EXAM assignment

Lecture: Atomistic Computer Modeling of Materials (ÚFV/APMM/19)

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Date: April 20, 2021

Submission Deadline: June 30, 2021 via email: *martin.gmitra@upjs.sk*

Assignment:

1. Calculate using density functional theory as implemented in Quantum Espresso code suite using Birch–Murnaghan equation of state

$$E_{\mathrm{tot}}(a) = E_0 + \frac{9V_0B_0}{16}\left(\left[\left(\frac{a_0}{a}\right)^2 - 1\right]^3 B_0' + \left[\left(\frac{a_0}{a}\right)^2 - 1\right]^2 \left[6 - 4\left(\frac{a_0}{a}\right)^2\right]\right)$$

equilibrium lattice constant a_0, bulk modulus at zero pressure B_0, and B_0' (which is $B_0' = (\partial B/\partial P)_T$) for cooper simple cubic crystal and face-centered crystal. V_0 is the equilibrium volume. Optimize number of k-points on accuracy of the ground state energy E_{tot} for lattice constant a close to equilibrium lattice constant. Converge the ground state energy value with precision below 10 meV.

2. Compare results for LDA and PBESOL exchange-correlation functionals. Discuss results and compare to known results from literature.

3. Calculate electronic band structures for the simple cubic and face-centered crystal at equilibrium for PBESOL. For k-path along the high symmetry lines connecting high-symmetry points in 1st Brillouin zones refer, e.g., to Bilbao crystallographic server.

Evaluation:

- 5% construction of the input files
- 15% finding optimal k-point sampling
- 20% relaxation of the simple cubic structure (LDA, PBESOL)
- 20% relaxation of the face centered structure (LDA, PBESOL)
- 20% finding a_0, B_0, and B_0' for LDA and PBESOL
- 20% calculate band structures
- +20% bonus, online oral exam covering theory topics given on lectures, please submit the requested files 2 days before oral exam.

Submit:

- input files, output files for equilibrium structures only
- a short text report (pdf/odt/doc) with results figure/table declaring obtained results

Exam conditions:

Scale: A: 100% - 90% B: 89% - 75% C: 74% - 60% D: 59% - 40% E: 39% - 20% FX: 19% - 0

Note**:** For pseudopotentials use the following inputs:

https://www.quantum-espresso.org/upf_files/Cu.pz-dn-kjpaw_psl.0.2.UPF
https://www.quantum-espresso.org/upf_files/Cu.pbesol-dn-kjpaw_psl.1.0.0.UPF

For energy cutoffs use the values as can be found in headers of the pseudopotentials files.

- **Input files**

For Cu SC:

```
&CONTROL
        calculation = 'scf'
        restart_mode = 'from_scratch',
        pseudo_dir = 'C:\Program Files\Quantum ESPRESSO 64-bit 5.2.1…',
        outdir = '.\tmp',
        prefix = 'Cu_SC_LDA'
/
&SYSTEM
        ibrav = 1
        celldm(1) = 6.830
        nat = 1
        ntyp = 1
        ecutwfc = 40.0
        occupations = 'smearing'
        smearing = 'marzari-vanderbilt'
        degauss =   0.05,
/
&ELECTRONS
diagonalization = 'david'
        mixing_beta = 0.7
        conv_thr = 1.D-6
/
ATOMIC_SPECIES
        Cu     63.546 Cu.pz-dn-kjpaw_psl.0.2.UPF
ATOMIC_POSITIONS crystal
        Cu          0.0000000000       0.0000000000       0.0000000000
  K_POINTS automatic
        7 7 7 0 0 0
```

