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

Exercise 14: Brillouin zone integration

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 as a **homework** exercise, to be performed at the “PC pool” during its opening hours. While the background section of the script is long, the actual exercise should be short as far as the computations go.

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

In a periodic potential, Bloch’s theorem states that the effective single-particle eigenfunctions have the following form:

$$\varphi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}). \quad (1)$$

Here, $u_{n,\mathbf{k}}(\mathbf{r})$ is a function that has the exact same periodicity as the potential itself. Only the phase of the eigenfunction will be different in different unit cells. \mathbf{k} denotes the “crystal momentum”, a continuous quantum number whose unique values are restricted to a single unit cell of the reciprocal space. Conventionally, one discusses the first Brillouin zone (the Wigner-Seitz cell of the reciprocal lattice), but in fact any other unit cell of reciprocal space would do as well.

For a *given* periodic potential, \mathbf{k} is a good quantum number, and the effective single-particle equations can be solved independently for any given \mathbf{k} , without the solutions from any other $\mathbf{k} \neq \mathbf{k}'$ interfering. Eigensolutions at different \mathbf{k} -points are decoupled. We only have to solve one \mathbf{k} -point at a time, not all of them at once.

For each \mathbf{k} -point, the single-particle Schrödinger equation still has multiple different solutions, just like in a non-periodic system. Different states n label these different solutions $\{\varphi_{n,\mathbf{k}}(\mathbf{r})\}$ with different eigenvalues $\epsilon_{n,\mathbf{k}}(\mathbf{r})$.

1.1 Relevance for density-functional theory

Happily, our “most productive” workhorse theory, Kohn-Sham density-functional theory, relies on solving effective single-particle equations. We can do this in a periodic potential. The Kohn-Sham eigenfunctions and eigenvalues then take exactly the form above: $\{\varphi_{n,\mathbf{k}}(\mathbf{r}), \epsilon_{n,\mathbf{k}}(\mathbf{r})\}$. For a *given* potential $v_{\text{eff}}(\mathbf{r})$, these solutions can be obtained independently at each \mathbf{k} -point. Formally, they are decoupled.

Only when we use the solutions $\varphi_{n,\mathbf{k}}(\mathbf{r})$ from all \mathbf{k} -points to create a new density $n(\mathbf{r})$ and, subsequently, a new potential $v_{\text{eff}}(\mathbf{r})$ in a self-consistency cycle we do couple results from different \mathbf{k} -points. But this is only an implicit coupling to get to the self-consistent density $n_0(\mathbf{r})$. Once we have $n_0(\mathbf{r})$, the actual Kohn-Sham equations are still decoupled.

This is an excellent result. A macroscopic solid has $O(10^{23})$ particles, and if one were to solve the full many-body Schrödinger equation with all electrons explicitly, their motion would *not* be spatially periodic. Sure, the time average of their motion (their density and their correlation functions) would be periodic, but one could not decouple the electrons in different unit cells from one another in a simple way.

Density-functional theory is different: We have hidden the correlated motion of all the “real” electrons inside a simple potential $v_{\text{xc}}(\mathbf{r})$. As a result, the physical ground state density is periodic, the effective potential is periodic, and we can use Bloch’s theorem to describe the effective single-particle states of the Kohn-Sham equations. Instead of having to describe all unit cells together and explicitly, we only need to describe the contents of a single unit cell explicitly. For the observable quantities—in Kohn-Sham theory, the ground state total energy E_0 and the ground-state density $n_0(\mathbf{r})$ —we are still exact, as long as we make no approximations to $v_{\text{xc}}(\mathbf{r})$.

Of course, in practice we must approximate $v_{\text{xc}}(\mathbf{r})$, but the approximations that we have can be very good indeed. Bloch’s theorem and density-functional theory give us an excellent starting point for a theory of real materials, as long as they are (somewhat) periodic.

