Lab 2. Check numerical convergence

We have in the first lesson obtained many results that seem to be reasonable, at least qualitatively. But can we trust them quantitatively? As an example, were the calculated energies the "true" DFT energies (at the GGA level using the PBE potential), or were the values affected by numerical parameters? On the other hand, were the numerical parameters well suited to the problem, or did we overshoot the accuracy? If we use a numerical grid that is much denser than what is needed to achieve sufficient precision, we may waste computational resources. This is not important for the small unit cell of bulk Si, but if we are going to run large supercells with hundreds or even thousands of atoms, we need to know exactly the appropriate level of accuracy. But then another question arises: what is "sufficient" precision?

We will not be able to answer all these questions completely, but we will systematically assess the most important sources of error and how to achieve control of them.

We are going to start testing convergence of the energy cutoff in the next section, so a good name of the new directory is e.g. "cutofftest". We will use bulk SiO_2 as our test case, so you can copy input files from ~olem/fm4111/datalab/sio2_bulk/. You can use the script vaspdist for this purpose:

```
> vaspdist ~olem/fm4111/datalab/sio2_bulk/ cutofftest
```

This script copies the five input files from the input directory (".") to the directory called cutofftest. Remember that this only work if you are located in the correct folder – the cutofftest folder should be listed when you write ls.

You are expected to write a brief report on this exercise, with answers to the questions embedded in the following text.

1 Use emacs to change text files

It is now necessary to manipulate the input files somewhat. To do this, we have access to a number of convenient scripts, which can be used simply by typing commands at the shell prompt. But you will also need to change entries in the files themselves, using a text editor. The recommended editor in this course is emacs, but you are of course free to use other unix based editors like vi, pico, gedit or xemacs.

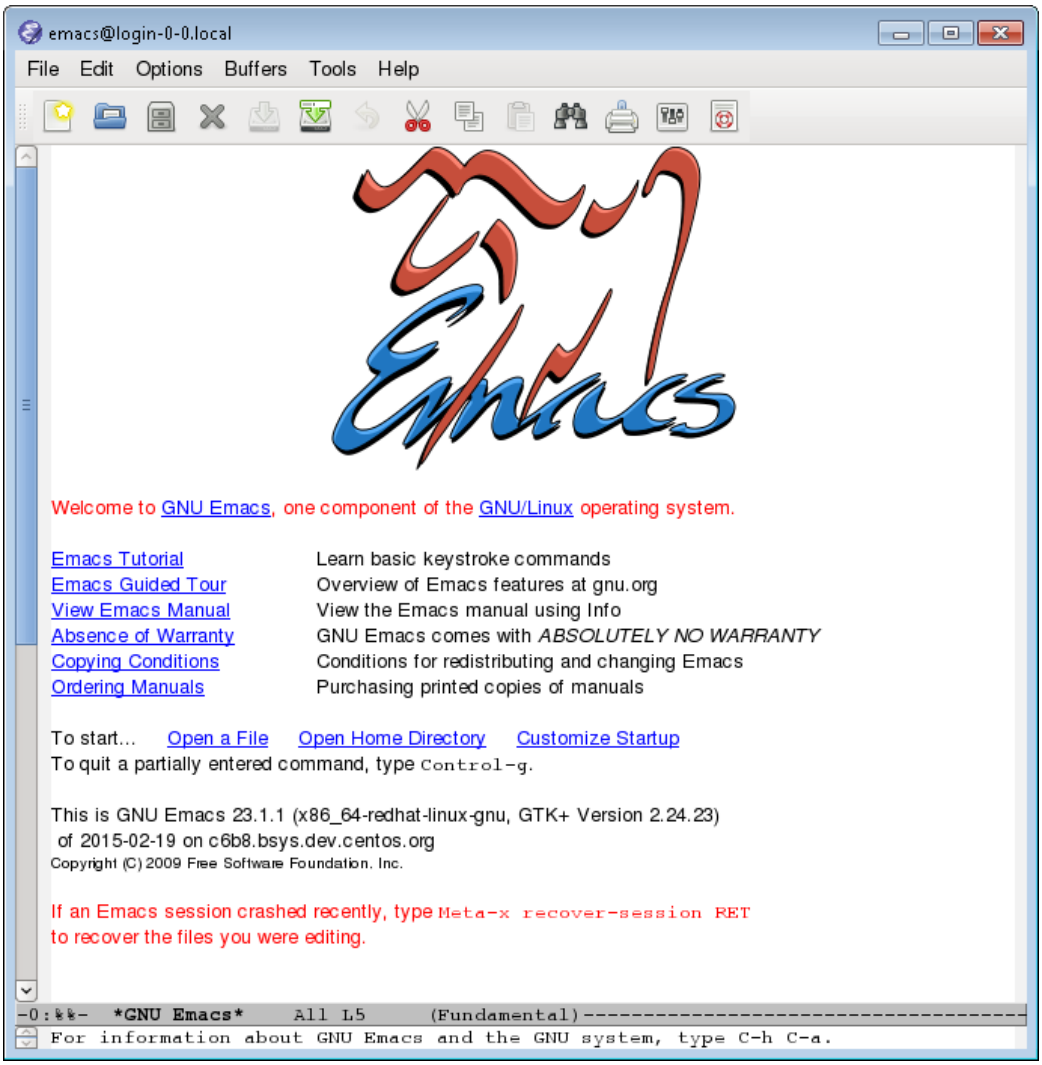
First, create a new directory for the file manipulation, e.g "Lab2". Then start emacs from the command line:

```
> emacs &
[1] 4536
```

