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

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Today's Themes:

- 1) Performing band structure calculations
 - 2) DFT calculations for metals: smearing parameters
 - 3) XC functionals: LDA and PBE
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Topics of the session

- 1. Performing band structure calculation
 - 2. Performing metallic calculation: smearing
 - 3. Exchange correlation functional
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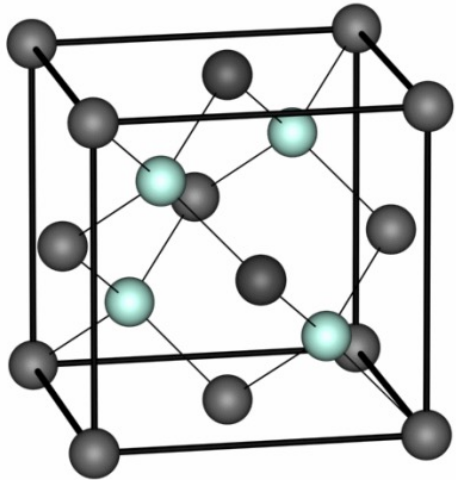
Exercise 1

Performing band structure calculations, example for
Silicon and 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 continuous 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

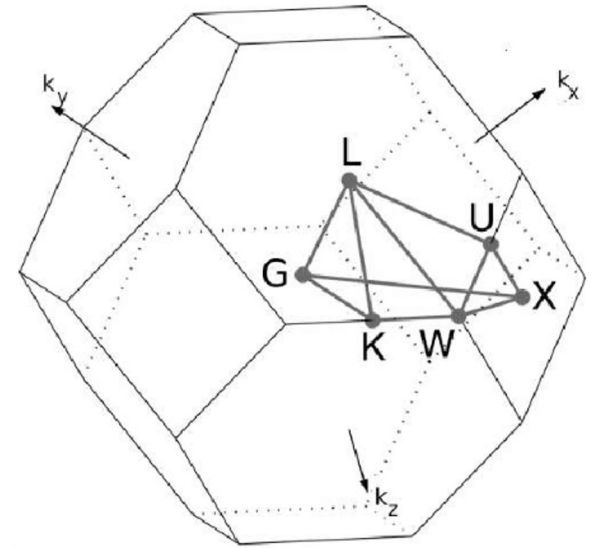
K_POINTS {crystal_b}
6

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: $W - \Gamma - X - W - L - \Gamma$;
 4. Specify how many k points to be calculated (Ex: 100)
 5. Save the k-path to file. (.pwsf 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`".

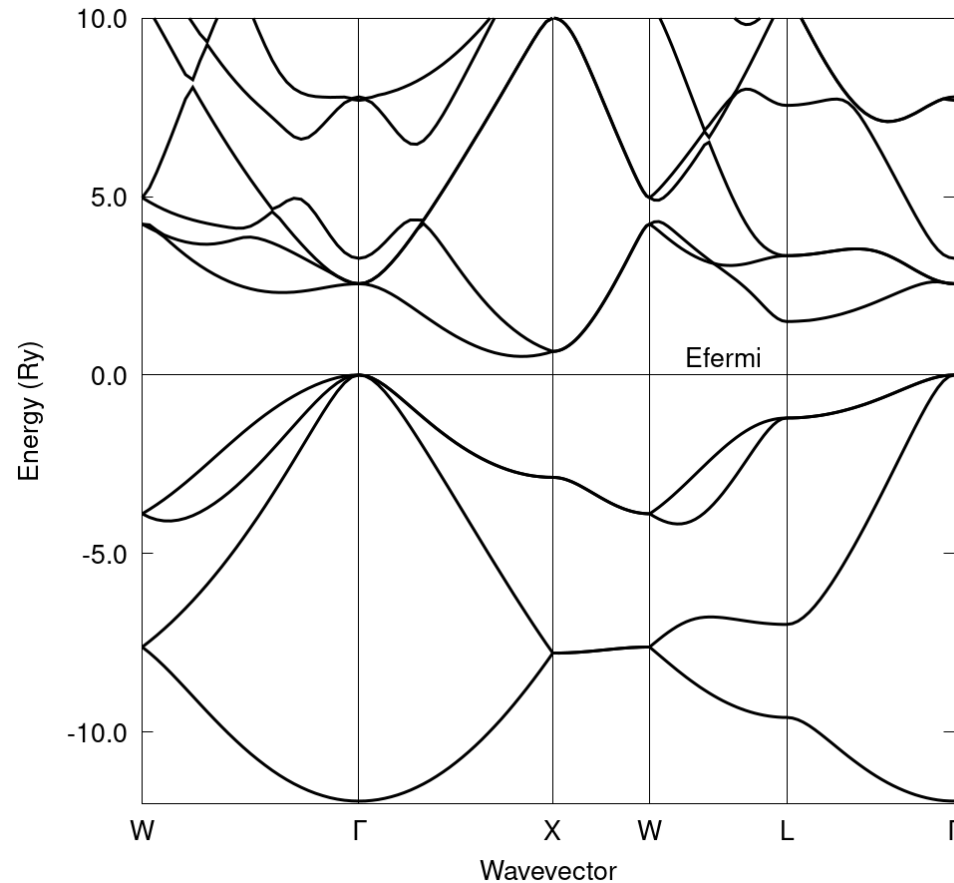
Bands data are stored in three files with different formats, among which we have `bands.dat.gnu` (can be plotted with gnuplot) and `bands.dat` can be visualized using the program `plotband.x`.

