Problem Set 2: First-Principles Energy Methods

Due date: 3/17/2019

Problem 1 (10 points): Convergence of *absolute energies* with respect to cutoff energies.

A Using the Quantum ESPRESSO PWscf package, calculate the energy of Ge in the diamond structure as a function of plane-wave cutoff energy. A good range to try is 5-80 Ry, doing calculations at increments of 5 Ry. For now, you may set the lattice parameter equal to its experimental value and use a k-point grid of 4x4x4. When changing the cutoff, make sure to keep the other variables (lattice constant, k-points, etc) fixed and to record them. Record and plot your final results. Specify when you reach the level of convergence of around 5 meV/atom (convert this to Ry/atom). Note that the code calculates total energy.

B Do you see a trend in your calculated energies and calculation time with respect to the cutoff? Is this what you expect and why?

C In Problem Set 1, we used a cubic unit cell. Here, we use the primitive cell. What are the advantages and disadvantages of both methods?

Problem 2 (10 points): Convergence of *absolute energies* with respect to k-points.

A Using PWscf, calculate the energy as a function of the size of the k-point grid used to integrate the Brillouin zone. For each grid, record the number of unique k-points. Record the computational time. When changing the size of the k-point grid, make sure to keep your other variables fixed (lattice constant, plane-wave cutoff, etc). One may choose a lower cutoff than the "converged" cutoff in the last problem. There are some "cross effects" in doing so, however we assume these are small.

B Do you see a trend in your calculated energies and computation times with respect to the k-point grid size? If you see a trend, is this what you expect and why?

Problem 3 (10 points): Convergence of *forces* with respect to plane-wave cutoff energies.

Oftentimes we are interested in quantities other than energies. In this problem, we will be calculating forces on atoms. Displace a Ge atom +0.05 in the z direction (fractional coordinates). Keeping other parameters fixed, calculate the forces on a Ge atom as a function of the kinetic energy cutoff. A good force value would be converged to within around 10 meV/Angstrom (convert this to Ry/bohr, since PWscf gives forces in Ry/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 (10 points): Convergence of *forces* with respect to k-points.

Using PWscf, calculate the force on a Ge atom displaced +0.05 in the 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 (5 points): 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. Using PWscf, calculate the energy difference between two Ge cyrstals at different lattice parameters, as a function of cutoff. For example, you could calculate the energy of Ge at the experimental lattice parameter (10.70 bohr), and then calculate the energy using another value close to it (10.75 bohr, for example), take the difference between the two energies, 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 around 5 meV/atom (convert this to Ry/atom).

Problem 6 (10 points): Comparing Problems 1, 2, 3, 4, and 5.

How do the cutoff requirements change when looking at absolute energies, looking at forces, and looking at energy differences? How do the k-point grid requirements change? Can you explain the differences in the requirements and the rates of convergence?

Problem 7 (45 points): Equilibrium lattice constant and bulk modulus.

In this problem you will calculate the equilibrium lattice constant and bulk modulus of Ge. Usually, we are interested in quantities such as forces or energy differences, not absolute energies. Therefore, for this problem use the cutoff and k-point criteria that you determined for the force and energy difference calculation. (In general, to be absolutely safe you should test convergence specifically for the quantity you are interested in. So, ideally, we would test convergence of lattice constant as a function of energy cutoff and k-point grid size, but we are not going to do this.)

A Calculate the equilibrium lattice constant of Ge in the diamond structure from first principles using PWscf. The experimental value is 10.7 bohr. 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 Ge in the diamond structure. Here you will need to derive some (simple) equations and then apply them to compute a material's property, a very typical scenario in computational science.

The bulk modulus is a measure of the stiffness of a material. It is defined as

$$B = -V_0 \frac{\partial P}{\partial V},$$

where P is the pressure on the material, V is its volume, and V_0 is its equilibrium volume. Derive an expression for the bulk modulus that you can use it. Use finite difference approximation for derivatives. How does your value compare with the experimental value of ≈76 GPa?

C Solve problem 7A by directly minimizing the energy using structure optimization capability of Quantum Espresso. Think about what type of calculation the code should do, find the required parameters in the online documentation and modify the Python workflow accordingly. Compare with the results of problem 7A where you directly scanned over lattice parameter values.

Hints: Remember that $P = -\partial E/\partial V$. Remember that PWscf calculates energies per primitive unit cell. Be careful about unit conversions.

OPTIONAL Extra Credit Question 1 (20 points):

Calculate the elastic constants C_{11}, C_{12}, and C_{44} for Ge using first-principles energy methods. You will need to perform proper deformations of the unit cell and to lower the symmetry. You will have 8 atoms in the unit cell for diamond structure. Use the same (reduced) symmetry for the original (not deformed) unit cell in order to make correct energy comparisons. You may want to look up convenient expressions relating the elastic constants specifically in cubic crystals.

OPTIONAL Extra Credit Question 2 (20 points):

Compute and plot the band structure of Ge. You will need to change the original calculation mode to

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calculation = 'bands'
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and provide the list of k points along high some symmetry directions (in section K_POINTS) for which you want to compute the Kohn-Sham eigenvalues. The proper format of the input file is very important. The details can be found in the PWscf manual. Look up the relevant high symmetry directions and special k-points for the diamond crystal, which is the same space group as Si and Ge. Include the valence bands and the 4 lowest conduction bands. (change parameter *nbnd*) Compare your result with the band structure found in the literature.