

HOMEWORK 6**Using Quantum Espresso (PWscf) for DFT Calculations in Solids****Due: Monday March 9th, 4:30 p.m.****Problem 1 - Convergence issues for absolute energy-calculation with respect to cutoff energies for first-principles (DFT) based calculations**

- A. Using PWSCF, calculate the energy of diamond as a function of cutoff energy. Use an energy increment of ~ 10 Ryd and a range of 10-140 Ryd. When changing the cutoff, make sure to keep the other variables (lattice constant, k - points, etc.) fixed. Record all relevant parameters such as lattice constant, k -points, etc. Record and plot your final results. Specify when you reach the level of convergence of ~ 5 meV/atom (convert this to Ryd).
- B. Do you see a trend in your calculated energies with respect to cutoff? Is this what you expected and why? If not, why?

Problem 2- Convergence of absolute energies with respect to k-points.

A. Using PWSCF, calculate the energy of diamond as a function of k -point grid size. For each grid, record the number of unique k -points. This gives a measure of how long your calculation will take - calculations scale as K , where K =number of unique k -points. When changing the size of the k -point grid, make sure to keep your other variables fixed (lattice constant, cutoff, etc.) . One may choose a lower cutoff than the “converged” cutoff in problem 1. There are some cross effects in doing so, however we assume these are small.

B. Do you see a trend in your calculated energies with respect to grid size? Is this what you expected and why?

Problem 3- Convergence of forces with respect to cutoff energies.

In this problem, we will be calculating forces on atoms. Displace a C atom $+0.05$ in the z direction (fractional coordinates). Keeping other parameters fixed, calculate the forces on C as a function of cutoff. A good force value would be converged to within ~ 10 meV/Angstrom (convert this to Ryd/bohr - PWSCF gives forces in Ryd/bohr). Record relevant parameters (lattice parameter, k -points, unique k -points etc.). A good k -point grid to use is $4 \times 4 \times 4$. Plot and record your results.

Problem 4- Convergence of forces with respect to k-points.

Using PWSCF, calculate the force on a C atom (displaced +0.05 z direction in fractional coordinates) as a function of k -point grid size. Keep all other parameters fixed. Record your relevant conditions (lattice parameter, cutoffs, etc.) .

Problem 5 - Convergence of energy differences with respect to energy cutoffs.

In practice only energy differences have physical meaning, as opposed to absolute energy scales, which can be arbitrarily shifted. Therefore, it is important to understand the convergence properties of energy differences. Using PWSCF, calculate the energy difference between diamond structures at two lattice parameters as a function of cutoff. For example, you could calculate the energy of diamond at the experimental lattice parameter (6.74 bohr), then calculate the energy at 6.70 bohr (or any lattice parameter close to the minimum), take the difference between the two, and repeat for many energy cutoffs. Make sure to keep your other variables (lattice constant, k points, etc.) fixed while changing the cutoff. Record all relevant parameters such as the lattice constant, k -points, and so on. A good energy difference is converged to ~5 meV/atom (convert this to Ryd).

Problem 6 - Comparing Probs. 1, 2, 3, and 4, and 5

How do the cutoff requirements change when looking at absolute energies vs. looking at forces vs. energy differences? How do the k -point grid requirements change? Can you explain this?

Problem 7 - Equilibrium lattice constant and bulk modulus of diamond.

This problem has you calculating the equilibrium lattice constant and bulk modulus of diamond. Usually, we are interested in quantities such as forces or energy differences. We are not usually interested in absolute energies. For this reason, use the cutoff and k -point criteria that you determined for the force and energy difference calculation for this problem. However, note that to be absolutely safe you should test for the quantity you are interested in (here e.g. would test convergence of lattice constant as a function of energy cutoff and k -point grid size). For this problem, just use the force criterion.

A. Calculate the equilibrium lattice constant of diamond using PWSCF. The experimental value is 6.74 bohr. Use the cutoff and k -point grid criteria you obtained from the force convergence calculations. How does the experimental value compare with the calculated value? Is this expected? Make sure to record all the relevant parameters (k -points, cutoffs, etc..).

B. Calculate the bulk modulus of diamond and compare with available experimental data.