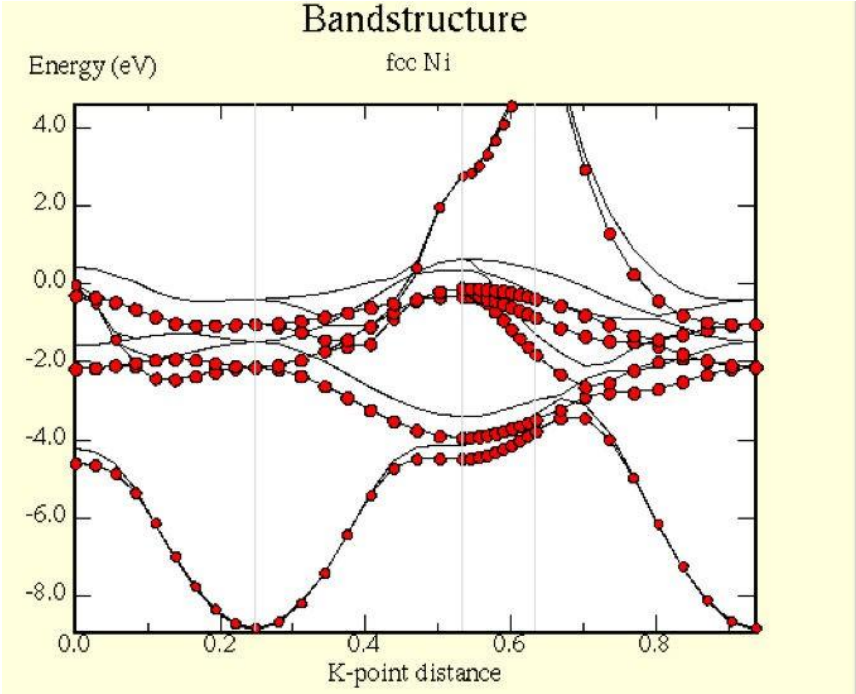
2020

Practicals for Condensed Matter – Introduction to VASP



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Numerical practical work in solid-state physics - Electronic structure of solids and molecules

This document presents practical exercises related to the study of the electronic structure of solids using the VASP software. A brief reminder of essential concepts is also presented before the exercises.

Course of practical work

The aim of the practicals is to quickly go over the key steps to find the equilibrium structure of a material and calculate its electronic properties such as the density of states or the band diagram. These practicals also aim to choose the optimal computation conditions to have sufficiently reliable results for relatively short computation times.
The various calculations proposed have for the most part a duration of less than one minute with a sequential version of VASP. DOS calculations can be a bit longer (5 or 10 min) We will use a parallelized version on the UFC compute cluster (mesocount). In each part, an archive containing the input files necessary to perform the calculations is made available to the user.

Useful scripts for analyzing results or preparing calculations

In some parts, scripts are proposed for the analysis of the results or to prepare some repetitive calculations for the optimization of the conditions of calculation. They are available in the archive containing the input files. However, the user can modify them according to their programming skills.

To interpret the results, you can use the VMD or p4vasp softwares to visualize crystal structures and the p4vasp software to illustrate the electron density of solids. These software are easily installed under linux, macOS or windows. It is advisable to use them directly on your computer by downloading the files to avoid delays due to the network.

Introduction to the VASP sofware

VASP ("Vienna Ab initio Simulation Package") is a software for simulating the electronic properties of condensed matter which is based on the density functional theory (DFT) and the use of 3D-periodic conditions. The wave functions are developed on a plane wave basis and the core electrons are represented by PAW (Plane Augmented Waves) type pseudopotentials.

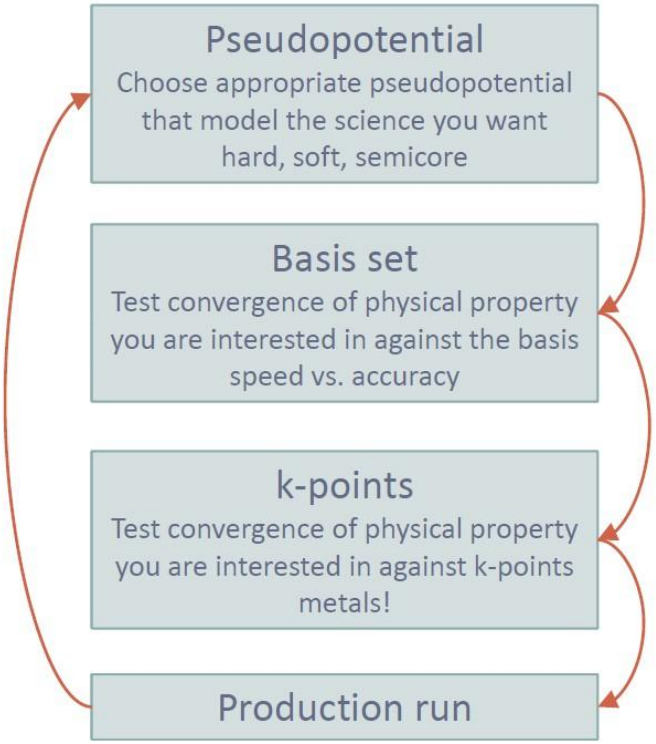
Some useful links around the VASP software:

- VASP web site : https://cms.mpi.univie.ac.at/wiki/index.php/The_VASP_Manual
- Official documentation and usefull key words : https://cms.mpi.univie.ac.at/wiki/index.php/Category:INCAR

During the practicals, it is strongly recommended to regularly consult the keyword list to familiarize yourself with the content of the input files. Some of the exercises proposed here are taken from the examples of calculations offered on the VASP wiki.

The theoretical course on DFT showed that to solve a problem, it was necessary:

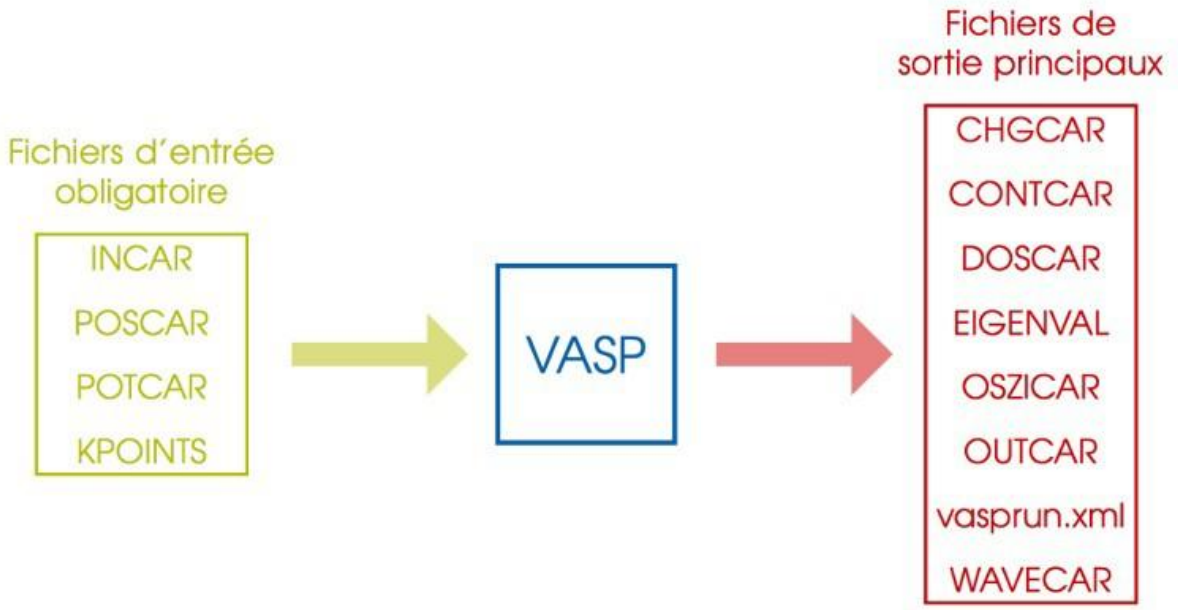
- Choose an exchange-correlation functional (precision LDA <GGA <Hybrid)
- Choose Pseudo-potentials (replace nuclei and core electrons with an effective potential)
- Choose an "Energy Cutoff" parameter that controls the size of the plane wave base used
- Choose points k in the First Brillouin Zone
  - Convergence increases with a sufficient number of points k
  - For metals, also choose the correct “smearing” method
    - “Tetrahedron” method for precise total energy results.
    - “Gaussian, Methfessel-Paxton, etc” methods for relaxation and precision calculations on geometric quantities.


Pseudopotential
Choose appropriate pseudopotential that model the science you want hard, soft, semicore
Basis set
Test convergence of physical property you are interested in against the basis speed vs. accuracy
k-points
Test convergence of physical property you are interested in against k-points metals!
Production run

Input/Output files

Overview

VASP requires multiple input files with a prescribed name and format. They should be in the code execution folder. Several output files are created during code execution and are also located in the execution folder. Some files are only present under certain conditions. Here is a general input / output diagram with the main output files:



It is recommended to create a file for each new calculation, unless you want to overwrite the data present in the file.

Input files in VASP

INCAR : Type of calculation and parameters of the calculation

POSCAR : Initial positions of atoms

KPOINTS : Grid of k points used

POTCAR : Contains the pseudo-potentials used

In addition to these compulsory files, there will also be an executable file (often colored in green) and a script to start the calculation on the mesocenter.

⚠ the name of the files is imposed ⚠

Output files in VASP

Among the main output files are:

OUTCAR: Listing of the calculation, general information ...
OSZICAR: Electronic and ionic iterations, useful for following the convergence of the calculation
WAVECAR: binary file containing the final wave function.
CHGCAR: final electron density discretized on a grid.
CONTCAR: final structure
DOSCAR: Density of states
EIGENVAL: Eigenvalues of the Hamiltonian for each band and for each point k.
Vasprun.xml: This file contains all previous information except electron density and wave function, but in xml format. It is used by some post-processing tools, the xml language making its reading easier than that of the OUTCAR file

The INCAR file

The INCAR file contains the calculation parameters and therefore defines the type of simulation. The parameters are given in a key = value syntax. Almost all of the available keywords are present on the keyword list (https://cms.mpi.univie.ac.at/wiki/index.php/Category:INCAR).