The '&' character means the command will be started without blocking the command line. Without this character, the shell will wait for the command to be finished, and you will not be able to write other commands while emacs is running. Using the & character means you will be able to run a command, make small changes in emacs, run another command, etc., without ending and starting new emacs sessions. If you forgot writing the & character, you can suspend the program with Ctrl-Z, and then restart the program in the background with the bg (**b**ack**g**round) command:

```
> emacs
> <Ctrl-Z>
[1]+  Stopped                 emacs
> bg
[1]+ emacs &
```

When emacs is started, a new window appears, similar to this:



You can open files etc. through the menus, they should be rather self-explanatory. File->Open file… will place the cursor at the bottom line, where you can write the name of the file. Use <Tab> to complete names; it is e.g. enough to type I<Tab><Enter> to open the INCAR file. If you type something wrong on this line, you can escape with the Ctrl-g combination. When INCAR is open, you can simply make the changes (as described in the next section) and save the file with File->Save (current buffer). It is a good idea to have a window permanently open, since you can open files from many different directories from the same instance of emacs.

Go to e.g. http://tldp.org/HOWTO/Emacs-Beginner-HOWTO.html for more details on how to use emacs.

2 Convergence of forces, pressure, total energy and band gap with respect to the energy cutoff

We want to check convergence of various calculated properties with respect to the energy cutoff that is specified in the INCAR file with the ENCUT tag. For each value of ENCUT we need to perform a separate calculation with VASP. Thus, you should create separate folders for each of these values. The default cutoff for SiO_2 is 400 eV. (This is taken from the POTCAR file; ENCUT = Max(ENMAX).) So first create a folder for the ENCUT = 400 calculation. Copy the starting files to this folder with the vaspdist script. Submit the job to the batch queue with the "sub" command. Remember that you can see the status of your jobs with the "st" command.

When a job has finished, you can get out the most essential results with the "vaspout" command:

```
> vaspout 400/OUTCAR
MxForce Drift   Press   TOTEN           Filename
0.604   0.007   33.48   -71.146266      400/OUTCAR
```

MxForce is the maximal force in eV/Å calculated by VASP, using electrostatic interactions with the atoms. It is convenient to monitor this during a relaxation, to see if the remaining forces are decreasing. We will use MxForce as a representative calculated force to check its convergence.