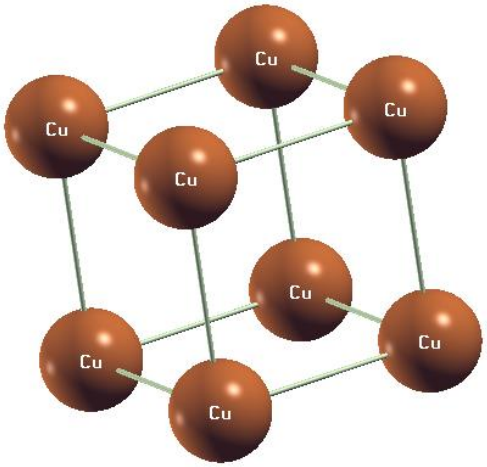

Fig. 1: Cu SC result in XCrySDen

For Cu FCC:

```
&CONTROL
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        restart_mode = 'from_scratch',
        pseudo_dir = 'C:\Program Files\Quantum ESPRESSO 64-bit 5.2.1…',
        outdir = '.\tmp',
        prefix = 'Cu_FCC_PBESOL'
/
&SYSTEM
        ibrav = 2
        celldm(1) = 6.831
        nat = 1
        ntyp = 1
        ecutwfc = 40.0
        occupations = 'smearing'
        smearing = 'marzari-vanderbilt'
        degauss =   0.05,
/
&ELECTRONS
        diagonalization = 'david'
        mixing_beta = 0.7
        conv_thr = 1.D-6
/
ATOMIC_SPECIES
        Cu     63.546 Cu.pbesol-dn-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS crystal
        Cu          0.0000000000       0.0000000000       0.0000000000
K_POINTS (automatic)
        7 7 7 0 0 0
```

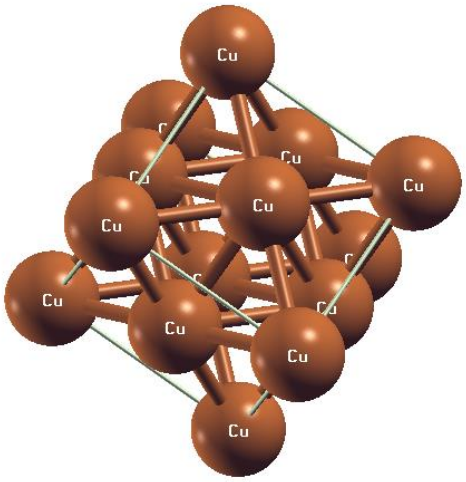

Fig. 2: Cu FCC result in XCrySDen

- **Optimal *k*-point sampling**

To achieve the required accuracy in the calculation of E_{tot}, the total energy shouldn't change significantly with increasing density of k-points. Using the results of total energy with different values of k-points, we can plot the relative calculation error, assuming that the maximum accuracy was achieved when using a grid of $\mathbf{10 \times 10 \times 10}$ k-points, to determine the optimal value of the number of k-points for the rational use of resources.

The formula by which the relative error was calculated is as follows:

$$\text{Relative error} = \left| \frac{E_{tot}(k) - E_{tot}(10)}{E_{tot}(10)} \right|.$$

Consider the case of a Cu SC:

