

Hands-on: Band structure and DOS metals/insulators

Tutors: Alberto Carta, Fatema Mohamed, Bryce
Rodrigue Malonda and George Manyali

Topics of Day3 hands-on session:

1. How to relax a structure (graphane and oxygen adsorption)
2. How to run post-processing calculations to plot DOS (dos.x), PDOS (projwfc.x) and band-structure (bands.x).
3. How to choose the smearing and the broadening parameters for metals.
4. How to compute forces and stresses.

Exercise 1

Forces and relaxation

Input file scf calculation

```
&CONTROL  
  calculation = 'scf',  
  prefix      = 'Graphane',  
  outdir      = '/tmp',  
  pseudo_dir  = '../pseudo',  
/
```

```
&SYSTEM
```

```
....  
....
```

```
/
```

```
&ELECTRONS
```

```
  conv_thr = 1.0d-8  
/
```

```
ATOMIC_SPECIES
```

```
  C 12.0107 C.pbe-rrkjus.UPF  
  H  1.00007 H.pbe-rrkjus.UPF
```

```
ATOMIC_POSITIONS alat
```

```
...
```

```
K_POINTS automatic
```

```
  9 9 1 0 0 0
```

Input file for relaxation

```
&CONTROL
```

```
  calculation = 'relax',  
  prefix      = 'Graphane',  
  outdir      = '/tmp',  
  pseudo_dir  = '../pseudo',  
/
```

```
&SYSTEM
```

```
....  
....
```

```
/
```

```
&ELECTRONS
```

```
  conv_thr = 1.0d-8  
/
```

```
&IONS
```

```
/
```

```
ATOMIC_SPECIES
```

```
  C 12.0107 C.pbe-rrkjus.UPF  
  H  1.00007 H.pbe-rrkjus.UPF
```

```
ATOMIC_POSITIONS alat
```

```
...
```

```
K_POINTS automatic
```

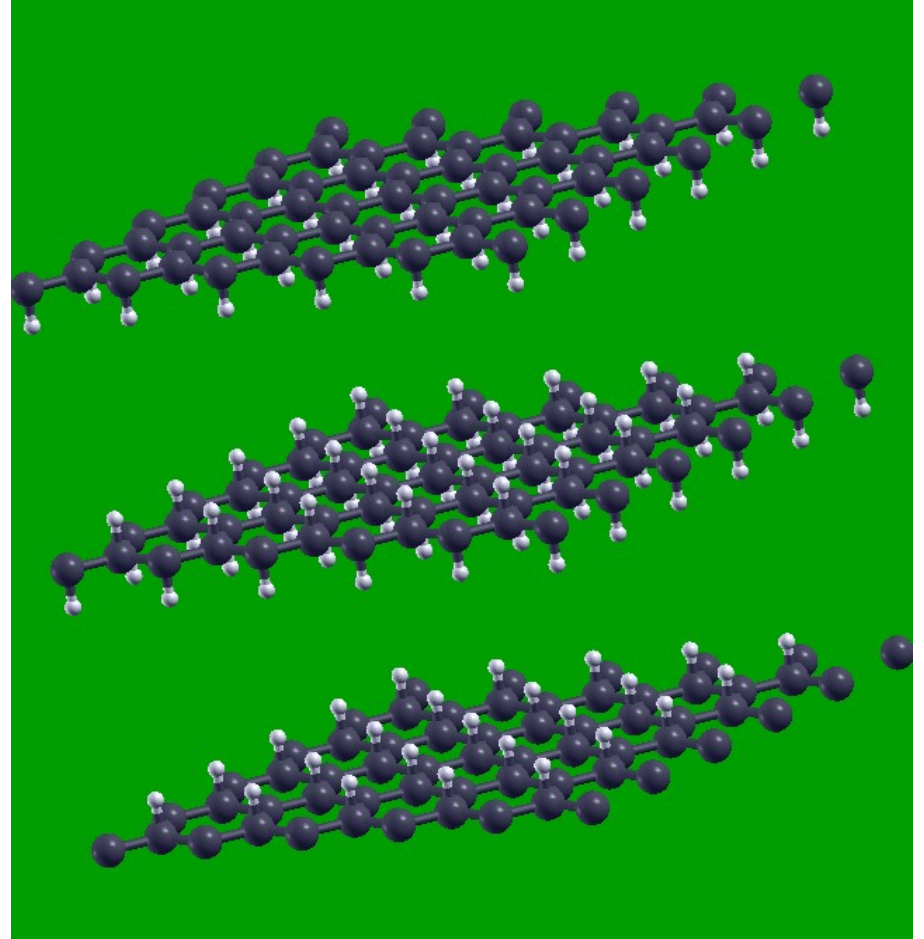
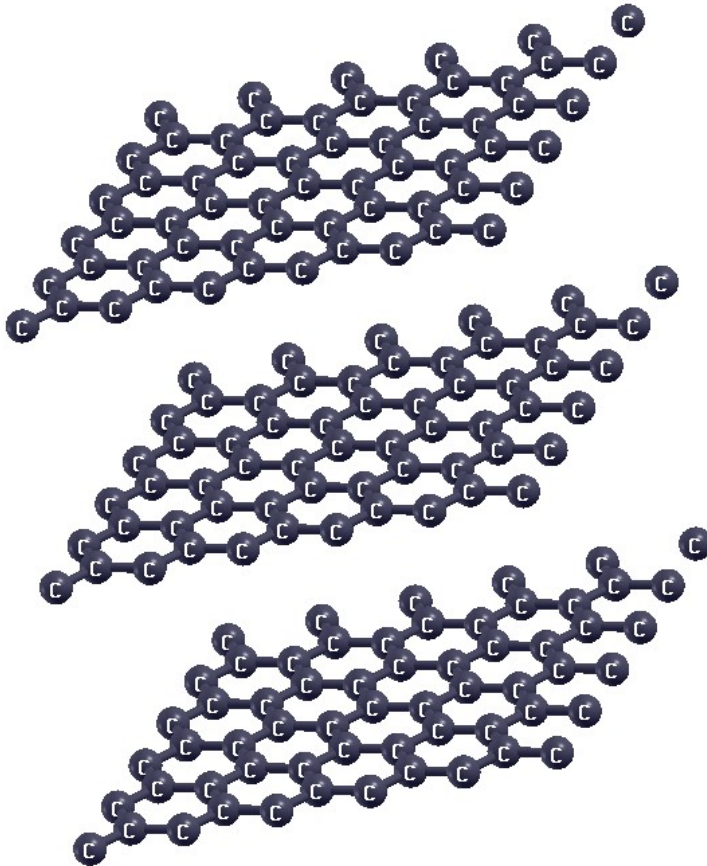
```
  9 9 1 0 0 0
```