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:

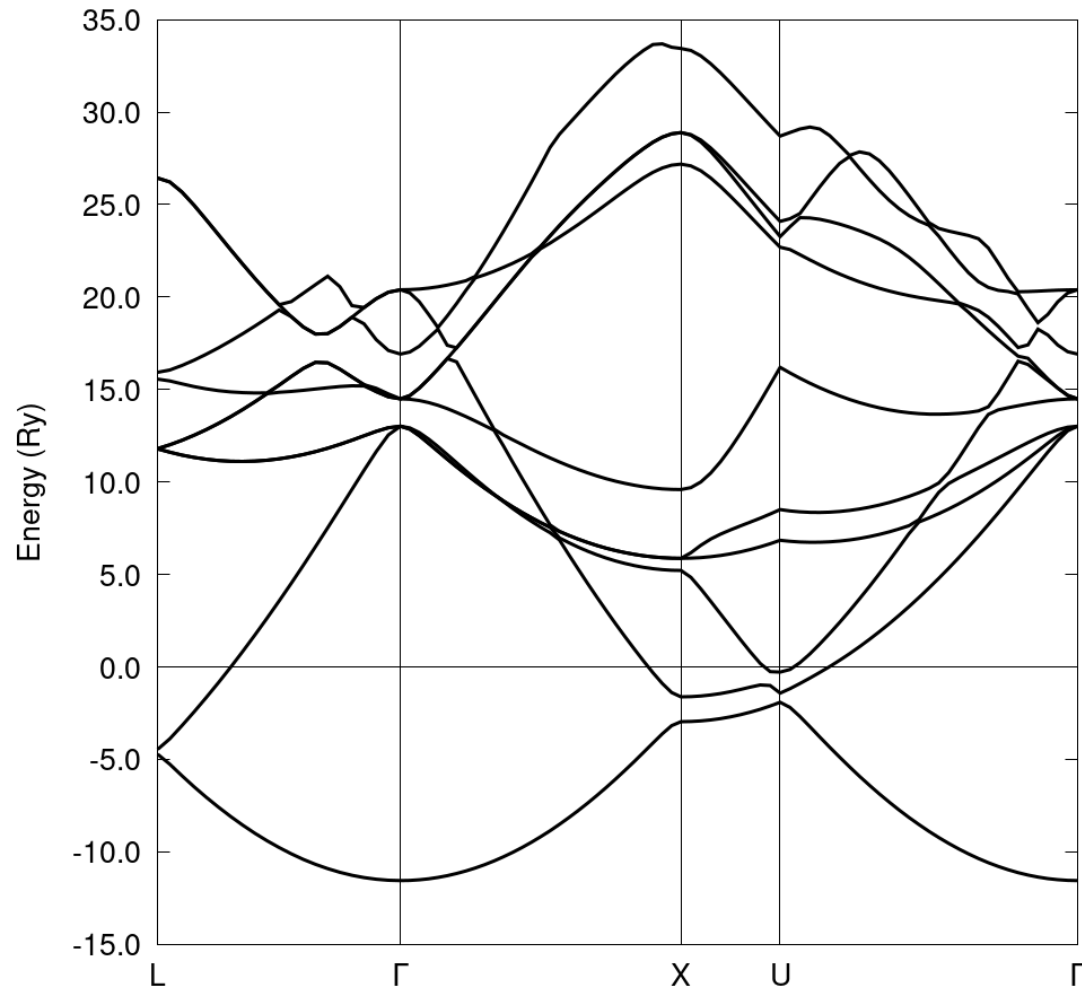
ASESMA2025/Day3/example1.bandstructure/ex2.Al

