Day 3 Hands-on: Bandstructures, metals and XC functionals

Tutors: Alberto Carta / Chiara Cignarella / Nelson Dzade / George Manyali / James Sifuna / Fatema Mohamed / Omamuyovwi Rita Jolayemi / Maram Ali Ahmed Musa

Today's Themes:

1) Performing band structure calculations
2) DFT calculations for metals: smearing parameters
3) XC functionals: LDA and PBE

Exercise 1

Performing band structure calculations

Exercise 1.1: band structure calculation

The scheme to compute the band structure is the following:

1. SCF pw.x calculation (calculation = 'scf')

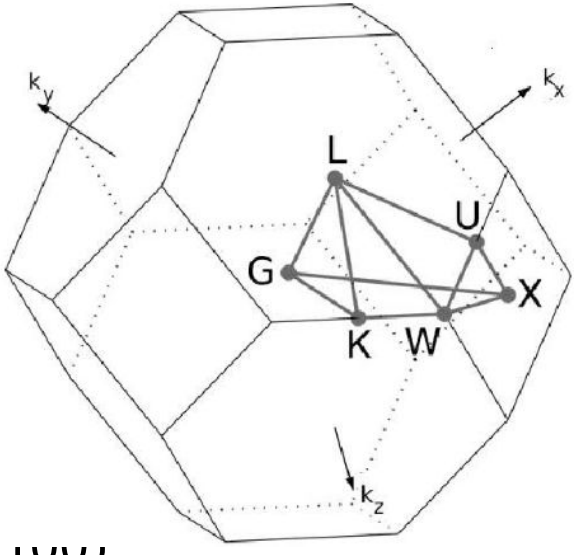
2. "bands"-type non-SCF pw.x calculation (fixed-potential) with:
   - calculation = 'bands'
   - number of bands (variable nbnd) is specified
   - a suitable path of k-points is specified in K-POINTS card. The k-point path must be continuous in k-space.

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.

Exercise 1.1: 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
4. symmetry points: W – Γ – X – W – L – Γ
5. Specify how many k points to be calculated (Ex: 100)
6. save the k-path to file. (.pwscf extension is required for
7. formatting the file for pw.x)

Exercise 1.1: band structure calculation

Input file: si.scf.in

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

[...]

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.bands.in

```
 &CONTROL
    calculation='bands'
    restart_mode='from_scratch',
    prefix = 'Si',
    pseudo_dir = '../../../../pseudo'
    outdir='./tmp'
    verbosity = 'high'
 /
[...]
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
```

Exercise 1.1: band structure calculation

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

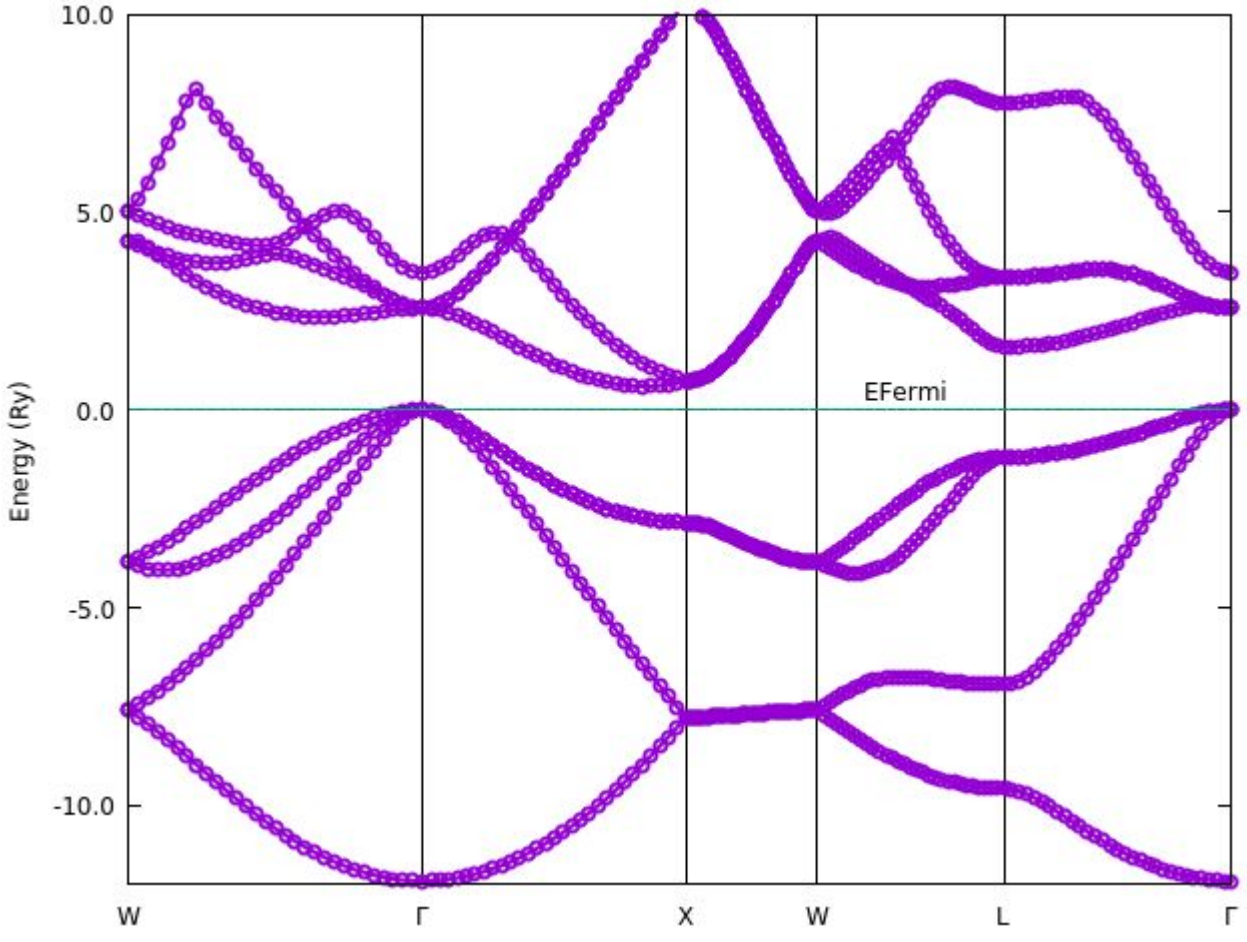
Contains data for bands

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.

Exercise 1.1: Si band structure



Si is an insulator, what about metallic systems?

Exercise 1.2: band structure of a metal

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/example1.bandstructure/ex2.Al directory
- read the pw.x input file al.scf.in
- notice the presence of new variables: occupations, smearing, degauss;
- run pw.x as:

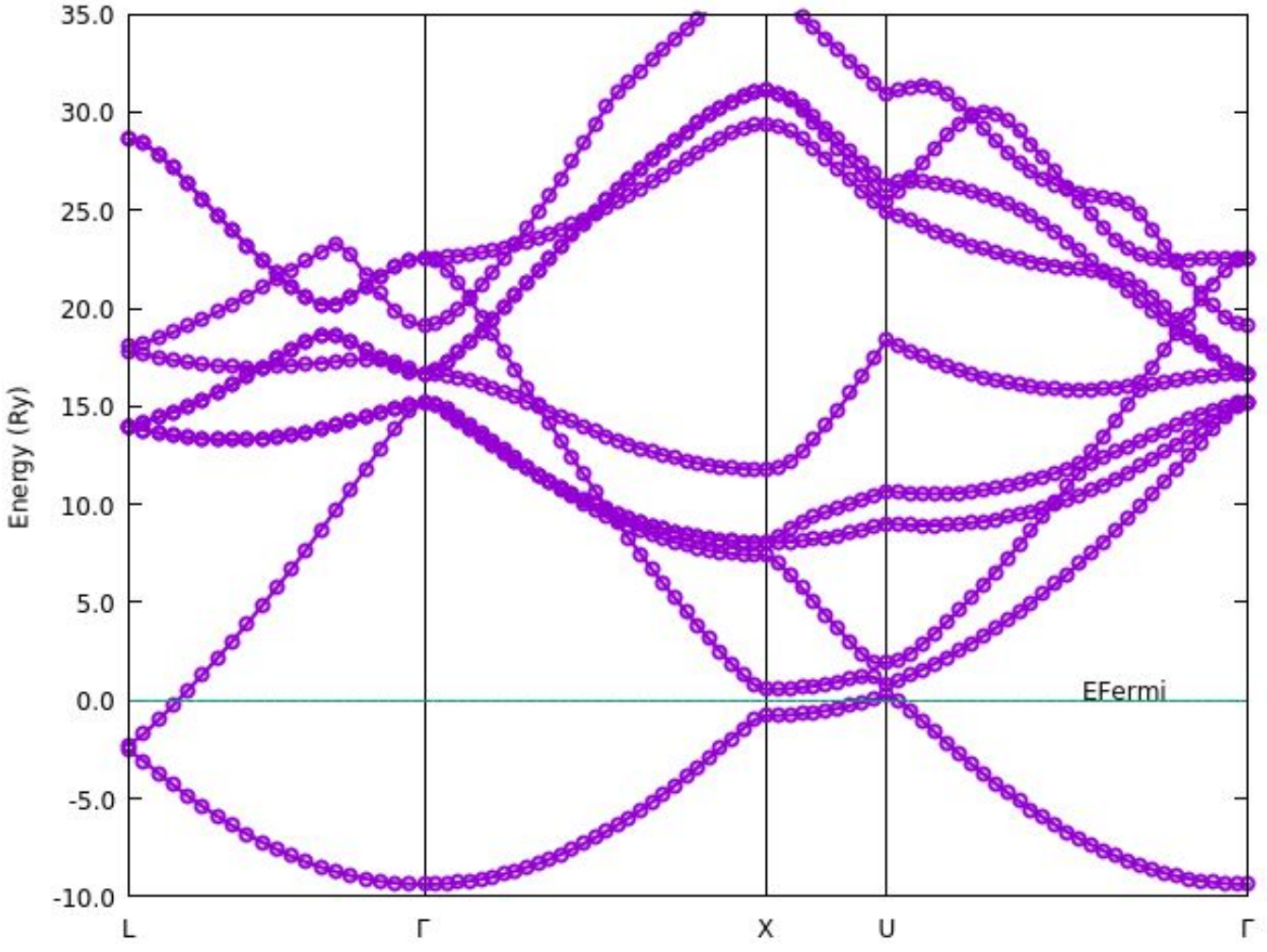
```
$ pw.x < al.scf.in | tee al.scf.out
```