1.2 Brillouin zone integrals

We wish to describe the properties of an infinite, periodic solid by solving the Kohn-Sham equations. If we look at the transition from non-periodic to periodic systems, we realize that some very important quantities now become integrals of the Brillouin zone. For example, the density:

$$n_0(\mathbf{r}) = \begin{cases} \sum_i f_i |\varphi_i(\mathbf{r})|^2 & \text{(non - periodic)} \\ \sum_n \int_{\text{BZ}} d^3k [f_{n,\mathbf{k}} \cdot |\varphi_{n,\mathbf{k}}(\mathbf{r})|^2] & \text{(periodic)} \end{cases} \quad (2)$$

or the sum of occupied eigenvalues:

$$\sum_n \int_{\text{BZ}} d^3k [f_{n,\mathbf{k}} \cdot \epsilon_{n,\mathbf{k}}] \quad , \quad (3)$$

which contains the kinetic energy $T_s[n]$.¹ i denotes the states of a non-periodic system, and the f_i and $f_{n,\mathbf{k}}$ denote the occupation numbers (for instance, from a Fermi function at finite temperature) in non-periodic and periodic systems, respectively.

We have thus circumvented the “big” problem of the full correlated solid, but a small problem remains. To obtain the density and total energy, we still have to solve continuous integral at (theoretically) infinitely many \mathbf{k} -points (all located in a single unit cell of reciprocal space). In practice, we thus need another approximation: We need to solve the resulting integrals, for instance by discretizing \mathbf{k} -space to a few \mathbf{k} -points only and rewriting the integral approximately as a weighted sum (an integral over a step function, as in elementary mathematics):

$$\sum_n \int_{\text{BZ}} d^3k F(\mathbf{k}) \rightarrow \sum_{\mathbf{k}} [w(\mathbf{k}) \cdot F(\mathbf{k})] \quad . \quad (4)$$

To evaluate this expression, we have to find “a few” \mathbf{k} -points that are spread across the Brillouin zone (or unit cell of reciprocal space), find their integration weights, and then evaluate the Kohn-Sham equations only at these chosen \mathbf{k} -points.

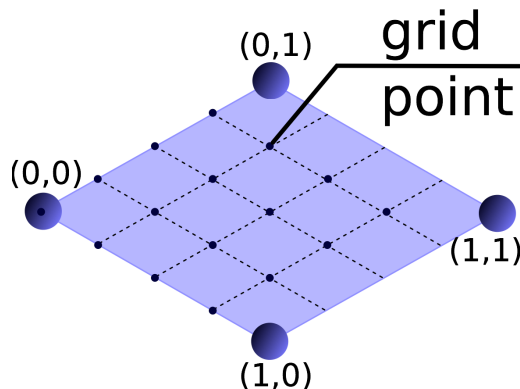


Figure 1: Reciprocal-space unit cell of a two-dimensional hexagonal lattice (easier to illustrate than the three-dimensional case), reciprocal lattice vectors (large blue dots) and even-spaced \mathbf{k} -point integration grid that covers the unit cell. We could also have drawn the first Brillouin zone (the Wigner-Seitz cell of the reciprocal lattice). The key point is that the k -space integration must cover a full unit cell area of reciprocal space.

The historically simplest choice to do so is an even-spaced integration grid of \mathbf{k} -points along the directions of the reciprocal lattice vectors. Figure (1) shows a two-dimensional example for the reciprocal-space unit cell of a hexagonal lattice. Here, we have chosen the following \mathbf{k} -space integration grid (small black dots):

$$\mathbf{k}(s_1, s_2, s_3) = (s_1/n_1) \cdot G_1 + (s_2/n_2) \cdot G_2 + (s_3/n_3) \cdot G_3 \quad . \quad (5)$$

G_i denote the reciprocal lattice vectors (large circles), and $0 \leq s_i \leq n_i$ are integers. To fully specify a grid of \mathbf{k} -points in this way, all we need to do is choose integers n_1, n_2, n_3 . The result is indeed an even-spaced \mathbf{k} -grid with equal integration weights $w(\mathbf{k})$ and a grand total of $n_1 \cdot n_2 \cdot n_3$ points. The number grows fast with the mesh refinement, but we have a definition. We will refer to such a mesh as a “ $n_1 \times n_2 \times n_3$ \mathbf{k} -point grid” below.

