Problem 3: Phonon dispersions and thermodynamic properties of Zn - PBEsol pseudopotential

In this exercise we study ab-initio the phonon dispersions of zinc. Zinc is an hcp crystal with two atoms in the unit cell. The experimental lattice parameters are $a = 2.66$ Å and $c = 4.95$ Å. We compute the total energy of zinc using density functional theory. You can use the pseudopotential `Zn.pbesol-spn-kjpaw_psl.1.0.0.UPF` from `pslibrary` for the PBEsol functional.

1. At the experimental structure, study the convergence of the total energy as a function of the kinetic energy cut-off of the wavefunctions and determine for which value the energy is converged within 1 mRy. Keep the charge density cut-off equal to 4, 6, or 8 times the cut-off for the wavefunctions. Discuss how the results change. For this calculation use a smearing parameter 0.02 Ry and a **k**-point mesh equal to $(12, 12, 8)$.

2. At the cut-offs determined at the previous point, study the convergence of the energy with the **k**-point sampling. Repeat the calculation for smearing parameters 0.02 Ry, 0.01 Ry, and 0.005 Ry. Discuss the convergence of the results and, if necessary, decrease or increase further the smearing.

3. Using the option `calculation='vc-relax'` in the `pw.x` input determine the equilibrium values of a and c/a at zero pressure. Discuss their convergence with the kinetic energy cut-offs and **k**-point sampling.

4. At the equilibrium values of a and c/a determine the phonon frequencies at the point Γ, K, M, A, H and L of the Brillouin zone. Study their convergence with the kinetic energy cut-offs and **k**-point sampling.

5. Using the parameters for which previous frequencies are converged within 3 cm^{-1} plot the complete phonon dispersions of zinc comparing with the experimental data in D. L. McDonald's, M. Elcombes and A. W. Pryors, J. Phys. C: Solid State Phys. **2**, 1857 (1969).

6. (optional) Compute the phonon frequencies on a thick mesh of **q** points and calculate the phonon density of states of zinc. Use the phonon density of states to calculate the vibrational contribution to the free energy, to the entropy and to the isochoric heat capacity.