- 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.

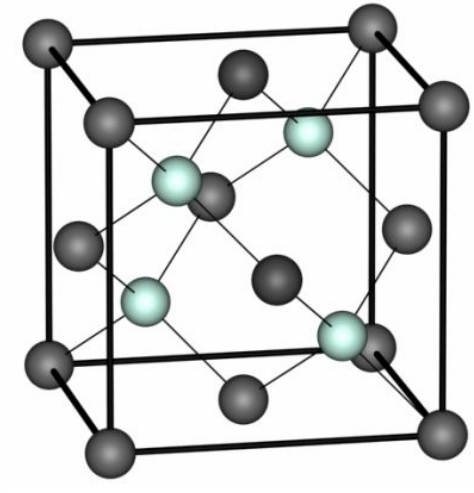
Exercise 1.2: band structure of a metal



1. Exercise 1: Silicon

To compute the band structure of Silicon, go to folder:

ASESMA2025/Day3/example1.bandstructure/ex1.Si



```
&CONTROL
calculation = 'scf',
...
/
&SYSTEM
ibrav = 2,
celldm(1) = 10.2,
nat = 2,
ntyp = 1,
ecutwfc = 20,

/
&ELECTRONS
/
ATOMIC_SPECIES
Si 28.086  Si.pbe-rrkj.UPF
ATOMIC_POSITIONS
Si      0.00.   0.00.   0.00
Si      0.25.   0.25    0.25
K_POINTS automatic
6 6 6   0 0 0
```

1. Exercise 1: Band structure of Silicon

The scheme to compute the bands is the following:

- **Perform the SCF Calculation:** Use pw.x to calculate the density (calculation = 'scf')

```
pw.x –in si.scf.in > si.scf.out
```

- **Perform a bands- type NSCF Calculation**: Use pw.x to with:
  - calculation = 'bands'
  - number of bands (variable nbnd) to be computed (if nothing is specified, the default is used)
  - a suitable path of k-points in specified K-POINTS card. The k-point path must be continuos in k-space.

- **Calculate Bands datafile**: Use bands.x, which, among others, produces data-files for the plot.

- **Plot the bands**: Use gnuplot to plot the band structures store in the file *bands.dat.gnu*.

Important: we must keep the prefix same outdir and prefix for "nscf" and "scf" pw.x and for the bands.x calculations!

1. Exercise 1: Silicon

- **Perform a bands- type NSCF Calculation**: : Use pw.x to with calculation= ‘bands’

```
pw.x –in si.bands.in> si.bands.out
```

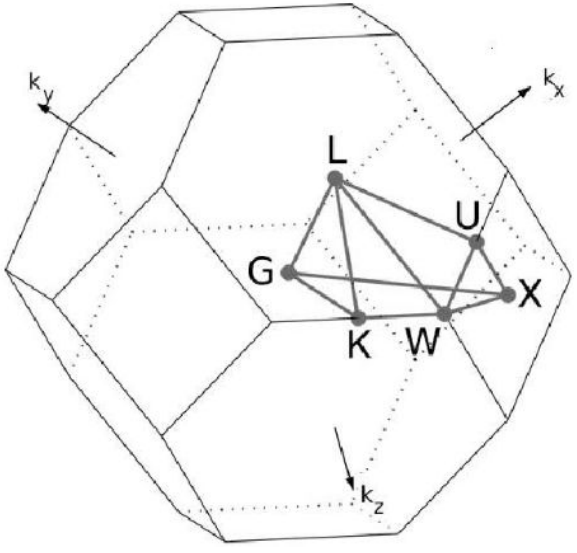
Input file for band calculation looks like this:

```
&CONTROL
   calculation='bands'
   prefix = 'Si',
   pseudo_dir = '../../pseudo'
   outdir='./tmp'
/
&SYSTEM
   ibrav = 2,
   celldm(1) = 10.262,
   nat =  2,
   ntyp = 1,
   ecutwfc = 12.0,
   ecutrho = 200.0,
   nbnd = 10
 /
&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
```

1. Exercise 1: Band structure of Silicon

How to specify the k-path for band structure calculation:



- Use the k-path selection tool of xcrysden:

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 – Γ – X – W – L – Γ ;
4. Specify how many k points to be calculated (Ex: 100)
5. Save the k-path to file. (.pwscf extension is required for formatting the file for pw.x).

- Insert manually, or use the Seek- Path tool online:

https://www.materialscloud.org/work/tools/seekpath

1. Exercise 1: Silicon

- **Calculate Bands datafile**: Use bands.x, which, among others, produces data-files for the plot.

```
bands.x –in bands.in> bands.out
```

An input file for the data post processing program bands.x:

```
&BANDS
outdir = ’./tmp’,
prefix=’Si’,
filband=’bands.dat’,
/
```

This program print the eigenvalues to the file specified in ”filband” .
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.

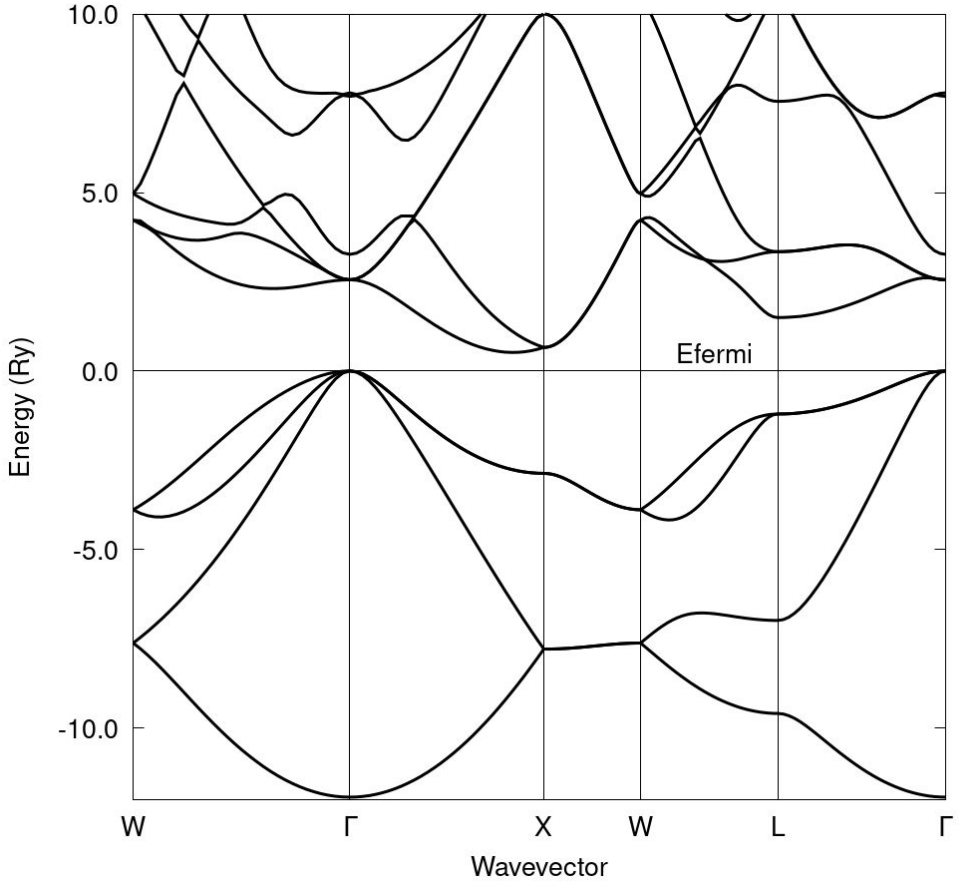
1. Exercise 1: Silicon

- **Plot with gnuplot**: run gnuplot plot_bands.gp

- The program plotband.x can be useful to obtain a postscript file of the band structure and a set of data files that can be plotted with xmgr. □ type plotband.x on the terminal, which prompts the terminal input:

```
Input file > bands.dat
Reading   10 bands at    151 k-points
Range:   -5.8760   17.7160eV  Emin, Emax, [firstk, lastk] > -5.8760 17.7160
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 > 6.0653
deltaE, reference E (for tics) 2, 6.0653
bands in PostScript format written to file bands.ps
```

1. Exercise 1: Silicon



- **Optional homework**: can you calculate the DOS of Silicon?

