Computational materials science

Practical work 2: Carbon nanotubes

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Contents I

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.

Carbon nanotubes

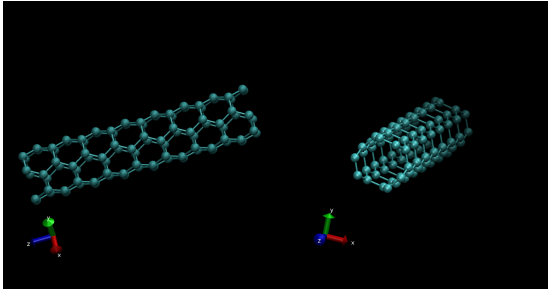
Carbon nanotubes I

Carbon nanotubes (CNTs) can be thought of as rolled-up graphene sheets. They are currently the focus of much research because they have many interesting properties, mainly concerning conductivity and molecular diffusion. Those properties can be tuned to some extent by changing the geometry of the tubes. In some configuration, they might behave as a metal, while in others they might behave as semiconductors. It is the goal of this practical work to show you some of this variability.

The geometry of a CNT is mainly defined by its *chirality*, describe by two numbers m and n. Qualitatively, chirality defines how much the CNT looks like a screw ; that is, it controls the pitch of a screw of hexagonal carbon cycles.

Carbon nanotubes II

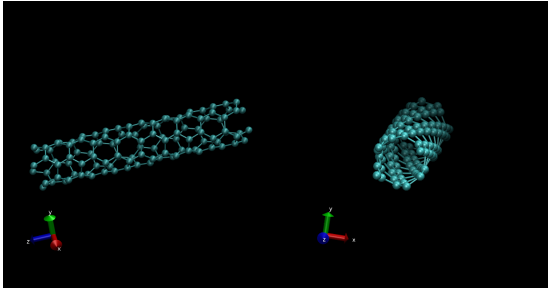
You will study two nanotubes, one with chirality $(3, 3)$ and one with chirality $(4, 2)$. The structure for those file were generated by a program online, and will be provided to you.
Here is a visualization of the $(3, 3)$ nanotube (in fact, a $1x1x8$ supercell) :



(a) CNT $(3, 3)$ (b) CNT $(3, 3)$

Carbon nanotubes III

And here is a visualization of the $(4, 2)$ nanotube (a $1x1x2$ supercell) :



(c) CNT $(4, 2)$ (d) CNT $(4, 2)$

Extracting the files

Extracting the files I

The files you will need to execute the various computations are contained in a TAR archive. You should create your own directory in the `WORK` directory, move there and type the following command to extract the files :

```
$ tar xvf ../PW2_Carbon_nanotubes.tar.xz
```

This will give you your own copy of the files, which you can modify as much as you like. Good luck !

CNT $(3, 3)$: ENCUT optimization

ENCUT optimization I

The first step is to choose a correct planewave cutoff as we did for silicon. Thus, the input files are similar to those we used back then. Let's take a look at some of those file. First, move to the `1_cnt33_ENCUT_optimization` directory.

New tag : `GGA`

Question 1: The `INCAR_template` file is almost the same as before (for silicon or diamond). There is a new tag however, `GGA`. What does the VASP wiki say about it ? What does the `PE` value correspond to ?

ENCUT optimization II

POTCAR

Question 2: Look at the first few lines of the `POTCAR` file (using the `head` command for example). The first line tells you which element the pseudopotential concerns, as well as the XC functional used to compute it (after the `PAW` string, which is just the name of the specific DFT method used). Are those consistent with your previous answer ?

POSCAR

Question 3: Finally, look at the `POSCAR` file, which definitely is different from silicon or diamond. How many atoms are there this time ?

ENCUT optimization III

You can now launch the cutoff optimization using `qsub` as before. This one should take around a few minutes.

Energy convergence

Question 4: As you did for silicon, retrieve the `energy.txt` file and plot the energy as a function of cutoff (don't forget to join your figure). What cutoff value seems to be a safe choice ?

For consistency, we will use a cutoff of 350.0 eV in the following. As a bonus, you can look at the time each computation took by using the grep command :

```
$ grep 'Total CPU time used (sec):' outputs/OUTCAR_*
```

Nothing is for free, is it ?

CNT $(3, 3)$: relaxation

CNT (3, 3) relaxation I

Move to the `cnt33_relaxation` folder and launch the job. The structure will be relaxed (both the positions and the lattice vectors), as we did for silicon.

Duration and ionic steps

Question 5: How long did the job take ? How many ionic steps were there ?

Energy

Question 6: Find the total energy at the first ionic iteration and at the last, what are their values ? Did we indeed relax the structure a bit ?

CNT $(3, 3)$: density of states

For this computation, you will use the previously obtained `CONTCAR` as the input `POSCAR` file. There is a new file, `plot_dos.sh` ; it is a small script which will extract the DOS from the `vasprun.xml` file. Move to the `3_cnt33_DOS` folder, and copy the relaxed `CONTCAR` to `POSCAR`. Launch the computation.

Fermi energy

Question 7: The fermi energy is a major property computed for a crystalline solid. VASP outputs it in the `OUTCAR` file near the end ; what is its value ? (*Hint : you can use `grep` to look for the 'E-fermi' string*).

Density of states

Question 8: Execute the `plot_dos.sh` script : `$ ./plot_dos.sh`
It will create a `dos.dat` file, which you should retrieve and plot. It's a good idea to shift your x-axis by the fermi energy, so that the band gap (if any) aligns with 0.

CNT $(4, 2)$: density of states

We can now move on to the $(4, 2)$ nanotube. Move to the `4_cnt42_DOS` folder.

POSCAR

Question 9: Take a look at the `POSCAR` file. How many atoms are there now ?

Because there are many more atoms than in the previous cases (and the unit cell is larger), working on this system with only 16 processors would be too long. Thus, the electronic density has been precomputed and provided to you, through the *CHGCAR* file.

INCAR

Question 10: Look at the new `INCAR` file, and more precisely the `ICHARG` parameter. Look it up on VASP's wiki, and explain with your own words what is the difference with the previous computations. Does it make sense that it's less expensive (in computing time) ?

Apart from that, everything works the same. You can launch the computation, and compute the density of states.

Fermi energy

Question 11: What is the fermi energy for this structure ?

Density of states

Question 12: Execute the `plot_dos.sh` script. Retrieve the `dos.dat` file, and plot it (don't forget to join it in your report, as awlays).

Discussion

Discussion

In a real paper, presenting results is not enough : you have to discuss them, place them into context and conclude.

Discuss

Question 13: You computed the DOS for CNTs with chirality $(3, 3)$ and $(4, 2)$. What information can you extract from them ? Can you tell what is the type of material for each nanotube ?

The end

Congratulations, you finished again !

If you finished in advance, you could give a bit more work to the Mesocentre and try relaxing the $(3, 3)$ or $(4, 2)$ nanotube...