

Lab 3. Crystal structures

You should read Sec. 2.1–2.4 in Sholl&Steckel before doing this exercise.

One of the exciting possibilities of DFT is to predict crystal structures. This is important if the crystal structure has not been determined experimentally, because it can be used to predict a large range of other properties like thermodynamic stability, band gap, elastic constants, etc. It can be done more or less dependent on experimental input, but it is still challenging to predict a crystal structure without any knowledge about the system from physical inspection. One important problem is that calculating the arrangement of atoms in a bulk crystal is a complex multidimensional optimization procedure, with many parameters that need to be optimized simultaneously: The unit cell size, the number of atoms, the lattice constants and angles, and the atomic positions. This means that you can sometimes not be certain that you find the global minimum of this multidimensional potential energy surface. You risk having found only a local minimum, and that a larger unit cell is more stable. You will often see that scientists claim to have “predicted” a crystal structure when they actually started out with a known unit cell and suggested crystal symmetry from experiment.

Another important point is that our calculations are usually performed without considering temperature. This means that we predict ground state structures that may be different from the structures at room temperature (or whatever relevant temperature). This is possible to solve by introducing temperature by allowing the atoms to move. Such calculations are orders of magnitude more expensive, and temperature has therefore often been neglected in the past. Modern methods involving phonon calculations, however, have made temperature dependent predictions more available.

Nevertheless, the DFT predicted ground state crystal structure is surprisingly often similar to what can be seen at room temperature. We will in this lesson show how one can quite clearly distinguish between different atomic models of bulk Pt by using the total electronic energy as calculated by VASP.

The lab corresponds partially to Exercise 1 on p. 46 in Sholl&Steckel, but we will do more. We will first relax the structures automatically, using forces calculated by VASP. Then we will use a more cumbersome method which not only gives the equilibrium properties but also the

1 Generate the input files

From the previous labs we recall that four input files with fixed name are needed by VASP: POSCAR, POTCAR, INCAR, and KPOINTS. In addition, you need a job script, which we will usually call jobfile. Most of these files can be easily created in a standard way, but in this lab the POSCAR file needs particular attention, since this is defining the crystal structure. You can make this for simple crystal structures simply by typing the information into a text file, or you may need to generate it from a crystal structure database.

We will in this lab compare four different crystal structures of platinum (Pt): simple cubic (sc), body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close-packed (hcp). The only information you will get to make life simpler is that the typical interatomic distance in Pt is around 2.8 Å. Oh, and you will also get POSCAR files and INCAR files as starting points for your calculations. You can find the

input structures here: `~olem/fm4111/datalab/pt/`. You should copy the files to a set of new directories. (Use `cp -r` to copy a directory with files and subdirectories.) Now go to one of the directories you have created (e.g. `bcc`). It should contain a POSCAR file:

```
> ls
POSCAR
```

Once you have a POSCAR file, you can generate a KPOINTS file automatically with the `makekpoints` script like in the following example. Note that you have to be located in a directory with an existing POSCAR file for this script to work:

```
> makekpoints
9 9 9
> ls
KPOINTS  POSCAR
```

The POTCAR file can be generated in a similar vein. You then need to specify the directory and the different elements included in the POSCAR file. In our case, there is only one element; Pt:

```
> makepot . Pt
ls
KPOINTS  POSCAR  POTCAR
```

The only missing files are INCAR and the jobfile script. Use the same jobfile as you did in the previous datalab. (You have to copy it from your own directory or from `~olem/fm4111/datalab/.`) The INCAR file depends on what we would like to do, so this will be different in the next two sections.

2 Relax the crystal structures automatically

The first task in most projects is to relax the bulk crystal structure(s) of the compound(s) you are interested in. You should do this now for the four hypothetical crystal structures of Pt. In each of the four directories you should perform the following procedure:

1. Create a subdirectory "relax1". Copy KPOINTS, POSCAR, POTCAR, and jobfile to this directory. Copy "INCAR_relax" from `~olem/fm4111/datalab/pt` to the same directory, but change the name to INCAR. (VASP only looks for files with exactly the correct names.) Submit the job. When the job has finished (check this with the `st` command), you will find the relaxed crystal structure in the "CONTCAR" file.
2. Create a subdirectory "relax2". Copy INCAR, POSCAR, POTCAR, and jobfile from relax1 to relax2. When the first job has finished, copy CONTCAR from relax1 to POSCAR in relax2. Submit the job.
3. Create a subdirectory "toten". Copy POSCAR, POTCAR, and jobfile from relax2 to toten. When the previous job has finished, copy CONTCAR from relax2 to POSCAR in toten. Copy "INCAR_toten" from `~olem/fm4111/datalab/pt` to toten, but change the name to INCAR. Run the job.

This is a very standard procedure in VASP, and you may save some time later on if you create a script that performs the above steps.

The second step is necessary because the numerical grids depend on the initial lattice constants. If they change significantly during the first relaxation, there may be artificial remaining forces or pressure that will be removed in the second step. In cases where the volume is not relaxed, e.g. in low-dimensional materials, this step can be skipped.

The third step is required to obtain reliable total energies, since the energy resulting from a relaxation run is not always accurate. The calculated pressure should be as low as possible in a relaxed structure. Pressure is not reliably calculated in this step and should only be reported from the relaxation steps.

You should check how many ionic steps are used by VASP to reach equilibrium structures, using the `vaspout` script. Was it really necessary to use the second relaxation step in this case? Did the total energy change much from the relaxation steps to the final step? Which structure seems to be the most stable one judging from the total energy per atom?

