Problem 2: Phonon dispersions of bcc, fcc, and hcp Hf

In this exercise we want to study ab-initio the phonon dispersions of Hafnium in the three most common metallic structures fcc, bcc, and hcp. Experimentally Hf is an hcp crystal with two atoms per unit cell. The experimental crystal parameters are $a = 3.196$ Å and $c = 5.051$ Å.

1. Compute the total energy of Hf as a function of the volume for fcc and bcc Hf using the Density functional theory method. You can use the pseudopotential `Hf.pz-spn-kjpaw_psl.1.0.0.UPF` from `pslibrary` for the LDA functional. Check your results with respect to the computational parameters: kinetic energy cut-offs, number of **k**-points, and smearing parameter.

2. In both cases fit the energy with a Murnaghan equation and determine the theoretical lattice constant at the minimum energy. Plot the pressure as a function of the volume.

3. Now determine the energy versus volume curve for hcp Hf. In this case for each volume determine a and c/a which optimize the energy. Fit the energy versus volume curve with a Murnaghan equation and determine the crystal parameters at the minimum energy. Plot the pressure as a function of the volume. Which is the most stable phase of Hf at zero temperature and pressure according to LDA?

4. At the equilibrium volume compute the phonon frequencies of hcp Hf at the points Γ, K, M and A of the Brillouin zone. Study the convergence of these frequencies with the cut-off energies, **k**-point sampling, and smearing.

5. At the equilibrium volume, and using the computational parameters determined in the previous point, compute the phonon dispersions of hcp Hf along a few high symmetry lines of the Brillouin zone. Compare with the experimental and theoretical phonon dispersions that you can find in the literature (see for instance Computational Materials Science **157**, 121 (2019)).

6. At the equilibrium volume found for the fcc and bcc structures, and using the computational parameters determined at previous point, compute the phonon dispersions of fcc and bcc Hf along a few high symmetry lines of the Brillouin zone. Are these phases dynamically stable?