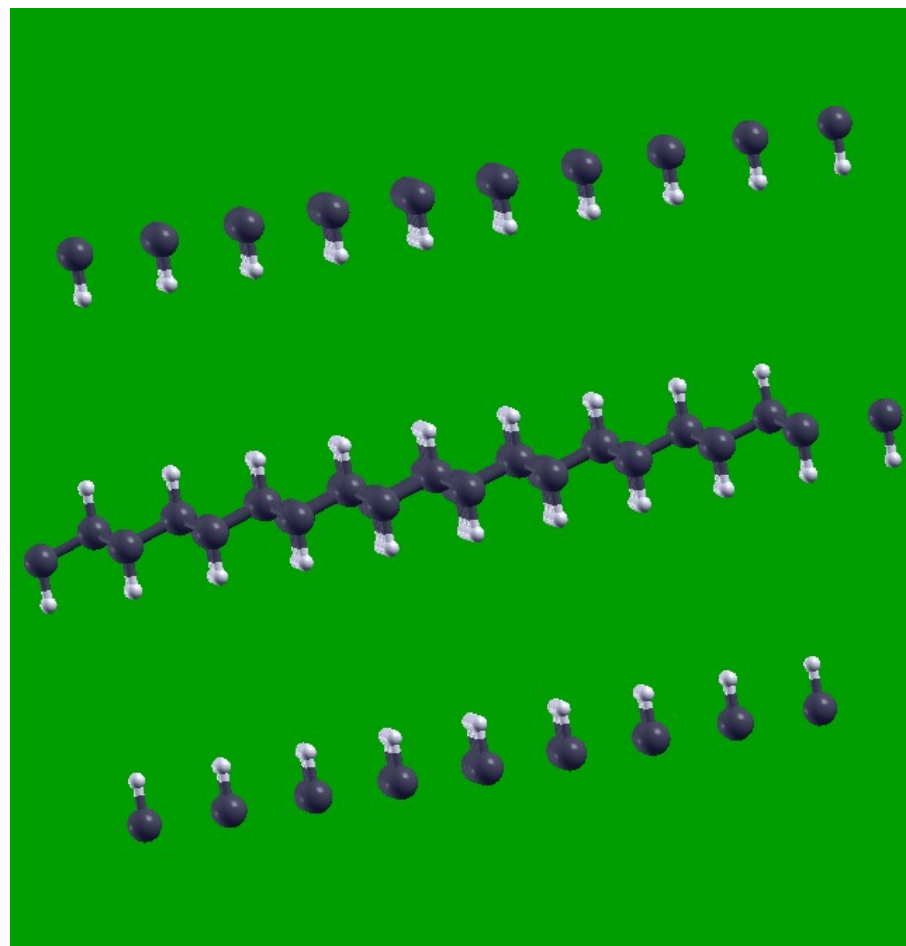
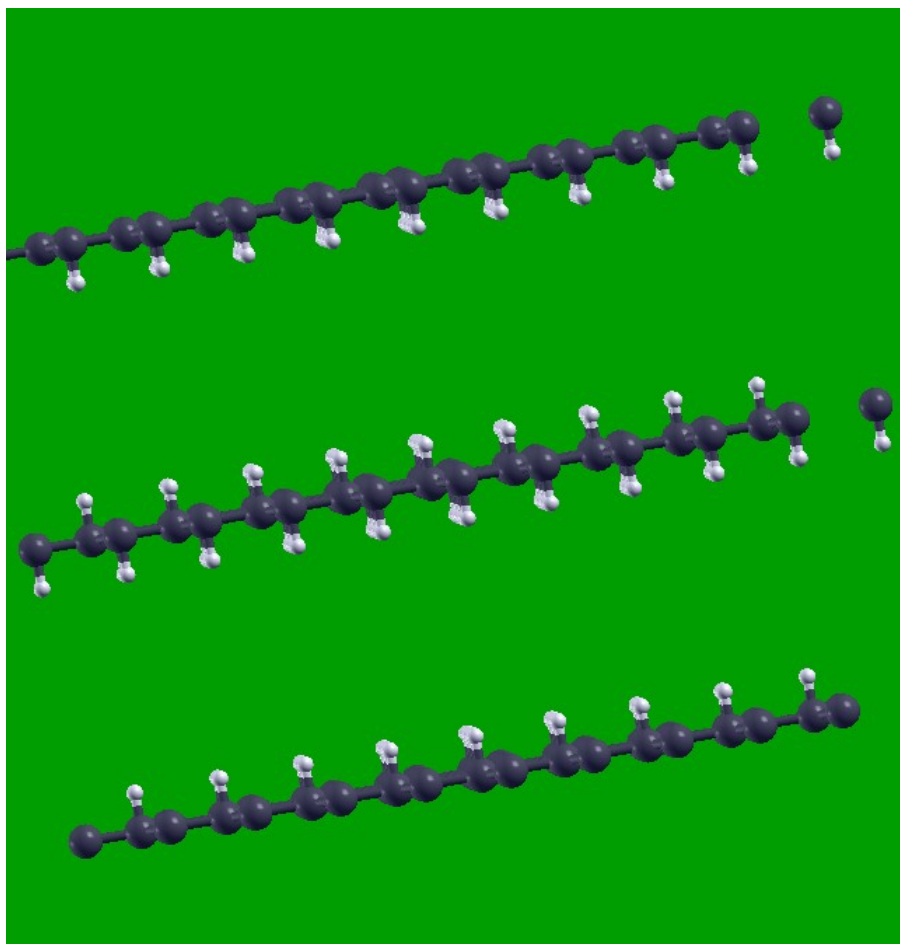
Ions is jargon for atoms, this cell must appear!

Buckling of graphane

Graphane is hydrogenated graphene → hydrogen saturates double-bonds / pi-delocalized cloud

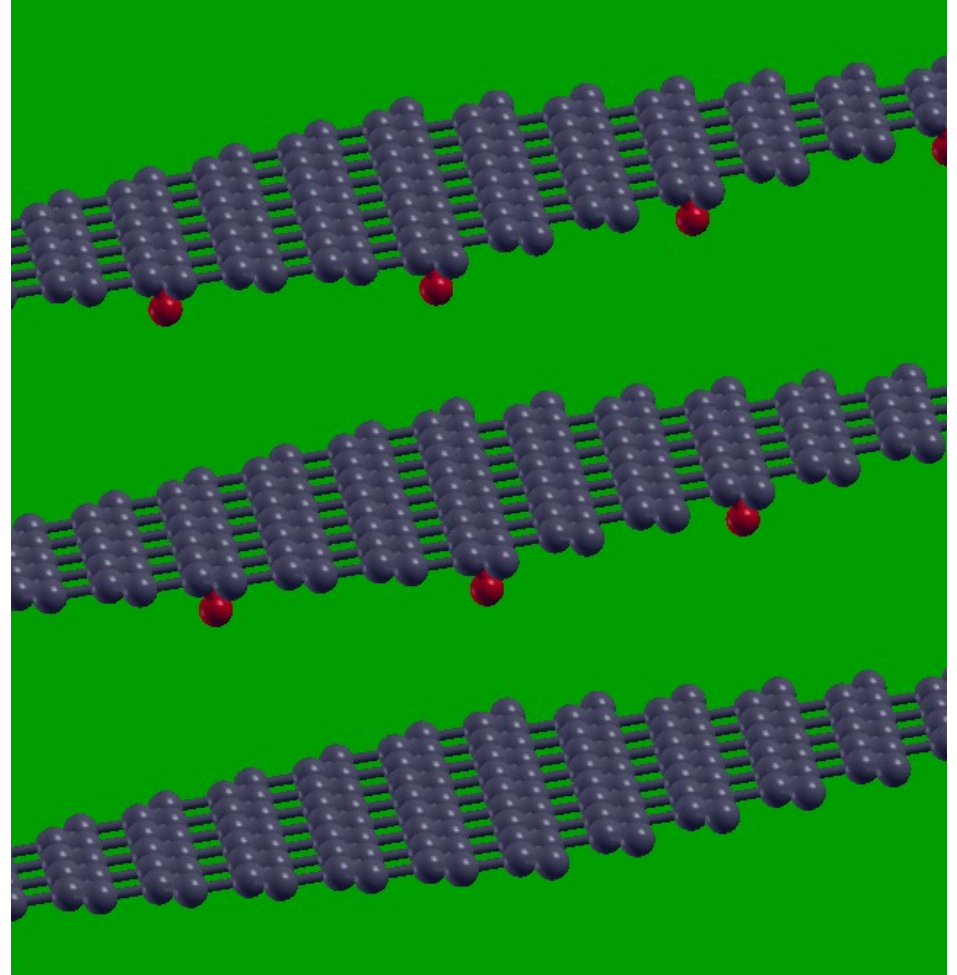
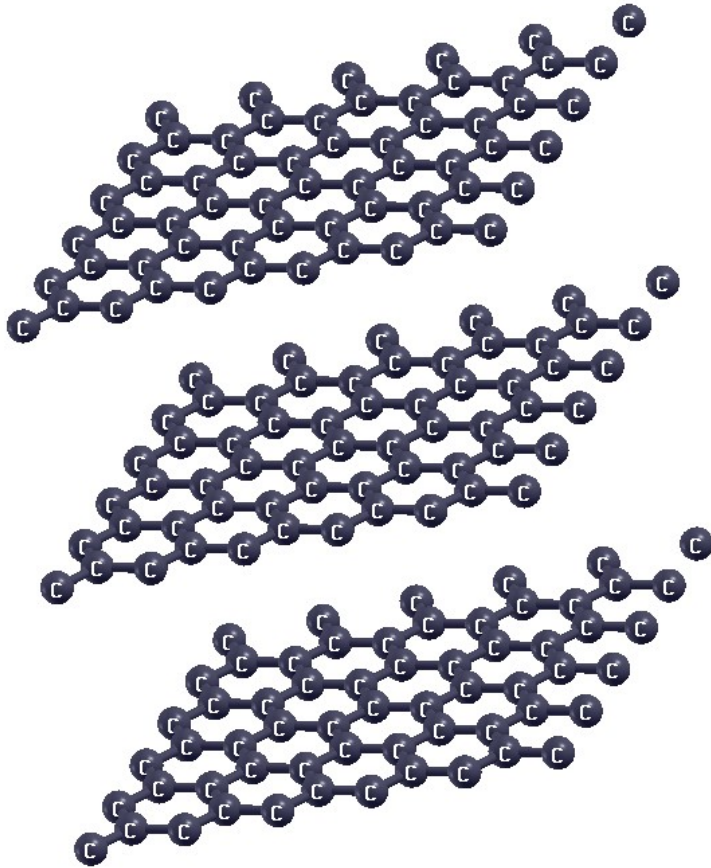


