Exercise for Computational Materials Sciences

Exercise 2, November 5th, 2024. Discussion on November 19th, 2024

This week's exercise focuses on density functional theory calculations. Our goal is to understand the electronic structure (band structure and density of states) as well as crystal structure/some mechanical properties (lattice constant and bulk modulus) for two example systems: diamond and graphene.

In the exercise class on November 12th we will familiarize ourselves with the computational environment needed for that, particularly the cluster login, loading of modules, the DFT package "Quantum ESPRESSO" (QE) and its in-shell/interactive execution, and the analysis of resulting band structures, density of states and total energies.

1) Diamond — C as fcc structure

Diamond is an allotrope of carbon, where carbon atoms crystallise in the so-called diamond lattice, which is an fcc lattice with two C atoms per primitive unit cell; the primitive unit cell is depicted on the right.

One possible choice of primitive basis vectors is given by

$$\vec{a}_1 = \frac{a}{2} \begin{pmatrix} -1 \\ 0 \\ -1 \end{pmatrix}, \qquad \vec{a}_2 = \frac{a}{2} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}, \qquad \vec{a}_3 = \frac{a}{2} \begin{pmatrix} -1 \\ 1 \\ 0 \end{pmatrix},$$

where $a = 3.57\,\text{Å}$ is the lattice constant. We choose to position one carbon atom at the origin of the coordinate system and the second one along the long spate diagonal:

$$\vec{r}_1 = 0 \cdot (\vec{a}_1 + \vec{a}_2 + \vec{a}_3) \; ; \qquad \vec{r}_2 = \frac{1}{4} \cdot (\vec{a}_1 + \vec{a}_2 + \vec{a}_3)$$
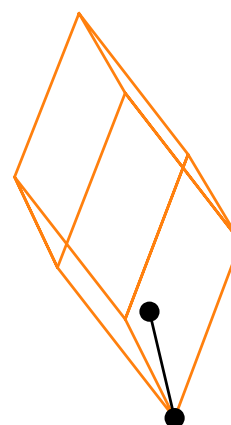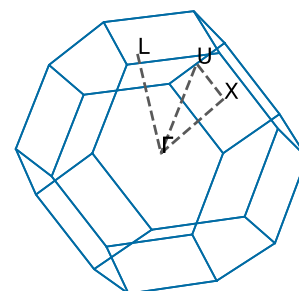
a) Calculate the DFT band structure of diamond using QE. To this end, generate first a self-consistent charge density and use this one to obtain the band structure.

Pursue the following steps.

- Take a look at the file `scf.in` and see whether you can identify physical parameters like lattice constant, number of atoms in the primitive unit cell, type of atoms, and real space position of the atoms. Run the self-constistent field calculation.

- Next, define the high-symmetry points of the Brillouin zone in terms of coefficients to the reciprocal vectors $\vec{b}_{\{1,2,3\}}$ along the path L $\to \Gamma \to$ X $\to$ U $\to \Gamma$. Add the coefficients to the `K_POINTS` block at the end of the file `bscf.in`. Then run the non-SCF band structure calculation and the postprocessing to extract the band structure.

  You can use the Python script `BZ_vis.py` to check your choice of the k-path.

- After the run is finished, you can find the files `bands.out.gnu` and `bands.out.rap` besides others. Use these files for plotting the band structure of diamond.

  Check the results of the bands obtained. Does the calculation predict diamond to be an indirect insulator with a band gap of size $5.4\,\mathrm{eV}$?

b) Add the information on the density of states to your obtained band structure by calculating it explicitly. Again, first a SC charge-density has to be generated, from there an energy surface is calculated by means of a non-self-consistent fields calculation and subsequently the DOS can be extracted.

Run the calculations in the order described above; SCF → nSCF → DOS. Visualise the DOS and comment on whether you would expect the result to look like it does.

c) Due to the simplicity of the diamond structure it is possible for you to find an optimal lattice constant a_{opt} by means of anlaysing how the total energy obtained from SCF calculations depends on the choice of a.

