Computational materials science

Practical work 1: Silicon

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Introduction

Format of these practical works

- These slides give you the instructions, not the explanations; see the Survival Guide for that.
- Don't write a full report as you're used to (we know you have lots of them). Simply answer the questions.
- We expect your reports at the end of the last session (we have 5 in total).

VASP : the Vienna Ab initio Simulation Package

We will be using the VASP software packagage for these practical works. Here is a very short description of its features.

- Commonly-used package for solid state physics and materials science, written in Fortran.
- Uses a planewave basis.
- Implements DFT, and many other methods (HF, TDDFT, ...).
- Can compute single-point energies, geometry and cell optimizations, molecular dynamics, and a few more things.
- Parallelized with MPI (distributed memory parallelism).
- You provide a set of input parameter files, launch VASP, and analyze the resulting output files.

Input file : INCAR

INCAR

- General parameters for the computation.
- Most important ones : computation type, XC functional, planewave cutoff, timestep, convergence criteria...
- Like most files in VASP : old, Fortran-friendly format (used to be punched on cards !)
- Also, many VASP filenames end in "CAR" ; nobody really knows why...

Input file : POSCAR

POSCAR

- Describe the nature and position of atoms in your computation.
- If the atoms move, this gives the initial position.
- Again, old-style format and rules.
- Can be displayed in visualization programs like VMD.

Input file : POTCAR

POTCAR

- Describes the chemical species and associated pseudopotentials in your computation.
- Not written by hand ; VASP provides a set of POTCAR files for each atom, which you can combine depending on the chemical species in your system.
- The order of the atoms in the file must be the same as in the POSCAR file. Otherwise, strange things will happen (an oxygen atom with the effective potential of a sodium atom can't be good).

Brillouin zone sampling : KPOINTS

KPOINTS

- You may remember from your solid state class that in a crystal, all the interesting properties can be computed from the first Brillouin zone (thanks to Bloch's theorem).
- Numerically speaking, to have accurate properties you need to sample the first Brillouin zone accurately ; this is done with *k-points*.
- The KPOINTS file indicates which points to use. You won't manipulate those files in these practicals, but in general you should know that the points can be generated automatically (for relaxations for instance), or specified manually (when computing band structures).

Output file : OUTCAR

OUTCAR

- Most of what VASP has to say goes into this file.
- General informations about the computation : progress (which eletronic/ionic step), duration of each step, errors if any...
- It repeats the parameters (both from `INCAR` and the default ones), in case you're not sure what you launched.
- Also some computed properties, like the Fermi energy.
- First place to look at when there is a problem.

Output file : OSZICAR

OSZICAR

- Repeats information from OUTCAR, but in a more compact form.
- Shows the convergence of each electronic step, and does so for each ionic step.
- Good place to keep watching to (clearly) see your computation's progress.

Output file : CONTCAR

CONTCAR

- When moving atoms (*i.e.* relaxation or molecular dynamics), contains the last computed atomic positions.
- Useful when restarting a long running job : restart with last positions, and not the first ones again !
- Same format as POSCAR.

First computation : FCC silicon

Connect to Mesocentre and setup your workspace

Connect to Mesocentre and setup your workspace

- First, we need to connect to Mesocentre. Use SSH to connect to user `tpchrono` using the provided password :

  ```
  $ ssh -CX tpchrono@mesologin1.univ-fcomte.fr
  ```

- There, create a folder for your group, in which all your files will be stored, and set the working directory to that folder :

  ```
  $ mkdir PracticalWork1_Name1_Name2
  $ cd PracticalWork1_Name1_Name2
  ```

- Copy the files we prepared for this practical work, and `cd` to the first folder :

  ```
  $ cp -r ~/PW1_files ./
  $ cd 1_FCC_Silicon
  ```

INCAR file I

```
SYSTEM = FCC Silicon

PREC = Normal
ISTART = 0
ICHARG = 2

ENCUT = 240.0 eV
ALGO = normal
NELMIN = 4
NELM = 100
EDIFF = 1e-6
LREAL = .FALSE.

ISMEAR = 0
SIGMA = 0.1
```

Using `cat`, you can display the contents of the `INCAR` file, which is reproduced on the left. It consists of a set of tags with (somehow) mnemonic names, given values to particular parameters. To keep files short, VASP provides a default value for most of them.
Documentation for those tags is available at `https://www.vasp.at/wiki/index.php/Category:INCAR_tag`.