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

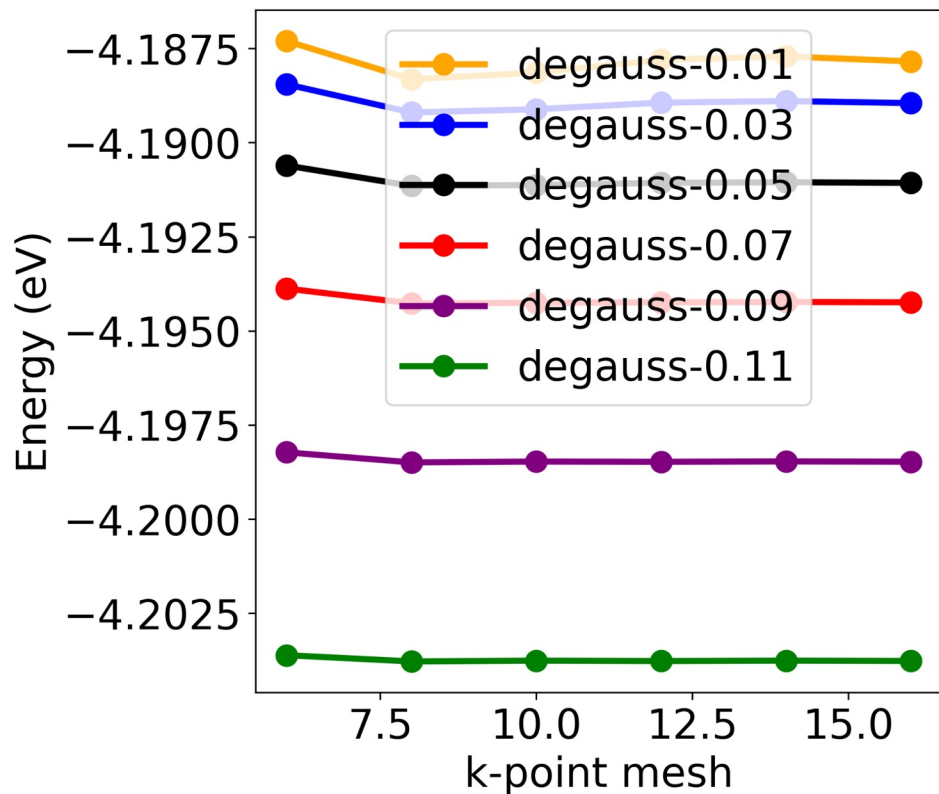
In this exercise we will compute the total energy for this fcc Al with the following values for degauss, k-point meshes and different smearing variables:

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

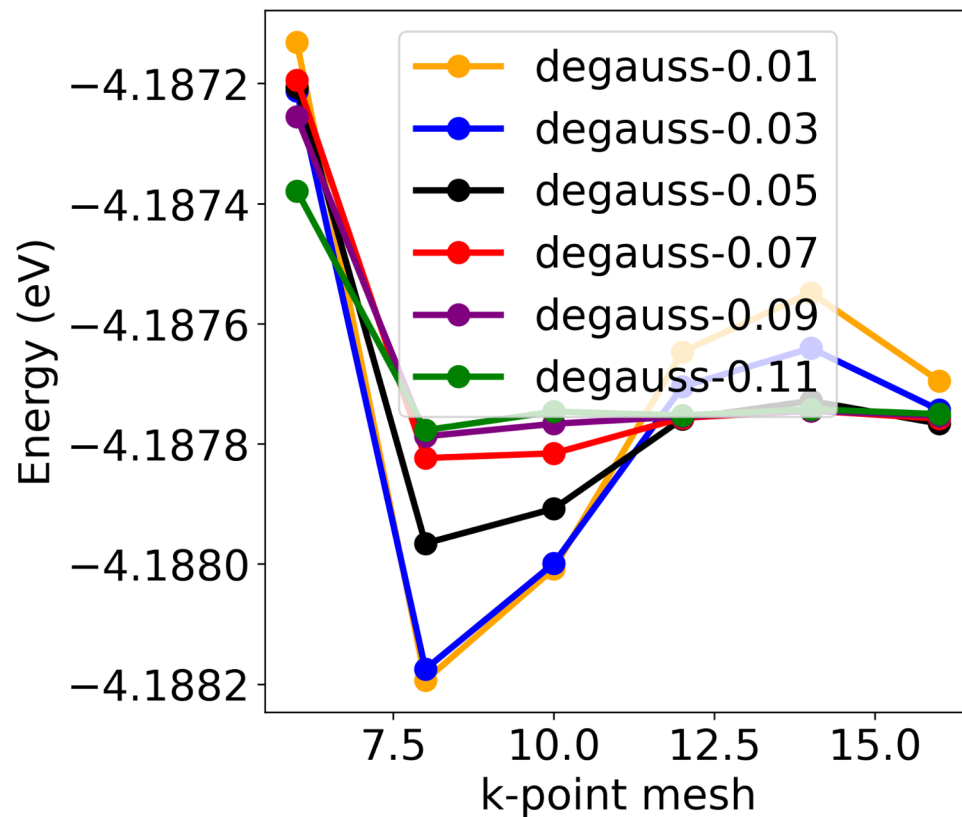
Plot the convergence of the total energy with respect to the number of k-points for the different smearing values.

