Hands-on session: Getting Introduced to VASP

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Login info

Log in onto the UGent molgate environment (`molgate.ugent.be`) using the account `nanoscale` and the password `KohnSham1516`. The port number is 45917. Go from molgate to either moldyn49, moldyn51, moldyn52 or moldyn53 by typing:

```
ssh nanoscale@moldynXX
```

After typing the password and logging in, load the ictce module:

```
module load ictce
```

Create a folder `<foldername>` for this hands-on session and enter it:

```
mkdir <foldername>
cd <foldername>
```

Copy the source files to the newly created folder and unpack them:

```
wget ‘http://users.ugent.be/~klejaegh/tutorial-vasp.tar.gz’
tar -xzvf tutorial-vasp.tar.gz
```

Code

This hands-on session is based on the VASP code (*Vienna Ab initio Simulation Package*), which employs the Projector-Augmented Wave (PAW) formalism. More information and a thorough manual can be found at `http://www.vasp.at/`. For visualization purposes, you might want to download VESTA from `http://jp-minerals.org/vesta/en/download.html`.

1 Setting up a single-point calculation

In order to perform a calculation with VASP, four distinct input files are needed:

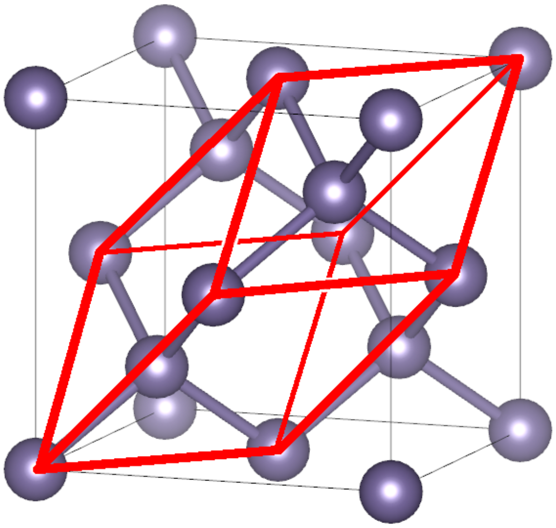
- **POSCAR**: This file contains all structural data about the input geometry, such as the lattice vectors and the atomic positions.
- **KPOINTS**: When using a plane-wave basis set, most properties are calculated in the reciprocal space. There, k space integrals are systematically replaced by summations over a discretized k grid. The sampling of the first Brillouin zone is given in the `KPOINTS` file.
- **INCAR**: This file steers the calculations. It contains all parameters for the desired DFT calculation: the plane-wave cut-off, the used optimization routine, whether a magnetic calculation should be performed, ...
- **POTCAR**: The `POTCAR` file tells VASP which potential to use. Several well performing PAW potentials are included with the VASP package. All necessary `POTCAR` files for this hands-on session have been provided in the source files.

When invoking VASP, the program will look for the required input files (with these exact filenames!) and, if everything goes well, start a calculation. Afterwards you can look for the results you want in the generated output files.

Now try a calculation yourself. All files have been provided in order to compute germanium in its ground-state crystal structure, i.e. in the diamond phase.

```
cd exercise1
cat POSCAR
```

You see that the 2-atom primitive unit cell is used as input, rather than the conventional 8-atom unit cell. This will allow us to achieve a high speed even for the most intensive calculations. The relation between the primitive and the conventional unit cell for diamond-type crystals is depicted below.



By having a closer look at the first lines of the `POTCAR` file,

```
head -n25 POTCAR
```

you see that this is a calculation with the PBE functional (`LEXCH`). This particular PAW potential takes into account 14 valence electrons (`ZVAL`), including the $3d$ electrons (hence the header of the file, `Ge_d_GW`). The modifier `GW` indicates that this potential is also well suited to determine the unoccupied energy levels, which is necessary for methods like GW.

Have a closer look at the `INCAR` and `KPOINTS` as well. You usually need to test what the appropriate cutoff energy and number of k-points are to obtain numerically converged results, but we did that for you. What is the cutoff energy? How many k-points are included in the sampling of the first Brillouin zone?

```
cat INCAR
cat KPOINTS
```

We will now run a single-point VASP calculation. Just type

```
vasp
```

at the command line. VASP is now executed on a single processor. Because this is a very small unit cell, the calculation should be finished within less than a minute.