INCAR file II

Here is the meaning for some of the tags :

- `SYSTEM` : name of the system on which we work.
- `PREC` : precision of the computation (can also be high or low).
- `NELMIN` : minimum number of SCF (or electronic) iterations.
- `NELM` : maximum number of SCF iterations.

`ENCUT` and `EDIFF`

Question 1: Using the documentation, describe the meaning of the `ENCUT` and `EDIFF` parameters. Would you say they are important ?

POSCAR file I

```
FCC Silicon
 3.9
0.5 0.5 0.0
0.0 0.5 0.5
0.5 0.0 0.5
   1
cartesian
  0   0   0
```

Look at the POSCAR file. It describes the unit cell of face-centered cubic silicon. The lines after cartesian give the coordinates of your atoms, a single one in this case.

Data block

Question 2: Using the VASP wiki (look for "POSCAR"), explain the meaning of the block of number in the beginning :

```
 3.9
0.5 0.5 0.0
0.0 0.5 0.5
0.5 0.0 0.5
```

Launching the computation

You can now launch the computation. This is done by enqueuing a job in the Mesocentre, using a special command and a script describing the job (`RUN.sh`, already written). The command is :

```
$ qsub -ar <session_number> -l h_rt=03:00:00 RUN.sh
```

where `<session_number>` will be given the day of the practicals.
The computation should only take a few seconds. You can see the running jobs with the command :

```
$ qstat
```

Analyzing the OUTCAR I

VASP should be done with this simple job in a few seconds, and generates many files along the way. Here you just need to look at the `OUTCAR` to find the requested information (using the commands `less` or `more`).

Computation time

Question 3: How much time exactly did the computation take (look at the end of the file) ?

Analyzing the OUTCAR II

The grep command is very handy when analyzing large text files like the OUTCAR : it allows you to search for a string. VASP will output the total energy at every step of the SCF loop, as a variable named TOTEN. You can find the value of TOTEN for each step by using :

```
$ grep 'TOTEN' OUTCAR
```

Total energy

Question 4: The last line gives the value of total energy for the last iteration. What is its value ?

Converging parameters : ENCUT optimization

How to trust your results ? I

How does one know if a set of parameters is right for a given computation ? In general we can't be *sure*, but we can increase confidence by doing a *convergence study* : vary parameters until the results don't change anymore.
The size of the planewave basis is an example : the higher the number of planewaves, the higher their frequency and thus the more precise the results (hopefully). You should choose the maximum planewave frequency (or equivalently, maximum energy, in which case it is called *cutoff*) by a convergence study.

How to trust your results ? II

In this section, we will vary the cutoff through the `ENCUT` tag, until the total energy is converged. This can be done with the script provided in the folder for this part : `2_ENCUT_convergence`. So you should set your working directory :

```
$ cd ../2_ENCUT_convergence
```

A look at the RUN.sh file

Take a look at the RUN.sh script and try to understand what it does. As a hint, the sed command is used to substitute strings in a file. Here it is used to replace MY_ENCUT in the INCAR_template file.

Run script

Question 5: Summarize what this script does. What is the minimum ENCUT value that will be tested ? What is the maximum value ?

Job execution

Launch the computation as before :

```
$ qsub RUN.sh
```

It should take a bit longer. In addition, it generates the `energy.txt` file which gives the total energy as a function of the cutoff.

Energy convergence

Question 6: Plot the `energy.txt` file and comment on the curve you obtain. Above which cutoff value does the total energy seem to be converged ?

In a real study, we would do this for each system of interest, and each set of input parameters. Here we will use a unecessarily high cutoff of 500 eV, which isn't too much of a problem for such a small system.

