

Sheet 5

November 10, 2025

Please hand in a pdf for exercise 2 and the answers from 1, and the plots for exercise 1, which is named `<firstname>.<lastname>.sheet.<number>`.

The deadline is Monday, Nov. 18th, 12:00 (noon). Please hand in your solution via moodle.

1 DFT calculations for diamond

This exercise will introduce you to *density functional theory* (DFT) calculations, and especially the open-source DFT package *Quantum Espresso*. Quantum Espresso is already installed in the virtual machine. If you like, you can also install it on your personal computers. To get the source code and information about the installation, please go to <https://www.quantum-espresso.org/>. On Ubuntu you can alternatively install it from the repositories by executing `sudo apt install quantum-espresso`.

1. For many material properties, calculating only the valence electrons explicitly is sufficient. Therefore, and because it is computationally less expensive, in DFT often *pseudopotentials* are used. Pseudopotentials are a numerically efficient technique to describe core-valence interactions. Go to <http://www.pseudo-dojo.org/> and download the *norm conserving, scalar relativistic, PBE* pseudo potential for carbon.
Hint: Quantum Espresso requires the UPF format.
2. With this pseudopotential and the provided Quantum Espresso input file, run a self-consistent calculation of diamond.

```
pw.x < diamond.in > diamond.out
```

3. In the output file, find the total energy E_{tot} for each self-consistent iteration cycle n and plot E_{tot} as a function of n . 1.5 points

4. Find and explain the contributions to the total energy. 0.5 points

5. Identify the highest occupied and lowest unoccupied state by their band index. How many occupied bands do you expect for diamond? At which \vec{k} -points do you find the highest occupied and lowest unoccupied states? What are the direct and indirect band gaps in this material? 1 point

6. To calculate the ground state properties with DFT, a set of basis functions has to be introduced. You will learn about basis sets in the lecture. For crystals often *plane waves* are chosen. The basis function at a specific reciprocal lattice vector \vec{k} is

then given by $e^{i(\vec{k}+\vec{G})\cdot\vec{r}}/\sqrt{N\Omega}$. The number of plane waves included in the basis set is determined by the cut-off $|\vec{k} + \vec{G}|^2 \leq \frac{2m}{\hbar^2} E_{\text{cut}}$. Naturally, using a larger basis set is more precise, but also computationally more expensive. Therefore one wants to use as low an *energy cut-off* as possible. In order to determine a suitable value, one does a *convergence test*. I.e., one systematically changes the value until the change in the total energy due to an increase/decrease of the cut-off is less than a threshold. *Do a convergence study for the energy cut-off. Therefore plot the total energy as a function of the energy cut-off. What cut-off would you choose to achieve an accuracy of 2meV/atom? Remark: be cautious about units!*

1 point

7. Similarly, you also have a trade-off between precision and computational costs of a calculation when increasing the number of reciprocal lattice points explicitly included in your calculation. *Do a convergence test for the \vec{k} -point grid. How many k -points do you have to use for a precision of 2meV/atom.*

1 point

8. The equilibrium structure of a material is the one with the lowest total energy. *Vary the lattice constant of diamond to find the equilibrium lattice constant. Plot the total energy E vs the lattice constant.*

1 point

2 Dirac Exchange

On sheet 3 we derived the exact exchange energy for the homogeneous electron gas. The local density approximation (LDA) functional, the first real DFT-functional, is based on the approximation that the exchange energy density $\epsilon_X(\vec{r})$ is locally given by the exact exchange of a homogeneous electron gas. The total exchange energy is given by

$$E_X[n] = \int d^3r \epsilon_X(\vec{r}) n(\vec{r}). \quad (1)$$

Derive an expression for $\epsilon_X(\vec{r})$.

1. In sheet 3 we showed that the single-particle Fock-operator(i.e. the exact exchange operator) for the homogeneous electron gas, when applied to a momentum eigenstate $\phi_i(\vec{r}) = e^{i\vec{k}_i\cdot\vec{r}}$ is given by eq 2.

$$\hat{\mathbf{F}}_i \phi_i(\vec{r}) = \frac{k_F}{\pi} \left(1 + \frac{1}{2} \left(\frac{k_F}{k_i} - \frac{k_i}{k_F} \right) \ln \left(\frac{k_F + k_i}{k_F - k_i} \right) \right) \phi_i(\vec{r}). \quad (2)$$

In order to properly normalise the wave functions, we now assume the domain is a cube of volume $V = 1$, with periodic boundary conditions. Demonstrate that, for a countable number of single-particle states $\phi_i(\vec{r})$ and slater determinant $\Psi(\vec{r})$,

$$\int d^{3N}r \Psi^*(\vec{r}) \Psi(\vec{r}) = \prod_i \int d^3r \phi_i^*(\vec{r}) \phi_i(\vec{r}) = \int d^3r. \quad (3)$$

0.5 points

2. Calculate the expectation value

$$E_X[n] = \langle \sum_i \hat{\mathbf{F}}_i \rangle = \int d^{3N}r \Psi^*(\vec{r}) \sum_i \hat{\mathbf{F}}_i \Psi(\vec{r}), \quad (4)$$

where $\Psi(\vec{r})$ is a product state of plane waves, and $\hat{\mathbf{F}}_i$ is the single-particle exchange operator which applies to the i -th orbital of a product state

$$\hat{\mathbf{F}}_i \prod_j \phi_{a(j)}(\vec{r}_j) = \prod_{j < i} \phi_{a(j)}(\vec{r}_j) \left(\hat{\mathbf{F}}_i \phi_{a(i)}(\vec{r}_i) \right) \prod_{k > i} \phi_{a(k)}(\vec{r}_k), \quad (5)$$

You may assume that the sum over all occupied electronic states ϕ_i can be replaced with the integral $\frac{1}{(2\pi)^3} \int_{\Omega_{k_F}} d^3k$ as demonstrated in sheet 3.

Hint 1: The exchange energy density does not depend on \vec{r} in this model.

1.5 points

3. Calculate the integral over \vec{k} , and restate the result in the form of eq. 1 in order to find an expression for $\epsilon_X(\vec{r})$ as a function of the density. To get the exchange energy in the LDA we then merely assume that in this expression we can replace $n \rightarrow n(\vec{r})$.

Hint 2: You can remove dependence on k_F from the integral with a coordinate transform.

Hint 3: Remember the relation between k_F and the density.

2 points