Buckling of graphane



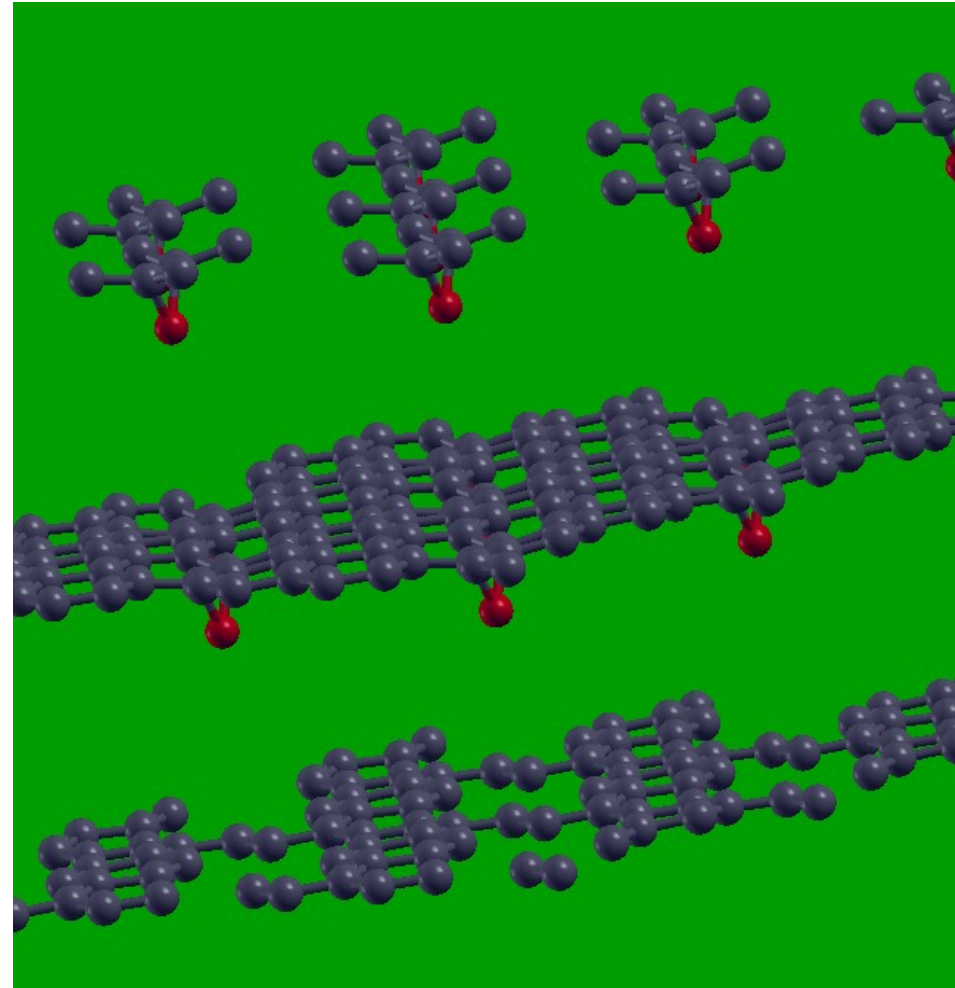
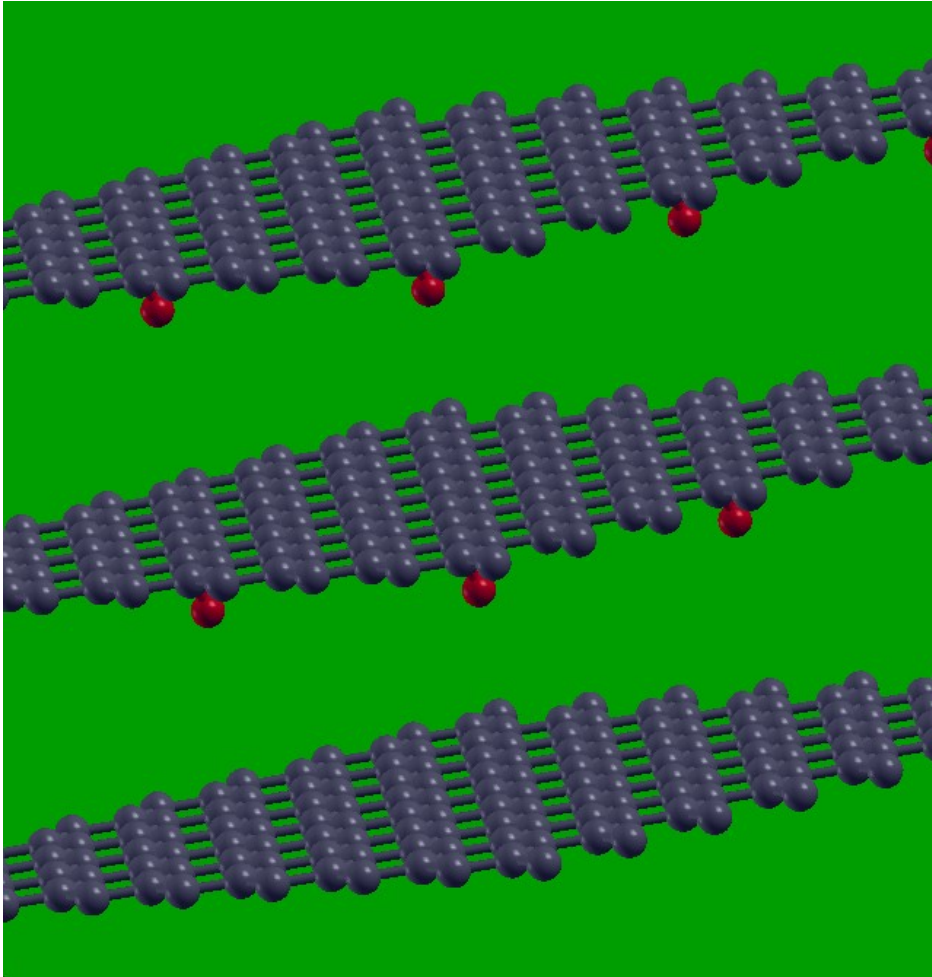
Oxygen adsorption on graphene