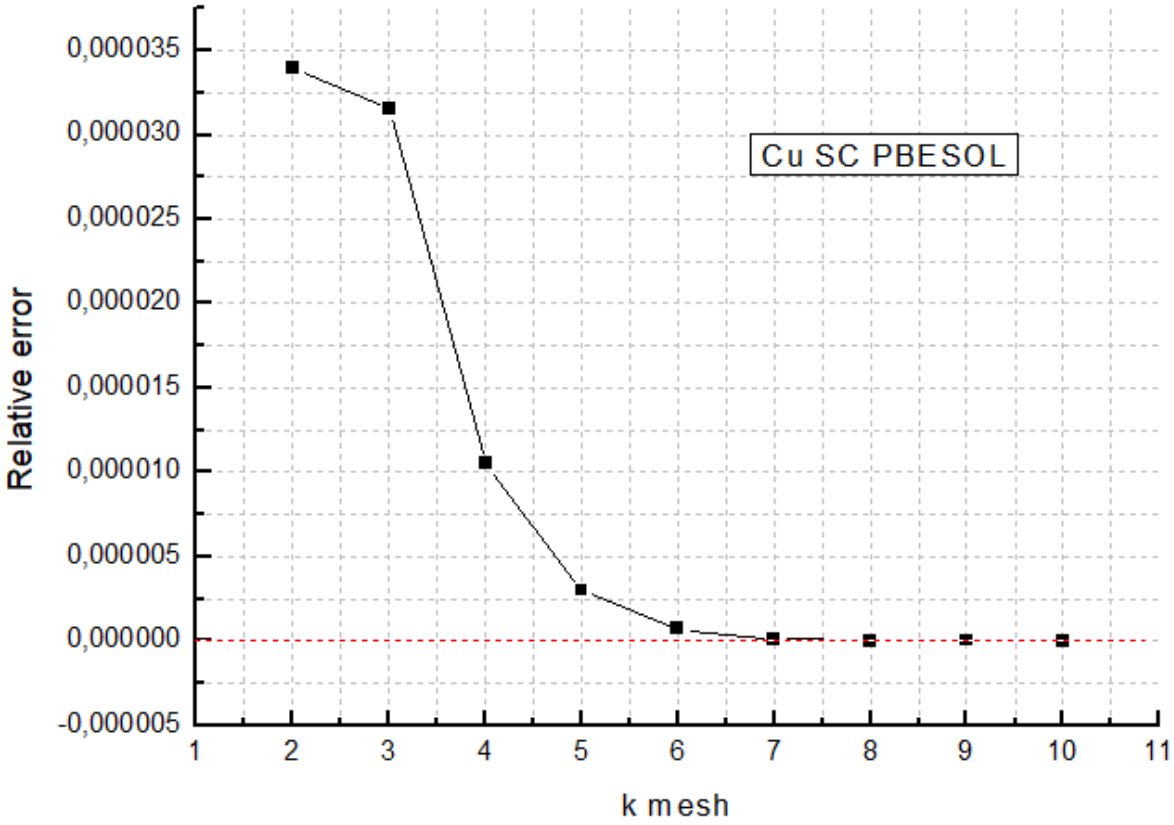

Fig. 3: Optimal *k*-point sampling for Cu SC

As you can see, the smallest value of the relative error can be observed after the values of $k = 7 \times 7 \times 7$. These calculations were carried out for the structure of Cu FCC, but the result was similar. That is why we will use $\mathbf{7 \times 7 \times 7}$ in further calculations.

- **Relaxation of the simple cubic structure (LDA, PBESOL)**

To determine the parameter of the unit lattice, we changed the size of the unit cell, assuming that at one atom in the unit cell will not act other interaction forces, as its environment is the same for different unit cell sizes. Then, it turns out that the total energy E_{tot} will depend on the interatomic distances, which are actually the size of an elementary cell.

Thus, having obtained the value of total energy at different values of the unit cell parameter, we can determine at which value of the lattice parameter, our system will have the minimum value of total energy, which will indicate the value in which our system will have the most stability.

Considering the values of the total energy for Cu SC in the case LDA, we have:

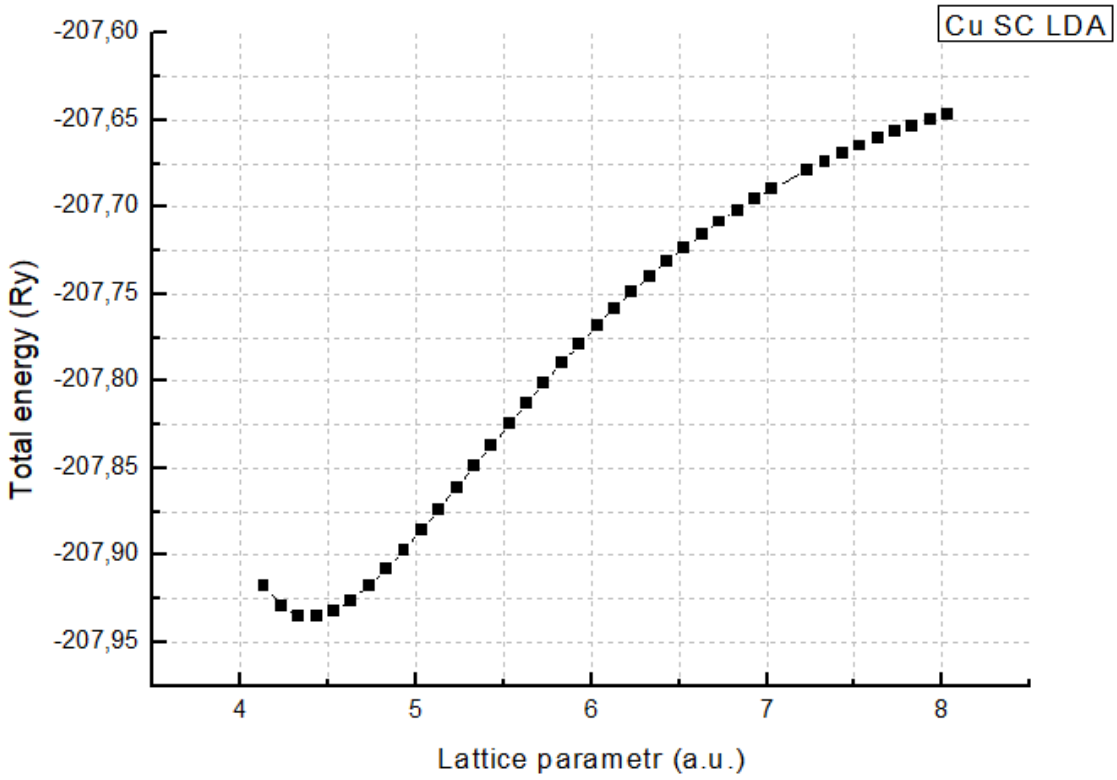

Fig. 4: Dependence of the total energy of the system on the lattice parameter (in the case of LDA, Cu SC)

As we can see, the most optimal choice would be **4.431** Bohr.

Consider the same dependence for the case of PBESOL:

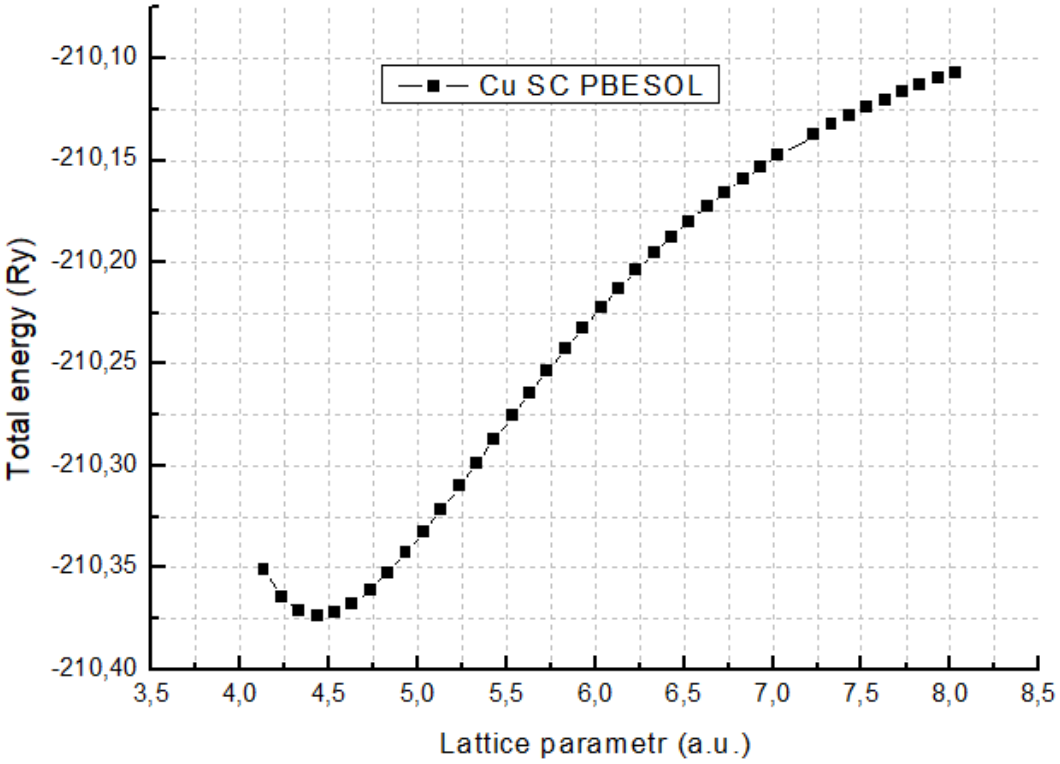

Fig. 5: Dependence of the total energy of the system on the lattice parameter (in the case of PBESOL, Cu SC)