In the following :

```
the first line is a title line
the keywords are grouped together when they act on the same part of the calculation
lines without an equal sign are treated as comments and are optional
```

The INCAR file contains at least the following lines

```
PREC = Normal
ENCUT = 300
LREAL = .FALSE.  or Auto
ISMEAR = 0 or 1 or -5
```

PREC: Check the global precision of the calculation

- = Normal (Default) - Standard calculation (accurate with errors less than 1 meV / atom)
- = Low - fast calculations not very precise
- = Accurate - Calculations with high precision

ENCUT: Controls the number of plane waves included in the base

- = ENMAX (Default) - the largest ENMAX in the POTCAR file
- = 1.3 * ENMAX - for relaxation calculations (change volume of the unit cell)

LREAL: Controls whether the calculations are done in the Reciprocal space (= AUTO) or in the real direct space (= .FALSE. By default)

- = AUTO - RD is used as soon as there are more than 20 atoms
- = .FALSE. –For calculations in the RR (default)

ISMEAR: Controls the weight given to each wave function during the calculation. This is a fairly sensitive parameter of this software.
Here are the recommendations from the VASP developers

- For semiconductor or insulating materials, it is preferable to always use “tetrahedron method” (ISMEAR = -5), if the unit cell is too wide (or if, only, one or two K-points are used) put ISMEAR = 0

Note: Avoid using ISMEAR> 0 for semiconductor or insulating materials, as this could lead to problems.

- For metal relaxation calculations, it is best to always use ISMEAR = 1 with an appropriate value of SIGMA (the entropy term should less than 1 meV per atom).
- For DOS and a very precise energy calculation, (no relaxation in metals) use the "tetrahedron method" (ISMEAR = -5).

Another parameter that can be changed here is SIGMA. For metals, a reasonable value is SIGMA = 0.2 (this is the default value but also the most used for transition metals).

In the calculation below, the structure is not relaxed (NSW = 0). Only the electron density is relaxed. So we just do a simple energy calculation.

```
Electronic
  PREC = Accurate
  EDIFF = 1e-6
  NELMIN = 4
  ENCUT = 400
  LORBIT = 11

Ionic relaxation
  NSW = 0

smearing
  ISMEAR = -5
```

One will note parameters specifying the precision of computation (ENCUT, PREC) or the threshold of convergence (EDIFF).
EDIFF specifies the stop condition for the electronic Self-consistent (SC) loop. The relaxation of the electronic degrees of freedom will be stopped if the total (free) energy change and the change of band structure energy ('change of eigenvalues') between two steps are both smaller than EDIFF. By default, EDIFF = 10^{-4} eV. There is no real reason to use a much smaller number.

In the following example we optimize the structure. The jargon used by VASP, ions generally refer to the nuclei of atoms. Here ionic relaxation therefore refers to the relaxation of the structure.

```
Ionic relaxation
Electronic
  PREC = Accurate
  EDIFF = 1e-6
  NELMIN = 4
  ENCUT = 400
  LORBIT = 11

Ionic relaxation
  NSW = 200
  ISIF = 2
  IBRION = 2
  EDIFFG = -0.01

smearing
  ISMEAR = 0
  SIGMA = 0.05
```

The new parameters indicate:

- The maximum number of iterations for the optimization of the structure (NSW),
- The algorithm used (IBRION)
  - IBRION = -1: no update.
  - IBRION = 0: molecular dynamics.
  - IBRION = 1: ionic relaxation (RMM-DIIS).
  - IBRION = 2: ionic relaxation (conjugate gradient algorithm).
  - IBRION = 3: ionic relaxation (damped molecular dynamics).
  - IBRION = 5 and 6: second derivatives, Hessian matrix and phonon frequencies (finite differences).
  - IBRION = 7 and 8: second derivatives, Hessian matrix and phonon frequencies (perturbation theory).
  - IBRION = 44: the Improved Dimer Method.

- Optimized structural parameters (ISIF)

ISIF determines whether the “stress tensor” is calculated or not. The forces are always calculated.
ISIF determines which are the degrees of freedom that the program must leave free to move (positions of the ions, volume of the cell, and cell shape).

The following table below summarizes the different possibilities:

ISIF	calculate		Degrees of freedom		
	forces	Stress tensor	positions	cell shape	cell volume
0	yes	no	yes	no	no
1	yes	trace only	yes	no	no
2	yes	yes	yes	no	no
3	yes	yes	yes	yes	yes
4	yes	yes	yes	yes	no
5	yes	yes	no	yes	no
6	yes	yes	no	yes	yes
7	yes	yes	no	no	yes

- and the expected precision (EDIFFG).

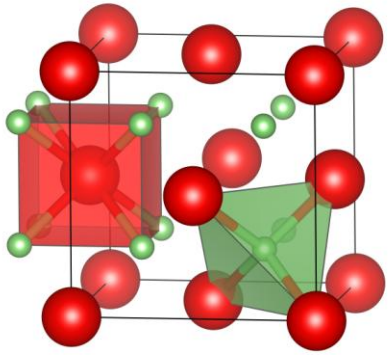
EDIFFG defines the shutdown conditions for the ion relaxation loop. Default EDIFFG = EDIFF × 10

The POSCAR file

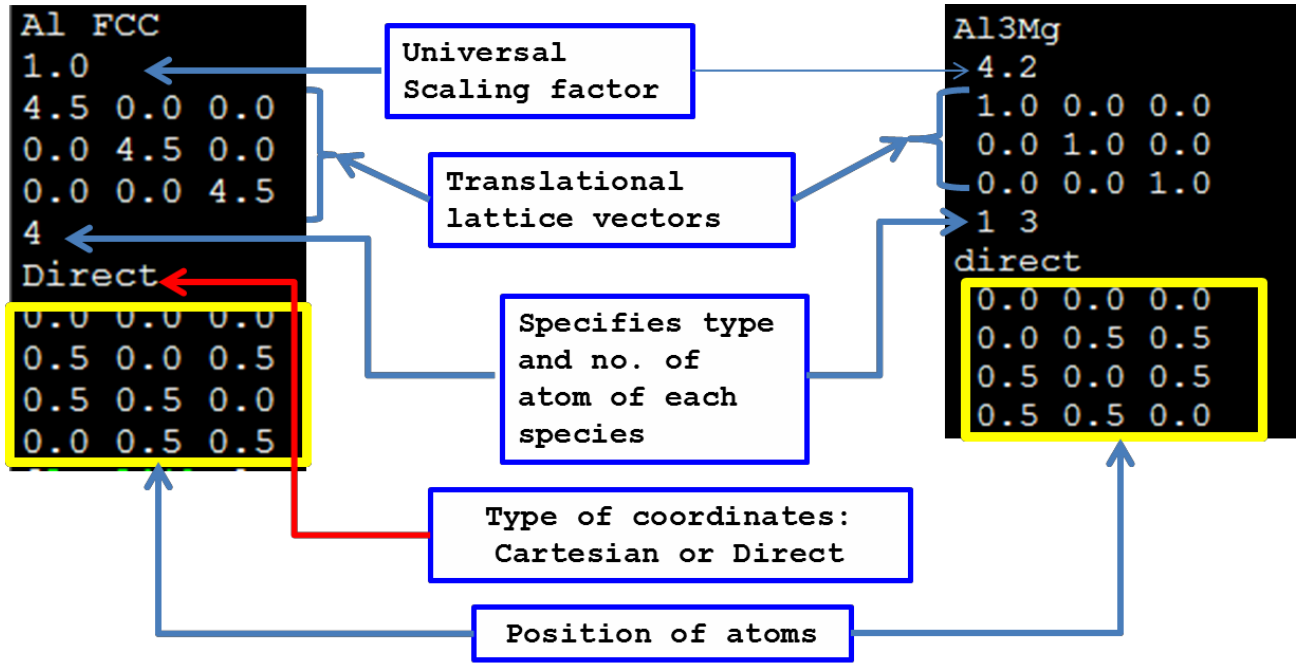
The POSCAR file defines the initial structure. It contains the bravais network and atomic positions. Let us examine the case of Li_20 whose structure is shown below. The POSCAR file of this structure in its representative unit cell is also given below

POSCAR

```
Li2O CFC                  → titre
  1.0                     → scaling factor
    4.619  0.0   0.0       } vecteurs de la maille
    0.0    4.619 0.0       } dans un repere cartesien
    0.0    0.0   4.619     }
 Li  O                    → types d'atomes
  8  4                    → nombre d'atomes de chaque type
Direct                    → Systeme de coordonnees
 0.25    0.25    0.25     }
 0.25    0.75    0.25     }
 0.75    0.25    0.25     }
 0.75    0.75    0.25     }  8 atomes de lithium
 0.25    0.25    0.75     }
 0.25    0.75    0.75     }
 0.75    0.25    0.75     }
 0.75    0.75    0.75     }
 0.0     0.0     0.0      }
 0.5     0.5     0.0      }
 0.0     0.5     0.5      }  4 atomes d'oxygène
 0.5     0.0     0.5      }
```



The following example refers to to fcc structures of Al et $Al(Mg)_3$



- In 'direct coordinates' the positions of atoms are given as fractions of the vectors of translations. In 'Cartesian coordinates' the positions of atoms are given in global coordinates.
- The "scaling factor" adjusts the volume of the unit cell
- The order of atoms in POSCAR MUST be the same as POTCAR
- The CONTCAR file is written in the same format as POSCAR.