Oxygen is strongly electronegative → electron acceptor



Oxygen adsorption on graphene

Oxygen is strongly electronegative → electron acceptor



Exercise 2

Follow up on silicon for Si

Input file scf calculation

```
&CONTROL
  calculation='scf',
  prefix='silicon',
  pseudo_dir='../pseudo/',
  outdir='../tmp'
/
&SYSTEM
 ibrav = 2,
  celldm(1) = 10.6,
  nat = 2,
  ntyp = 1,
  nbnd=10,
  ecutwfc = 36,
/
&ELECTRONS
/

ATOMIC_SPECIES
  Si 28.086 Si.pz-vbc.UPF
ATOMIC_POSITIONS
  Si 0.00 0.00 0.00
  Si 0.25 0.25 0.25
K_POINTS automatic
  6 6 6 1 1 1
```

Input file for relaxation of unit cell

```
&CONTROL
  calculation='vc-relax',
  prefix='silicon',
  pseudo_dir='../pseudo/',
  outdir='../tmp'
/
&SYSTEM
 ibrav = 2,
  celldm(1) = 10.6,
  nat = 2,
  ntyp = 1,
  nbnd=10,
  ecutwfc = 36,
/
&ELECTRONS
/
&IONS
/
&CELL
/

ATOMIC_SPECIES
  Si 28.086 Si.pz-vbc.UPF
ATOMIC_POSITIONS
  Si 0.00 0.00 0.00
  Si 0.25 0.25 0.25
K_POINTS automatic
  6 6 6 1 1 1
```

← Slightly different
calculation mode

← We need also a CELL section

Relax lattice constant for Si

Run ``pw.x < si.relax.in | tee si.relax.out`` and consider the following:

- Compare the lattice volume to the one we optimized on Day 2, are they the same?
- What is the code doing from iteration to iteration?
- The new lattice constant is given in terms of the starting one, try to compute the relaxed lattice constant from the output and compare with the one we optimized on Day 2.

Density of State (DOS) for Si

The procedure to compute the DOS is the following:

- Use `pw.x` to calculate the density (`calculation = 'scf'`)
- Use `pw.x` to calculate the electronic eigenvalues on more k-point grids (`calculation = 'nscf'`)
- Use `dos.x` to compute the total DOS, will be produced in a data-file.

Important: we must keep the prefix same `outdir` and `prefix` for “nscf” and “scf” `pw.x` calculations and for the `dos.x` calculation.

Input file si.scf.in

```
&CONTROL
  calculation='scf'
  restart_mode='from_scratch',
  prefix = 'Si',
  pseudo_dir = '../pseudo'
  outdir='./tmp'
/

&SYSTEM
 ibrav = 2,
  celldm(1) = 10.262,
  nat = 2,
  ntyp = 1,
  ecutwfc = 20.0,
  ecutrho = 200.0,
/

&ELECTRONS
/

ATOMIC_SPECIES
Si 28.086 Si.pbe-rrkj.UPF

ATOMIC_POSITIONS alat
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25

K_POINTS automatic
6 6 6 1 1 1
```

Input file si.scf.in

```
&CONTROL
  calculation='nscf'
  restart_mode='from_scratch',
  prefix = 'Si',
  pseudo_dir = '../pseudo'
  outdir='./tmp'
/

&SYSTEM
 ibrav = 2,
  celldm(1) = 10.262,
  nat = 2,
  ntyp = 1,
  ecutwfc = 20.0,
  ecutrho = 200.0,
  nbnd=-8
  occupations = 'tetrahedra'
/


&ELECTRONS
/

ATOMIC_SPECIES
Si 28.086 Si.pbe-rrkj.UPF

ATOMIC_POSITIONS alat
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25

K_POINTS automatic
12 12 12 1 1 1
```

to calculate unoccupied bands, look at
number of Kohn-Sham states in the
si.scf.out.



Input file si.dos.in

&dos

```
outdir = './tmp',  
prefix='Si',  
fildos='si.dos',  
/
```



The same as in the scf and nscf input

Data file si.dos

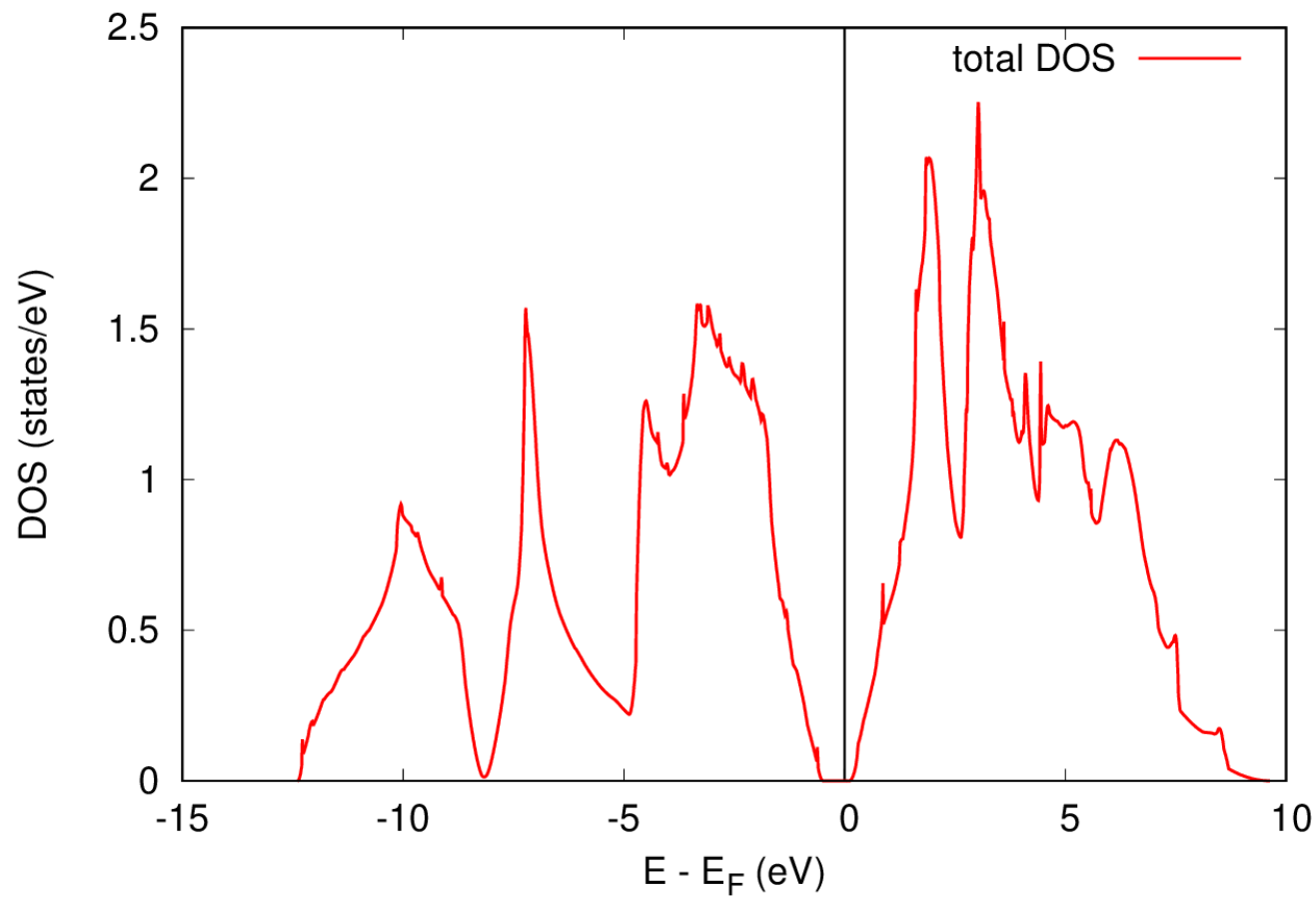
#	E (eV)	dos(E)	Int dos(E)	EFermi =	6.724 eV
	-5.667	0.0000E+00	0.0000E+00		
	-5.657	0.5876E-03	0.1959E-05		
	-5.647	0.2351E-02	0.1567E-04		
	-5.637	0.5289E-02	0.5289E-04		
	-5.627	0.9402E-02	0.1254E-03		
	-5.617	0.1469E-01	0.2448E-03		
	-5.607	0.2115E-01	0.4231E-03		
	-5.597	0.2879E-01	0.6719E-03		
	-5.587	0.3761E-01	0.1003E-02		
	-5.577	0.4760E-01	0.1428E-02		
	-5.567	0.1183E+00	0.2264E-02		
	-5.557	0.1378E+00	0.3596E-02		

Gnuplot script: plot_dos.gp

DOS is shifted such that the Fermi energy corresponds to zero of energy. Use the Fermi energy from the file si.nscf.out.