1. Exercise 2: Aluminum

To compute the band structure of Silicon, go to folder:

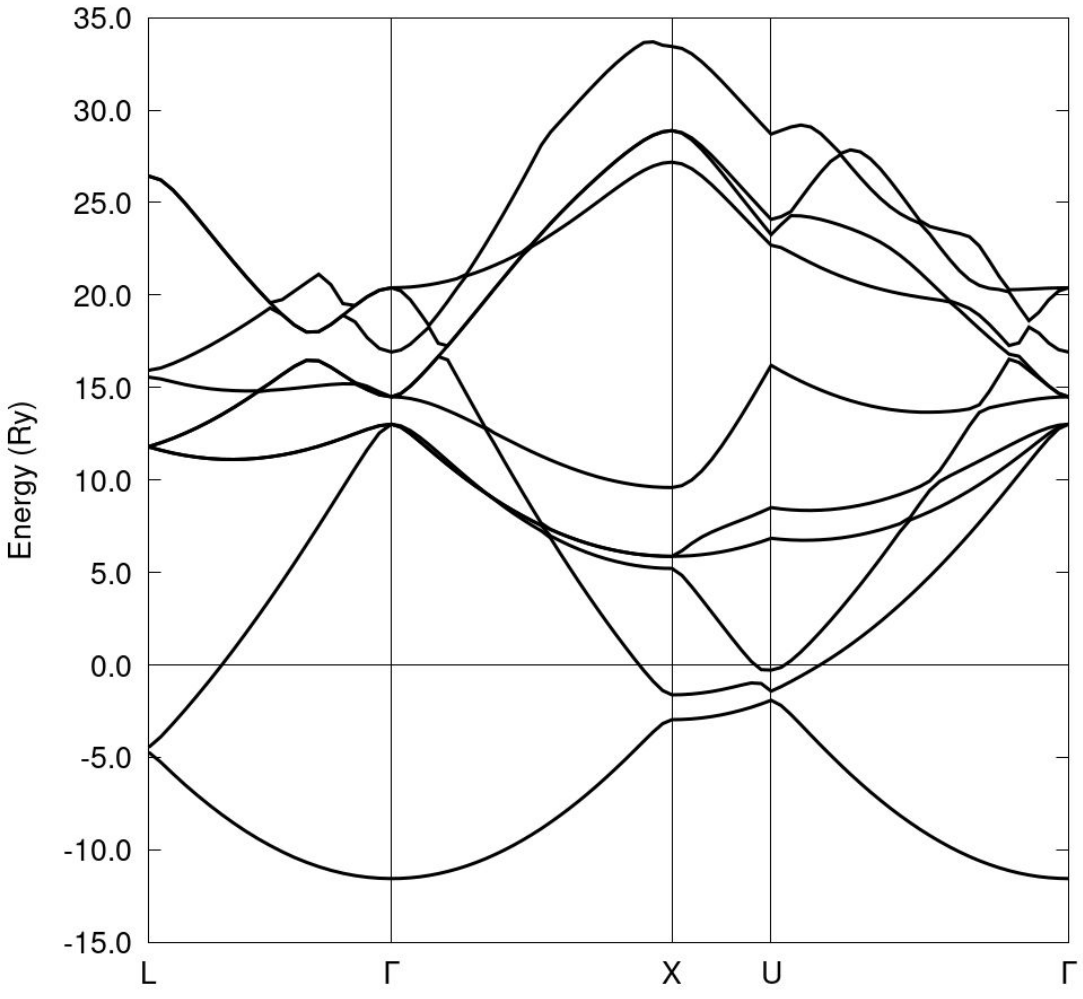
ASESMA2025/Day3/example1.bandstructure/ex2.Al

and use the same procedure for silicon:

- Self-consistent calculation (pw.x)
- Select a k-point path (i.e. by using XCrysDen, ...) and do “bands”-type non-SCF pw.x calculation
- Run a bands.x calculation
- Plot the results using gnuplot, or run plotband.x

Optional homework: converge the ecut_wfc and k-points for Aluminium, as done in Day2 (you find the scripts in folder *ex2.Al/convergence_test)*

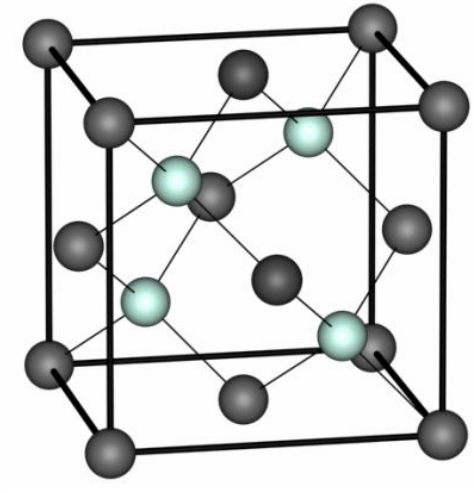
1. Exercise 2: Aluminum



1. Exercise 1: Silicon

To compute the band structure of Silicon, go to folder:

ASESMA2025/Day3/example1.bandstructure/ex1.Si



```
&CONTROL
calculation = 'scf',
...
/
&SYSTEM
ibrav = 2,
celldm(1) = 10.2,
nat = 2,
ntyp = 1,
ecutwfc = 20,

/
&ELECTRONS
/
ATOMIC_SPECIES
Si 28.086  Si.pbe-rrkj.UPF
ATOMIC_POSITIONS
Si      0.00.   0.00.   0.00
Si      0.25.   0.25    0.25
K_POINTS automatic
6 6 6   0 0 0
```

1. Exercise 1: Band structure of Silicon

The scheme to compute the bands is the following:

- **Perform the SCF Calculation:** Use pw.x to calculate the density (calculation = 'scf')

```
pw.x –in si.scf.in > si.scf.out
```

- **Perform a bands- type NSCF Calculation**: Use pw.x to with:
  - calculation = 'bands'
  - number of bands (variable nbnd) to be computed (if nothing is specified, the default is used)
  - a suitable path of k-points in specified K-POINTS card. The k-point path must be continuos in k-space.

- **Calculate Bands datafile**: Use bands.x, which, among others, produces data-files for the plot.

- **Plot the bands**: Use gnuplot to plot the band structures store in the file *bands.dat.gnu*.

Important: we must keep the prefix same outdir and prefix for "nscf" and "scf" pw.x and for the bands.x calculations!

1. Exercise 1: Silicon

- **Perform a bands- type NSCF Calculation**: : Use pw.x to with calculation= ‘bands’

```
pw.x –in si.bands.in> si.bands.out
```

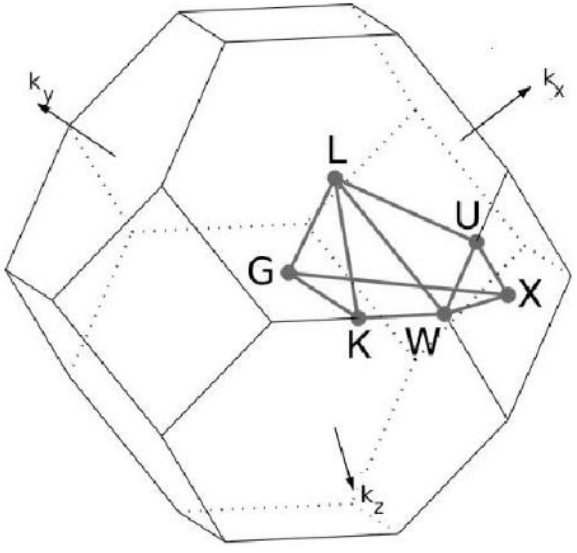
Input file for band calculation looks like this:

```
&CONTROL
   calculation='bands'
   prefix = 'Si',
   pseudo_dir = '../../pseudo'
   outdir='./tmp'
/
&SYSTEM
   ibrav = 2,
   celldm(1) = 10.262,
   nat =  2,
   ntyp = 1,
   ecutwfc = 12.0,
   ecutrho = 200.0,
   nbnd = 10
 /
&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
```

1. Exercise 1: Band structure of Silicon

How to specify the k-path for band structure calculation:



- Use the k-path selection tool of xcrysden:

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 – Γ – X – W – L – Γ ;
4. Specify how many k points to be calculated (Ex: 100)
5. Save the k-path to file. (.pwscf extension is required for formatting the file for pw.x).