The KPOINTS file

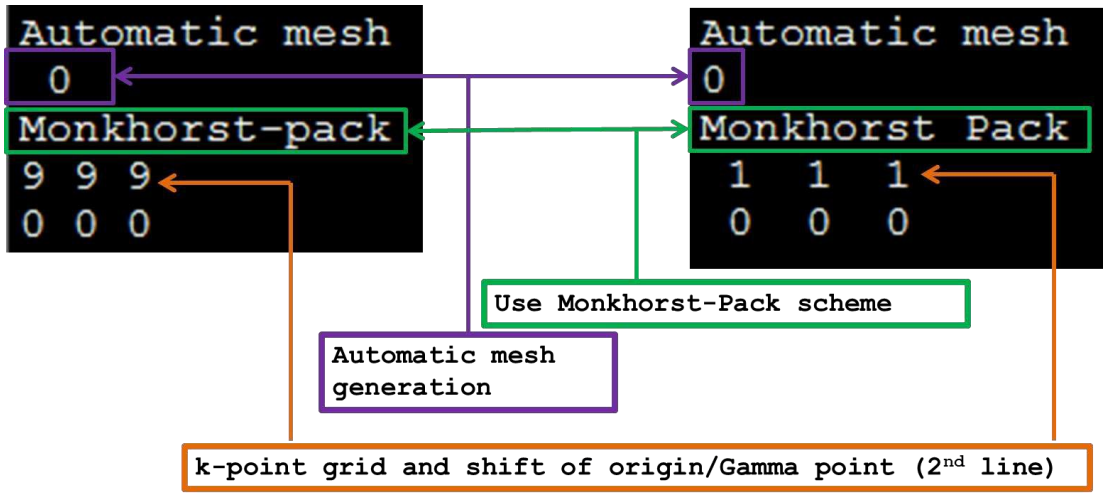
The KPOINTS file contains the grid of points k used to integrate the first Brillouin zone of the reciprocal space. This is the main difference between a periodic code like VASP and a molecular code (apart from the base).
The grid of points k must tessellate the first Brillouin zone. The size of the grid is a compromise between precision and computation time. Generally we ask VASP to create the grid automatically, the KPOINTS file is then the following, for a grid centered on point Γ (origin of the reciprocal network) with 6 points k in each direction (216 in total):

```
grille automatique
0
Gamma
 6 6 6
 0 0 0
```

In reality, VASP does not do the math for 216 k points. He looks for those which are in the irreducible part of the first Brillouin zone and weights these points k by the number of homologs which they induce in the first Brillouin zone.
In the KPOINTS file, we can also indicate the lines of high symmetry of reciprocal space to draw a band diagram.
Some general recommendations:

- Non-periodic system (molecule): a single point k, grid 1 × 1 × 1
- The number of points k required is related to the unit cell. The smaller the unit cell parameter, the more it takes a large number of points k.
- For the computation of a DOS it takes a large number of points k.
- For a hexagonal unit cell, center the grid at Γ.

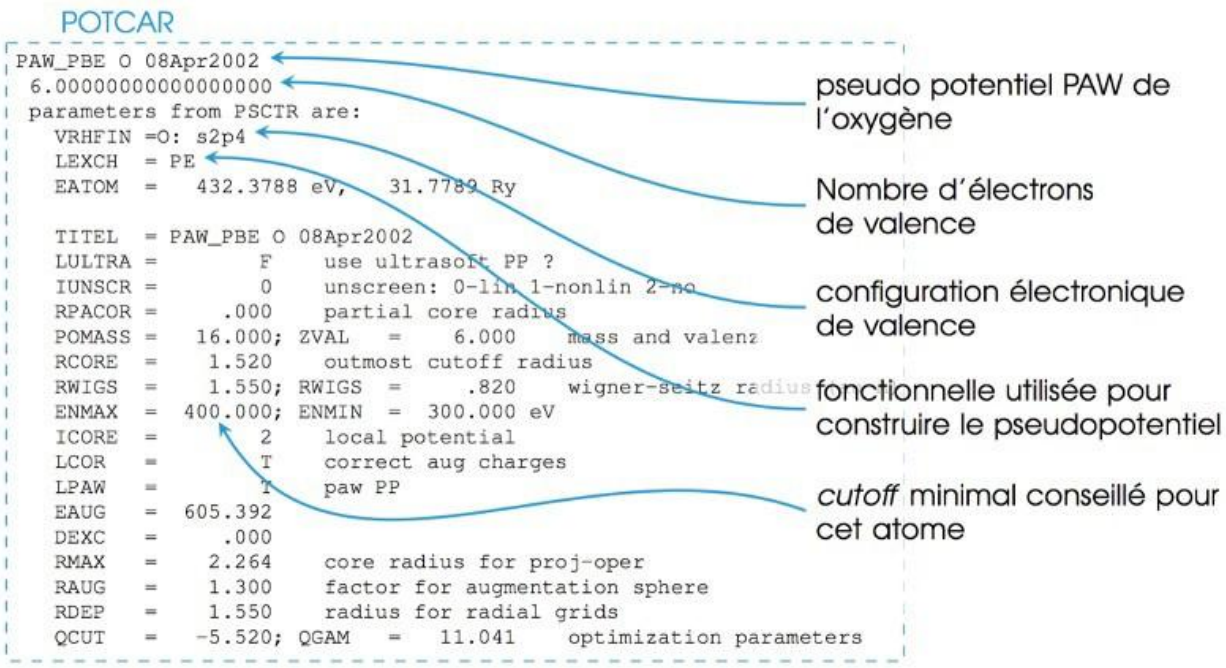
The following example relates to the KPOINTS file for aluminum either as a bulk or as an atom



*The grid of points k must be inversely proportional to the ratio of the base vectors (otherwise there will be calculation errors). For example if the base vectors are $a_1 = 3$ $a_2 = 9$ $a_3 = 21$ then the grid of points k should be 7: 3: 1

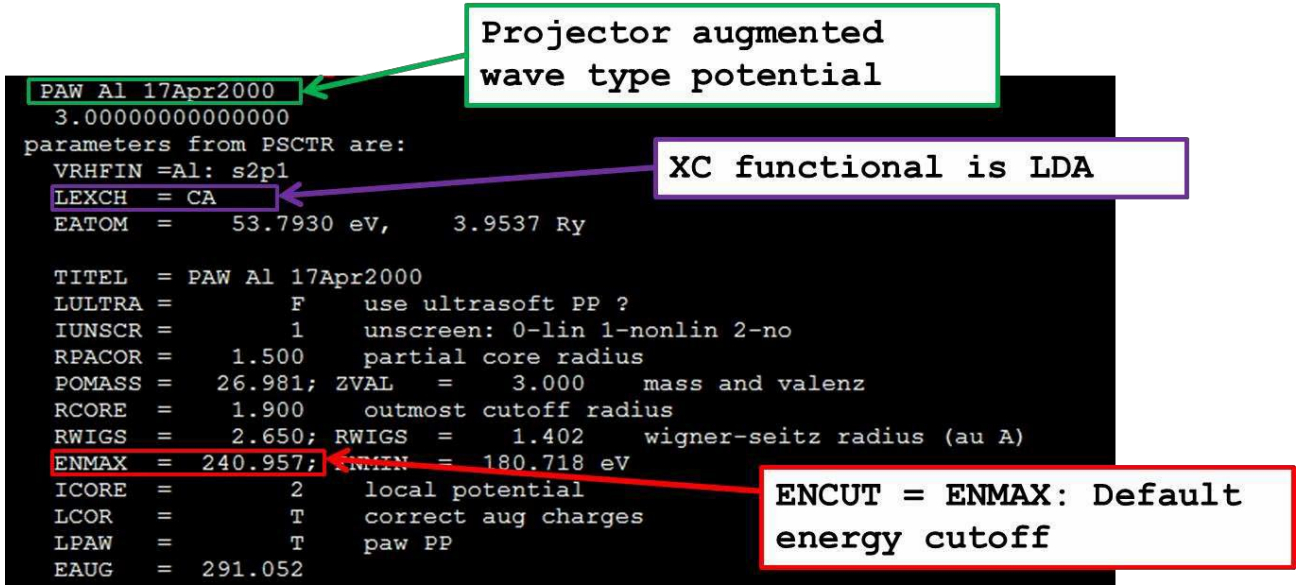
The POTCAR file

The POTCAR file contains the pseudo-potentials used for each atom of the calculation. For a given element, several pseudo-potentials may be available depending on the density functional used to construct it and the number of core electrons contained in the pseudo-potential. The following image gives an overview of a POTCAR file for the oxygen atom and a description of some elements it contains.



If several atoms are present in the system, we must concatenate the POTCAR files in the order of appearance of the atoms in the POSCAR file.

Below is another example of a POTCAR file for aluminum



Running VASP

VASP is available in several versions :

- sequential: monoprocessor version
- MPI: parallel version based on the Message Passing Interface library Gamma point only: a version optimized for calculations with a single k point

The parallelization of VASP is not the object of this practical work. We will just see here how to run VASP and describe the contents of the standard output files.

Connection to the calculation center “mesocomte”:

¶ • To access mesocomte, type the following command on a terminal: “**ssh -CX tpchrono@mesologin1.univ-fcomte.fr**” then enter the password: **Ietoog3x (capital i at the beginning)**

• Enter the WORK directory (command: **cd WORK**) to find the **Atoms-and-molecules and Bulk-systems folders**

• In the same WORK directory, create a folder with your name (Command: **mkdir TP_VASP_2020_yournames**) to which you will copy each time the folders or files necessary for the calculations you will perform.

• Copy the Atoms-and-molecules and Bulk-systems folders to your folder. Command: **cp -r Atoms-and-molecules Bulk-systems TP_VASP_2020_yournames**

⚠ Important: Make file changes only in YOUR folder ⚠

Atoms & Molecules

Examples:

- O atom
- O_2 molecule
- CO
- H_2O

Tasks:

- Single point total energy
- Relaxation
- Vibrational frequencies

VASP software is normally dedicated to periodic systems that require the use of plane waves to describe electrons. It is therefore not suitable in principle for the study of atoms and molecules whose description of the electrons located around the nuclei is generally done using atomic or molecular orbitals. However, it can be shown that if the input parameters of the software are correctly defined, we can still correctly describe molecular systems.