As a side remark, there are many works that attempt to go beyond this simple choice of \mathbf{k} -points, to exploit symmetry, or to go beyond this simple integration method. We can not go through all

¹As we saw on the last exercise sheet, the total energy can be obtained either from $T_s[n]$ or from the sum of eigenvalues. The sum of eigenvalues contains $T_s[n]$ completely, but one still needs to subtract the so-called “double-counting” terms to get to the total energy of the many-electron system.

these developments here. By and large, however, the method chosen above works despite all its potential flaws, and is, in a sense, still the *de facto* standard of the field. Since the “ Γ point” ($\mathbf{k}=(0,0,0)$) is explicitly included, the type of grid above is also referred to as a Γ -centered grid.

1.3 The upshot

We now have a simple recipe to investigate a bulk solid in density-functional theory. We choose

- the unit cell,
- the positions of the atoms inside the unit cell,
- and mesh factors n_1, n_2, n_3 for the \mathbf{k} -point grid.

The key point is that, of course, we wish to approximate the results of the continuous Brillouin zone integration, so we need to make sure that our mesh n_1, n_2, n_3 is chosen to be dense enough.

2 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.
- The calling sequence for FHI-aims is:

```
mpirun -np 1 aims.scalapack.mpi.x | tee calculation.out
```

This should be enough to produce the output needed. If you want to be adventurous and use two CPUs, you may try instead:

```
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.

3 Exercise 14a: The diamond phase of Si—total energy

Silicon is (arguably) the most popular solid in the world, at least when it comes to solid-state theory. We here focus only on its experimental phase, the diamond phase.

To set up a calculation for Si, we could simply use the conventional (cubic) unit cell of the fcc lattice and place two Si atoms at each of its sites. This choice, however, would give us a total number of eight Si atoms per unit cell, as the conventional fcc cell itself has four sites.

In practice, we can do better and use the *primitive cell* of the fcc lattice instead. It is easy to convince yourself that the following choice of geometry will do:

```

lattice_vector    0.0 2.715 2.715
lattice_vector    2.715 0.0 2.715
lattice_vector    2.715 2.715 0.0

atom      0.0 0.0 0.0 Si
atom      1.3575 1.3575 1.3575 Si

```

Looking over the numbers, you should see that these values correspond to a (conventional) lattice parameter of $a=5.43$ Å. You can visualize (and check) your input by:

```
jmol geometry.in &
```

Then, to repeat unit cell geometries and visualise periodic structures, press the right mouse button and choose from the menu the category

Symmetry

and then

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

Can you see the tetrahedron typical for the diamond structure?

We next need to think about our computational choices in `control.in`. For instance:

```

# 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 (to be adjusted)
k_grid    3 3 3

```

You have seen most of these settings in the earlier exercises.

Note our choice of the LDA exchange correlation functional for the present calculation. For the present exercise, it is critical that you choose LDA and not, by accident, Hartree-Fock theory. A calculation for bulk Si in Hartree-Fock theory can be done, but at the price of significantly more computer time and memory—as well as the need to deal with the Coulomb operator between electrons in different unit cells, which leads to significantly worse convergence with the number of k-points. In short, do not use Hartree-Fock theory.

The only interesting *new* choice is the `k_grid` tag. In the present example, it specifies a $3\times 3\times 3$ grid of k-points, which will be used for all Brillouin zone integrations.

Before we continue, we must still pick settings for the element Si. In the interest of time, we here do NOT use the “tight” settings that we used for the free atom exercises earlier. Instead, we use all default settings—including the basis set—from the “light” settings:

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

You are absolutely welcome to try out “tight”er settings for the solid, but this is not a requirement for the present exercise.

It is a good idea to generate a directory

```
mkdir Si_diamond
```

and enter the directory with:

```
cd Si_diamond
```

Copy your `geometry.in` file for silicon in diamond structure and your `control.in` file. Now you have all the pieces to run your first periodic calculation.

