NANO266 Lab 2 - Convergence of DFT calculations

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1 Introduction

In this lab, we will look at convergence issues in bulk calculations with respect to parameters such as the energy cutoff and k-point grid. We will be using QuantumEspresso (http://www.quantum-espresso.org/), an open scource first principles code. Note that all calculations in this lab are fairly simple and can be run on a modern desktop or laptop in serial mode, i.e., you do not actually need access to a supercomputing cluster to perform these calculations.

2 Initial setup

It is assumed that you have already followed the instructions in the README.md in the root labs folder and have access to PWSCF, either on XSEDE or on your own computer or virtual machine. Do a git pull so that you are up to date with the repo. Try typing `pw.x` in your terminal to make sure that everything is working. You may get a `Waiting for input...` message. Just hit Ctrl-C to cancel.

Once you are done with the above, make sure you are in the lab2 folder by doing:

cd <path/to/repo>/labs/lab2

3 Q1 (10 points): Convergence of *absolute* energies with respect to energy cutoff

Start by looking at the `Si.pw.in.template`, which is a template for the input file for PWSCF. You should get yourself familiar with the format, and what each of the sections and parameters mean. Note that some parameters have placeholders {xxx}, which will be replaced by our run script. A PWSCF_IO tutorial is provided in the tutorials folder of this

repo to help you understand the parameters. You may also wish to consult the QuantumEspresso online documentation. A quick explanation of the key parameters are given as follows:

```
&control                    # This is the control section
  calculation = 'scf' ,     # Specifies that we are doing a static SCF calculation.
  outdir = './tmp' ,
  pseudo_dir = './' ,       # Location of pseudopotential files.
  tprnfor = .True.,         # Specifies that you want forces to be printed. Used
  tstress = .True.,         # in subsequent questions.
/
&system                     # Specifies the structure
  ibrav = 2,                # For PWSCF, ibrav = 2 denotes an FCC cell.
  celldm(1) = {alat},       # This specifies the lattice parameter of the fcc cell.
  nat = 2,                  # We have two Si atoms per unit cell.
  ntyp = 1,                 # There is only one type of atom (Si)
  ecutwfc = {ecut} ,        # This stipulates the energy cutoff.
/
&ELECTRONS                  # These three sections are not used in this particular calcul
/
&IONS
/
&CELL
/
ATOMIC_SPECIES              # Specify the pseudopotential for each species.
  Si   28.055  {pseudopotential}
ATOMIC_POSITIONS crystal    # Specifies the atomic positions in frac. coords
  Si      0.00    0.00    0.00
  Si      0.25    0.25    0.25
K_POINTS automatic          # Specifies the k-point grid to be used
  {k} {k} {k}   0 0 0
```

We have also written a Python script called `run_pw.py` to help you in this simulation. Again, read through the script to understand what it does. It is heavily commented to aid you in your understanding. Note that this is a starting point. *You will need to understand enough to make changes in order to finish this lab.* A second script called `analyze.py` is provided to help you compile the results into a csv file, which can be opened with most spreadsheet programs for analysis. To run the scripts, you simply need to type

`python <script>.py <other parameters if necessary>`

1. Using PWSCF, calculate the energy of silicon as a function of cutoff energy. A good increment is ∼10 Ry, in the range of 10–100 Ry. When changing the cutoff, make sure to keep the other variables (lattice constant, k-points, etc.) fixed. Record and plot your final results. Specify when you reach the level of convergence of ∼5 meV/atom (you will need to take care of the unit conversions). Note that PWSCF calculates energy per primitive cell.

2. Do you see a trend in your calculated energies with respect to cutoff?

4 Q2 (10 points): Convergence of *absolute* energies with respect to *k*-points

1. Modify the script in Q1 to calculate the energy as a function of k-point grid size. For each grid, record the number of unique k-points. Note that this is not the same as the k specified in the script and input file. The `analyze.py` script reports the number of unique k-points extracted from the output files. Again, make sure to keep your other variables fixed. Record and plot your final results. Specify when you reach the level of convergence of $\sim$5 meV/atom.

2. Do you see a trend in your calculated energies with respect to grid size? If you see a trend, is this what you expect and why? If not, why?

3. Plot your calculation time against the number of k-points. Is there a relationship, and if so, what is that relationship? (You will need to figure out how to extract the calculation time from the output files.)

5 Q3 (10 points): Convergence of forces with respect to cutoff energies

Let us now investigate the convergence of forces on atoms with respect to cutoff. Displace a Si atom +0.05 in the z direction (fractional coordinates). Keeping other parameters fixed, calculate the forces on Si as a function of cutoff. A good force value would be converged to within $\sim$10 meV/Angstrom (note that PWSCF gives forces in Ryd/bohr). Use a k-point grid of 4x4x4. Plot and record your results, including all relevant parameters.

6 Q4 (10 points): Convergence of forces with respect to *k*-points

Repeat Q3, but this time, investigate the convergence of forces as a function of k- point grid size. Keep all other parameters fixed. Record your relevant conditions (lattice parameter, cutoffs, etc.)

7 Q5 (10 points): Convergence of energy differences

In practice, only energy differences have physical meaning. Let us now investigate the convergence of energy differences with respect to energy cutoff and k-points. For this exercise, compute the energy difference between silicon structures at two lattice parameters. You can

calculate the energies of silicon the experimental lattice parameter (10.26 Bohr), and at 10.30 Bohr, and take the difference between the two. Do a convergence study for both the energy cutoff and the k-point grid. Record all relevant parameters such as the lattice constant, k -points, and so on. A good energy difference is converged to $\sim$5 meV/atom.

8 Q6 (10 points): Selecting the right parameters

Look at the results from the preceding questions. Discuss the changes in the requirements in terms of cutoff, k-point grid, etc. when comparing absolute energies, forces and energy differences. Explain as far as possible any trends you see.

9 Q7 (15 points): Finding the equilibrium structure

Using an appropriate set of parameters (energy cutoff, k-point, etc.), determine the predicted equilibrium lattice constant for silicon by calculating the energy of the silicon structure at several lattice parameters. Note that you may need to use a finer grid near the equilibrium point to get a more accurate answer.

Also, it should be pointed that PWSCF allows you to specify `calculation = 'vc-relax'` to automatically perform a full cell relaxation. But it is important that you understand how to do it using static SCF energy calculations at different lattice parameters as a demonstration of the variational principle. You will be using this in the next step and your next lab.

10 Q8 (15 points): Bulk modulus of silicon

Calculate the bulk modulus of silicon at the equilibrium lattice constant using the PBE functional. Remember that the bulk modulus is given by:

$$K = V\frac{\partial^2 E}{\partial V^2}$$

Think about how you can obtain K from the E vs a plot. Be careful that PWSCF reports energies per *primitive cell*, and you will need to make sure you do appropriate unit conversions ans scaling.

Compare it to the experimental value of 97.6 GPa. (Hopcroft, M. a; Nix, W. D.; Kenny, T. W. J. Microelectromechanical Syst., 2010, 19, 229–238, doi:10.1109/JMEMS.2009.2039697.)

11 Q9 (10 points): Choice of functional

The calculations you have been doing thus far is based on the PBE GGA functional. Redo Q7 and Q8, but now use the `Si.pz-n-kjpaw_psl.0.1.UPF` (LDA) pseudopotential instead. Comment on any differences in the predicted equilibrium lattice constant.