• We will start with a simple study of the oxygen atom that you will find in the Oatom folder. (enter the folder with the command: **cd Atoms-and-molecules / Oatom**)

For the oxygen atom, consult the input files (POSCAR, INCAR and KPOINTS) which are provided to you, you can use the commands: less, nano or vi (vi if you are used to Linux) to open the files on your terminal.

- less: only to consult
- nano: to view and modify
- vi: view and modify (more complicated)

Tip: If you are unfamiliar with Linux, use the "less [file]" command to view only, to avoid editing the file by mistake. To quit "less", press the "Q" key.

Q.1 Explain the choices that are made. Which XC functional (information you will find in the POTCAR file) is used for the oxygen atom ?

POSCAR	INCAR	KPOINTS
O atom in a box 1.0 8.0 0.0 0.0 0.0 8.0 0.0 0.0 0.0 8.0 1 Cart 0 0 0	SYTEM = O atom in a box ISMEAR = 0	Gamma-point only 0 Monkhorst-Pack 1 1 1 0. 0. 0.

- Start the calculation corresponding to these input files. To do this, type the command:

  qsub -ar [n° to be communicated] -l h_rt=06:00:00 VASP-script

-VASP-script is the submission file of your calculation. In particular, it indicates the name you want to give to your script or the number of cores you want to use to perform its calculation. We won't have to change the settings for this file just yet.

-06:00:00 is the number of hours left before the end of the session, it will be modified as the session progresses.

Different output files make it possible to follow the progress of the calculation:

• xxx.o [job-number] (where "xxx" is the name given to the script in the submission file),
• OSZICAR
• OUTCAR

The OUTCAR file in which we find the information contained in the first two describes the progress of the calculation in more detail and allows to see, for example, at which stage it stopped in the event of an interruption or problem. .

At the end of each calculation, you are advised to save in a folder of your workstation all the filesn except : CHG, CHGCAR, the submission script and the executable file.

For this, two methods are possible:
• Launch the FileZilla software which allows file transfer between two computers, then enter the following information: Host: mesologin1.univ-fcomte.fr, Username: tpchrono, Password: Ietoog3x, Port: 22

! If you are on Windows OS ignore the following point, use FileZilla.

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- Or on your computer's terminal, go to the desired directory on your workstation where you want to transfer your data and type the following command (to transfer a folder between Linux computers):
  "**scp -r username @ source_computer: path / to / the / folder / source . (point)**", the password requested is the one you use to connect to the mesocomte account. -r is to specify that you are copying a folder, the point indicates that you want to move your folder to the current directory.

- Look at the file with **xxx.o[job number]**

  You should obtain something like :

```
 entering main loop
       N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1     0.384469664751E+02     0.38447E+02   -0.96726E+02     16   0.293E+02
DAV:   2     0.345965628955E+01    -0.34987E+02   -0.34942E+02     32   0.450E+01
DAV:   3    -0.244485866931E+00    -0.37041E+01   -0.34307E+01     16   0.308E+01
DAV:   4    -0.312557021227E+00    -0.68071E-01   -0.66914E-01     16   0.508E+00
DAV:   5    -0.313520305300E+00    -0.96328E-03   -0.96311E-03     32   0.506E-01    0.286E-01
DAV:   6    -0.314540466589E+00    -0.10202E-02   -0.17853E-03     16   0.332E-01    0.142E-01
DAV:   7    -0.314637222361E+00    -0.96756E-04   -0.22710E-04     16   0.134E-01
   1 F= -.31463722E+00 E0= -.16037490E+00  d E =-.308525E+00
 writing wavefunctions
```

Q.2 What do DAV, N, E,dE, F represent ? Why does the calculation stop ?

In the same directory (still on the mesocomte), create a new folder that you will call "suite" (command: mkdir suite) and copy into the files: CONTCAR, INCAR, POTCAR, KPOINTS, WAVECAR and the VASP-script file (command : cp [file] [destination_folder]).

• Modify the name of the CONTCAR file to POSCAR (command: **mv CONTCAR POSCAR**)
• Perform a run of this calculation again and show that when you restart VASP, the WAVECAR file is reread and the run continues with the previously determined "wavefunctions".

Q.3 What is the consequence? (Compare the output files of the two calculations)

Observe the eigenvalues of the electronic Hamiltonian. To do this, look for the following block in the OUTCAR file:

```
 E-fermi :  -8.8431    XC(G=0):   -0.8043    alpha+bet :  -0.1463
          k-point     1 :       0.0000    0.0000    0.0000
           band No.  band energies     occupation
               1     -23.8439      2.00000
               2      -8.9040      1.33333
               3      -8.9040      1.33333
               4      -8.9040      1.33333
               5      -0.4676      0.00000
               6       1.8633      0.00000
               7       1.8633      0.00000
               8       1.8633      0.00000
```

Q.4 Identify the energy levels and interpret the occupancy obtained with this calculation. Is this normal or aberrant?

In the OUTCAR output file, find the total energy of the system appearing in the following block:

```
 FREE ENERGIE OF THE ION-ELECTRON SYSTEM (eV)
  ---------------------------------------------------
  free  energy   TOTEN  =        -0.31463722 eV
  energy  without entropy=       -0.00611258  energy(sigma->0) =        -0.16037490
```

Q.5 Calculate the entropy of this system and compare this value to the free energy.

This entropy value is not physical. The cause of this error stems from the basis of pseudo-potentials which are built on the assumption of spinless atoms.

In fact, the O atom has a valence shell with 2 unpaired electrons.

• Exit the Oatom folder (repeat the command: '**cd ..**' until you exit the folder).
• Create a new folder that you will name '**OatomSpin' (mkdir [name_folder]**)

⚠ Reminder: do not forget to create a folder of the same name on your personal computer in order to save back your files.

• Copy into this new folder the files: POSCAR, INCAR, KPOINTS, POTCAR and the VASP-script from the first **Oatom** folder.

To do this, perform the following commands:
• Enter the OatomSpin folder you just created (**cd OatomSpin**)
• Type "**pwd**" to display the path that leads to this folder which will be in the form **/ Home / Users /… / Atoms-and-molecules / OatoSpin**.
• Now go to the Oatom folder then type the following command "**cp [document] [path_to _destination folder]**"
• You can copy multiple files at the same time by writing them one after the other (separated by a space).

Enter the **OatomSpin** folder.

Type the command "**nano INCAR**" to open and modify INCAR and add the line "**ISPIN = 2**" at the end of the file. Press "**ctrl + X**" to exit then the "**O**" key when prompted to save changes.

It will also be necessary to modify the name of the job in the VASP-script file, open the file in order to be able to modify it and replace "**TP_Oatom**" by "**TP_OatomSpin**". Exit then save the modification.

Restart the appropriate VASP run. You should get something like:

```
           N       E                     dE             d eps       ncg     rms          rms(c)
  DAV:   1     0.389725012498E+02    0.38973E+02   -0.10098E+03    32   0.259E+02
  DAV:   2     0.317912429240E+01   -0.35793E+02   -0.35786E+02    64   0.438E+01
  DAV:   3    -0.119085682530E+01   -0.43700E+01   -0.36686E+01    32   0.328E+01
  DAV:   4    -0.126198272139E+01   -0.71126E-01   -0.69189E-01    32   0.508E+00
  DAV:   5    -0.126284205021E+01   -0.85933E-03   -0.85925E-03    48   0.504E-01    0.653E+00
  DAV:   6     0.164008071667E+00    0.14269E+01   -0.32208E+00    32   0.894E+00    0.151E+00
  …     …       …
  DAV:  13    -0.167302579657E+01   -0.25698E-03   -0.13177E-05    32   0.203E-02    0.956E-03
  DAV:  14    -0.167302926747E+01   -0.34709E-05   -0.34771E-06    32   0.116E-02
     1 F= -.16730293E+01 E0= -.15958981E+01  d E =-.154262E+00  mag=     1.9999
   writing wavefunctions
```

but also :

```
 E-fermi :  -7.1152     XC(G=0):  -0.7730     alpha+bet : -0.1463
 spin component 1

 k-point     1 :       0.0000    0.0000    0.0000
  band No.  band energies     occupation
      1     -25.0878       1.00000
      2     -10.0830       1.00000
      3     -10.0830       1.00000
      4     -10.0830       1.00000
      5      -0.4932       0.00000
      6       1.8213       0.00000
      7       1.8303       0.00000
      8       1.8303       0.00000
```

```
spin component 2

k-point     1 :       0.0000    0.0000    0.0000
 band No.  band energies     occupation
     1     -21.8396       1.00000
     2      -7.0543       0.33333
     3      -7.0543       0.33333
     4      -7.0543       0.33333
     5      -0.3594       0.00000
     6       1.9830       0.00000
     7       1.9830       0.00000
     8       1.9830       0.00000
```

To check if a word is present in a file, type the command "**grep [word] [file]**" and all the lines of the file containing this word will be displayed. For example, to search for the word “energy” in the OUTCAR file, just type **grep energy OUTCAR**.

Q.6 Explain the respective occupations obtained. Give the magnetization of the atom O. Having used the "spinpolarized" option stabilize the structure?

Reminder: retrieve and save your files

In GGA, most atoms are characterized by a break in symmetry. VASP, due to its initial construction for 3D solids, produces symmetrical charge electronic densities in accordance with the symmetry of the cell used.

Look at the OUTCAR file to find out what symmetry VASP used previously.
To break this symmetry as simply as possible, change the unit cell parameter (7.0, 7.5, and 8.0) in the POSCAR file. Reduce SIGMA to 0.01 (INCAR file).

To do this, exit the current folder and create a new folder that you will name: "**OatomSpin_lowsym**". Copy in the POSCAR, POTCAR, INCAR, KPOINTS and VASP-script files from the **OatomSpin** folder.

In the **OatomSpin_lowsym** folder open the POSCAR file and replace the unit cell parameter with:

7.0	0.0	0.0
0.0	7.5	0.0
0.0	0.0	8.0

In the INCAR file, add the line SIGMA = 0.01 before ISPIN = 2.
Finally in the VASP-script file, replace "TP_OatomSpin" with "TP_OatomSpin_lowsym".
Don't forget to save the changes.