After running the script, visualize the file DOS.eps using evince or okular command.

Density of State (DOS) for Si



Projected Density of State (PDOS) for Si

The PDOS allows us to get the contribution from each atom in the cell and/or each of their orbital contributions. We can achieve it using **projwfc.x**.

The calculation steps are similar, the differences are in the input files for dos and pdos.

Input file si.pdos.in

```
&PROJWFC
```

```
outdir = './tmp',
```

```
prefix='Si',
```

```
filpdos='si.dos',
```

```
/
```

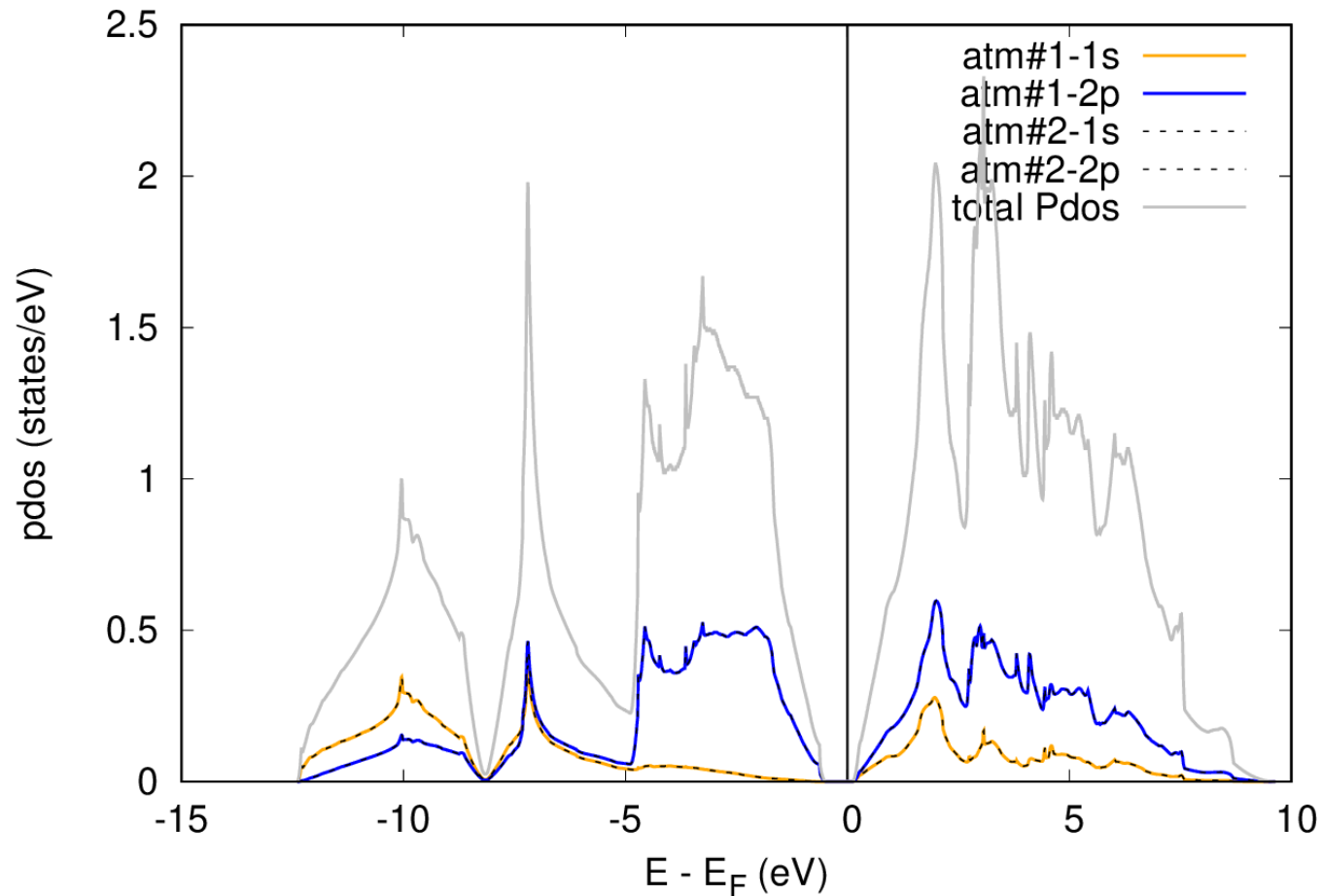
← See the difference w.r.t dos.x

run the PDOS calculation, execute '**projwfc.x**' as:

```
$ projwfc.x < si.pdos.in | tee si.pdos.out
```

Output: Have a look at **si.pdos.out** file. the PDOS values are written in the file **{filpdos}.pdos_atm#N(Si)_wfc#M(l)**, where N, M, and l are the atom number, wfc number, and atomic wavefunction read from pseudopotential file.

Projected Density of State (PDOS) for Si



To Plot the data: use **xFroggie** or gnuplot script **plot_pdos.gp** on your directory

Exercise 3

Band structure for Si

Band Structure of Silicon

The scheme to compute the band structure is the following:

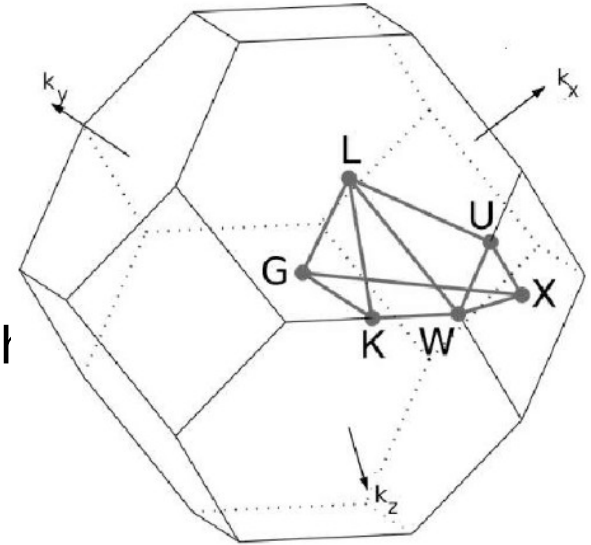
1. SCF **pw.x** calculation (**calculation = 'scf'**)
2. “bands”-type non-SCF **pw.x** calculation (fixed-potential) with:
 - **calculation = 'bands'**
 - number of bands (variable **nbnd**) is specified
 - a suitable path of k-points is specified in **K-POINTS** card. The k-point path must be continuous in k-space.
3. **bands.x** calculation, which, among others, produces data-files for the plot.