3 Vary the cell sizes manually

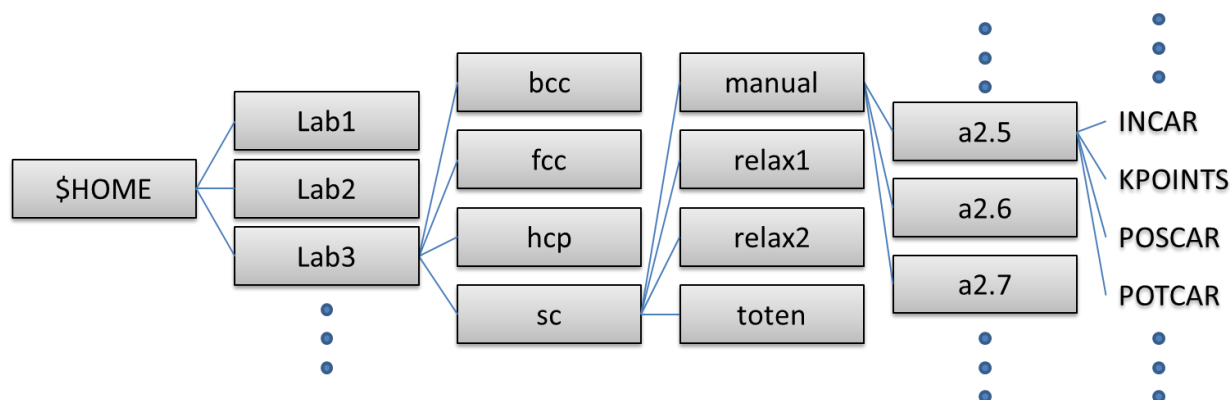
An alternative way to relax the unit cells is to vary the cell parameters manually and find the minimum energy from a fitted curve. This should now be done for the four candidate structures. For each structure start by creating a subdirectory "manual". Within this directory, create a number of directories with varying cell size. As an example, the `sc` structure starts with $a = 2.6 \text{ \AA}$. You can assume that this is close to the equilibrium size (or simply check from the relaxed structure in the previous section). Several jobs with different cell sizes will provide the total energy as a function of cell size. A distance of 0.1 \AA between the lattice constants is suitable, and you should use at least five different values.

In order to change the lattice constant, simply change the cell parameter on the second line of POSCAR. You can either change the POSCAR file in a text-editing program like `emacs`, or using a script (see below). In addition to this, you need the other input files in each subdirectory. This can be copied from your previous jobs; in this case use the "INCAR_toten" file when creating the INCAR file.

A crude example of a script that does this automatically is listed here. Remember that all five VASP input files have to be in the same directory as the script.

```
#!/bin/sh -f
for a in 2.4 2.5 2.6 2.7 2.8
do
mkdir a$a
sed s/2.6/$a/ POSCAR > a$a/POSCAR
cp INCAR KPOINTS POTCAR jobfile a$a/
cd a$a
sbatch jobfile
cd ..
done
```

When you have run all these jobs, your directory tree should look a bit like this:



When VASP has finished, you should find the following files in the a2.6 directory:

```
> ls
CHG          DOSCAR      INCAR        OSZICAR      POSCAR        vasprun.xml
CHGCAR       EIGENVAL    jobfile      OUTCAR        POTCAR        XDATCAR
CONTCAR      IBZKPT      KPOINTS      PCDAT        slurm-JOBID.out
```

You can find the total electronic energy with the toten script:

```
> toten OUTCAR
Total energy (eV)      F      E0
OUTCAR                 -5.605233  -5.605233
```

When you have repeated this for different values of a , you can use the toten script to find out how the total energy varies with a (the wildcard $*$ matches any sequence of characters):

```
> toten a*/OUTCAR
Total energy (eV)      F      E0
a2.6/OUTCAR            -5.605233  -5.605233
...
```

The optimal lattice constant with lowest energy can be read out of the data if the grid is dense enough. However, it is much more efficient to use curve fitting to find this. You can use this simple python script as a starting point for such fitting: [~olem/fm4111/datalab/pt/fitcurve.py](#). Copy this file to your directory with results and check that everything in the script is compatible with your file names etc. Then run the script with this command:

```
> module load python2/2.7.10.gnu
> python fitcurve.py
```

You only need to load the python module before the first time you run a python script in the session.

Repeat this for all the crystal structures. If you have time, you can also vary the c/a ratio in the hcp cell. The default value is the ideal ratio of $\sqrt{8/3} \approx 1.63$. Check the relaxed c/a ratio to provide reasonable values.

4 Report

Write a brief report presenting the results. Use the standard format with introduction, results, discussion, and conclusion. The minimum content is:

1. Answer the questions in the text.
2. The optimized lattice constant a of the bcc, fcc, and sc crystal structures, preferably with curves supporting the results. Compare the automatic relaxation with the manual one.
3. The lowest total energy E of each of the structures (both automatic and manual). This should be reported per atom in order to be directly comparable.
4. A brief discussion of how this compares to the experimental crystal structure. You can find this e.g. in many periodic tables.

In addition, you may want to present the following results:

5. The optimized lattice constants a and c and the lowest total energy E of the hcp structure.
6. The bulk modulus B_0 of some or all of the crystal structures. A crude approximation to that can be found from the equation $B_0 = \frac{2}{9}(1/a_0)\beta$, where a_0 and β are the fitting parameters in Eq. (2.2) on p. 38 in Sholl&Steckel: $E(a) \cong E_0 + \beta(a - a_0)^2$.