Exercise 2: smearing

Gaussian

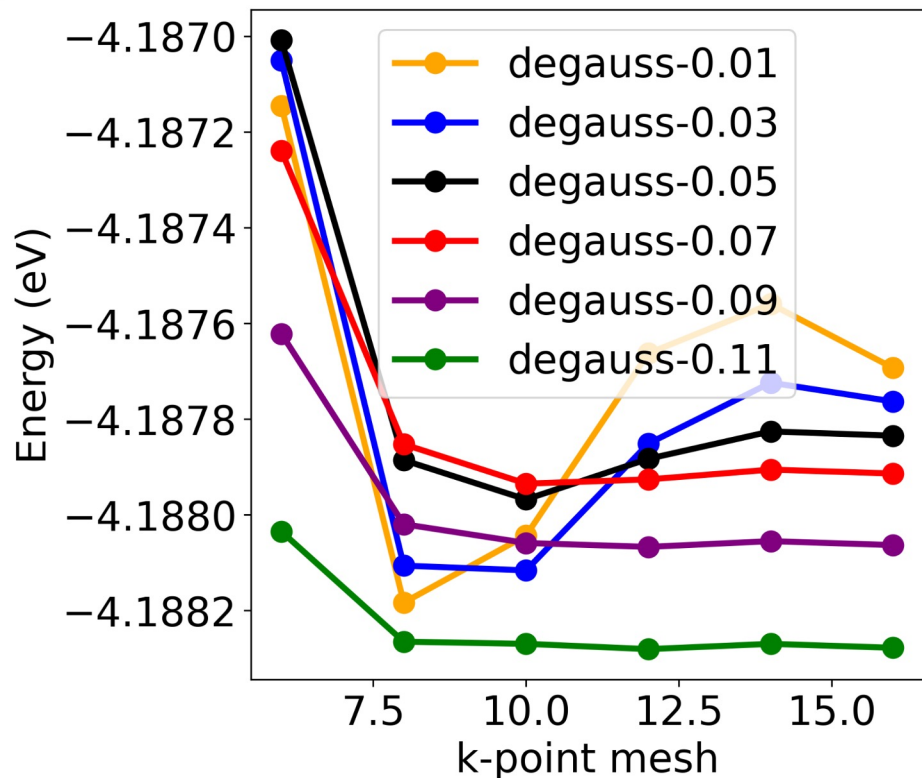


Methfessel-Paxton

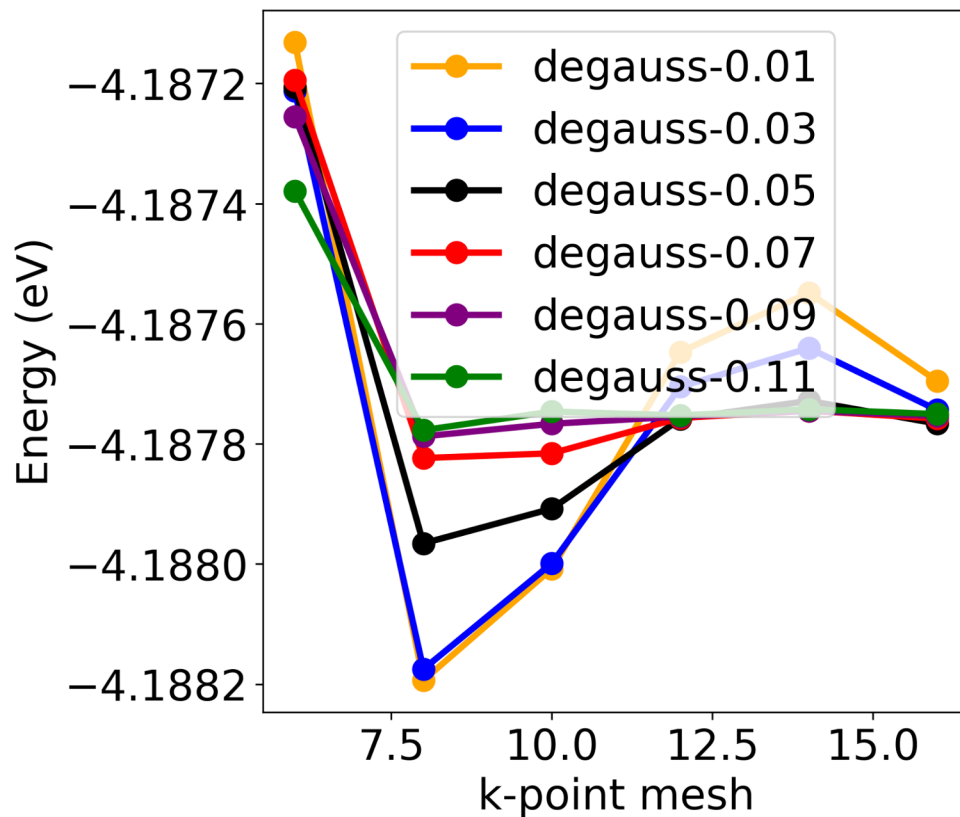


Exercise 2: smearing

Marzari-vanderbilt

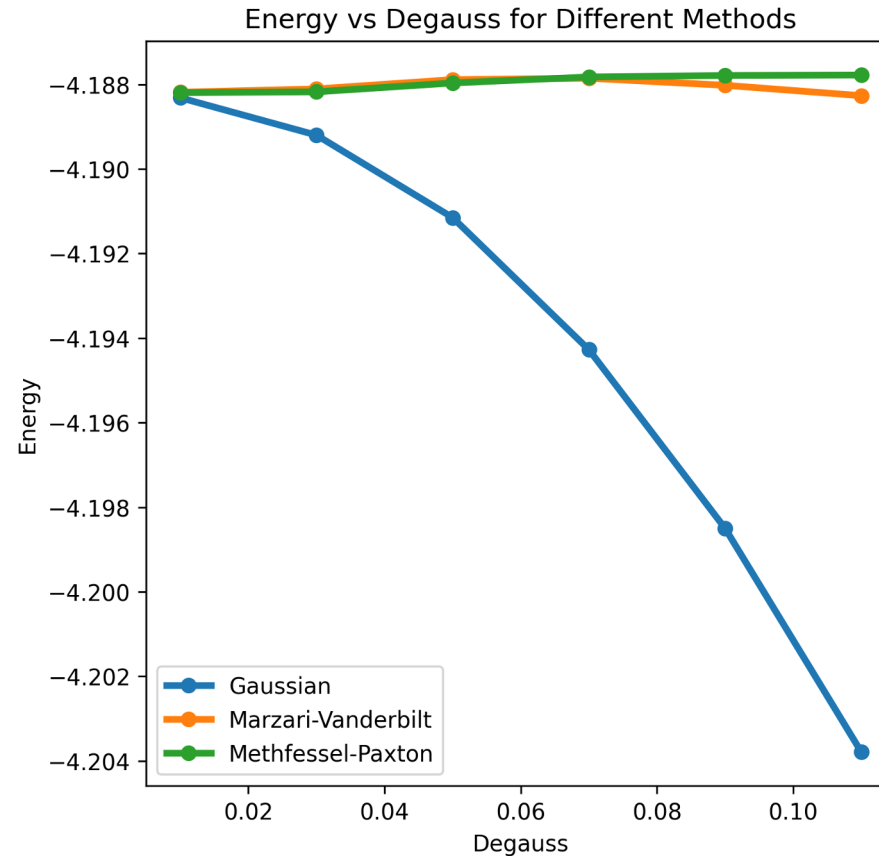


Methfessel-Paxton



Exercise 2: smearing

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