Important: we must keep the prefix same **outdir** and **prefix** for “nscf” and “scf” **pw.x** calculations and for the **bands.x** calculation.

k-path for Band Structure calculation

The **k-path** in BZ for fcc crystal can be specified using **xcrysden** as follow:

1. Open the file **si.scf.in** with **xcrysden**.
2. Select: Tools → k-path selection
3. Select the path by clicking on a sequence of high symmetry points: $W - \Gamma - X - W - L - \Gamma$
4. Specify how many k points to be calculated (Ex:
5. save the k-path to file. (.pwscf extension is required for formatting the file for pw.x)



Input file si.bands.in

&CONTROL

calculation='bands'

restart_mode='from_scratch',

prefix = 'Si',

pseudo_dir = '../pseudo'

outdir='./tmp'

verbosity = 'high'

/

&SYSTEM

ibrav = 2,

celldm(1) = 10.262,

nat = 2,

ntyp = 1,

ecutwfc = 12.0,

ecutrho = 200.0,

nbnd=8

/

&ELECTRONS

/

ATOMIC_SPECIES

Si 28.086 Si.pbe-rrkj.UPF

ATOMIC_POSITIONS alat

Si 0.00 0.00 0.00

Si 0.25 0.25 0.25

K_POINTS {crystal_b}

6

0.50 0.25 0.75 30 !W

0.00 0.00 0.00 30 !G

0.50 0.00 0.50 30 !X

0.50 0.25 0.75 30 !W

0.50 0.50 0.50 30 !L

0.00 0.00 0.00 30 !G

An input file for the data post processing program **bands.x**. This program print the eigenvalues to the file specified in "**filband**"

&BANDS

```
outdir = './tmp',  
prefix='Si',  
filband='si_bands',  
/
```

← The same as in the scf and bands input

← Contains data for bands

Run the postprocessing calculation (**bands.x**):

```
$ bands.x < bands.in | tee bands.out
```

bands data are stored in three files with different formats, among which we have **bands.dat.gnu** (can be plotted with **gnuplot**) and **bands.dat** can be visualized using the program **plotband.x**.

The program **plotband.x** can be to obtain a postscript file of the band structure and a set of data files that can be plotted with xmgr

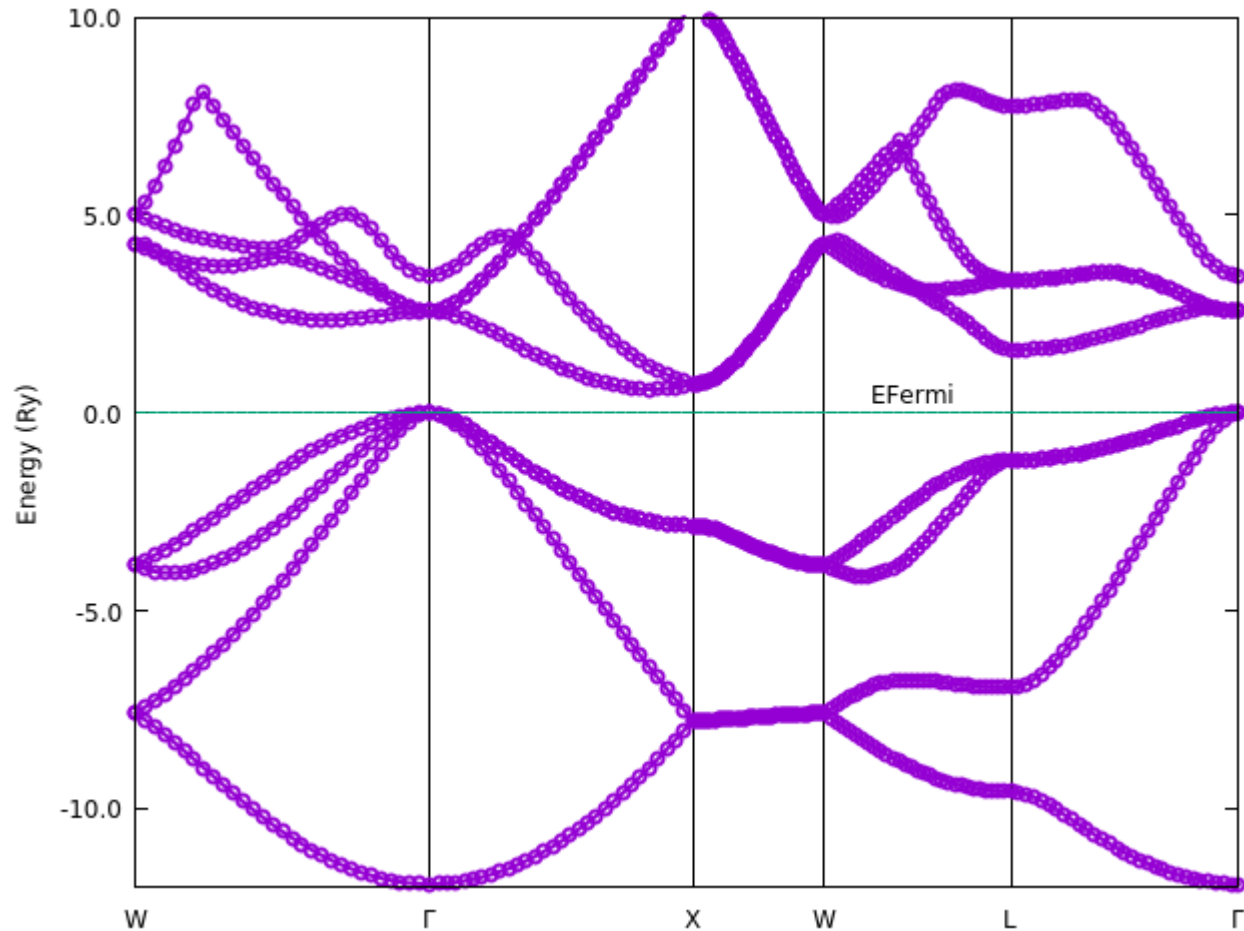
plotband.x prompts for terminal input:

\$ plotband.x

```
Input file > bands.dat
Reading 8 bands at 151 k-points
Range: -5.6670 16.3610eV Emin, Emax, [firstk, lastk] > -5.6670 16.3610
high-symmetry point: -1.0000 0.5000 0.0000 x coordinate 0.0000
high-symmetry point: 0.0000 0.0000 0.0000 x coordinate 1.1180
high-symmetry point: -1.0000 0.0000 0.0000 x coordinate 2.1180
high-symmetry point: -1.0000 0.5000 0.0000 x coordinate 2.6180
high-symmetry point: -0.5000 0.5000 0.5000 x coordinate 3.3251
high-symmetry point: 0.0000 0.0000 0.0000 x coordinate 4.1912
output file (gnuplot/xmgr) > Si.bands.dat
bands in gnuplot/xmgr format written to file Si.bands.dat
```

```
output file (ps) > bands.ps
Efermi > 6.239
deltaE, reference E (for tics) 2, 6.239
bands in PostScript format written to file bands.ps
```

Band Structure of Silicon



Try to plot with xFroggie: <https://xfroggie.com/>

Exercise 2

A metallic example: Aluminum

A metallic example: Aluminum

Let us consider **Aluminum**, in the **fcc** phase. It is a metal, only valence bands and a few k-points will not suffice.

- move to the **Day3/example2.Al** directory
- read the **pw.x** input file **al.scf.in**
- notice the presence of new variables: **occupations**, **smearing**, **degauss**;
- run **pw.x** as:

```
$ pw.x < al.scf.in | tee al.scf.out
```

- in the output file notice that
 - the **number of bands** (Kohn-Sham states) is automatically set to a value larger than the number of electrons divided by 2
 - the **Fermi energy** is computed.