Restart the VASP calculation. You should find a much lower energy:

```
…       …       …
DAV:   15     -0.189071145737E+01    -0.29321E-03    -0.39183E-05     48    0.478E-02     0.995E-03
DAV:   16     -0.189098921147E+01    -0.27775E-03    -0.39294E-05     40    0.290E-02     0.541E-03
DAV:   17     -0.189104076616E+01    -0.51555E-04    -0.34087E-06     48    0.132E-02
   1 F= -.18910408E+01 E0= -.18910408E+01   d E =-.309633E-20  mag=     1.9998
```

The O_2 molecule

We are now going to do a relaxation of the oxygen molecule, the files of which you will find in the **Odimer** folder.
Consult the input files (POSCAR, INCAR & KPOINTS) provided to you.

Q.7 Explain the choices that are made. What kind of calculation are we going to do now?

POSCAR	INCAR
O atom in a box 1.0 8.0 0.0 0.0 0.0 8.0 0.0 0.0 0.0 8.0 2 Cart 0 0 0 0 0 1.22	SYSTEM = O2 dimer in a box ISMEAR = 0 ISPIN = 2 NSW = 5 IBRION = 2 SYSTEM = O2 dimer in a box ISMEAR = 0

You should obtain results like :

```
DAV:    1      0.517118590134E+02     0.51712E+02    -0.31393E+03     80    0.366E+02
…       …      …
…       …      …
DAV:   14     -0.985349953776E+01    -0.15177E-03    -0.57546E-06     64    0.125E-02    0.371E-03
DAV:   15     -0.985357023804E+01    -0.70700E-04    -0.22439E-06     64    0.741E-03
   1 F= -.98535702E+01 E0= -.98535702E+01  d E =-.985357E+01  mag=     2.0000
 curvature:   0.00 expect dE= 0.000E+00 dE for cont linesearch  0.000E+00
 trial: gam= 0.00000 g(F)=  0.113E+00 g(S)=  0.000E+00 ort = 0.000E+00 (trialstep = 0.100E+01)
 search vector abs. value=  0.113E+00
 bond charge predicted
…       …      …
…       …      …
   2 F= -.96234585E+01 E0= -.96234585E+01  d E =0.230112E+00  mag=     2.0000
 trial-energy change:    0.230112  1 .order    0.190722   -0.113406    0.494850
 step:   0.1397(harm=   0.1864)  dis= 0.00731  next Energy=    -9.861386  (dE=-0.782E-02)
 bond charge predicted
…       …      …
…       …      …
   3 F= -.98607735E+01 E0= -.98607735E+01  d E =-.720327E-02  mag=     2.0000
 curvature:  -0.09 expect dE=-0.900E-05 dE for cont linesearch -0.900E-05
 trial: gam= 0.00000 g(F)=  0.969E-04 g(S)=  0.000E+00 ort =-0.331E-02 (trialstep = 0.828E+00)
 search vector abs. value=  0.969E-04
 reached required accuracy - stopping structural energy minimisation
```

Q.8 Explain these values. Why does the calculation stop?

The final positions are in CONTCAR.

Q.9 Compare the value of the bond length obtained with the data in the literature.

The CO molecule

Here we will do a relaxation of the bond length of the CO molecule.
You will find the necessary files in the folder named "**CO**"

Q.10 Justify the POSCAR file for this molecule.

Prepare the POTCAR file by concatenating the POTCARs of the individual species. You will find the POTCAR file you will need for each atom in the **potpaw_VASP** folder.

To concatenate the files, type the command:
"**Cat POTCAR-O POTCAR-C> POTCAR**". This command means that the two POTCAR files for oxygen atom (POTCAR-O) and carbon (POTCAR-C) are combined into one file which will be called POTCAR.

⚠ Pay attention to the order in which you do the concatenation, here the order in POTCAR will be POTCAR-O first, followed by POTCAR-C. It is important to keep the same order for the atoms in the POSCAR file. So the first coordinate line will belong to the oxygen atom and the second will belong to the carbon atom. ⚠

Check that the ENCUT cut-off (cut-off energy) is the maximum of the ENMAX of the two species.
To do this, find the value of ENMAX in the POTCAR file by typing the command: "**grep ENMAX POTCAR**".
Relax the structure as in the previous case (O2 molecule).

In order to see the number of iterations performed, type the command "**grep Iteration OUTCAR**". An iteration corresponds to an ionic relaxation (a relaxation step). There can be several electronic relaxations between two ionic relaxations. For example, the first iteration includes about fifteen electronic relaxations. You will notice this in the OSZICAR file.

Q.11 Plot the free energy against the relaxation steps. Have we reached equilibrium?

Q.12 Give the length of the bond at equilibrium. Compare with data from the literature.

We now want to calculate the vibration frequencies of this molecule.

Go to the **COvib** folder**.**

Q.13 Interpret the INCAR, KPOINTS and POSCAR files that are provided. Briefly re-explain how to calculate frequencies. How many displacements will be calculated to evaluate the vibration frequencies in this case?

INCAR

```
SYTEM = CO molecule in a box
ISMEAR = 0
IBRION = 5
NFREE = 2
POTIM = 0.02
NSW = 1
```

POSCAR

```
CO molecule in a box          Header (comment)
1.0                           Overall scaling constant
8.0 0.0 0.0                   lattice vector a(1)
0.0 8.0 0.0                   lattice vector a(2)
0.0 0.0 8.0                   lattice vector a(3)
1 1                           Number of atoms for each species
Sel                           Selective dynamics
Cart                          Positions in cartesian coordinates
0 0 0     F  F  T           first atom
0 0 1.143 F  F  T           second atom
```

Start the calculation and find the frequencies in the OUTCAR file for the following information:

```
SECOND DERIVATIVES (NOT SYMMETRIZED)
------------------------------------
               1Z           2Z
 1Z  -114.737304   114.737304
 2Z   114.458316  -114.458316


Eigenvectors and eigenvalues of the dynamical matrix
----------------------------------------------------


  1 f  =   63.887522 THz   401.417139 2PiTHz 2131.058277 cm-1    264.217647 meV
             X          Y          Z           dx          dy          dz
     0.000000   0.000000   0.000000            0           0   -0.655280
     0.000000   0.000000   1.143000            0           0    0.755386

  2 f/i=    0.038494 THz     0.241864 2PiTHz    1.284016 cm-1     0.159198 meV
             X          Y          Z           dx          dy          dz
     0.000000   0.000000   0.000000            0           0    -0.755386
     0.000000   0.000000   1.143000            0           0   -0.655280
```

Q.14 What do these two frequencies correspond to? Can you compare them to data from the literature?

Repeat the frequency calculation by changing the step (**POTIM** larger or smaller).
In order not to overwrite the output files of the previous calculation, create a different folder for each POTIM value in the current directory and copy the necessary input files into it.
Also try to increase the convergence criterion for the electronic part (**EDIFF = 10^{-5} eV**) and the precision (**PREC = ACCURATE**).
Run this new calculation in a new folder.

Reminder: don't forget to upload the files to your computer.

The PROCAR file gives information on the wave functions of electrons and the electron density. To create it, you must specify the LORBIT line in the INCAR file.

LORBIT = 10	DOSCAR and *l*-decomposed PROCAR file
LORBIT = 11	DOSCAR and lm-decomposed PROCAR file

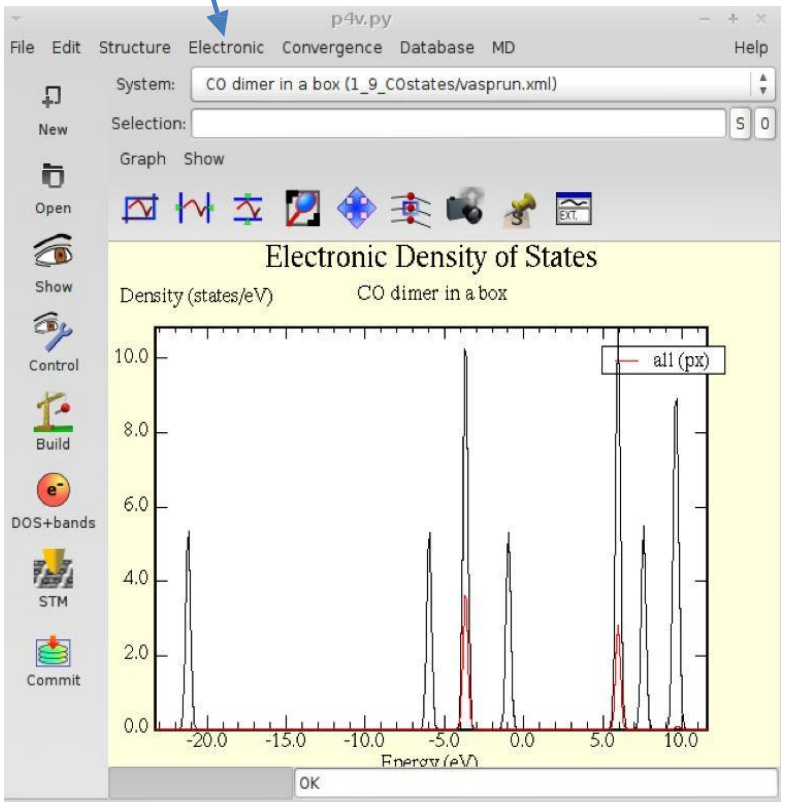
We try to see the decomposition into atomic orbitals and in particular to distinguish the p_x and p_y states. You can either open the PROCAR file, or use the p4vasp software (p4v [vasprun.xml]).

Before that we will calculate the density of state of our molecule.