Exercise 3

Exchange correlation functional

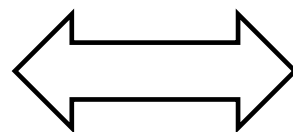
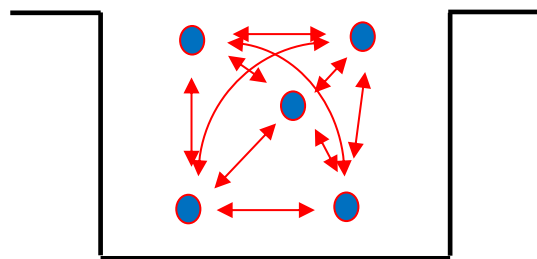
DAY 3: Exchange Correlational Functional

- Go to the exercise 3 folder

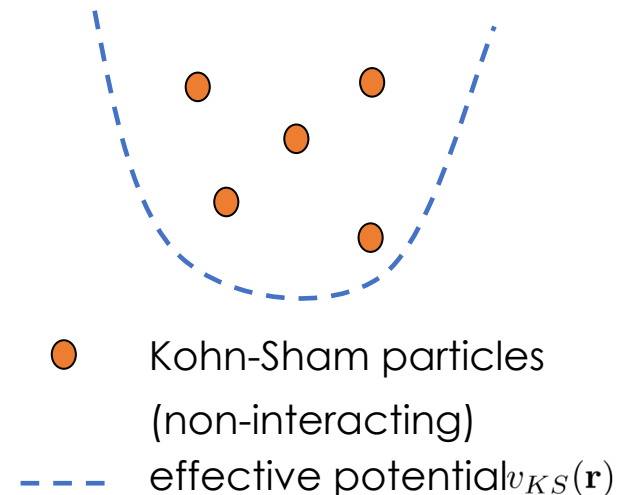
```
cd ASESMA2025/Hands-on-basic/Day3/
```



