
Theoretical Material Science: Electronic Structure Theory at the Computer

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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.

If you are fast, you may finish the exercise below in the actual exercise class. If not, we ask you to try finish as much as you can, and then come back at another point, follow the script, and finish the exercise.

You can do the actual computations and hand in your solutions to the exercise in pairs of two. 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. You can just qualitatively draw the plots by hand in your homework or print them on paper or screenshot them and then hand-in your homework electronically via email as PDF.

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

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1 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.

2 Background

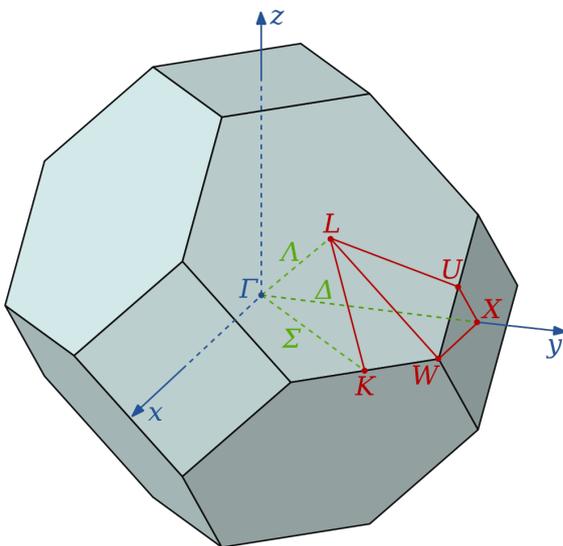


Figure 1: Brillouin zone of the fcc lattice. (taken from Wikipedia)

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 \mathbf{k} -points). These are the lines along which one typically plots and interprets the band structure $\epsilon_n(\mathbf{k})$ of compounds with an fcc lattice symmetry. 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.

In this exercise, we will use the structure predictions of exercises 14 and 15 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., the *GW* approximation) instead.

However, proper *GW* calculations are (still) expensive and they are not exact, either. In

3 Reminder: FHI-aims in the Virtual Machine

As a quick reminder, here is (again) an overview of the most important pieces needed for FHI-aims:

- To run the code, create the necessary input files (`control.in` and `geometry.in`) in a working directory of your choice.
- The calling sequence for FHI-aims is:

```
aims | tee calculation.out
```

As before, although you should not need it, there is a complete manual (pdf) for the FHI-aims code located in `/home/theory/fhi-aims.160328.3/FHI-aims.pdf`.

In this exercise sheet, we will use a *python* script to visualize and plot band structures and densities of states. This requires additional python libraries that you can install with the command:

```
sudo apt-get install python-matplotlib python-scipy
```

For this purpose, you will be requested to enter the password (“theory”) and to acknowledge the installation of additional, required packages (just press “Y” when asked for it). If you encounter any problems, e.g. “E: Could not get lock /var/lib/dpkg/lock”, reboot the virtual machine with the command: `sudo shutdown -r now`

After reboot, the commands

```
sudo dpkg --configure -a  
sudo apt-get install python-matplotlib python-scipy
```

should do the trick. Alternatively, you can just re-download and re-install the updated virtual machine instance that already contains these packages from <https://thcloud.rz-berlin.mpg.de/s/kElVkeik4aSfMEQ>. Please note that deleting the old virtual machine will also delete the data that you created with it during the previous exercises.

4 Exercise 16: Electronic Structure of Semiconductors

We have learned some of the basics regarding the electronic properties of materials namely, band structure 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 band structure and DOS of real materials. In this exercise, we will achieve this goal for semiconductors.

4.1 Exercise 16a: Band Structure 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 previous exercise sheet 5. You may use $a_0=5.416$ Å for that purpose. We have already ascertained that a \mathbf{k} -space integration grid of $12\times 12\times 12$ is more than sufficient for accurate calculations of diamond Si.

4.1.1 Calculating the Band Structure 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 5. 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 band structure and DOS in `FHI-aims`:

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

# SCF settings
sc_accuracy_eev  1E-2
sc_accuracy_rho  1E-4
sc_accuracy_etot 1E-5
sc_iter_limit    40

# 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 band structure 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 $12 \times 12 \times 12$ \mathbf{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, i.e., the integration, is however not trivial to evaluate numerically. For one thing, the \mathbf{k} space integration grid is discrete in our case. Furthermore, the Dirac δ function is similarly hard to represent in a numerical approach. For a finite \mathbf{k} -space grid, we thus compute:

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

where the integral has been replaced by a sum over \mathbf{k} -points on a grid that spans the Brillouin zone. The Dirac δ function has been replaced by a Gaussian function w (width the broadness σ) that approximates the Dirac δ , and that “smears out” the discrete eigenvalues at given \mathbf{k} -points. For increasingly denser \mathbf{k} -grids and narrower widths σ , this continuous expression systematically approaches the true expression given in 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 values ϵ , here 1000. Finally, the Gaussian function w has a width (“broadening”) of 0.1 eV.

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

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 band structure, 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 \mathbf{k} -vectors are written in relative coordinates of the reciprocal basis vectors. **name_start** corresponds to the name of the starting \mathbf{k} -vector and **name_end** corresponds to the name of the ending \mathbf{k} -vector.