Convergence with respect to k-points, degauss, and smearing

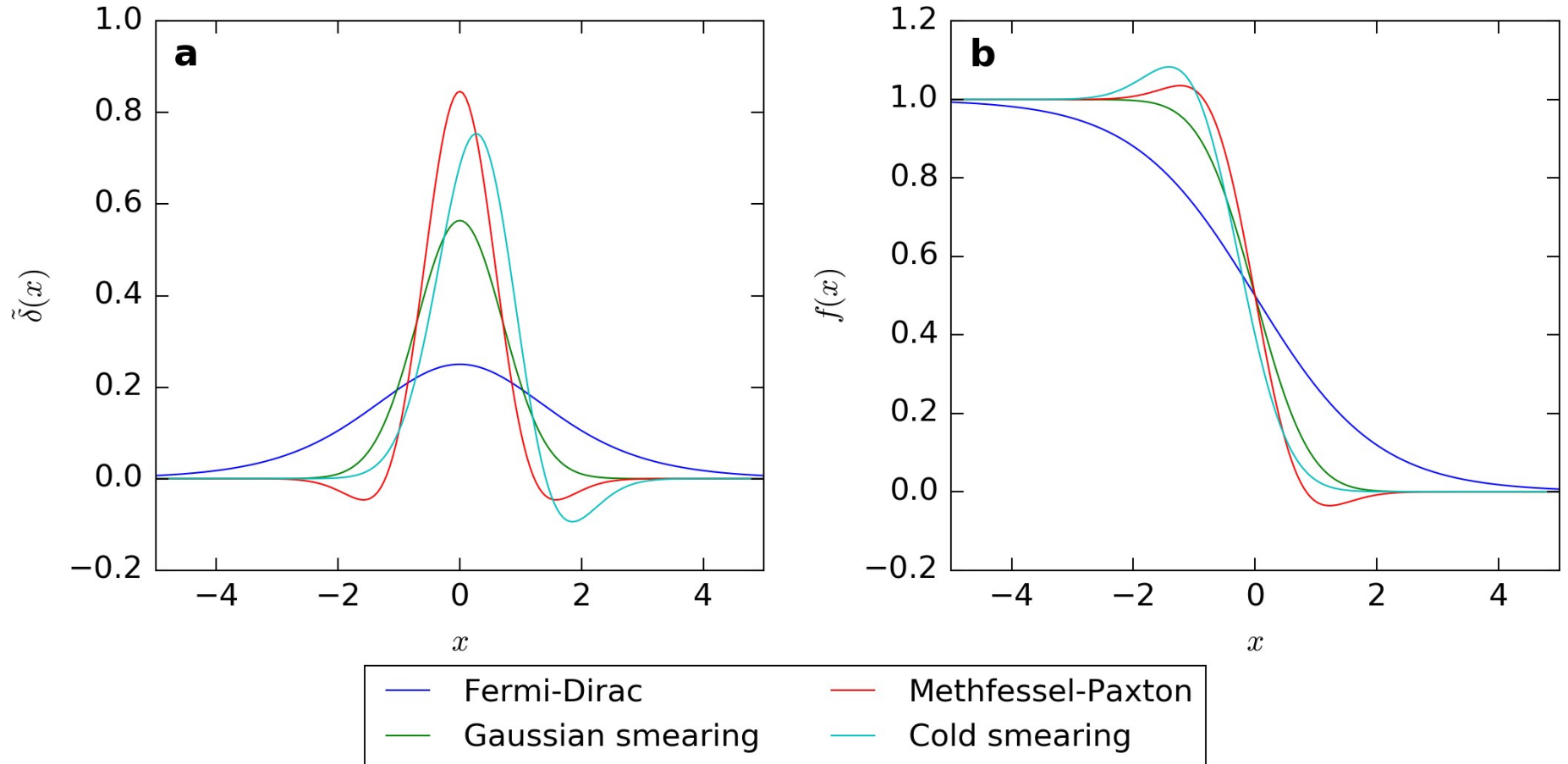
In this exercise we will compute the total energy for this fcc Al with the following values for degauss, k-point meshes and different smearing variables:

- degauss variable, in range from 0.01 to 0.11
- k-points: $N \times N \times N$ ($1 \times 1 \times 1$) with $N=6,8,10, \dots, 16$
- smearing variable, possible values: 'gauss' (or 'g'), 'marzari-vanderbilt' (or 'm-v'), 'methfessel-paxton' (or 'm-p')
- run **pw.x** for **run-al** file at different directories in **ex1-conv**:

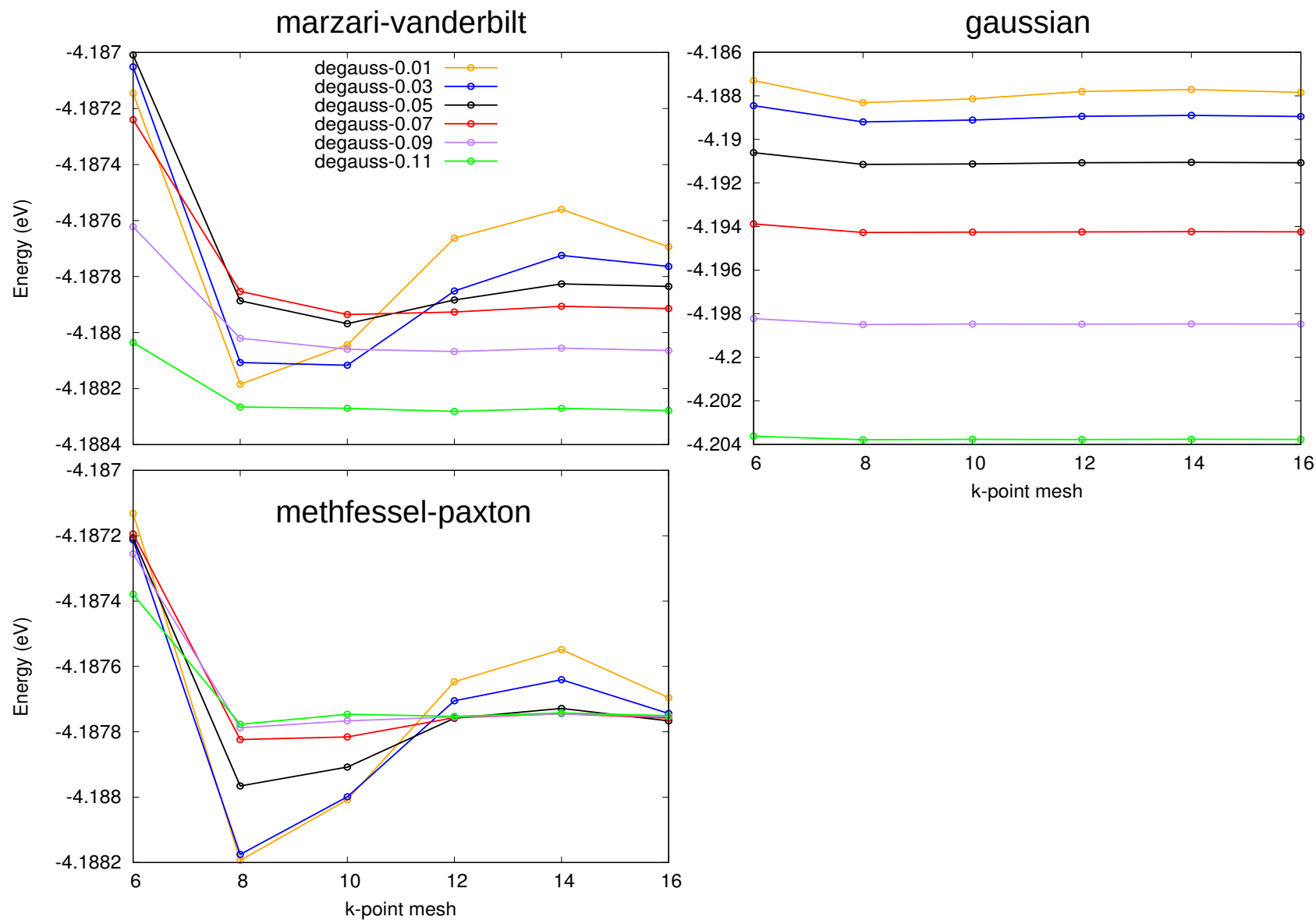
Plot the convergence of the total energy with respect to the number of k-points for the different smearing values.