Kohn-Sham DFT



KS MAPPING



- electron
- ↔ 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 \mathbf{r} is locally approximated with that of a homogeneous electron gas with density $n(\mathbf{r})$

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



The exchange and correlation energy functional

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

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

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

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



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

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

The exchange and correlation energy functional

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

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

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

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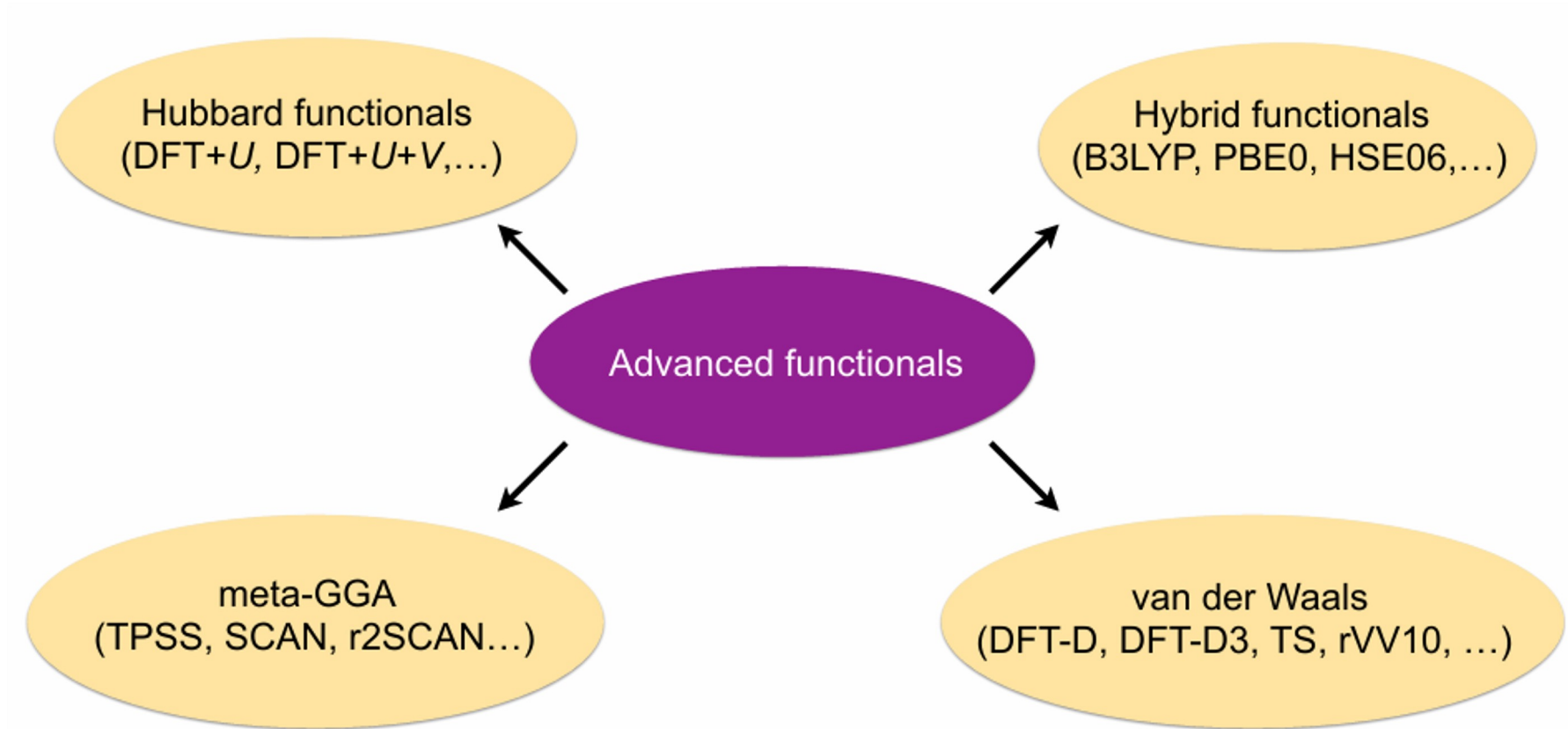
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$$E_{\text{xc}}^{\text{mGGA}} = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau) \quad \tau = \frac{1}{2} \sum_i |\nabla \psi_i(\mathbf{r})|^2$$

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

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

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
 - ...