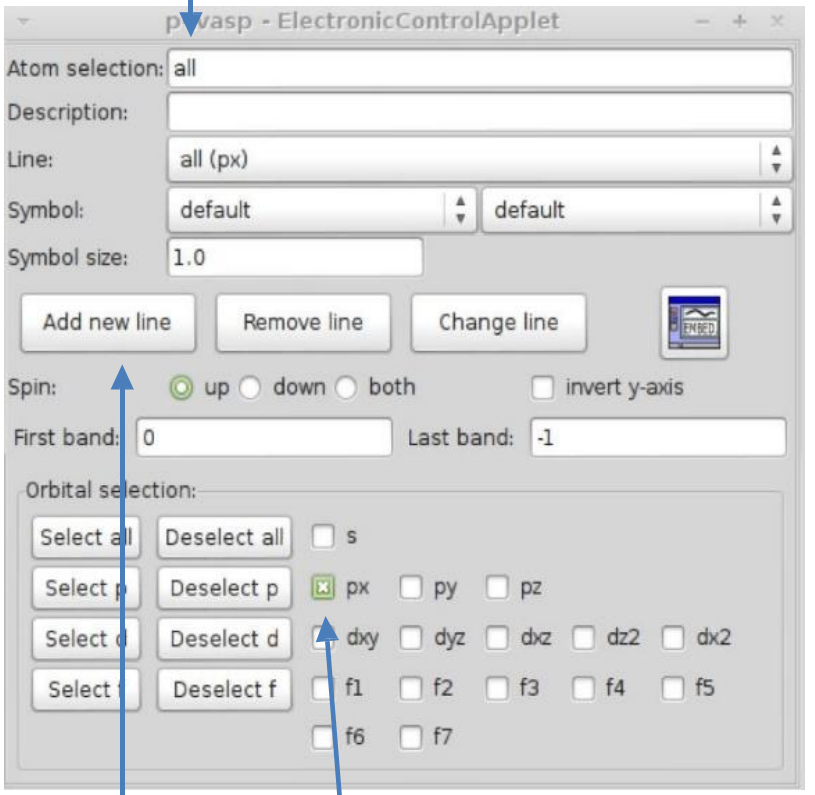
- Start the calculation in the **CO-DOS** folder then transfer the folder to your local computer.
- On your computer open a terminal and enter the **CO-DOS** folder you just transferred to launch p4vasp, type **"p4v". (For LINUX users)**
- Click on the "Show" tab to view the molecule.
- Follow the steps below to plot the electron state density of the molecule on p4vasp.
- Save the graph you get.

On cherche à voir la décomposition en orbitales atomiques et notamment à distinguer les états p_x et p_y. On peut soit ouvrir le fichier PROCAR, soit utiliser le logiciel p4vasp (p4v [vasprun.xml]).

Step 1 : go to Electronic/Local DOS+bands control



Step 2 : select atoms : “all”, “C”, “O”, “1”, “2,…



Step 3 : select orbital character

Step 4 : and add new line

The H_2O molecule

We are now going to study the water molecule in order to find the best parameters to optimize it.
You will find the files for this part in the **H2O** folder.

- Build the INCAR file as shown below then run the optimization calculation.

POSCAR

```
H2O molecule

0.52918

15.0   0.0   0.0
 0.0  15.0   0.0
 0.0   0.0  15.0

1 2

Select

Cart

0.00   0.00   0.00   F F F
1.10  -1.43   0.00   T T F
1.10   1.43   0.00   T T F
```

- Q.15 Explain the POSCAR file opposite.

- Q.16 Give the value of the OH bond and the characteristic length of the cell in the same unit.

Build and give in your report the INCAR file corresponding to an electronic relaxation in standard precision, a cut-off of 400 eV, a relaxation of the structure using the DIIS algorithm on a maximum number of 10 steps with a criterion of convergence on the forces of 0.02 Å eV-1. We will minimize the structure according to 2 degrees of freedom (x, y). The molecule is forced to remain plane in (x, y). We will also take ISMEAR = 0 and SIGMA = 0.1

Q.17 Give the energy and bond lengths of the optimized water molecule.

Open the **VASP-script_ENCUT.sge** script for editing. This script allows you to vary the cut-off between 200 and 700 eV in the INCAR file.

In the line "VASPDIR = $ WORK / VOTRE_REPERTOIRE / Atoms-and-molecules", replace "YOUR_REPERTOIRE" with the name of your directory.

• Redo the previous calculation by launching it with the submission script **VASP-script_ENCUT.sge**

Q.18 Plot the energy and length of the OH bond as a function of the cut-off. Give your conclusions.

• Redo the computation by using this time for the electronic part a stronger precision (PREC = ACCURATE) and a stronger convergence criterion (EDIFF = 10^{-5} and 10^{-6} eV).

Q.19 Compare your results and comment on them without forgetting the execution times. Plot the energy and length of the OH bond against EDIFF. Give your conclusions.

• Repeat the calculation, this time using a structural relaxation with the conjugate gradient method.

Q.20 Give your conclusions. Also compare the run times between these two optimization methods.

Bulk Systems

Examples:

- fcc Cu
- fcc Si and cd Si

Expected goals:

- Equilibrium structure of solids & volume of the unot cella t equilibrium
- DOS Density of states
- Band Structures

Equilibrium Structure of Cu FCC

For this part, go to the **Bulk-Systems/fccCu** folder.

We are trying to determine the equilibrium structure of copper knowing that it crystallizes in the FCC system.

First, we try to determine the sensitivity of the calculations to the various input parameters (size of the Plane waves base set, grid of points k). We simply calculate the energy without trying to optimize the structure ("single point energy" calculation)

We give for that:

INCAR	KPOINTS	POSCAR
System = fccCu ENCUT = 273.214 ISMEAR = 0 SIGMA = 0.1	K-Points 0 Monkhorst-Pack 11 11 11 0. 0. 0.	fcc Cu: 3.62 0.5 0.5 0.0 0.0 0.5 0.5 0.5 0.0 0.5 1 cartesian 0 0 0

Influence of ENCUT

• Start the calculation with the script “VASP-script-ENCUT.sge” (after modifications) which allows ENCUT to be varied from 200 to 800 eV in the INCAR.

An energy-f-ENCUT.dat file will be created, it gives energy according to the cut-off.

Q.21 Plot the energy as a function of the cut-off value. Deduce a converged value for the cut-off.

• If you have time, repeat the previous calculations using the Cu_pv pseudopotential.

Q.22 What is the particularity of this pseudopotential?

Q.23 Compare and justify the results obtained.

Influence of the grid of points k

In this part we will use the cut-off value determining the optimal size of the base, which was determined previously. The goal now is to optimize the geometry by changing the grid of points k.

• Do a calculation for a grid ranging from 1x1x1 to 10x10x10. (using the appropriate script after modifying the appropriate line).

Q.24 Observe the convergence of energy. Conclude.

The energies values can also be found in the OUTCAR or OSZICAR output files. (Command: **grep ‘’ free energy ’’ OUTCAR**, be careful there is a double space between “free” and “energy”).

Optimization of the structure

Create a new folder for this part which you will name "**opt-fccCu**" for example.
Copy the INCAR, KPOINTS, POTCAR input files into it.
Modify the INCAR and KPOINTS files according to the results of the calculations you obtained previously.
The goal now is to optimize the geometry more finely using this grid of points k and this value of ENCUT.
One can for example “scan” in an automatic way the volume of the unit cell (thus the parameter of unit cell for a rhombohedral unit cell)

• The example script below builds the POSCAR file corresponding to this operation.
• Perform an optimization calculation by choosing values of the initial parameters corresponding to the previous tests. You can adapt the example script by making the necessary changes.
• For each calculation, note:
• The energy at the end of the optimization

Optimisation de la structure

Créez un nouveau dossier pour cette partie que vous nommerez « **opt-fccCu** » par exemple.
Copiez dedans les fichiers d'entrées INCAR, KPOINTS, POTCA.
Modifiez les fichiers INCAR et KPOINTS d'après les résultats des calculs que vous avez obtenus précédemment.
Le but est maintenant d'optimiser plus finement la géométrie en utilisant cette grille de points k et cette valeur de ENCUT.
On peut par exemple « scanner » de manière automatique le volume de la maille (donc le paramètre de maille pour une maille rhomboédrique)

- L'exemple de script ci-dessous construit le fichier POSCAR correspondant à cette opération.
- Faire un calcul d'optimisation en choisissant des valeurs des paramètres initiaux correspondant aux tests précédents. Vous pouvez adapter le script donné en exemple en faisant les modifications qu'il faut.
- Pour chaque calcul, noter :
  - L'énergie à la fin de l'optimisation
  - Optimized unit cell parameters

```
#!/bin/bash -l
#
#$ -V
#$ -q parallel.q
#$ -pe mpi 16
#$ -l h_vmem=2.0G
#$ -o $JOB_NAME.$JOB_ID.out
#$ -e $JOB_NAME.$JOB_ID.err
#$ -N Cu_vol


# chargement des modules
module purge
module load vasp/5.3

# path definition
VASPDIR=$WORK/VOTRE_REPERTOIRE/bulk-systems
WORKDIR=$VASPDIR/fccCu/opt-fccCu/$JOB_NAME
if [ ! -d $VASPDIR/fccCu/opt-fccCu/$JOB_NAME ]; then
  mkdir $VASPDIR/fccCu/$JOB_NAME
fi

cd $WORKDIR

for ((i=30;43-$i;i++))
do

a=$(echo "$i*0.1+0.02"|bc -l)
cat > POSCAR <<!
fcc Cu:
 $a
0.5 0.5 0.0
0.0 0.5 0.5
0.5 0.0 0.5
Cu
 1
Cartesian
0 0 0
!

###############################################
# exÃ©cution
time mpirun -n $NSLOTS Home/Users/tpchrono/WORK/Executable/vasp
###############################################

cp OSZICAR OSZICAR-$a
cp OUTCAR OUTCAR-$a
cp POSCAR POSCAR-$a
E=`tail -1 OSZICAR` ; echo $a $E >>energy-f-maille.dat

done
```

The POSCAR file is not given because we do not know the value of the unit cell parameter. We must "scan" different values of lattice parameters to approach the equilibrium value (the one that gives the lowest energy). We will therefore calculate the total energy for different lattice parameters. One gives here the script (called VASP-script-vol.sge) which will generate unit cell parameter values in a folder named Cu_vol.

