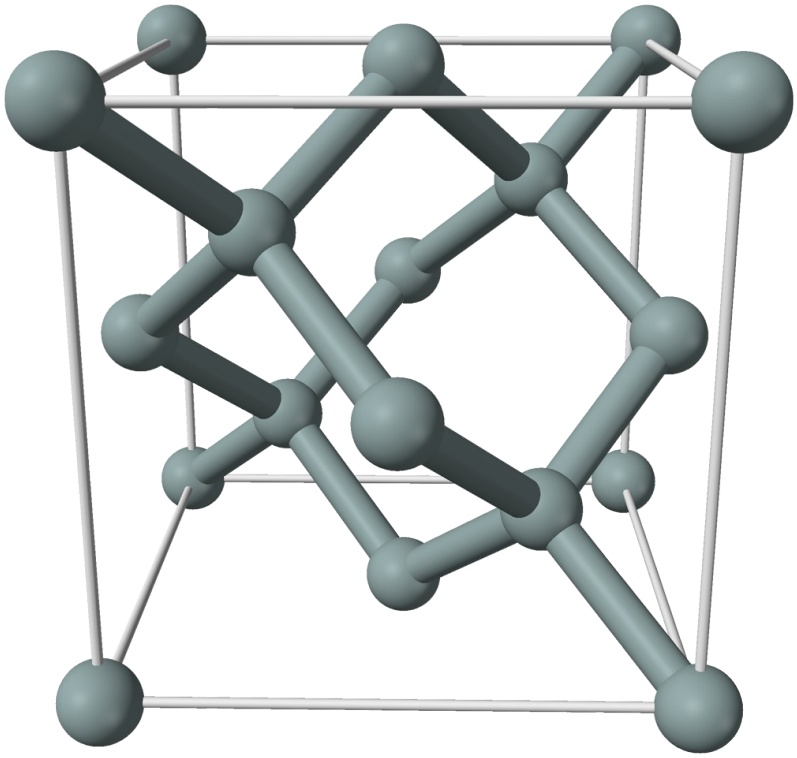
Lab #1 Assignment: Total-Energy Calculations with Quantum-Espresso

For our sample problem, we will be determining the zero-temperature, zero-pressure equilibrium lattice parameter of silicon by doing a series of DFT total-energy calculations. First, we will determine proper values for the plane-wave energy cutoff and for the density of the Monkhorst-Pack ***k***-point grid by examining convergence of interatomic forces. Then we will calculate the energy as a function of varying lattice parameter and fit the results to a known equation-of-state curve.

The diamond-structure unit cell of silicon is shown below for your reference.



For each of these calculations, you may use the sample input file Si.sample.in as a starting template for your calculations. Although you may edit this file manually for each calculation you perform, you may find it easier to use scripts to automate the process. If you choose to use scripts instead, a sample script Si.sample.sh is provided as a template.

Part I: Understanding convergence with respect to plane-wave energy cutoff

1) Copy the template input file Si.sample.in and edit it.
2) Set your ***k***-point mesh to a value which is large enough to ensure any error because of poor sampling will be small. A value of 6 x 6 x 6 should be sufficient for this part of the problem. To begin with, set the lattice constant celldm(1) to the room-temperature experimental value for silicon (look on http://www.webelements.com).
3) Systematically vary your plane-wave energy cutoff ecutwfc and calculate the energy of the system for each value of ecutwfc. Try values between 5 and 35 Ry, sampling at intervals of 5 Ry.

4) Save your results from (2). Now revise your script to calculate the energy of the system as a function of ecutwfc for a unit cell of silicon which is compressed by 5% in each cubic direction. (Note that there is no need to revise the positions of the atoms in the script, since these are given in units of the lattice constant and will scale automatically when you change celldm(1)).
5) For each value of ecutwfc, calculate the energy difference ΔE between the structure of (1) and that of (2). Collect your results and plot ΔE as a function of the plane-wave energy cutoff ecutwfc. Is the convergence trend monotonic?
6) Assume that using 35 Ry gives a good approximation for the fully converged value of ΔE. What is the *lowest* energy cutoff that gives a value for ΔE that is within 1% of the value for a 35 Ry cutoff? This is the value you should choose for all subsequent calculations.

Part II: Understanding convergence with respect to *k*-point mesh density

1) Now repeat the basic procedure from Part I, except this time systematically vary the Monkhorst-Pack ***k***-point mesh density instead of the plane-wave energy cutoff. Try automatic ***k***-point meshes of 1 x 1 x 1, 2 x 2 x 2, 3 x 3 x 3, ... , up to 6 x 6 x 6. Keep the offset at 1,1,1. (Note that since silicon is a cubic cell, ***k***-point sampling should always be even in each of the three Cartesian directions.) Be sure to use the plane-wave energy cutoff you found in Part I. As before, perform one complete set of calculations for silicon at the experimental lattice parameter and a second one for the system under compression.
2) For each ***k***-point mesh density, calculate the energy difference ΔE between the larger structure and the compressed structure. Collect your results and plot ΔE as a function of the linear ***k***-point mesh density. Is the convergence trend monotonic?
3) Assume that an 6 x 6 x 6 ***k***-point mesh gives a good approximation for the force at full convergence. What is the *smallest* ***k***-point mesh that gives a value for ΔE that is within 1% of the value you obtained using the 6 x 6 x 6 mesh? This is the mesh you should choose for all subsequent calculations.

Part III: Obtaining the equilibrium lattice constant

1) Now insert the values for the plane-wave energy cutoff and the Monkhorst-Pack ***k***-point mesh density that you obtained in Parts I & II. Calculate the total energy of your system as a function of the lattice parameter. Test values for the lattice parameter in the range 9.8 to10.8 Bohr, sampling at intervals of 0.2 Bohr.
2) Plot the energy as a function of the lattice parameter.
3) Use the ev.x utility provided with Quantum-Espresso to fit the energy-versus-lattice constant data to a Birch-Murnaghan equation of state. Note that the input to this utility should be a file with two columns: the lattice parameter in units of Bohr and the energy in units of Rydbergs. Look at the output to ev.x and record the resulting lattice constant and the energy of the system at equilibrium.

Part IV: The consequences of poor convergence

1) Repeat the procedure you used in Part III, except this time use a plane-wave energy cutoff of only 5 Rydbergs. Plot the resulting energy as a function of the lattice parameter, and record the values of the lattice constant and the energy of the system at equilibrium.
2) Repeat the procedure once again, returning the plane-wave energy cutoff to its proper value but decreasing the ***k***-point mesh to 1 x 1 x 1. Plot the resulting energy as a function of the lattice

parameter, and record the values of the lattice constant and the energy of the system at equilibrium.

3) How does poor convergence affect the results? Pay particular attention to the shape and position of the energy-versus-lattice-constant curve.
4) Suppose we were to double the size of the silicon unit cell that we used in each dimension, resulting in a new unit cell with 8 times the volume of the original. Based on your findings of Parts I & II, what plane-wave energy cutoff and ***k***-point mesh density should you use for your new cell? Justify your answer.