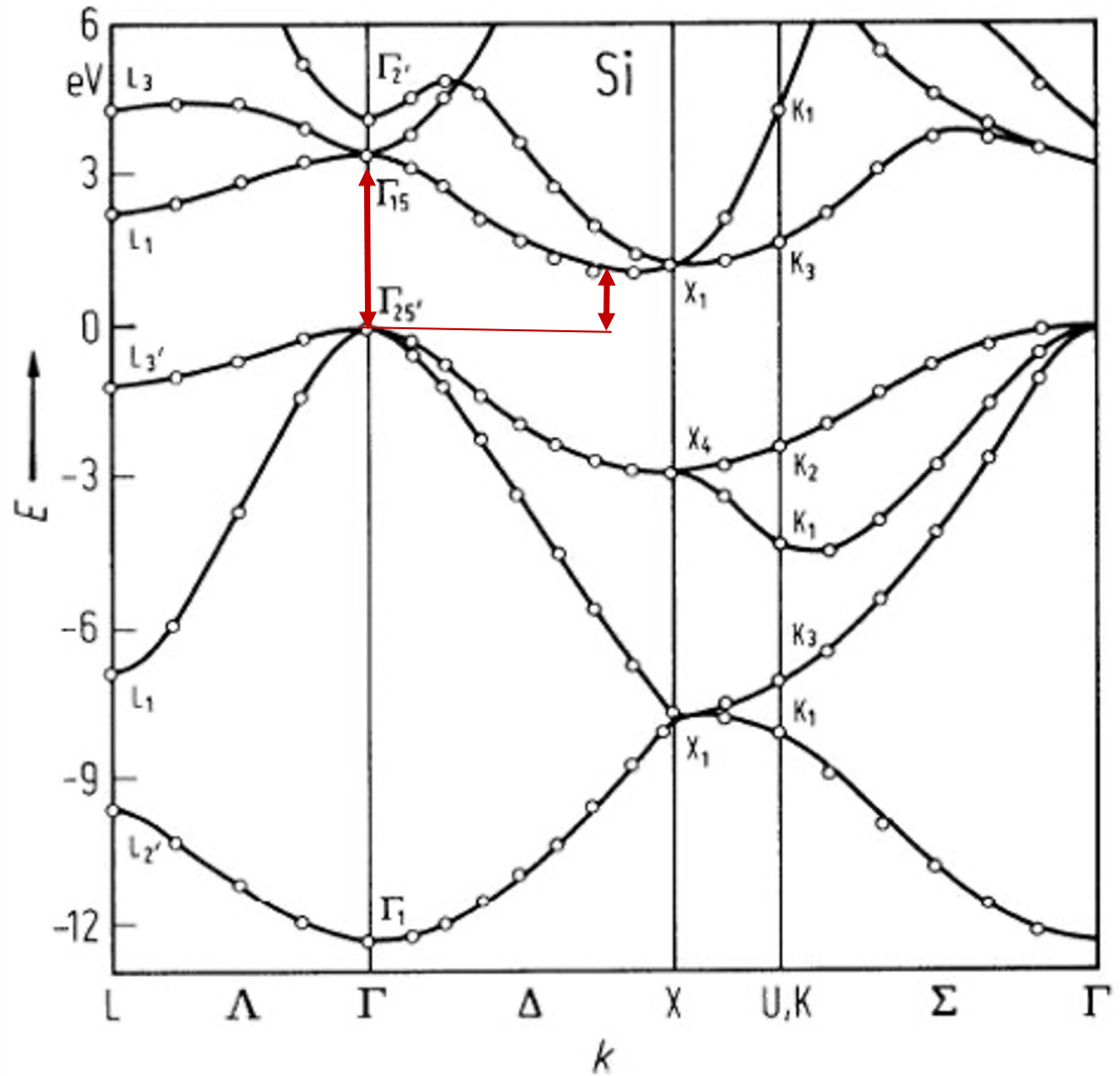
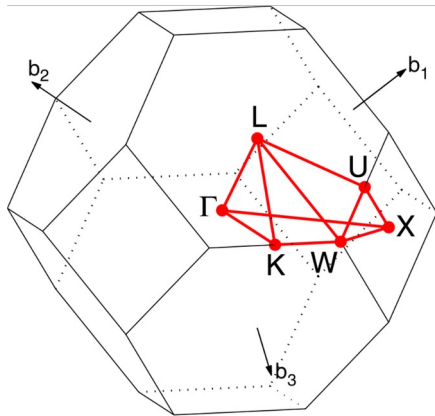
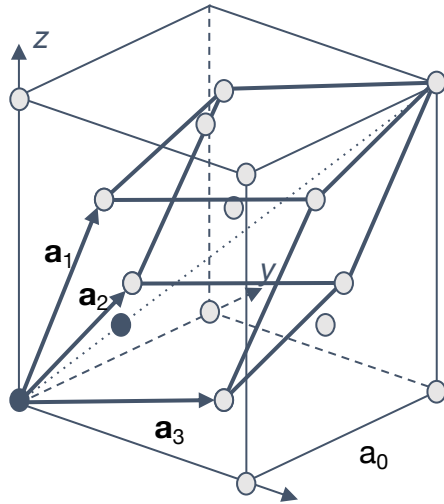
Lack of non-locality