```
> mpirun -np 2 aims.scalapack.mpi.x | tee Si_diamond_kgrid_3x3x3.out
```

Then, repeat the calculations for different k -grids, for example:

- `k_grid 3 3 3`
- `k_grid 4 4 4`
- `k_grid 6 6 6`
- `k_grid 12 12 12`
- `k_grid 24 24 24`

For each calculation, record the final total energy value—the one given in the last self-consistency cycle. How does the total energy converge with the k -grid? Which level do you consider sufficient for bulk Si?

In the exercise, we are actually interested in the cohesive energy. This energy is defined as:

$$E_{\text{coh}} = E_{\text{tot}} - N_{\text{Si}} \cdot E_{\text{free atom}} \quad , \quad (6)$$

where E_{coh} and E_{tot} are taken *per unit cell*, N_{Si} is the number of Si atoms per unit cell, and $E_{\text{free atom}}$ is the energy of a free (isolated) Si atom.

For the free atom reference, please use exactly the same total energy that you found in exercise number 8, for LDA, tight settings, and a tier 2 basis set, which yielded a spherical free atom. Be sure to NOT use the total energy from a Hartree-Fock calculation by accident.

4 Exercise 14b: The diamond phase of Si—electron density

The *other* physical quantity to be obtained from Kohn-Sham density-functional theory is the density $n_0(\mathbf{r})$ itself. We will here only visualize the density. In the “real world”, the density would give you immediate access to structure factors in X -ray diffraction, charge transfer (in less simple solids, that is), and many other quantities.

To visualize the electron density, go back to one of the previous calculations that you consider “converged”, and add the following lines to `control.in`:

```
output cube total.density
cube filename total.density.cube
```


Visualize the result (using jmol). Remember (from exercise 8):

In jmol, you will have to open the “Console” from the “File” menu. Once you have this console, you can use typed commands to specify which isosurface of the density you would like to see.

Once you have opened “jmol” and the “Console”, type:

```
load "total_density.cube"
```

Now we still have to tell jmol which “isosurface” of the electron density we would like to see. For example:

```
isosurface cutoff 0.1 "total_density.cube"
```

Interestingly, you may find that 0.1 gives you a slightly puzzling result. To visualize the density in a better way, increase the cutoff value to perhaps 0.5 ... what do you find? Did you expect this result?

It turns out that visualizing a total density on its own is often not the most informative choice when trying to understand a chemical bond. The density itself is large, and density *changes* are often small compared to the absolute density. You can easily verify this statement by looking at the total density for an underconverged \mathbf{k} -point grid, which still looks very similar to the converged one—although the total energy is clearly different.

We can learn some more by looking at a density difference—in this case the difference between the full crystal and the free atom:

$$\delta n(\mathbf{r}) := n(\mathbf{r}) - \sum_I n_{\text{free atom}}(|\mathbf{r} - \mathbf{R}_I|) \quad , \quad (7)$$

where $\{\mathbf{R}_I\}$ are the positions of all Si atoms in the entire crystal.² The free atoms are here taken to be spherically symmetric, as in exercise 8. Fortunately, FHI-aims supports this output of a difference density by default, by setting:

