the case of ZnSe:

```
> cat /media/public/TFKP_2012/species_defaults/light/30_Zn_default >> control.in
> cat /media/public/TFKP_2012/species_defaults/light/34_Se_default >> control.in
```

We can now run the calculation, for example:

```
> mpirun -np 2 aims.scalapack.mpi.x | tee GaAs.out
```

and later the same for ZnSe (in a different directory).

4.2.2 Visualizing the bandstructure and the DOS of GaAs and ZnSe

As before, to visualize the bandstructure and the DOS, run the `aimsplot.py` script, `geometry.in` and `control.in` should be in the same directory. Type:

```
> /media/public/TFKP_2012/bin/aimsplot.py
```

to see a graphic interface with the bandstructure and the DOS plots.

Visualize the bandstructure and the DOS for ZnSe in the same way.

Answer the questions in the corresponding Exercise Sheet.

- From the bandstructure, identify what type of semiconductors they are.
- By inspecting the location and occupation numbers of the “highest occupied” and “lowest unoccupied” levels in the final s.c.f. iteration, extract the LDA bandgap value and compare them with the experimental values values of 1.52 eV and 2.82 eV corresponding to GaAs and ZnSe respectively. Comment if you see any trend of LDA in predicting the bandgap of materials.
- Comparing the band structures of both materials, how different are they from one another and from Si? What is the effect of the d electrons of Zn and Ga? (Hint: The d bands are rather localized but still close to the valence range. They do not, however, participate directly in chemical bonding, as the d shell is closed for all atoms considered here. Thus, the d bands must be rather flat across the Brillouin zone and all contribute to the DOS for roughly the same energy only.
- Locate the minimum of the CB in both compounds (Γ point) and comment on the physical meaning of the curvature of the band centered at the Γ point.

5 Exercise 22: Electronic structure in metals

The purpose of this exercise is to show the drastic effect of the structure of a solid on its electronic (and, as a consequence, all other) properties. We here use fcc Si as an example, which is a metal. We will thus also learn about some features of a metallic band structure and DOS.

5.1 Bandstructure and DOS of the fcc phase of Si

To complete this exercise, we require the equilibrium lattice parameter a_0 corresponding to fcc phase of Si, which was computed in the Exercise Sheet 8 (use 3.834 Å). Use a k -space integration grid of density $12 \times 12 \times 12$.

Generate a directory

```
mkdir Si_fcc
```

and enter the directory with:

```
cd Si_fcc
```

We recall the geometry input file `geometry.in` for fcc:

```
lattice_vector    0.0 <0.5*a0> <0.5*a0>
lattice_vector    <0.5*a0> 0.0 <0.5*a0>
lattice_vector    <0.5*a0> <0.5*a0> 0.0

atom_frac         0.0 0.0 0.0 Si
```

We next recall our computational choices in `control.in` and add further settings related to the calculation of the bandstructure and DOS in FHI-aims:

```
# Physical settings
xc          pw-lda
spin        none

# SCF settings
occupation_type gaussian 0.1
empty_states 100
sc_accuracy_eev 1E-3
sc_accuracy_rho 1E-5
sc_accuracy_etot 1E-6
sc_iter_limit 100

# k-grid settings
k_grid 12 12 12

# Density of states
output dos -20 0 1000 0.1
dos_kgrid_factors 8 8 8

# High-symmetry k-points for diamond bandstructure output
output band 0.25 0.50 0.75 0.5 0.5 0.5 50 W L
output band 0.5 0.5 0.5 0.0 0.0 0.0 50 L Gamma
output band 0.0 0.0 0.0 0.0 0.5 0.5 50 Gamma X
output band 0.0 0.5 0.5 0.25 0.5 0.75 50 X W
```

Notice that we are using a denser k -space grid to integrate the DOS than for the case of semiconductors: The factors by which the original k -space grid from the s.c.f. cycle is increased are now (8, 8, 8). Together with the original k -grid of $12 \times 12 \times 12$, this makes for a $96 \times 96 \times 96$ integration mesh that is used for the DOS. Even this mesh is still at the low end of convergence for a metal, but it does generate a smooth-looking DOS. If we used a lighter Brillouin zone integration grid, the result would look noisy.

As we are dealing with a metal, we want to avoid a situation in which we obtain a Fermi level with fractional occupation numbers and possibly higher-lying states with a finite occupation (see last exercise sheet). We make the following choices:

- Add a finite “smearing” (broadening of occupation numbers) around the Fermi level.
`occupation_type gaussian 0.1`
- Include a larger number of Kohn-Sham orbitals than the default to the calculation above the Fermi level.
`empty_states 100`

Finally, we add “light” settings to complete the `control.in` file for Si:

```
> cat /media/public/TFKP_2012/species_defaults/light/14.Si_defaults >>
control.in
```

We can now run the calculation, for example:

```
> mpirun -np 2 aims.scalapack.mpi.x | tee Si.fcc.out
```

To visualize the bandstructure and the DOS, run the `aimsplot.py` script, `geometry.in` and `control.in` should be at the same directory. Type:

```
> /media/public/TFKP_2012/bin/aimsplot.py
```

You are able to answer the questions in the corresponding Exercise Sheet.

- Identify the metallic behaviour from the bandstructure and DOS.
- Look at the band structure and DOS and verify if and where it looks like the free electron case. You will also note areas where some bands become flat, known as van Hove singularities. Can you comment on their consequence for the DOS?