- Insert manually, or use the Seek- Path tool online:

https://www.materialscloud.org/work/tools/seekpath

1. Exercise 1: Silicon

- **Calculate Bands datafile**: Use bands.x, which, among others, produces data-files for the plot.

```
bands.x –in bands.in> bands.out
```

An input file for the data post processing program bands.x:

```
&BANDS
outdir = ’./tmp’,
prefix=’Si’,
filband=’bands.dat’,
/
```

This program print the eigenvalues to the file specified in ”filband” .
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.

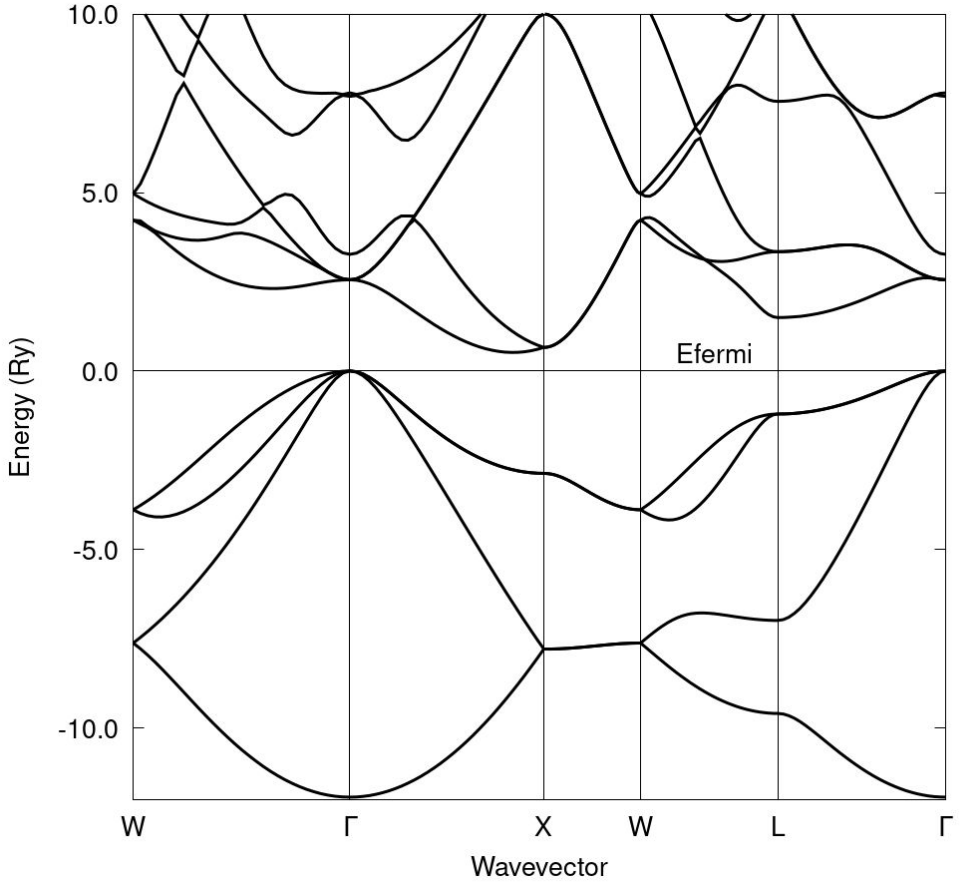
1. Exercise 1: Silicon

- **Plot with gnuplot**: run gnuplot plot_bands.gp

- The program plotband.x can be useful to obtain a postscript file of the band structure and a set of data files that can be plotted with xmgr. □ type plotband.x on the terminal, which prompts the terminal input:

```
Input file > bands.dat
Reading   10 bands at    151 k-points
Range:   -5.8760   17.7160eV  Emin, Emax, [firstk, lastk] > -5.8760 17.7160
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 > 6.0653
deltaE, reference E (for tics) 2, 6.0653
bands in PostScript format written to file bands.ps
```

1. Exercise 1: Silicon



- **Optional homework**: can you calculate the DOS of Silicon?

1. Exercise 2: Aluminum

To compute the band structure of Silicon, go to folder:

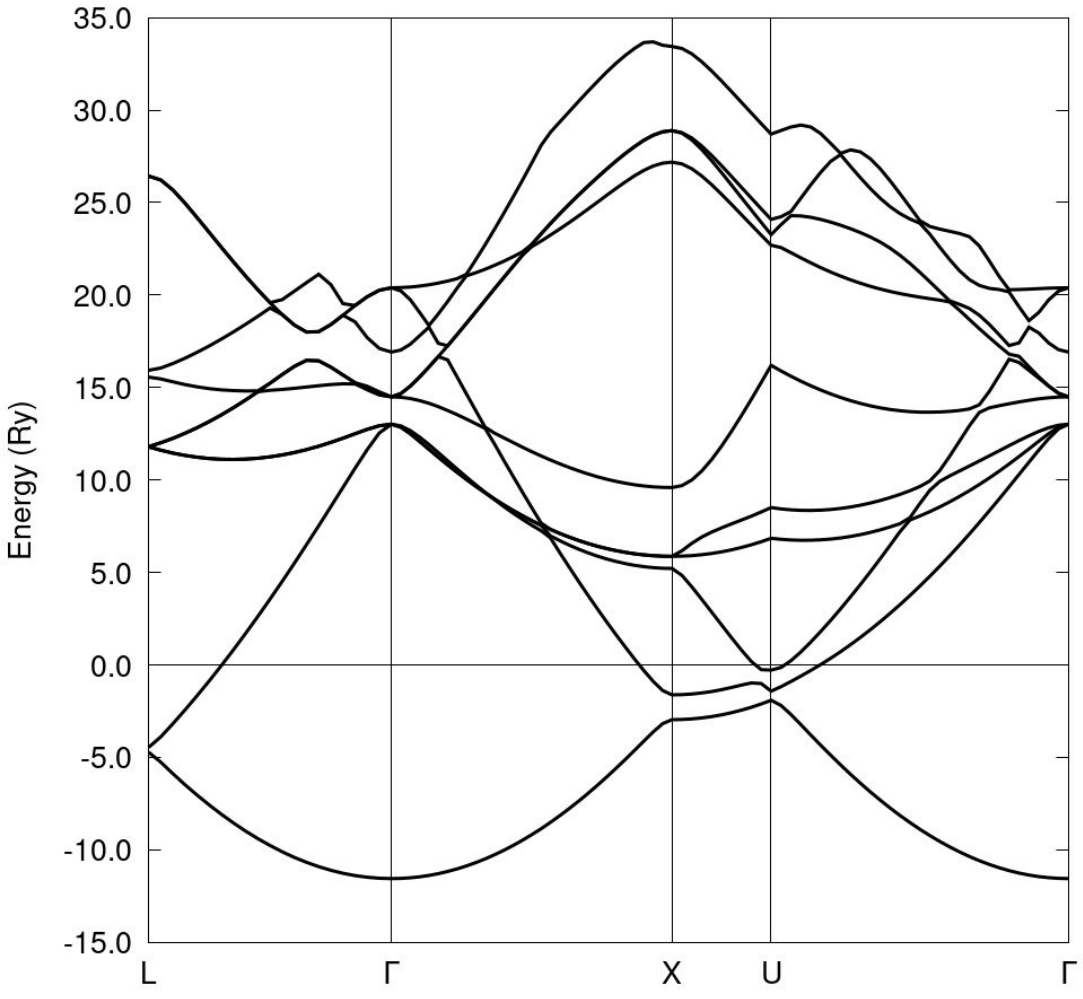
ASESMA2025/Day3/example1.bandstructure/ex2.Al

and use the same procedure for silicon:

- Self-consistent calculation (pw.x)
- Select a k-point path (i.e. by using XCrysDen, ...) and do “bands”-type non-SCF pw.x calculation
- Run a bands.x calculation
- Plot the results using gnuplot, or run plotband.x

Optional homework: converge the ecut_wfc and k-points for Aluminium, as done in Day2 (you find the scripts in folder *ex2.Al/convergence_test)*