As we can see, the most optimal choice would be **4.431** Bohr and the similarity of the results, which can be an indicator of the correctness of our calculations.

Here consider the case of a Cu FCC structure:

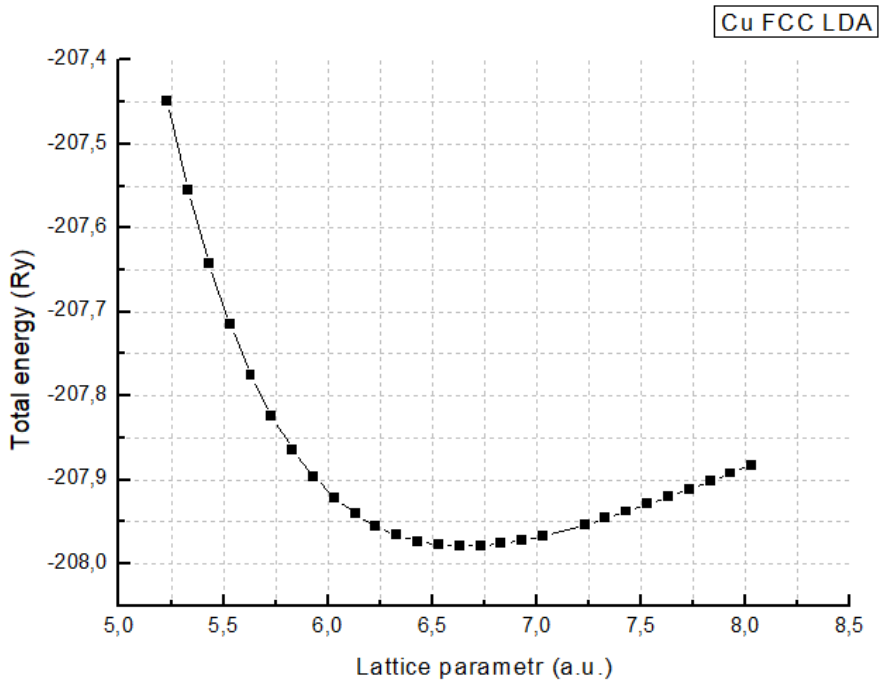

Fig. 6: Dependence of the total energy of the system on the lattice parameter (in the case of LDA, Cu FCC)

As we can see, the most optimal choice would be **6.631** Bohr.

For PBESOL, we have **6.731** Bohr, when the experimental data told about value of **6.831** Bohr.