Drift is a measure of the quality of the calculated force. It should always be lower than the lowest force we are aiming for in a relaxation.

Press is the calculated pressure in kbar calculated by VASP. If it is positive, it indicates that the unit cell experiences an external pressure, and that a relaxation will increase the cell volume.

TOTEN is the calculated total electronic energy in eV. It is the energy of the unit cell compared to that of all the atoms infinitely apart. A negative energy means that energy is gained, thus the structure is stable compared to the atoms.

Bandgap is the calculated band gap of the structure in eV. It is calculated as the difference between the conduction band minimum and the valence band maximum. Thus, it is possible to get out a "negative" band gap. This is not physical, but can be convenient for convergence tests etc.

Now create a new folder with ENCUT = 450 and copy input files to this folder. Open the INCAR file in emacs or another text editor. Change the energy cutoff in INCAR manually to 450, and save the file:

```
ENCUT  = 450       ! Cut-off energy for plane wave expansion
```

This job can now also be submitted with the "sub" command.

Repeat the procedure above for energy cutoffs up to 850 eV, separated by 50 eV. You will need to create folders, change ENCUT in INCAR, submit the job to the queue, and read out the results after each job. You may want to write a simple script that performs all these tasks automatically. A sample script may look like this (you could make a file called e.g. encuttest.sh with contents similar to this):

```
#!/bin/sh -f
```

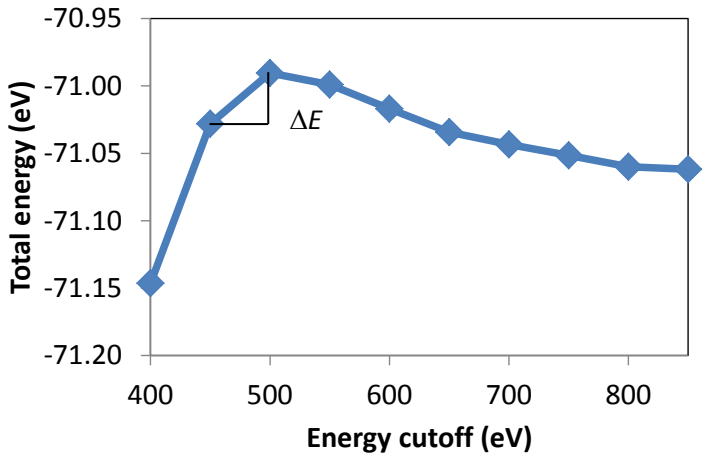
```
for encut in {400..850..50}
  do
    mkdir encut$encut
    sed s/400/$encut/ INCAR > encut$encut/INCAR
    cp POSCAR KPOINTS POTCAR jobfile encut$encut/
    cd encut$encut/
    sbatch jobfile
    cd ..
  done
```

The script can be run from the command line, but make sure it has executing access. Use the chmod (**ch**ange **mod**ification) command for that:

```
  > chmod u+x encuttest.sh
  > encuttest.sh
```

Save the data from vaspout in a new file called e.g. results.txt. You can create a new file in emacs using the menu File->Open file… To copy text from the terminal, mark the text with the left mouse button. To paste the text, simply click the middle mouse button.

We can now assess the convergence of the calculated pressure and the total energy with respect to the cutoff energy. We start with the **total energy**. This can be visualized by plotting the total energy as a function of the cutoff energy (you should plot this yourself by copying the data in results.txt to a spreadsheet or open it in a plotting program like gnuplot):



We see that the absolute change in calculated total electronic energy $|\Delta E|$ is more than 0.1 eV when we increase the cutoff from 400 to 450 eV; this is clearly not very well converged. If we require convergence of the total energy within e.g. 10 meV, this is obtained at 500 eV ($|\Delta E|$ is then 9 meV). When is the total energy converged within 3 meV?