The volume is still not quite right (20 Å^3/atom), but we don't bother with that for our first calculation. Do notice, however, that the volume can be set in the `POSCAR` file, by typing it in the second line with a minus before it. If you don't use a minus sign, VASP will interpret your number as a scaling factor for the lattice constant and the atomic positions.

The `OUTCAR` file contains the most important output data. What is the external pressure corresponding to this configuration (kB = kbar)? What is the energy? What are the total forces on the ions and can you explain these values? Use your favourite text editor to scroll through the output, or use

```
grep '<search term>' OUTCAR
```

2 Setting up a relaxation run

As mentioned in the previous exercise, the provided volume of 20 Å^3 per atom is not yet optimal. It is possible to find structures with a different volume and a lower energy. Look at the external pressure you found in the previous exercise. It is the pressure needed to remain in the current configuration (such that it doesn't evolve towards its optimal volume). Do you expect the germanium to expand or to shrink?

We will now try to find the equilibrium volume of the Ge cell. Move to the folder of exercise 2,

```
cd ../exercise2
```

This folder contains the same files as exercise 1. When using VASP, it is always wise to perform different calculations in different folders, since the input and output files have fixed names and would be overwritten.

In order to relax our Ge cell, we keep all settings from the previous calculation. However, we add some keywords to the `INCAR` file, which tell VASP that it should relax the volume:

`IBRION = 2`	*relax by means of the conjugate gradient algorithm*
`ISIF = 7`	*only relax the volume, keep the internal coordinates and cell shape fixed*
`EDIFFG = 1E-4`	*relax until the change in energy is smaller than* 10^{-4} *eV/Å*
`NSW = 10`	*stop the relaxation if no convergence is found after 10 ionic steps*

Run VASP again after modifying the `INCAR`. What is the external pressure now?

The `CONTCAR` file contains the data of the optimized geometry. Can you calculate the new volume from these optimized cell parameters? Do not forget to take into account the scaling factor. Have a look (afterwards) in the `OUTCAR` file if your calculation of the volume corresponds to the result written there. Did the volume increase or decrease? Was this what you expected?

Have a look at the energy in the `OUTCAR` file. It is indicated by the keyword `energy(sigma->0)`, on the line starting with `energy  without entropy`. Note that there are two spaces between `energy` and `without`, to make it easier to search the file for the final value. The purpose of this volume relaxation was to obtain a lower energy. Did we succeed?

3 Finding the equilibrium volume with an equation of state

Keep working with the same structure. You have already optimized the volume V_0, but we will now show that this value is sometimes not precise enough. In this exercise, we will demonstrate a better way to determine it.

Go to the folder of exercise 3, and copy the input files from the relaxation run to it (see section 2). Use the `CONTCAR` as a new `POSCAR` file.

```
cd ../exercise3
cp ../exercise2/CONTCAR POSCAR
cp ../exercise2/INCAR .
cp ../exercise2/KPOINTS .
cp ../exercise2/POTCAR .
```

Change the `INCAR` file to perform a single-point calculation and run VASP. This should give the same result as the relaxation run. Look at the energy. What do you find? Was this to be expected?

The difference between the current energy and the previous one is due to the so-called Pulay effect. It arises because of the finiteness of the plane-wave basis set: a limited set of plane waves was chosen to represent the wave functions in the unit cell, but when the volume of the cell changes, that of the reciprocal cell changes as well. The plane waves in the basis set should therefore be redetermined to yield a constant resolution (in terms of the maximum wave vector G_{max}, or equivalently the cutoff energy E_{cut}). Instead, a relaxation run keeps the used plane-wave basis set fixed. As a result, small volumes have too low energies (because E_{cut} is too large) and large volumes too high energies (because E_{cut} is too low), leading to an equilibrium volume that is too small. Since VASP uses the (incorrect) energy gradient to determine the stress tensor, the Pulay effect can be noticed there too. As a result, what you think to be the optimal volume can sometimes differ significantly from reality, especially for soft materials.

Pulay stresses can be minimized by choosing a large energy cutoff (and thus a large plane-wave basis set), but this is computationally not always feasible. When performing $E(V)$ calculations and fitting an *equation of state*, this problem does not occur at all.