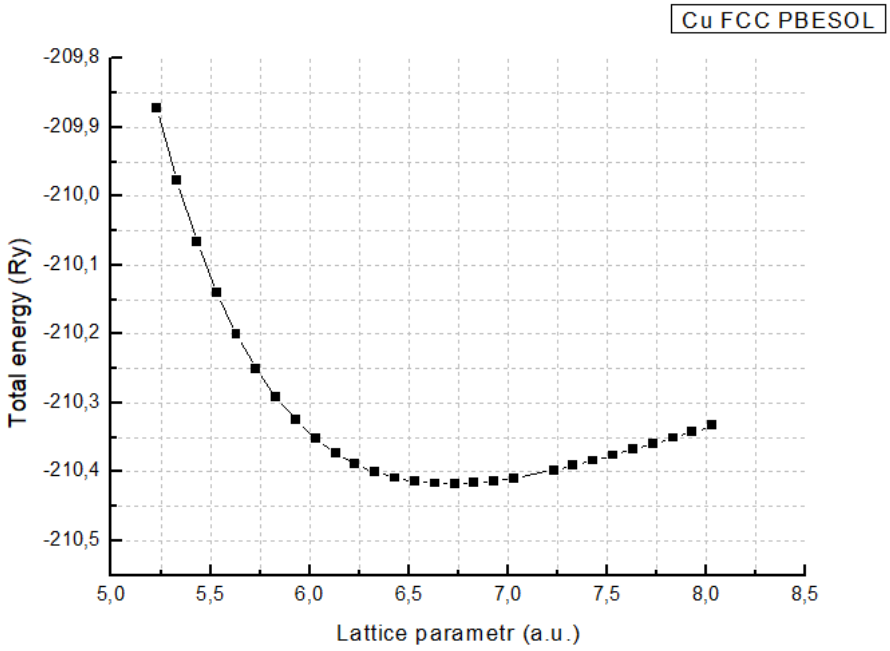

Fig. 7: Dependence of the total energy of the system on the lattice parameter (in the case of PBESOL, Cu FCC)

Based on the data obtained, we can find the volume of the equilibrium state.

- **Electronic band structures**

Using the results obtained in the calculations of "*scf*" (the value of the Fermi energy), we can start using the calculations of "bands", but for this it is necessary to use the crystallographic data to compile "*k*-path" in the input file.

After calculating the "*bands*" we were able to obtain files with a "high-symmetry point" and a file with the "dat.gnu" format, which stores the data for building the "Electronic band structure".

Below are the results that were obtained during the assignment.