Note that we have increased the cutoff energy in steps of 50 eV. If we used another step, we would need to specify the convergence criterion differently. In other words: since we are interested to know at which point the slope of the curve above is less than a certain value, we need to know both ΔE and the cutoff

energy step size. So if someone says that their calculation is converged within 1 meV with respect to the cutoff energy, this does not actually say much. If $|\Delta E| < 10$ meV when the step size is 10 eV, this is much less strict than if the step size is 100 eV. With this in mind, we can formulate our preliminary convergence criterion above in the following manner:

$$\frac{\Delta E_{\mathrm{Tot}}}{\Delta E_{\mathrm{Cutoff}}} < \frac{3\,\mathrm{meV}}{50\,\mathrm{eV}}.$$

What about the calculated **pressure**? The pressure is printed out in kbar, and a reasonable convergence criterion for the pressure is that the change in pressure ΔP is less than 3 kbar when we increase the cutoff energy by 50 eV:

$$\frac{\Delta P}{\Delta E_{\mathrm{Cutoff}}} < \frac{3\,\mathrm{kbar}}{50\,\mathrm{eV}}.$$

When is the pressure converged with respect to the cutoff energy?

The pressure is not among the most important properties we can calculate. But it is used for relaxation of the unit cell size (VASP will then aim to decrease the calculated pressure below a certain value P_{max}). In that case, the error originating from numerical parameters like the cutoff energy should not be larger than P_{max}. Numerical convergence of the pressure is also important when elastic properties of materials (elastic moduli) are calculated.

One of the most important tools we are going to use later on is relaxation of **forces**. This can be used to predict crystal structures and local geometric structures in nanomaterials. It is also important to perform calculations of electronic structure etc. without internal stress and large remaining forces in the structure, since this can influence many of the other properties.

The forces are given in eV/Å, and a typical criterion for numerical convergence is:

$$\frac{\Delta F_{\mathrm{Max}}}{\Delta E_{\mathrm{Cutoff}}} < \frac{0.05\,\mathrm{eV/Å}}{50\,\mathrm{eV}},$$

where ΔF_{Max} is the change in maximal force when the cutoff is increased (the maximal force F_{Max} is printed out by the vaspout script in the "MxForce" column). When is the force converged with respect to the cutoff, if we use this criterion? What if the criterion is one order of magnitude more strict (0.005 eV/Å), which is needed in calculations of e.g. phonon vibrations?

Our last parameter in this section is the **band gap**. When is the band gap converged to within 0.01 eV with respect to the energy cutoff?

3 Convergence of relative energies with respect to the energy cutoff

The calculations in the previous section were all done on the same structure. The total energy of one structure is not interesting to us – the absolute value is somewhat arbitrary, and can almost never be

compared between different programs or methods. We are on the other hand always interested in relative energies. As an example, we were interested in the energy difference between various crystal structures of Pt in Lab 2.

One simple way to generate an energy difference is to move one atom slightly away from the equilibrium position. You should prepare a series similar to the one in the previous section, only with this slightly different structure. Thus, create a new folder (e.g. "cutofftest2") with subfolders corresponding to ENCUT = 400 to 850 and repeat the calculations. Change the structure by moving the first Si atom by 0.02 in the y coordinate:

```
      0.46980000  0.02000000  0.66667000
```

We now have two sets of test calculations for slightly different structures, using a series of cutoff energies. This can be used to evaluate the convergence of **relative energies** with respect to the cutoff. More generally, relative energies can e.g. be formation energies (comparing the energy of a compound with its constituents), transition barriers (comparing the energy at a saddle point with that at a nearby energy minimum), surface energies (comparing the energy of a slab with that of the bulk), adsorption energies (comparing the energy of an adsorbed molecule with the sum of a the energy of a pure surface and that of the molecule), etc. Thus, in most cases we would be satisfied with the convergence of relative energies within, say:

$$\frac{\Delta E_{\mathrm{Rel}}}{\Delta E_{\mathrm{Cutoff}}} < \frac{1\,\mathrm{meV}}{50\,\mathrm{eV}}.$$

Our relative energy E_{rel} is defined as the difference between the energy of the input structure of bulk SiO_2 (cutofftest) and that of bulk SiO_2 with one atom moved away from equilibrium (cutofftest2). When do we achieve numerical convergence of this relative energy with respect to the cutoff?