Q.25 Interpret it and improve it if necessary (especially the path).

The result of the scrip should gives something like :

```
3.5 1 F= -.44256712E+01 E0= -.44233993E+01 d E =-.454388E-02
3.6 1 F= -.46614699E+01 E0= -.46600410E+01 d E =-.285796E-02
3.7 1 F= -.47979864E+01 E0= -.47959298E+01 d E =-.411323E-02
3.8 1 F= -.48645042E+01 E0= -.48630063E+01 d E =-.299564E-02
3.9 1 F= -.48773847E+01 E0= -.48758538E+01 d E =-.306176E-02
4.0 1 F= -.48487436E+01 E0= -.48481092E+01 d E =-.126878E-02
4.1 1 F= -.47852634E+01 E0= -.47844854E+01 d E =-.155599E-02
4.2 1 F= -.46936947E+01 E0= -.46922530E+01 d E =-.288339E-02
4.3 1 F= -.45831167E+01 E0= -.45811837E+01 d E =-.386598E-02
```

Q.26 Plot the energy per atom against the lattice parameter and comment on your values.

• Adjust your POSCAR file with the equilibrium value you found and redo a VASP run to verify your calculation (use the normal **VASP-script**.

Equilibrium Structure of Si FCC

The purpose of this part is analogous to the previous work on copper. This is to optimize the geometry of silicon assuming it crystallizes in the FCC system. We give the grid of points k and the value of ENCUT optimal below.

INCAR	KPOINTS
System = fcc Si ISTART = 0 ICHARGE = 2 ENCUT = 240 ISMEAR = 0 ; SIGMA = 0.1	K-Points 0 Monkhorst-Pack 11 11 11 0. 0. 0. K-Points 0

As in the previous case, one can “scan” automatically the volume of the unit cell.

• Adapt the previous script to build the POSCAR file and scan the unit cell parameter between 3.5 and 4.3 Å.
• For each calculation, note the energy at the end of the optimization
• Draw the energy curve as a function of the unit cell parameter

The equilibrium distance is close to 3.9 Å. Redo an optimization with this value by adjusting your POSCAR file with this value.

• Keep your CHGCAR file for the next part concerning the calculation of the DOS of Cu CFC

Density of states of Si FCC

• Create a new **"fccSidos"** folder.
• Copy into this new folder the CONTCAR, INCAR, POTCAR, WAVECAR, CHGCAR files from the previous calculation as well as the VASP-script submission script.
The following calculation will be done from the **fccSidos** folder.

To calculate the density of states (DOS), we read the electron density found previously in the electron optimization calculation.
One does not modify it for this calculation of the DOS (ICHARG = 11). Each point k is treated independently.

• Edit the INCAR and KPOINTS files as shown below.

```
System = fcc Si

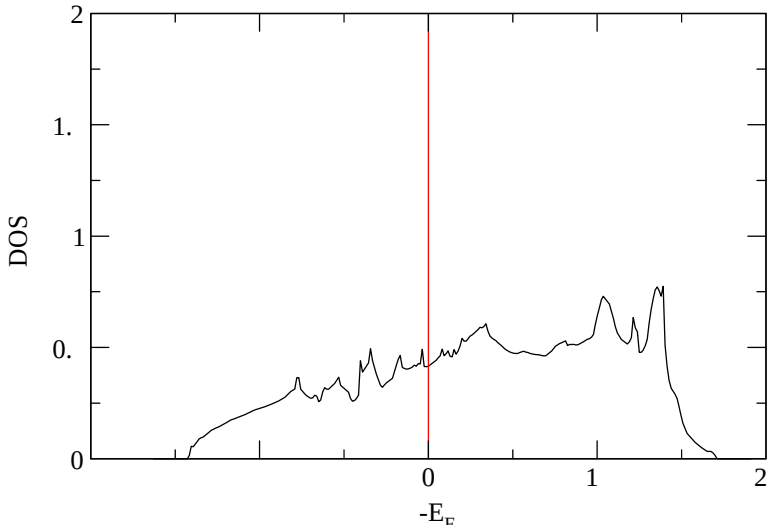
ICHARG = 11          Read charge density from previous
                     run, and keep it fixed during this
                     calculation

ENCUT = 240          energy cutoff: 240 eV (see POTCAR)

ISMEAR = -5          Use the tetrahedron method with
                     Blöchl corrections

LORBIT=11
```

```
K-Points
0
Monkhorst-Pack
21 21 21
0. 0. 0.
```

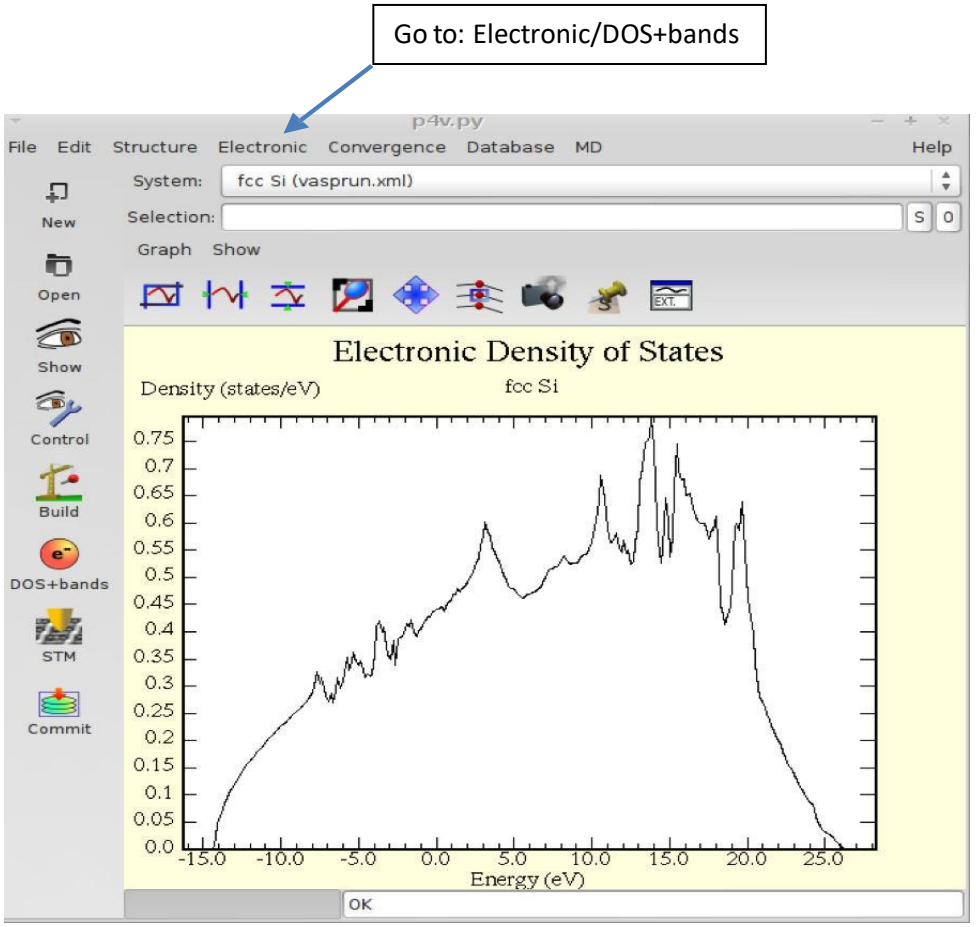


N.B .: copy the electronic charge density that you found previously in your current directory

- It is recommended to use the "Tetrahedron" method for the calculation of the DOS
- You have to increase the "k points sampling" for a DOS calculation

Density of states of Si FCC

After having transferred your data to the appropriate directory on your local workstation, open from this same directory the program p4vasp and follow the instructions below to view DOS (**For LINUX users**)



Band Structure of Si FCC

We will now look at the band structure of our system.
• Copy the CHGCAR file obtained during the calculation of the DOS into the fccSiband folder.
You will find the following information in the KPOINTS file.

```
L-G-X-U K-G                          Header (comment)

10                                   10 points per line segment

Line                                 Switch for bandstructure

reciprocal                           begin/end-points in reciprocal coordinates

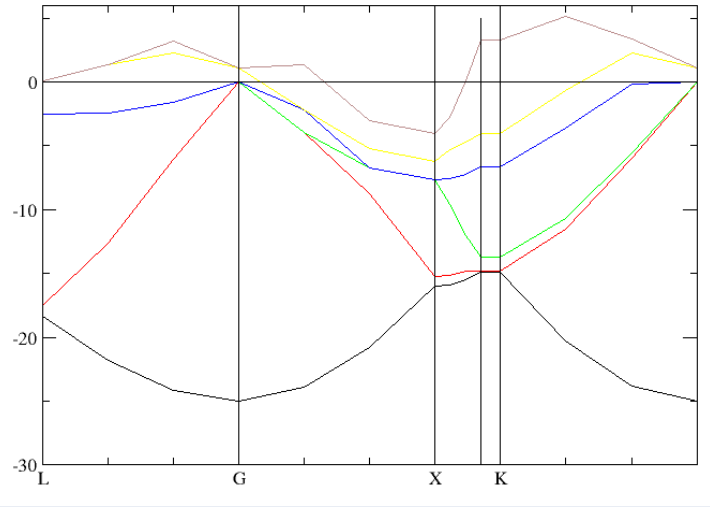
0.50000  0.50000  0.50000   1       L-point
0.00000  0.00000  0.00000   1       G-point

0.00000  0.00000  0.00000   1       G-point
0.00000  0.50000  0.50000   1       X-point

0.00000  0.50000  0.50000   1       X-point
0.25000  0.62500  0.62500   1       U-point

0.37500  0.75000  0.37500   1       K-point
0.00000  0.00000  0.00000   1       G-point

                                     All points are weighted  "× 1"
```