Convergence with respect to k-points, degauss, and smearing

Different smearing schemes

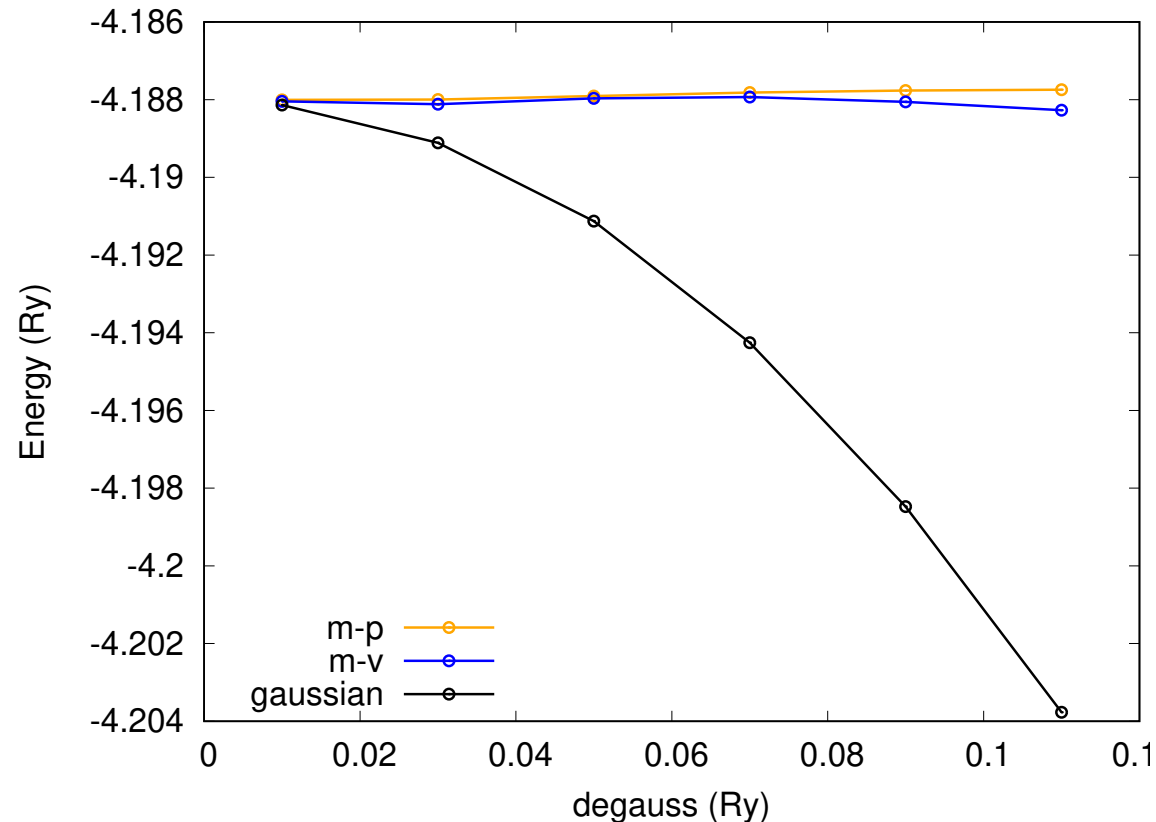


Convergence with respect to k-points, degauss, and smearing



Convergence with respect to k-points, degauss, and smearing

Choose a suitable k-point mesh and plot the total energy as a function of degauss for Marzari-Vanderbilt and Gaussian smearing.

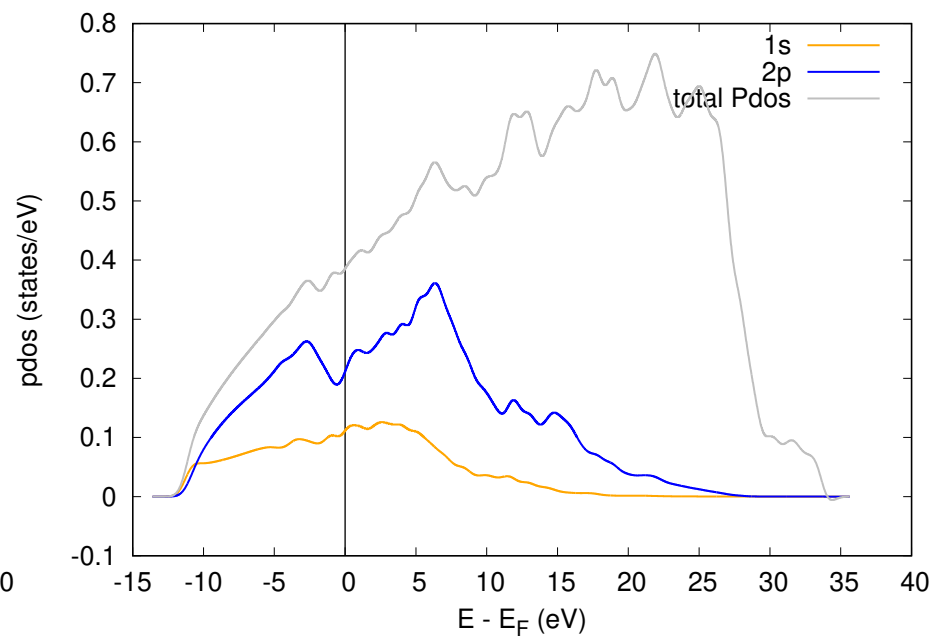
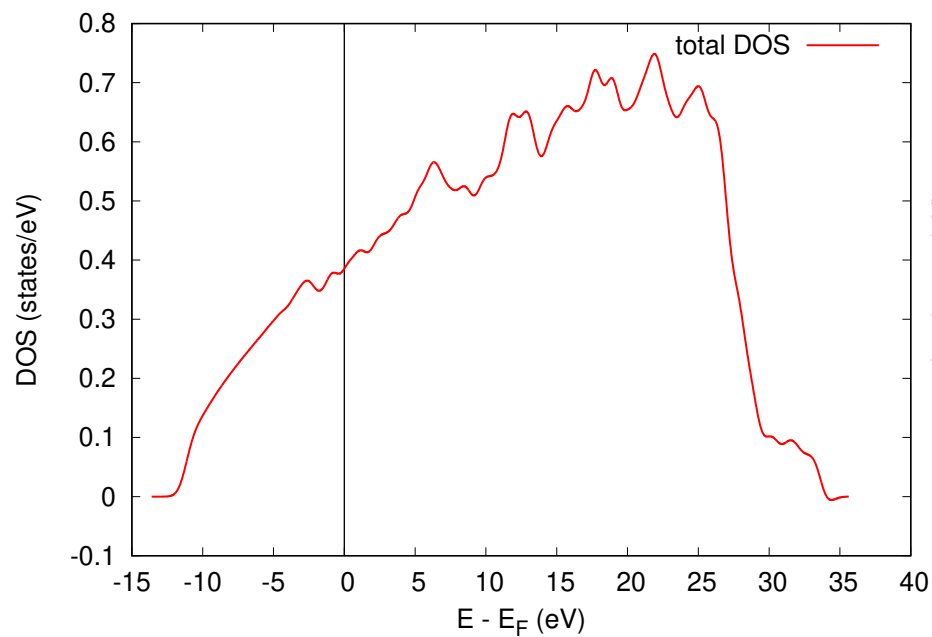


Density of state (DOS) and Projected DOS (PDOS) for Al

Use the procedure given in the instructions for **example1**:

- move to Day3/example2.Al/ex2.dos/ directory and
- Self-consistent calculation (**pw.x**)
- Select a finer mesh of k points by doing Non self-consistent calculation (**pw.x**)
- a **dos.x** calculation to calculate DOS
- a **projwfc.x** calculation to calculate PDOS projected to atomic states

Density of state (DOS) and Projected DOS (PDOS) for Al



Band structure for Al

Use the procedure given in the instructions for **example1**:

- move to Day3/example2.Al/ex2.bands/ directory and
- Self-consistent calculation (**pw.x**)
- Select a k-point path (i.e. by using XCrysDen, ...) and do “bands”-type non-SCF **pw.x** calculation
- a **bands.x** calculation print the eigenvalues and plot them using gnuplot or
- Use the program **plotband.x**

Band structure for Al