The behavior of relative energies is usually quite similar to what we have seen for bulk SiO_2 above; they are normally well converged numerically at a much lower cutoff energy than the total energy. This is good news, since it shows that we can usually cope with a quite low cutoff energy; both the band structure and the relative energies are well converged at rather low energies.

But our data also give a reason to be concerned. Even if a quantity has shown to be converged within a certain limit, we are never guaranteed that this quantity does not vary with more than this limit when the cutoff energy is increased even further. We should thus be cautious, both when performing our calculations and when interpreting (our own and others') results. If a certain precision is important, we should make sure that numerical convergence is at least as good as the precision, preferably significantly better. And when someone claims to have well-converged results: always ask what it means quantitatively, and keep in mind the possibility that the error bars may be larger than the "proven" precision.

4 Convergence with respect to the k point density

You should now be familiar with the concept of numerical convergence, and checking the convergence of important quantities like the forces and relative energies with respect to the **k** point density should be

relatively straightforward. This time we need two directories ktest and ktest2 with the two different structures above in their respective directory. Use 400 eV as cutoff (you have hopefully found that this is sufficient for most of the properties we are interested in).

This time you need to change the KPOINTS file. For this we can use the makekpoints script with the -d option:

```
> makekpoints -d 2
```

This creates a distribution of integration points in reciprocal space (k points) where the density of points is at least 2 points per $Å^{-1}$ in each direction. For SiO_2 this gives a KPOINTS file which looks like this:

```
k-density: 2.0
0
Gamma
 3 3 3
 0  0  0
```

Prepare a folder for k-point densities ranging from 1 to 6. Submit the jobs to the queue. When they have finished, use vaspout to read out the results.

We define convergence with respect to the **k** point density with respect to increasing the number of points along each direction N_k by unity[1]:

$$\frac{\Delta E_{\text{rel}}}{\Delta N_k} < \frac{1\,\text{meV}}{1}.$$

You should now be able to answer the following questions: When is the relative energy converged according to the criterion above? When is the force converged to within 0.05 eV/Å? And 0.005 eV/Å? Which **k** point density is required to obtain pressures converged to within 1 kbar? And band gaps within 0.01 eV?

Before moving on, we should check what we can gain by choosing a proper cutoff and **k** point density. A simple measure of the computational cost is the CPU time used by the job. This is printed in OUTCAR, and can easily be accessed with the cpu script:

```
> cpu */OUTCAR
```

Check this for the ktest2 directory, since this is where most time is used (due to the lower symmetry of this structure). How many CPU seconds were needed to achieve a converged relative energy (as defined in the section above)? How much is this increased if the **k** point density is increased by 1 or 2?

It is important to note here that a relatively large part of the CPU resources for very short jobs like these, goes to start-up procedures and stuff that does not matter when the job size is increased significantly. Real tests of the effect of **k** point densities on the performance should thus be made with jobs that would use in

[1] Sometimes we have to make sure the grid is even- or odd-numbered. We do not need to take that into account here.

the order of hours to finish. One would then find that a lot of time can be saved by choosing the appropriate level of numerical accuracy, both when it comes to cutoff energy and **k** point density.

5 Report

Write a brief report on which values you found to be needed for bulk SiO_2 for proper convergence of the total energy, pressure, relative energy, band gap and force with respect to the cutoff energy and the **k** point density. Use tables and/or plots to support your results.