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

```
> cat /home/theory/fhi-aims.160328.3/species_defaults/light/14.Si_defaults >>
control.in
```

We can now run the calculation, for example:

```
> aims | tee Si_diamond.out
```

4.1.2 Visualizing the Band Structure and the DOS

After a calculation with FHI-aims is performed, some postprocessing is required in order to visualize the band structure 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 band structure and the DOS, run the `aimsplot.py` script, `geometry.in` and `control.in` *should be in the same directory*. Simply type:

```
> /home/theory/fhi-aims.160328.3/utilities/aimsplot.py
```

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

In case of problems with `aimsplot.py`, please see Sec. 3.

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 value is a purely technical thing here and determined by the occupation numbers near the Fermi level.

You are able to answer the questions in the corresponding exercise sheet, now.

- Take a look at the DOS and identify the semiconductor behaviour (“Is there a band gap?”).
- Search for the maximum of the valence band (VB) and the minimum of the conduction band (CB) in the band structure and identify if you are dealing with a direct or indirect band gap semiconductor. Mark your findings in the plot.
- By inspecting the location and occupation numbers of the “highest occupied” and “lowest unoccupied” levels, extract the LDA band gap value, compare it with the experimental value of 1.17 eV, and comment on it. Note that FHI-aims now gives you two values for the band gap: One after the final s.c.f. iteration (“ESTIMATED overall HOMO-LUMO gap:”) and one after the band structure calculation (“Band gap of total set of bands:”). Do they give the same value? If not, why?

4.2 Exercise 16b: Band Structure 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 5. Use a \mathbf{k} -space integration grid of $12 \times 12 \times 12$ in both cases.

4.2.1 Calculating the Band Structure 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 is the equilibrium lattice parameter calculated in exercise sheet 5. 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 band structure 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-2
sc_accuracy_rho  1E-3
sc_accuracy_etot 1E-5
sc_iter_limit    40

# k-grid settings
k_grid  12 12 12

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

# High-symmetry k-points for diamond (and zincblende) band structure 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 LDA, as well as a $12 \times 12 \times 12$ \mathbf{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 band structure along the high symmetry points as mentioned in the exercise sheet.

Note: So far, 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 /home/theory/fhi-aims.160328.3/species_defaults/light/31_Ga_default >>
control.in
> cat /home/theory/fhi-aims.160328.3/species_defaults/light/33_As_default >>
control.in
```

For ZnSe, use:

```
> cat /home/theory/fhi-aims.160328.3/species_defaults/light/30_Zn_default >>
control.in
> cat /home/theory/fhi-aims.160328.3/species_defaults/light/34_Se_default >>
control.in
```

We can now run the calculation:

```
> aims | tee GaAs.out
```

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

4.2.2 Visualizing the Band Structure and the DOS of GaAs and ZnSe

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

```
> /home/theory/fhi-aims.160328.3/utilities/aimsplot.py
```

to see a graphic interface with the band structure and the DOS plots.

In case of problems with `aimsplot.py`, please see Sec. 3.

Visualize the band structure and the DOS for ZnSe in the same way.

Answer the questions in the corresponding exercise sheet.

- From the band structure, identify what type of semiconductors they are.
- By inspecting the location and occupation numbers of the “highest occupied” and “lowest unoccupied” levels, extract the LDA band gap values and compare them with the experimental values of 1.52 eV and 2.82 eV of GaAs and ZnSe, respectively. Compare the values after the final s.c.f. iteration (“ESTIMATED overall HOMO-LUMO gap:”) and the one after the band structure calculation (“Band gap of total set of bands:”). Do they give the same value? If not, why? Comment if you see any trend of LDA in predicting the bandgap of materials (e.g., an almost constant shift or factor).
- Comparing the band structures of both materials, how different are they from one another and from Si (How broad are the bands)? 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 are rather flat across the Brillouin zone and 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 (Hint: “effective mass”).

5 Exercise 17: 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 Band Structure and DOS of the FCC Phase of Si

To complete this exercise, we require the equilibrium lattice parameter a_0 corresponding to the fcc phase of Si, which was computed in exercise sheet 5 (use 3.834 Å). Use a \mathbf{k} -space integration grid of $12 \times 12 \times 12$.

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 band structure 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-2
sc_accuracy_rho 1E-4
sc_accuracy_etot 1E-5
sc_iter_limit 40

# 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 band structure 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 an even denser \mathbf{k} -space grid to integrate the DOS than in the case of semiconductors: The factors by which the original \mathbf{k} -space grid from the s.c.f. cycle is increased are now (8, 8, 8). Together with the original \mathbf{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 an almost 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 make the following choices (see exercise sheet 5):

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

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

```
> cat /home/theory/fhi-aims.160328.3/species_defaults/light/14.Si_defaults >>
control.in
```

We can now run the calculation:

```
> aims | tee Si_fcc.out
```

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

```
> /home/theory/fhi-aims.160328.3/utilities/aimsplot.py
```

In case of problems with `aimsplot.py`, please see Sec. 3.

You are able to answer the questions in the corresponding exercise sheet.

- Identify the metallic behaviour from the band structure and DOS (“Is there a band gap?”).
- 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 (How does the DOS look there and why?)?