1. Exercise 2: Aluminum



Exercise 2

Performing metallic calculations: smearing

Exercise 2: smearing

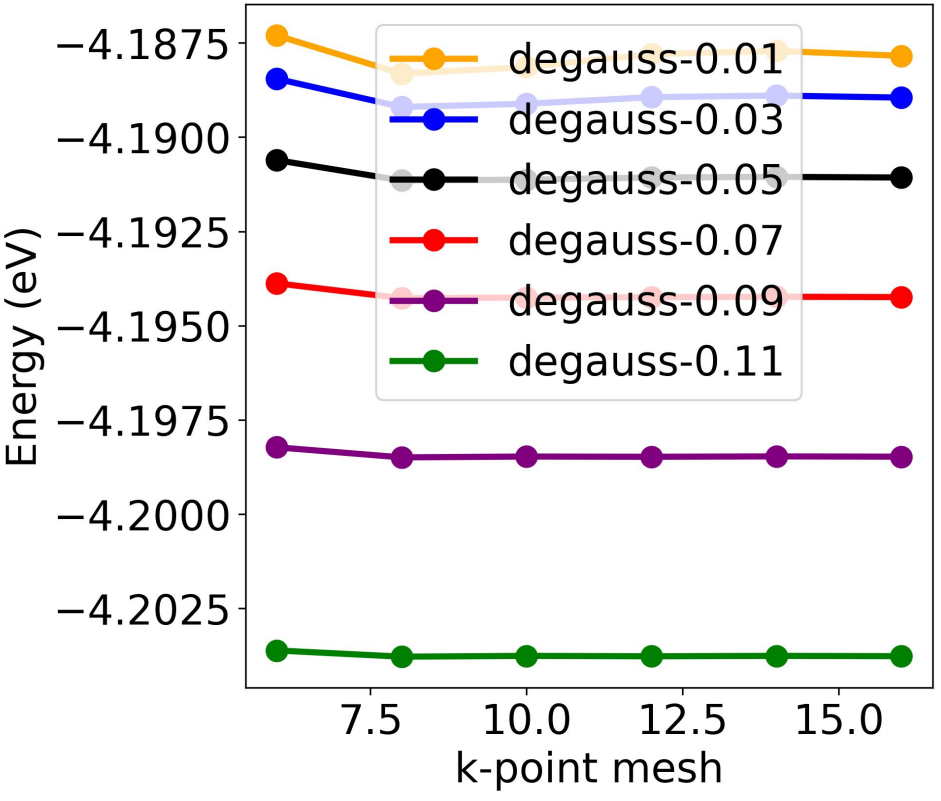
In this exercise we will compute the total energy for this fcc Al with the following values for degauss, k-point meshes and different smearing variables:

- degauss variable, in range from 0.01 to 0.11
- k-points: N×N×N (1×1×1) with N=6,8,10, …, 16
- smearing variable, possible values: 'gauss' (or 'g'), 'marzari-vanderbilt'
- (or 'm-v'), 'methfessel-paxton' (or 'm-p')
- Follow the instructions in example2.smearing:

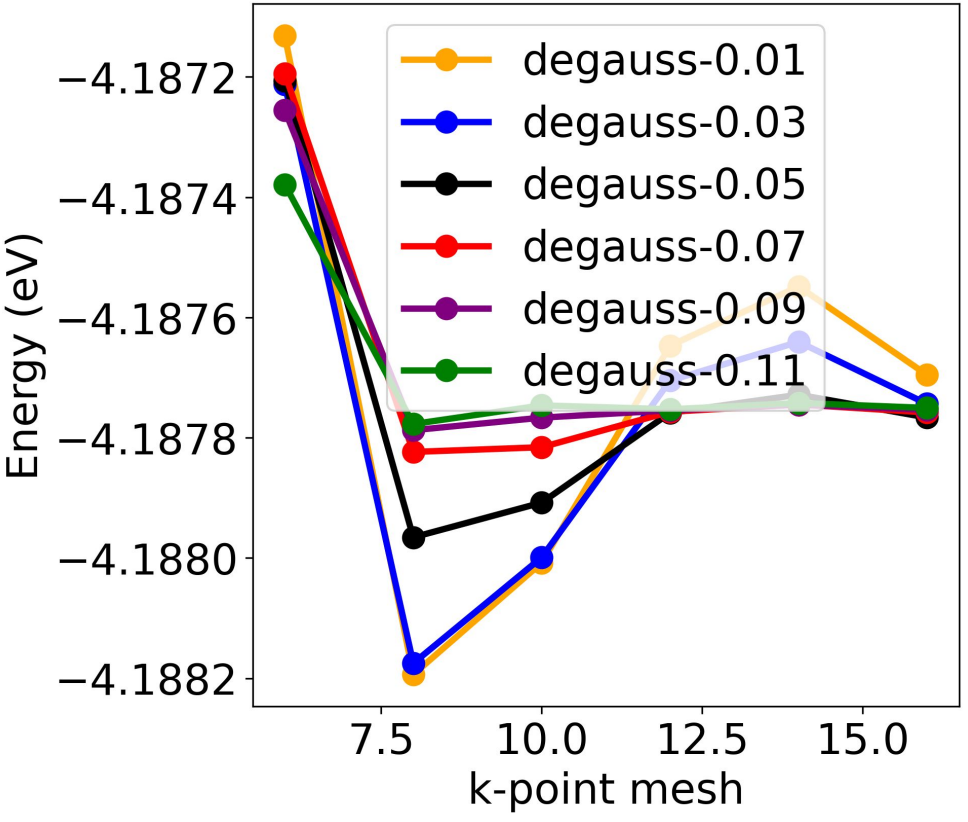
Plot the convergence of the total energy with respect to the number of k-points for the different smearing values.