FCC silicon band structure

FCC silicon band structure I

One of the most interesting property you can compute for a crystal is the *band structure*. This is typically done by reusing previously computed orbitals, and a different set of KPOINTS. To keep things simple, we will launch a completely new job here.
Go to the `3_FCC_silicon_band_structure` folder and execute the script using `qsub` as before.

FCC silicon band structure II

This time, you will need to transfer some files from the Mesocentre to your local machine, which you can do with the `scp` command. The files you need to get are `plot_band_structure.py`, `KPOINTS` and `vasprun.xml`. The Python script will compute and display the band structure using the two other files.

Band structure

Question 7: Download your files and execute the Python script. You should see the band structure ; save it to a file, and don't forget to send it along your report. Comment on the band diagram you obtain. Is it a metal, a semiconductor or an insulator ? Does that experimentally correspond to silicon ?

Real silicon structure and relaxation

Real structure and relaxation I

The conclusions from the previous computation should be a strong hint that the structure we have used for silicon so far, is actually not its real structure. To test this theory, we can try another structure : diamond-like silicon, in which silicon atoms occupy the same positions (in relative coordinates) as carbon atoms in diamond. Go to the `4_Real_silicon` directory, and look at the input files. Apart from the `POSCAR`, the rest is similar to previous computations.

New `POSCAR` file

Question 8: Read the `POSCAR` file in more details. What changed compared to before ?

Real structure and relaxation II

INCAR

Question 9: Look at the `INCAR` file. This is a different kind of computation than before. Use the VASP wiki to found exactly what it is ; in particular, you should read what it has to say about `IBRION` and `ISIF` for the values in the `INCAR` file.

You can now launch the computation with usual command.

Results

Question 10: How many ionic steps were performed before reaching the ionic convergence criteria ?

Real structure and relaxation III

Let's look at the *OUTCAR* file a bit.

Total energy

Question 11: Find the final total energy in the *OUTCAR* file. Compare it to the total energy previously computed for FCC silicon ; is it higher or lower ? Does this make it a better candidate structure for silicon ?

New unit cell dimensions

Question 12: The *OUTCAR* file also contains the dimensions of the relaxed unit cell near the end. Find the "*VOLUME and BASIS-vectors*" section, and report the new vector lengths. (*Hint : those are for silicon's unit cell, while in the litterature the lattice parameter is usually given for the conventional cell.*)

Real silicon band structure

Real silicon band structure

As we did before for FCC silicon, let's compute the band structure. Go to the `5_Real_silicon_band_structure` ; use the `CONTCAR` file of the previous simulation as `POSCAR` to this one (you just need to rename it to `POSCAR`). Execute the job, and download the plotting script, `KPOINTS` and `vasprun.xml` files to your local machine.

Silicon band structure

Question 13: Execute the *plot_band_structure.py* script, and save the figures (don't forget to send them along your report). What kind of material is described by this band structure ? Does it correspond to the experimental properties of silicon ? The script also outputs some useful information in the terminal ; for instance, what band gap does it report ?

Diamond structure relaxation

Diamond structure relaxation I

The last structure we will work upon is actual diamond. Just like silicon, it has the diamond structure (obviously), and the only difference is that silicon is replaced by carbon (and consequently, the lattice parameter is different). Again, we will use a high value for the cutoff, but in practice you should always do converge studies when starting to work on something new.
Go to the `6_Diamond_optimization` folder, and look at the hopefully now-familiar input files.

Input

Question 14: What was changed in the `POSCAR` file ? Is the `POTCAR` file the same as before ?

Diamond structure relaxation II

Launch the computation.

Output

Question 15: Again, what is the final total energy ? What is the final lattice parameter ? Compare the initial volume to the final volume.

Diamond band structure

Diamond band structure

Switch now to the last folder, `7_Diamond_band_structure`. Use the `CONTCAR` file of the previous simulation as `POSCAR` for this one (you just need to rename it to `POSCAR`). You can then launch the job.
Once done, download and plot the band structure as before.

Diamond band structure

Question 16: Don't forget to save your band structure plots. Again, comment on the bands you obtain. Do we have a semiconductor, metal or insulator ? What band gap does the plotting script extract ?

The end

Congratulations, you're done with the first practical work !