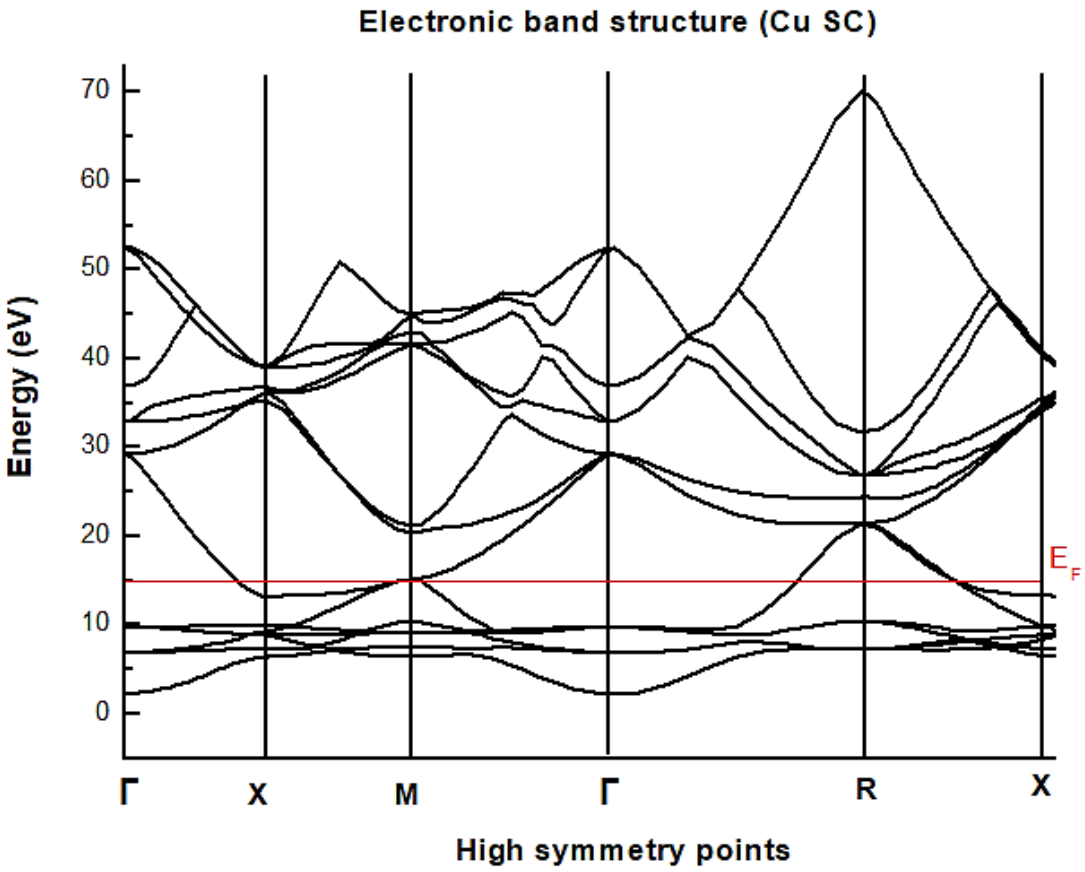

Fig. 8: Electronic band structure for Cu SC (in the case of PBESOL).

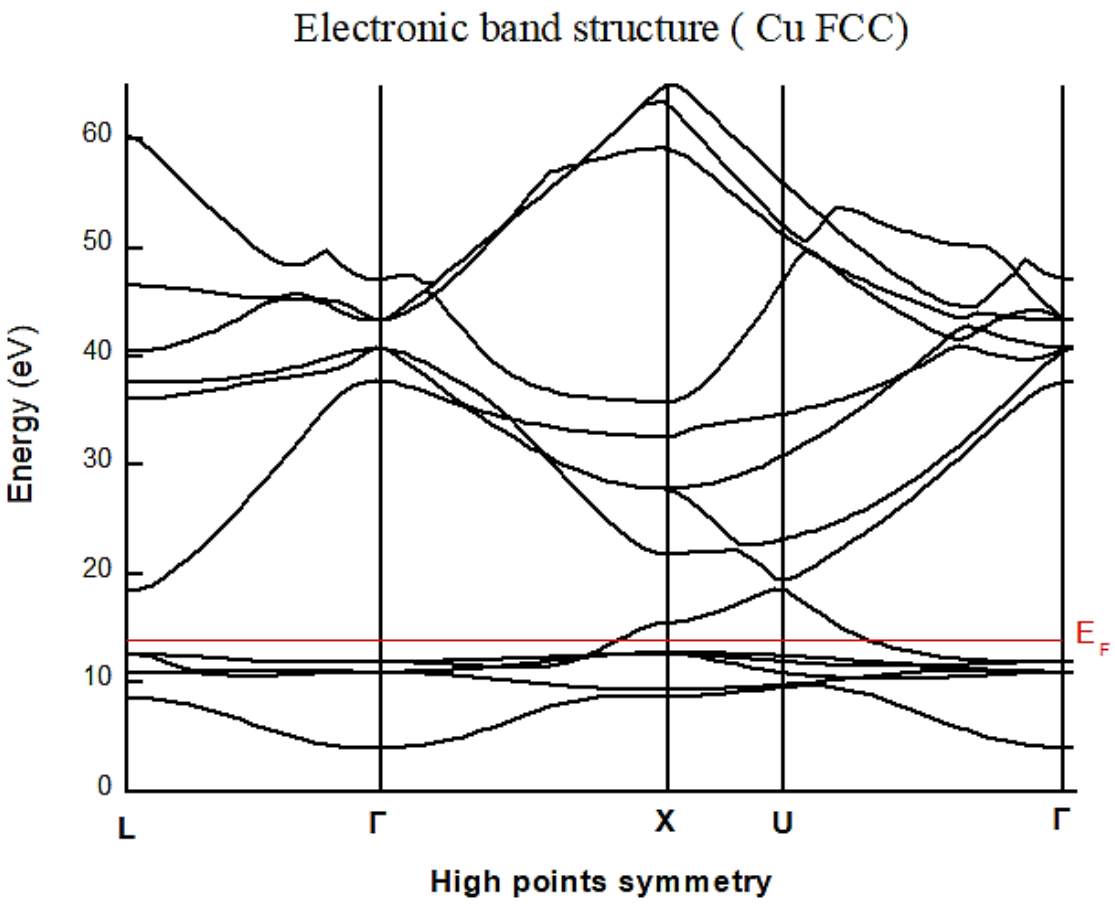

Fig. 9: Electronic band structure for Cu FCC (in the case of PBESOL).