

## 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. Make sure that all of you are able to use the PHYsnet cluster and have some basic knowledge about how to navigate a computer in a terminal instead of a graphical interface.

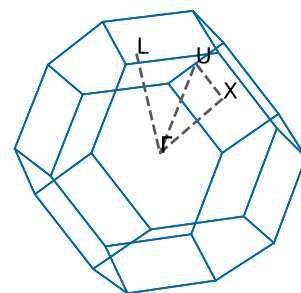
### 1) Diamond — C as fcc structure

- a) Before you start: Take a look at the files in the provided zip-container. In `C_bulk.fcc/bands/` you can find `scf.in`, `bscf.in`, `bands.in` and `bands.sub`.

In the second file, add the information on the  $k$ -path. Consider the fact that the fcc basis vectors in QE are given by

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

where  $a = 3.57 \text{ \AA}$  is the lattice constant. Define the high-symmetry points of the lattice in terms of coefficients to the reciprocal vectors  $\vec{b}_{\{1,2,3\}}$  along the path  $L \rightarrow \Gamma \rightarrow X \rightarrow U \rightarrow \Gamma$ . You can use the Python script `BZ_vis.py` to check your choice.



Submit the band structure calculation using the provided `bands.sub` file. 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 eV?

- b) In the folder `dos` use the provided files. Run the calculations by submitting the `dos.sub` file. Use the resulting `C_fcc_16.dos` data file and add the DOS to your band structure. Would you expect the result to look like this?
- c) Navigate to the folder `E_tot`. You can find the file `scf_3.50.in` and a submit file there. In the SCF calculation file, vary the lattice parameter `a` in the `system` block between 3.4 Å and 3.7 Å. Copy the SCF calculation file, change its name and add all calculation runs to the submit file. Extract the converged total energy  $E_{\text{tot}}$  from all files and plot it over the lattice parameter  $a$ . Determine the optimal lattice constant  $a_{\text{rel}}$  by fitting a parabola to your data points.
- d) Navigate back to the DOS folder. Change the numbers in the last line of SCF and nSCF files from  $n_{k,\{1,2,3\}} = 16$  to  $n_{k,i} \in \{4, 8, 32\}$ . 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  $n_{k,i} \in \{4, 32\}$  in the study of  $E_{\text{tot}}(a)$ . Compare the resulting curves and fit results.

- e) Finally, fix  $n_{k,\{1,2,3\}} = 16$  again and vary the kinetic energy cut-off  $E_{\text{cut}}$  between 50 Ry and 110 Ry for calculations of the DOS and  $E_{\text{tot}}(a)$ . Analyse the resulting DOS, highest occupied and lowest unoccupied levels as well as the resulting minimal lattice constant.

## 2) Graphene — C as hexagonal 2D structure

- a) Next up is graphene. Navigate to the folder `C_m1_hex/bands`. Add to the `scf` and `bscf` files information about the number of atoms per unit cell `nat`, the positions of those atoms in crystal coordinates, and the positions of the high-symmetry points of the path through reciprocal space  $\Gamma \rightarrow \text{M} \rightarrow \text{K} \rightarrow \Gamma$  in reciprocal coordinates. Keep in mind that Quantum Espresso uses

$$\vec{a}_1 = a \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \vec{a}_2 = \frac{a}{2} \begin{pmatrix} -1 \\ \sqrt{3} \\ 0 \end{pmatrix}, \quad \vec{a}_3 = c \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix},$$

where  $a$  is the in-plane lattice parameter of the hexagonal grid and  $c$  is the orthogonal lattice parameter (QE is a 3D DFT code but can be used for 2D structures by having a large enough layer distance). Run the band structure calculation and plot your results. How does it compare to the band structure of sheet 1, exercise 3?

- b) Add the aforementioned missing information to the files in the `dos` folder. Run the calculations and add the density of states to your obtained band structure. Again, compare to sheet 1, exercise 3.
- c) Perform a study of  $E_{\text{tot}}(a)$  and find  $a_{\text{min}}$ . Start by keeping  $n_{k,\{1,2,3\}}$  and  $E_{\text{cut}}$  fixed, varying  $a$  between 2.40 Å and 2.55 Å.

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

- d) Repeat the variation for the DOS calculation using  $n_{k,i} \in \{3, 6, 12, 18, 24\}$  and  $E_{\text{cut}}$  between 50 Ry and 110 Ry.