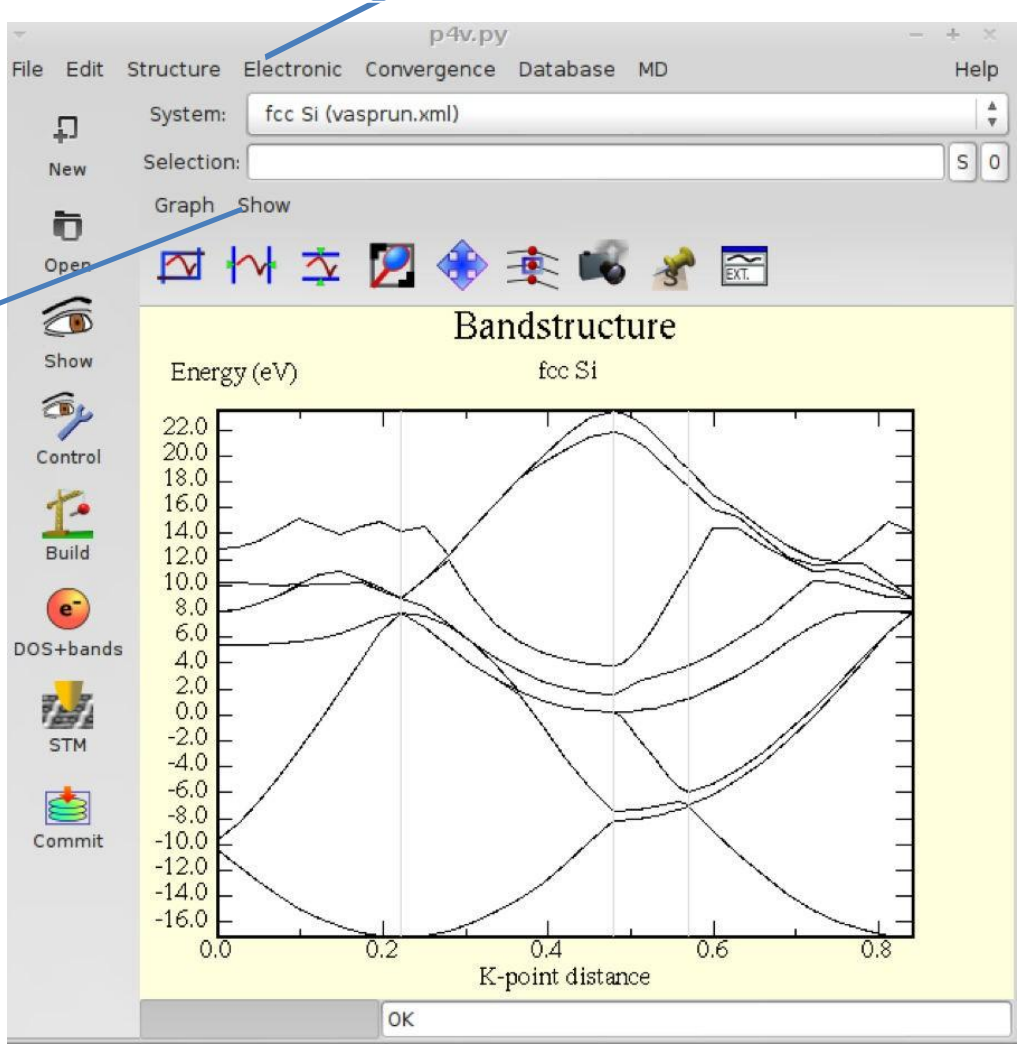
N.B : copy the self-consistent charge density of the previous example (fcc Si DOS) to your current working directory.

Band Structure of Si FCC

At the end of your calculation you can visualize the band structure of the Si FCC with p4vasp by following the following instructions

Step 1.) Go to: Electronic/DOS+bands

Step 2) Go to : Show/Bands



Equilibrium Structure of diamond-like Si

Silicon does not actually crystallize in a CFC system but rather in a “diamond” type structure.

• Redo the previous calculations (equilibrium structure and DOS) for this structure
• Create a new folder that you will call **“diamondSi”**, copy into it from the **fccSi** folder the input files necessary for the calculation.

We will first determine the unit cell parameter at equilibrium (make variations between 5.2 and 5.8 Å), then the DOS.

• You can either create a script as in the previous calculations, or create a folder for each unit cell parameter value (longer) in order to be able to plot at the end the energy of the structure as a function of the unit cell parameter.

Q.27 Comment out the following POSCAR file:

```
cubic diamond

5.5

0.5 0.5 0.0
0.5 0.0 0.5
0.5 0.5 0.0

2

Direct

-0.125 -0.125 -0.125
 0.125    0.125  0.125
```

We should obtain something like :

```
-.10528151E+02 E0= -.10528137E+02 d E =-.274709E-04
5.3 1 F= -.10713281E+02 E0= -.10713280E+02 d E =-.218410E-05
5.4 1 F= -.10806685E+02 E0= -.10806685E+02 d E =-.114401E-06
5.5 1 F= -.10823039E+02 E0= -.10823039E+02 d E =-.429842E-08
5.6 1 F= -.10775102E+02 E0= -.10775102E+02 d E =-.204668E-09
5.7 1 F= -.10673578E+02 E0= -.10673578E+02 d E =-.112715E-10
5.8 1 F= -.10528393E+02 E0= -.10528393E+02 d E =-.552513E-11
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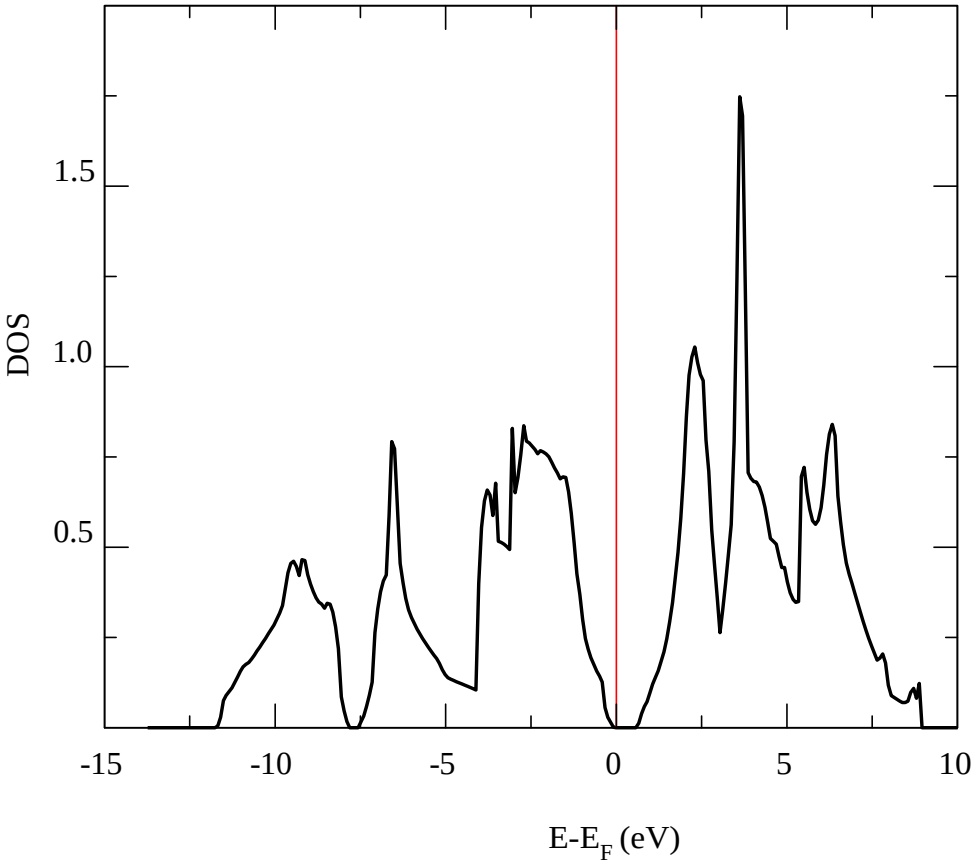

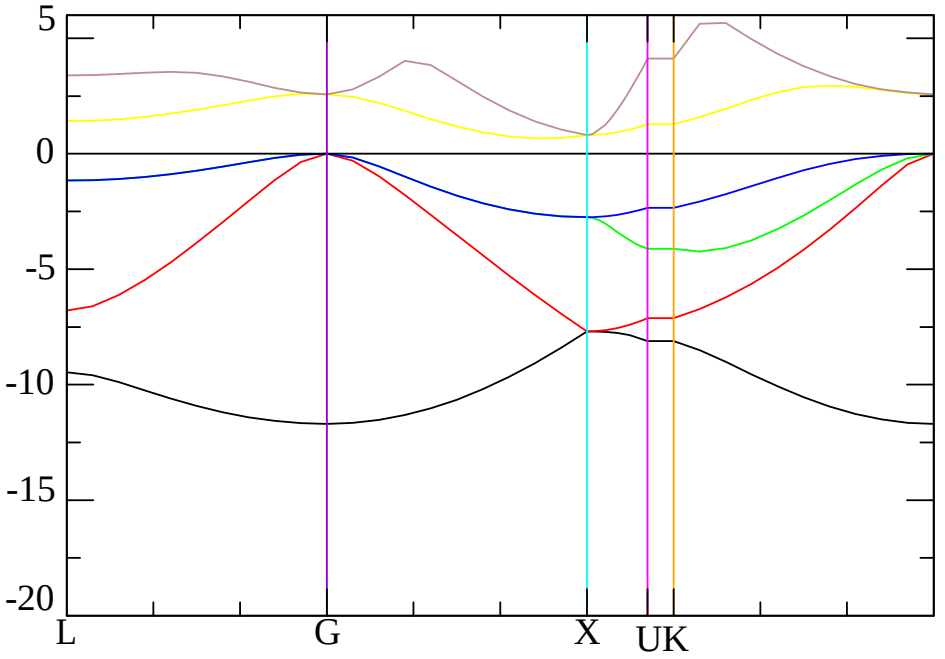

Q.28 What can you deduce from these graphs: Metal? Semiconductor? Insulating? Give the value of the gap, and compare to the experimental value