```
output cube delta_density
cube filename delta_density.cube
```

in `control.in`. Visualize the result in jmol and play with the cutoff parameter for isosurfaces. (Hint: choose a smaller value than what was needed for the full density.) What is the result? Where is the difference density concentrated? Does this match your expectations for a diamond Si crystal?

5 Exercise 14c: The diamond phase of Si—“band gap” in LDA

The “band gap” of an insulating or semiconducting solid is defined as:

$$E_{\text{gap}} = I - A = E(N - 1) + E(N + 1) - 2E(N) . \quad (8)$$

Here, I is the ionization potential (energy needed to remove an electron from the solid), A is the electron affinity (energy needed to add an electron to the solid), and $E(N - 1)$, $E(N)$, and $E(N + 1)$ are the energies of the singly positive, neutral, and singly negative *entire solid*, where N is the number of electrons in the neutral case.

²Yes, this sum converges. For instance, the ground state densities of exact free atoms fall off exponentially with the distance from the nucleus. In LDA, the decay behaviour is not exponential—one of the “failures” of LDA for free atoms—but the decay is still fast enough to converge.

The band gap, as written above, is an inconvenient quantity to compute exactly (see lecture script), as (i) the entire solid is involved, and (ii) there is a technical problem with most simple density functionals that would simply “delocalize” that single electron until, by virtue of Janak’s theorem, only the difference between the highest occupied and lowest unoccupied Kohn-Sham eigenvalue of the neutral crystal remains:

$$E_{\text{gap}}^{\text{naive}} = \epsilon_{\text{CBM}} - \epsilon_{\text{VBM}}. \quad (9)$$

We have here used the conventional abbreviations “VBM” for “valence band maximum” and “CBM” for “conduction band minimum” in solids, which in practice mean the highest unoccupied level in the Brillouin zone, and the lowest unoccupied level in the Brillouin zone.

We will come back to the fine details of “band structures” later, but for the specific integration grid used in a particular calculation, FHI-aims gives you its “best estimate” (only an estimate, as we are not sampling the full, continuous Brillouin zone!) of $E_{\text{gap}}^{\text{naive}}$, ϵ_{CBM} , and ϵ_{VBM} . In the output, look for the following section:

```
Highest occupied state (VBM) at      -5.77245422 eV (relative to internal zero)
| Occupation number:      2.00000000
| K-point:      1 at      0.000000      0.000000      0.000000 (in units of recip. lattice)

Lowest unoccupied state (CBM) at      -5.13991586 eV (relative to internal zero)
| Occupation number:      0.00000000
| K-point:      7 at      0.333333      0.000000      0.333333 (in units of recip. lattice)

Overall HOMO-LUMO gap:      0.63253836 eV between HOMO at k-point 1 and LUMO at k-point 7
| This appears to be an indirect band gap.
| Smallest direct gap :      2.52459934 eV for k_point 1 at      0.333333      0.000000      0.333333
```

How do these values evolve with the \mathbf{k} -grid used? What do you learn about the relative locations of VBM and CBM?

Note that only the *difference* between eigenvalues has a clear physical meaning in solids. The absolute location is shifted by an arbitrary amount: The $G = 0$ component of Ewald’s potential. Without knowing the boundaries of an experimental crystal (surface orientation etc.), it is not possible to relate this value to an absolute “vacuum level.”

Note also that we have here taken the Kohn-Sham eigenvalues themselves as indicative of a measurable quantity: The band gap. We learned earlier that Kohn-Sham eigenvalues, strictly, have no guaranteed physical meaning, and this is in fact the case. When comparing Kohn-Sham band gaps to experimentally measured values (e.g., from photoemission spectroscopy), one can go horribly wrong.

On the other hand, Kohn-Sham eigenvalues are the simplest quantity to be compared, and they do arise from a physically motivated potential. Thus, they are still often used for a qualitative look at the “electronic structure” of real solids. Take a look at the “naive band gap” values you extracted for bulk Si. How close are they to experimental values?

http://en.wikipedia.org/wiki/Band_gap

The question whether and how much the eigenvalues of a hypothetical “exact” Kohn-Sham theory would or would not reproduce an experimental band gap is still a hotly contested issue today. ($E(N - 1)$, $E(N)$, and $E(N + 1)$ are ground state properties of some system, after all.) We will not touch this issue in detail here, but you may ask the author of the present script for his opinion.