Exercise 2: smearing

Gaussian

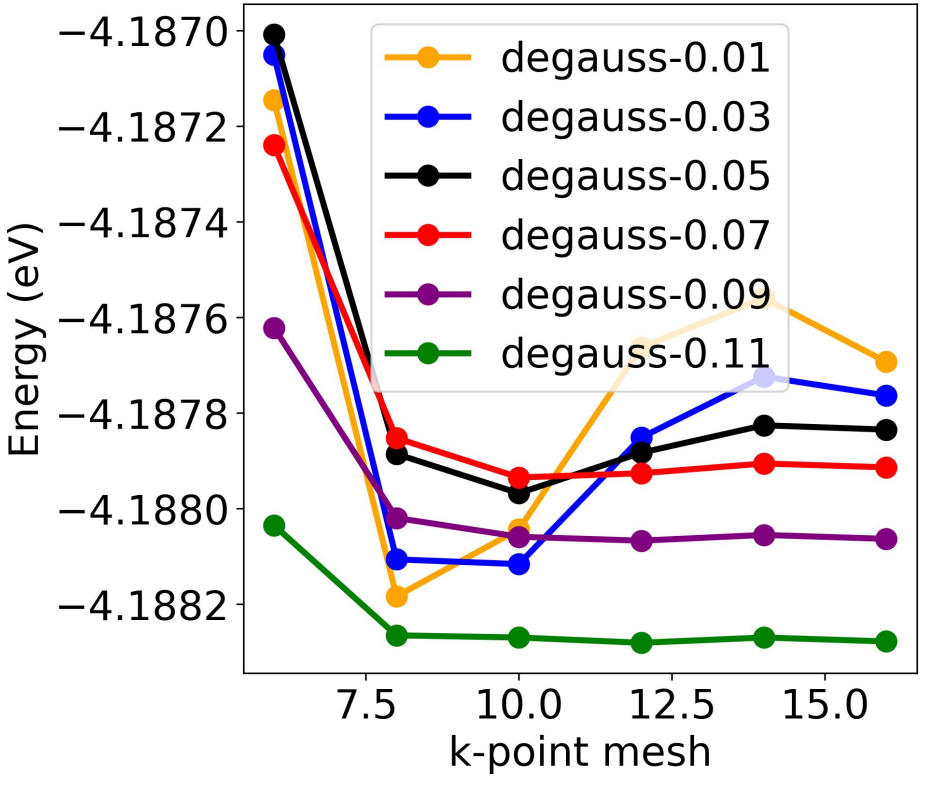


Methfessel-Paxton

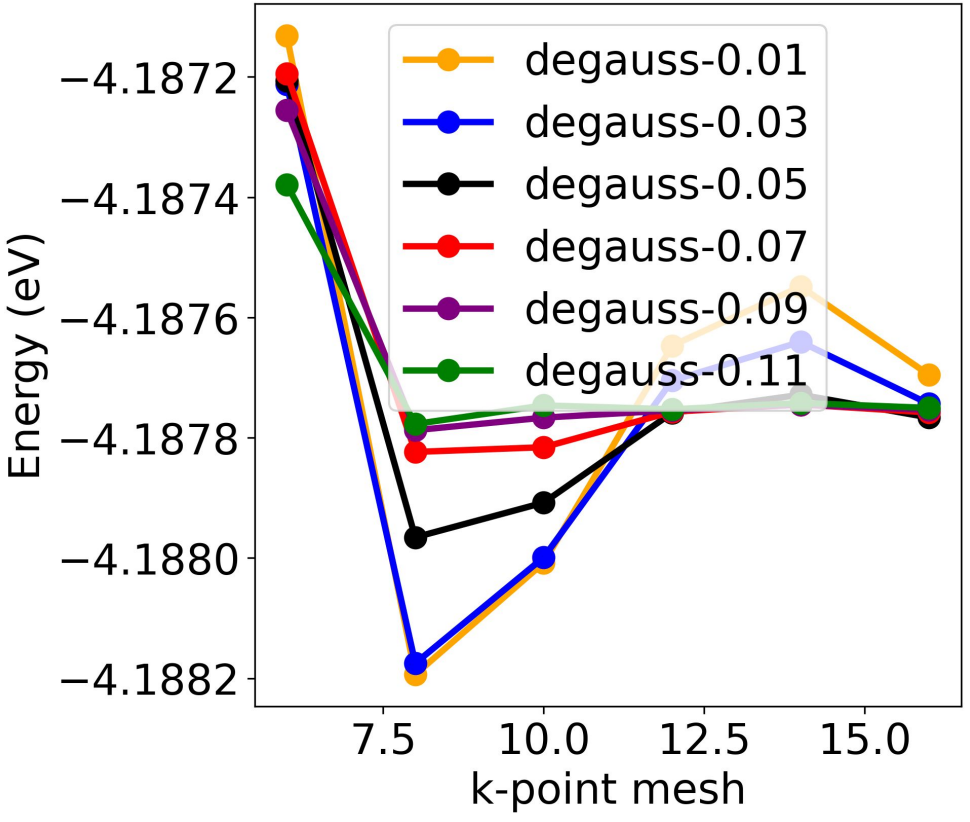


Exercise 2: smearing

Marzari-vanderbilt

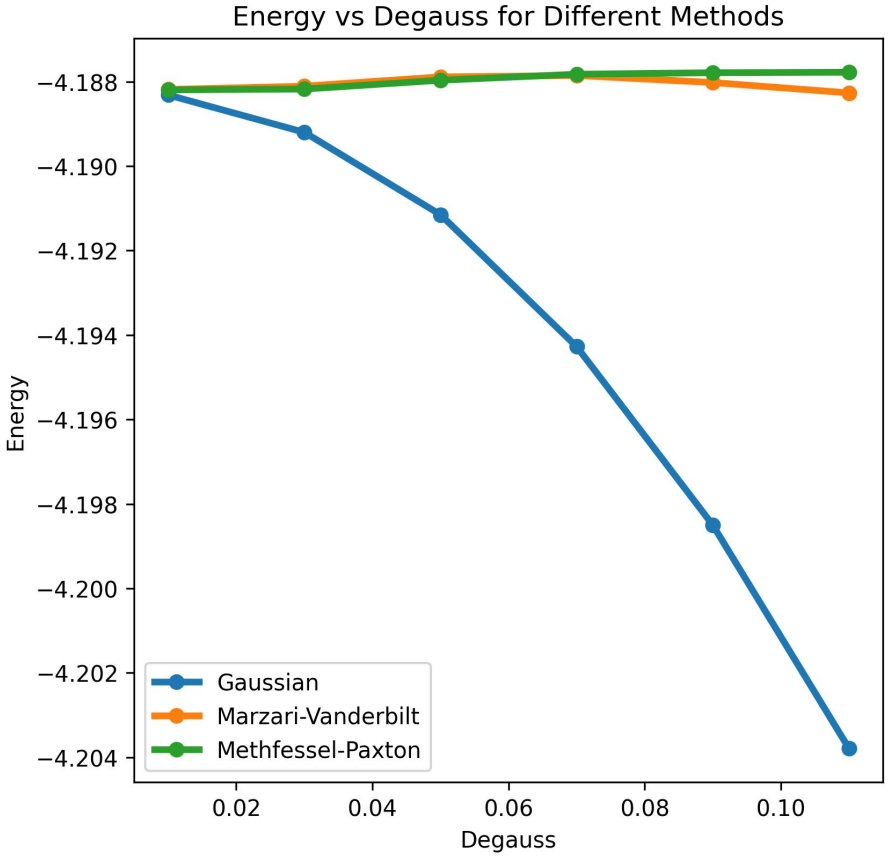


Methfessel-Paxton



Exercise 2: smearing

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



Exercise 3

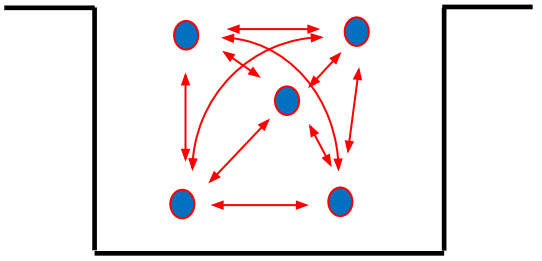
Exchange correlation functional

DAY 3: Exchange Correlational Functional

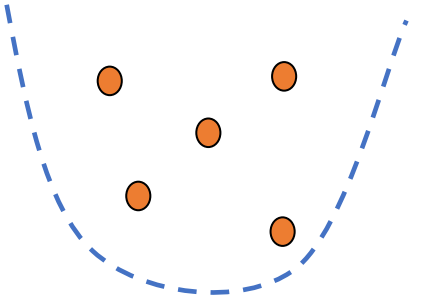
- Go to the exercise 3 folder

```
cd ASESMA2025/Hands-on-basic/Day3/
```

Kohn-Sham DFT



KS MAPPING



electrons

interaction

external potential $v_{ext}(\mathbf{r})$

Kohn-Sham particles (non-interacting)

effective potential $v_{KS}(\mathbf{r})$

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + v_{KS}[n](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$v_{KS}[n](\mathbf{r}) = V_{ext}(\mathbf{r}) + e^2\int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

The exchange and correlation energy functional

- **LDA**: The xc energy density of the inhomogeneous system in **r** is locally approximated with that of a homogeneous electron gas with density n(**r**)

$$E_{\mathrm{xc}}^{\mathrm{LDA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{HEG}}(n(\mathbf{r}))$$

The exchange and correlation energy functional

- **LDA**: The xc energy density of the inhomogeneous system in **r** is locally approximated with that of a homogeneous electron gas with density n(**r**)

$$E_{\mathrm{xc}}^{\mathrm{LDA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{HEG}}(n(\mathbf{r}))$$

- **GGA:** include the dependence on the gradient of the density

$$E_{\mathrm{xc}}^{\mathrm{GGA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r})) = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{HEG}}(n(\mathbf{r})) F_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

The exchange and correlation energy functional

- **LDA**: The xc energy density of the inhomogeneous system in **r** is locally approximated with that of a homogeneous electron gas with density n(**r**)

$$E_{\mathrm{xc}}^{\mathrm{LDA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{HEG}}(n(\mathbf{r}))$$

- **GGA:** include the dependence on the gradient of the density

$$E_{\mathrm{xc}}^{\mathrm{GGA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r})) = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{HEG}}(n(\mathbf{r})) F_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

- **Meta-GGA**: include the dependency on the laplacian of the density and kinetic energy density

$$E_{\mathrm{xc}}^{\mathrm{mGGA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau) \qquad \tau = \frac{1}{2} \sum_i |\nabla \psi_i(\mathbf{r})|^2$$

The exchange and correlation energy functional

- **LDA**: The xc energy density of the inhomogeneous system in **r** is locally approximated with that of a homogeneous electron gas with density n(**r**)

$$E_{\mathrm{xc}}^{\mathrm{LDA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{HEG}}(n(\mathbf{r}))$$

- **GGA:** include the dependence on the gradient of the density

$$E_{\mathrm{xc}}^{\mathrm{GGA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r})) = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{HEG}}(n(\mathbf{r})) F_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