Calculate the total energy for 7 different volumes (+9%, +6%, +3%, 0%, −3%, −6% and −9% of the previously determined V_0). Do this is in separate subfolders.

It is now possible to fit the data points you have calculated to e.g. a Birch-Murnaghan equation of state. This is a fit of the energy to a third-order polynomial in $V^{-2/3}$. One easy way of performing this fit, is by means of the provided `eos` script. Collect all the volume and energy results of your 7 calculations into one file, `<volumefilename>`. Put the volumes in the first column and the energies in the second. Now type

```
python eos <volumefilename> 1 1
```

Have a look at `<volumefilename>.eosout`. What is the fitted equilibrium volume? Is the difference with the VASP optimization large?

4 The cohesive energy

We will now determine one of the basic stability criteria for our crystal. The cohesive energy or atomization energy represents the energy needed to form the crystalline structure from (infinitely separated) atoms:

$$\Delta E_{coh} = E_{crystal} - E_{atom}$$

$E_{crystal}$ represents the crystal energy for one atom.

A negative cohesive energy corresponds to a stable unit cell. In nature the crystal with the lowest cohesive energy is the one that exists at zero kelvin.

In order to calculate the cohesive energy, two quantities are needed, $E_{crystal}$ and E_{atom}. The former we have already determined in exercise 3, but we still need a value for the atomic energy. With a non-periodic code such as Gaussian, this might seem easy, but for a periodic package like VASP, some unexpected issues arise.

4.1 An atom in a cubic cell

The first problem is the size of the unit cell. We can simulate a single atom by taking a large box and placing the atom in the middle, but how large does that box have to be? We have to make it big enough, to prevent interactions with periodic neighbours, but too large a cell and it will take forever to compute. We will choose 10 Å as a compromise between precision and time.

Navigate to the folder of exercise 4 and set up your own `POSCAR`: make a cubic unit cell with the germanium atom in the middle. Create an appropriate `INCAR` file, and add the following keywords:

`ISPIN = 2`	*enable a spin-polarized solution*
`MAGMOM = 3`	*initial magnetic moment in* μ_B
`LORBIT = 11`	*write out the magnetic moment per orbital*

We initialize the magnetic moment a bit above the expected value of $2\,\mu_B$ to make it easier for VASP to converge.

Use a single k point ($1 \times 1 \times 1$). More k points are not needed, since they only describe the interaction with periodic images better. For a single atom these do not exist, however. Since only one k point is used, the tetrahedron smearing scheme does not work. Be sure to use `ISMEAR=0` and add `SIGMA=0.05`.

Have a look at the `OUTCAR` file. What is the energy? What is the final magnetic moment? What is the occupation of the different energy levels? There is a line **`band No. band energies occupation`** at the end of your `OUTCAR` file for each of the two spins.

4.2 An atom in an orthorhombic cell

A second issue is the cell symmetry. The shape of the unit cell influences the electronic wavefunctions in a crystal. In the case of a single atom these symmetry restrictions are unphysical, and they can have an undesired influence on the electronic ground state.

Repeat you calculation of the single atom (in a separate (sub)folder), but in an orthorhombic unit cell (different lattice parameters a, b and c). Choose the lattice constants close to the original 10 Å (e.g. an 0.1 Å difference). How do the total energy and band occupations differ?

In order to get the occupation of the energy levels right, we have to force the system into the correct solution. Use `ISMEAR=-2` in your INCAR file and add `FERWE = 1 1 ...  1 0 0 ...  0` and `FERDO = 1 1 ...  1 0 0 ...  0`. There should be as much zeros and ones as the number of bands, 1 standing for an occupied state and 0 for an unoccupied one. Make sure the calculation starts from the correct magnetic moment, by including `MAGMOM=2`. Now do the computation of the single atom again. Is the energy lower or higher? Does this make sense according to the variational principle?

Compute the cohesive energy. How does it compare to experiment? Experimentally, the cohesive energy of Ge in the diamond structure is known to be $\Delta E_{coh} = -375\,\mathrm{kJ/mol}$.

As a final note, we want to emphasize that neither calculation for the Ge atom is really physical. To accurately describe the distribution of 2 p-electrons over the p_x, p_y and p_z levels, a multideterminant scheme is required (i.e., going beyond DFT).