Use a set of SCF runs with lattice parameters chosen between $3.4\,\text{Å}$ and $3.7\,\text{Å}$, i.e. compress and stretch the diamond structure. Extract the converged total energy E_{tot} from the output files and plot it over the lattice parameter a. Determine the optimal lattice constant a_{opt} by fitting a parabola to your data points. Extract also the bulk modulus B_0 of diamond from this optimisation.

d) Investigate how DOS, a_{opt} and B_0 are influenced by the choice of k-grid.

On the technical side this is achived by changing the numbers in the last line of SCF and nSCF files from $n_{k,\{1,2,3\}} = 8$ to $n_{k,i} \in \{4, 16, 32\}$ (note that the runs for the latter two can take some time to finish). Analyse the resulting DOS. Extract the information on the highest occupied and lowest unoccupied level of the insulator from the nSCF runs and compile DOS and those levels into one plot together with the previously obtained band structure. What do you observe?

Do the same for $n_{k,i} \in \{4, 16\}$ in the study of $E_{\mathrm{tot}}(a)$. Compare the resulting curves and fit results.

e) Last but not least, fix $n_{k,\{1,2,3\}} = 16$ and determine how the kinetic energy cut-off E_{cut} has influence on DOS, a_{opt} and B_0.

Vary E_{cut} between $50\,\mathrm{Ry}$ and $110\,\mathrm{Ry}$. Analyse the resulting DOS, highest occupied and lowest unoccupied levels as well as a_{opt} and B_0.

2) Graphene — C as hexagonal 2D structure

Graphene is another allotrope of carbon. This time, the carbon atoms crystallise in a two-dimensional honeycomb structure. To be more precise a hexagonal lattice with again two atoms per primitive unit cell. The primitive unit cell viewed along $\vec{a}_3$ can be seen on the right and the primitive vectors are given by

$$\vec{a}_1 = a \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad \vec{a}_2 = \frac{a}{2} \begin{pmatrix} -1 \\ \sqrt{3} \\ 0 \end{pmatrix}, \qquad \vec{a}_3 = c \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix},$$
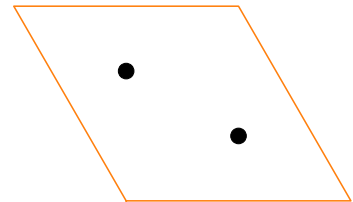
where $a = 2.46\,\text{Å}$ is the in-plane lattice constant and c the lattice parameter perpendicular to the honeycomb sheet, i.e. the interlayer separation for van-der-Waals materials.

a) Calculate the band structure of graphene along the path $\Gamma \to M \to K \to \Gamma$. Go through the same steps as in 1.a). How does it compare to the band structure of sheet 1, exercise 3?

This time, you have to add a bit of information into the input files yourselves. Specifically, the number of atoms per unit cell `nat`, the positions of those atoms in crystal coordinates (reconstruct them from the primitive cell depicted above), and the k-path.

b) Determine the density of states and add it to your band structure plot. Again, compare to sheet 1, exercise 3.

c) The structure of graphene is almost as simple as diamond. By assuming the system to be a monolayer of graphene, the meaning of $\vec{a}_3$ and c can be neglected. Study the influence of a on the total energy and try to find a_{opt} as well as B_0 of graphene.

Start by keeping $n_{k,\{1,2,3\}}$ and E_{cut} fixed, varying a between $2.40\,\text{Å}$ and $2.55\,\text{Å}$.

Next, repeat for varying $n_{k,i} \in \{6, 8, 10\}$ and determine a_{opt} as well as B_0. Fix $n_{k,i} = 12$ again and vary E_{cut} between $50\,\text{Ry}$ and $110\,\text{Ry}$; determine a_{opt} and B_0.

Technical side note: You might have noticed that c was chosen to be over five times a and the carbon atoms sit at $z = \frac{c}{2}$. This way, QE effectively runs a 2D-calculation although the system is 3D.

d) Study the influence of k-grid choice and kinetic energy cut-off on the DOS of graphene.

Run DOS calculations using $n_{k,i} \in \{3, 6, 12, 18, 24\}$ and E_{cut} between $50\,\text{Ry}$ and $110\,\text{Ry}$.