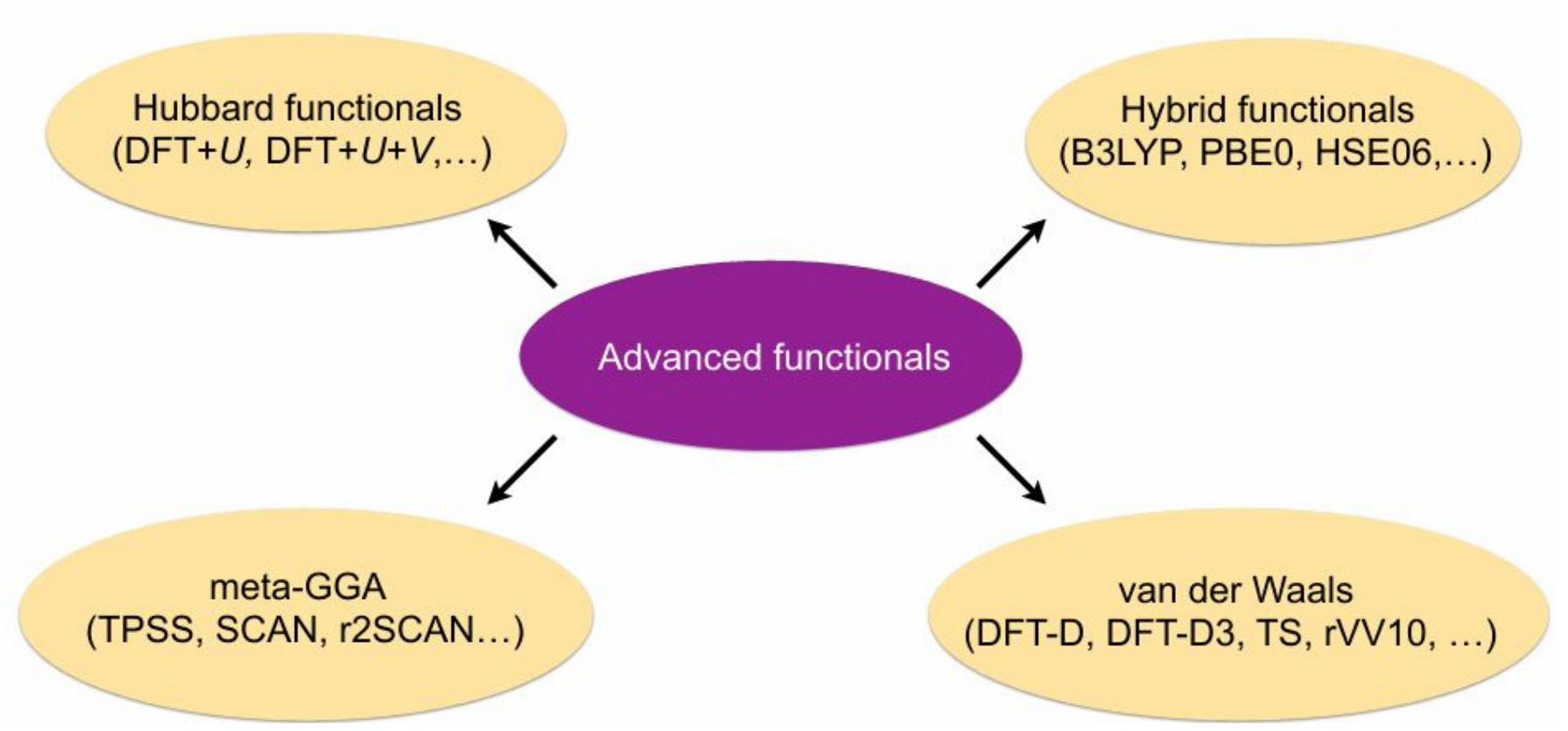
- **Meta-GGA**: include the dependency on the laplacian of the density and kinetic energy density

$$E_{\mathrm{xc}}^{\mathrm{mGGA}} = \int d\mathbf{r}\, n(\mathbf{r}) \varepsilon_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau) \qquad \tau = \frac{1}{2} \sum_i |\nabla \psi_i(\mathbf{r})|^2$$

- **Hybrid functionals**: include a fraction of Fock exchange

$$E_{\mathrm{xc}}^{\mathrm{hyb}} = (1 - a_0) E_{\mathrm{x}}^{\mathrm{DFT}} + a_0 E_{\mathrm{x}}^{\mathrm{HF}} + E_{\mathrm{c}}^{\mathrm{DFT}}$$

Some advanced exchange-correlation functionals



Some drawbacks of LDA / GGA

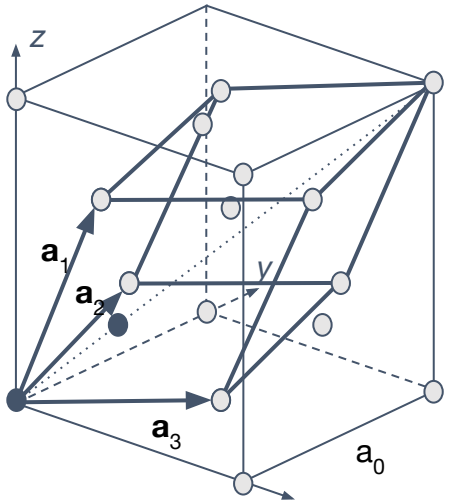
Self-interaction errors

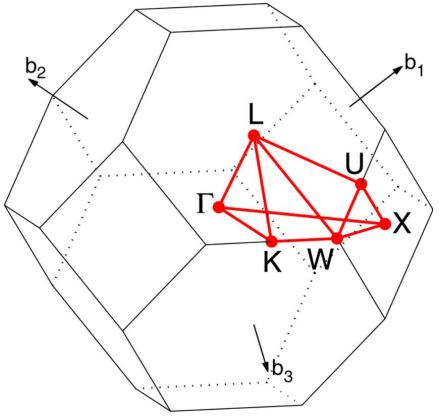
Consequences: - over delocalization of electrons (*d* and *f*)
- incorrect description of charge transfer
- incorrect energetics of chemical reactions
- underestimation of band gaps
- …

Lack of non-locality

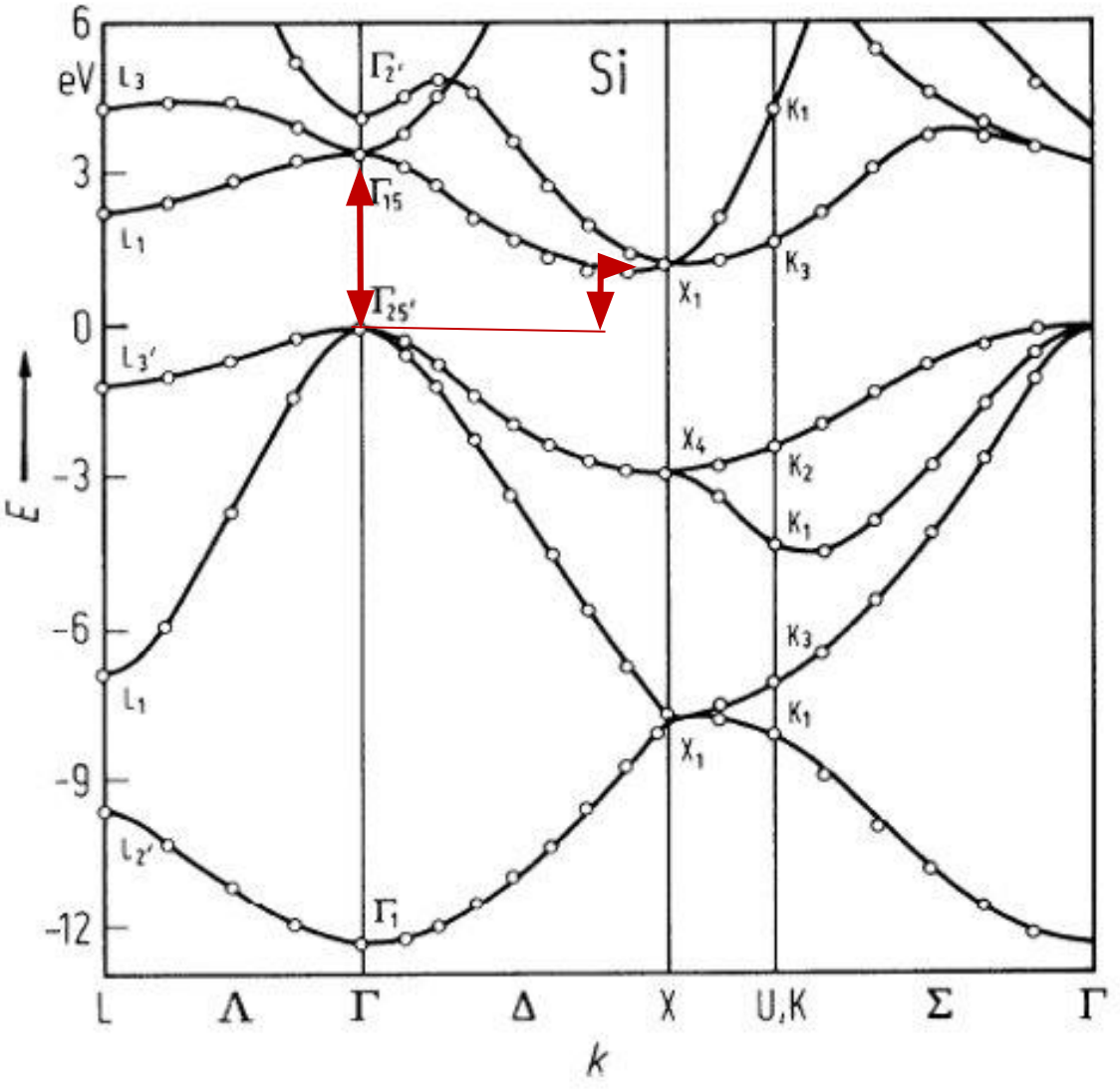
Consequences: - incorrect description of weak long-range (Van der Waals) interactions
- inadequate description of bond breaking and formation
- no Rydberg series
- …

FCC Silicon

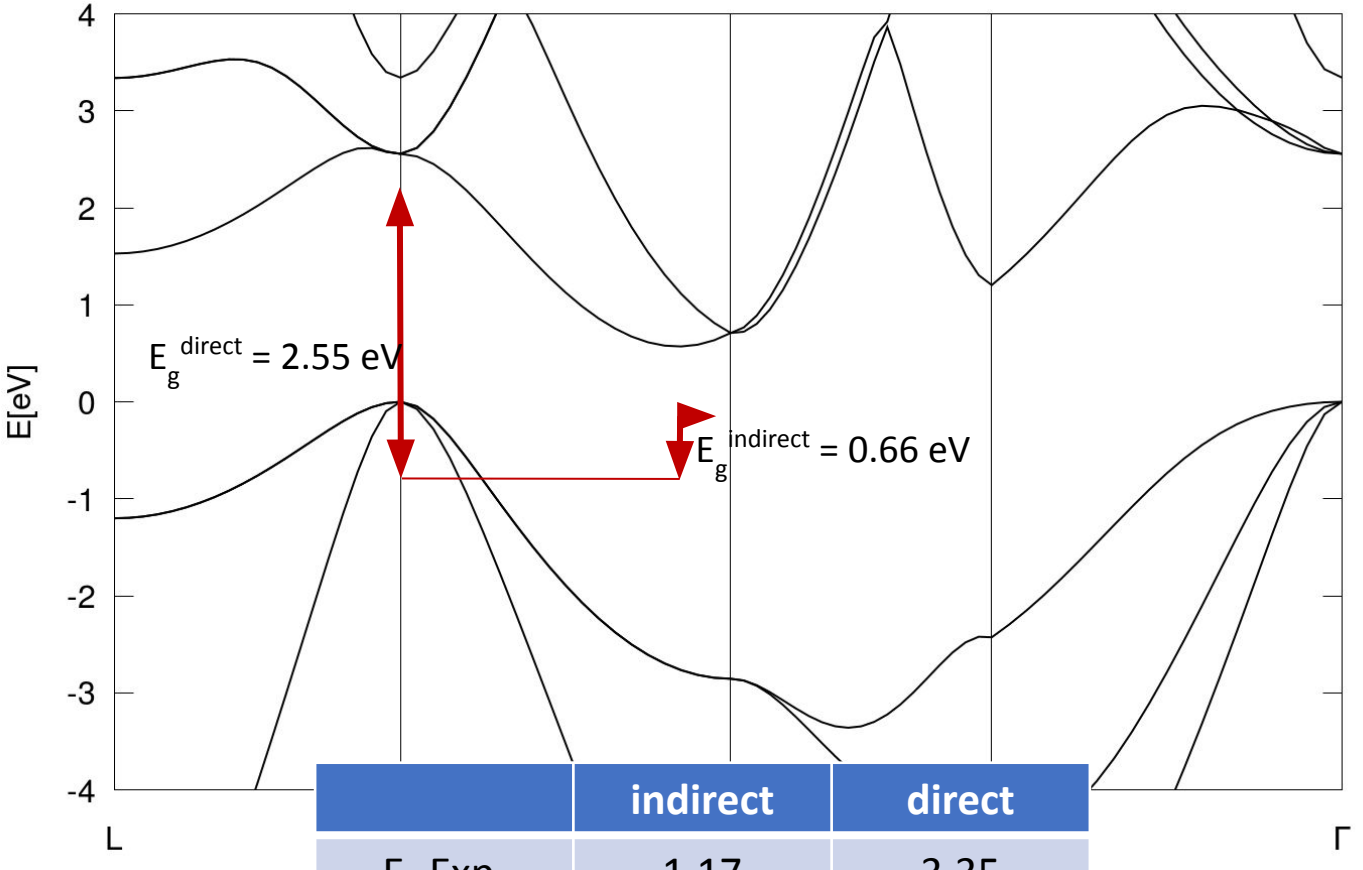




Goal of exercise3

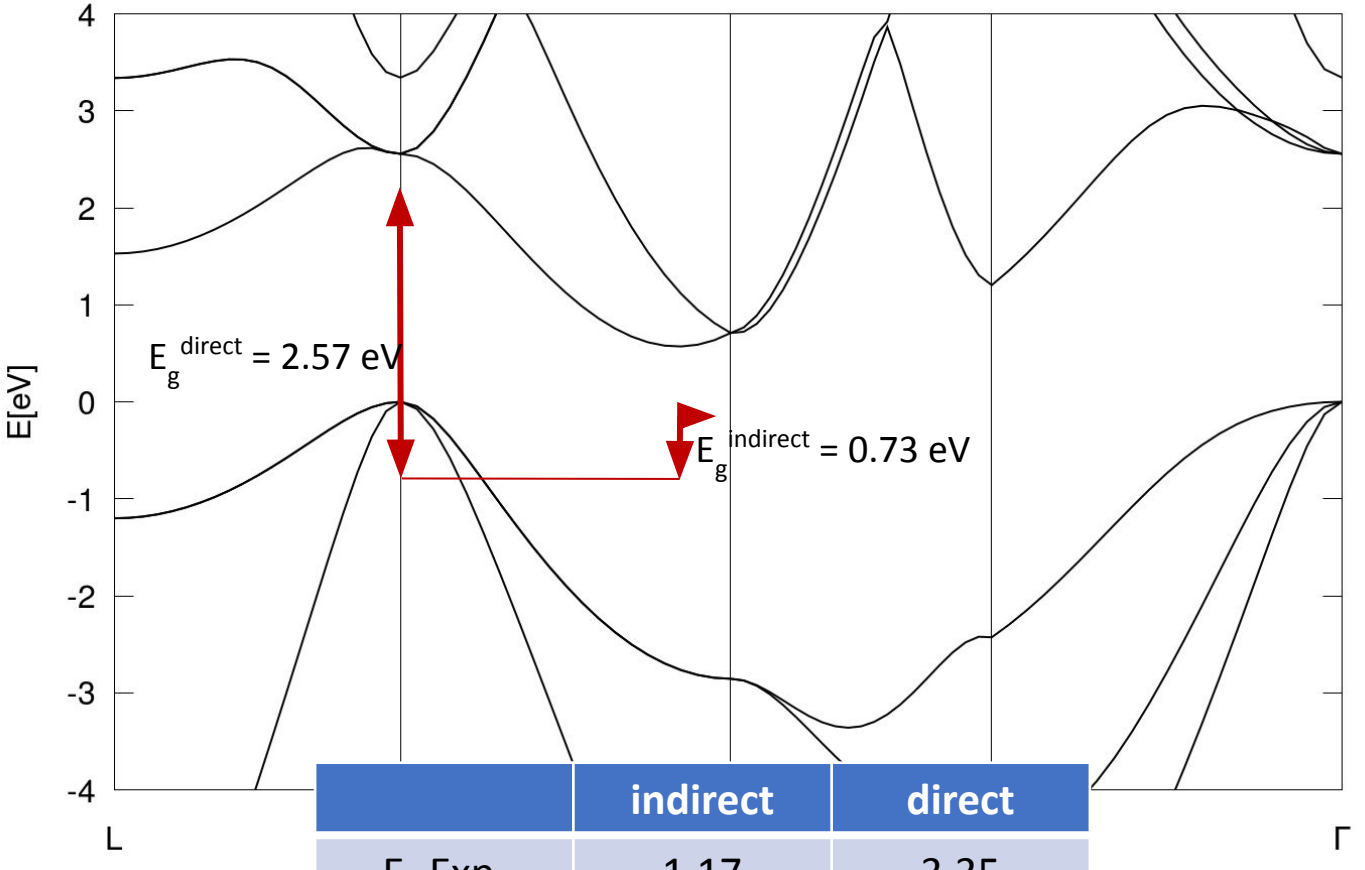


LDA Silicon band structure



	indirect	direct
E_g Exp.	1.17	3.35

GGA Silicon band structure



	indirect	direct
E_g Exp.	1.17	3.35

Silicon band Gap: summary

ecut = 20 Ry, k mesh: 6 x 6 x 6

Functional	indirect Gap	Direct Gap	Band width
LDA	0.66	2.55	11.94
GGA	0.73	2.57	11.90
Exp.	**1.17**	**3.35**	**12.5**

Silicon Lattice Parameter: summary

ecut = 36 Ry, k mesh: 6 x 6 x 6

Functional		
LDA	5.401	93.2
GGA	5.476	85.8
Exp.	**5.431**	**90.0**