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

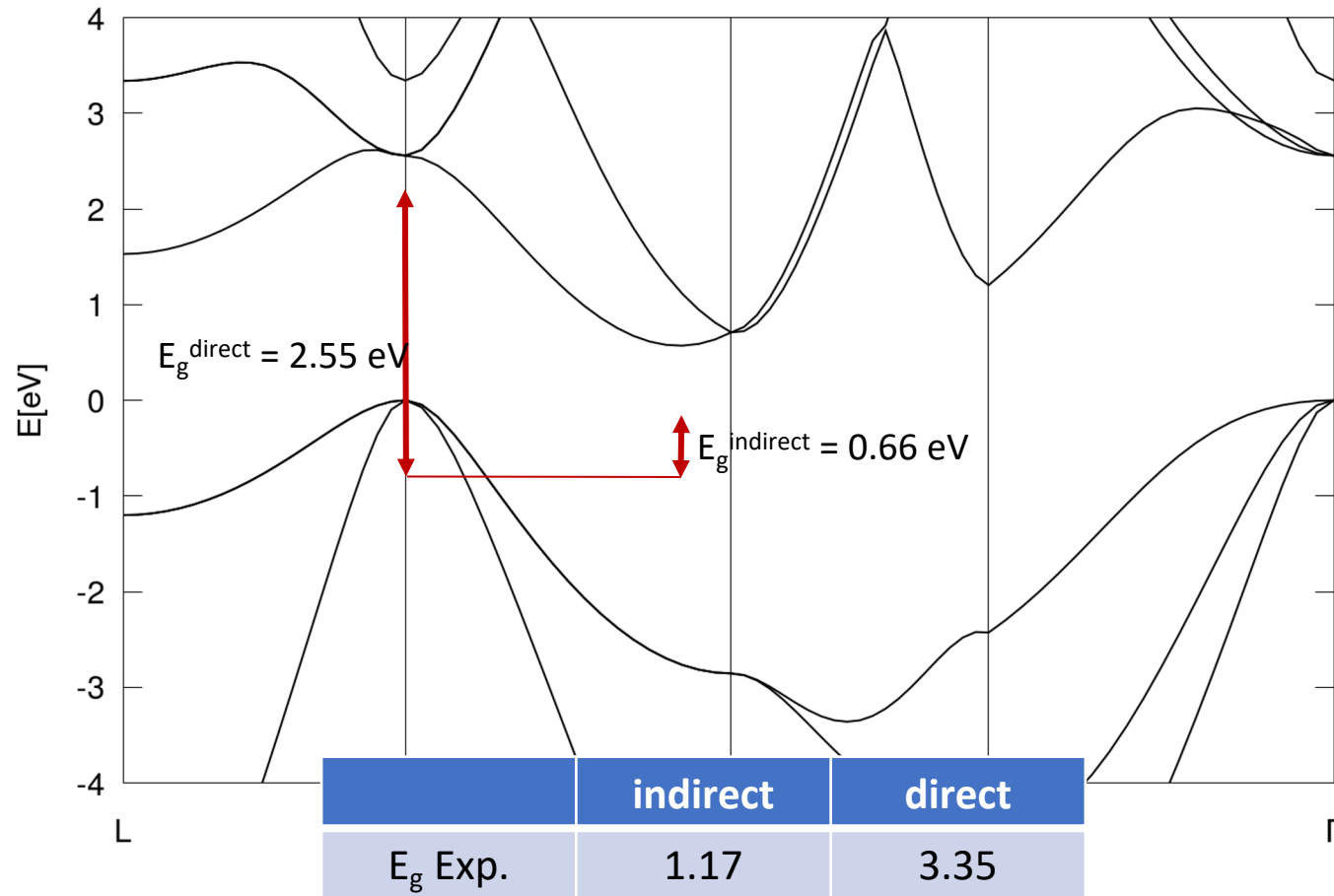


FCC Silicon

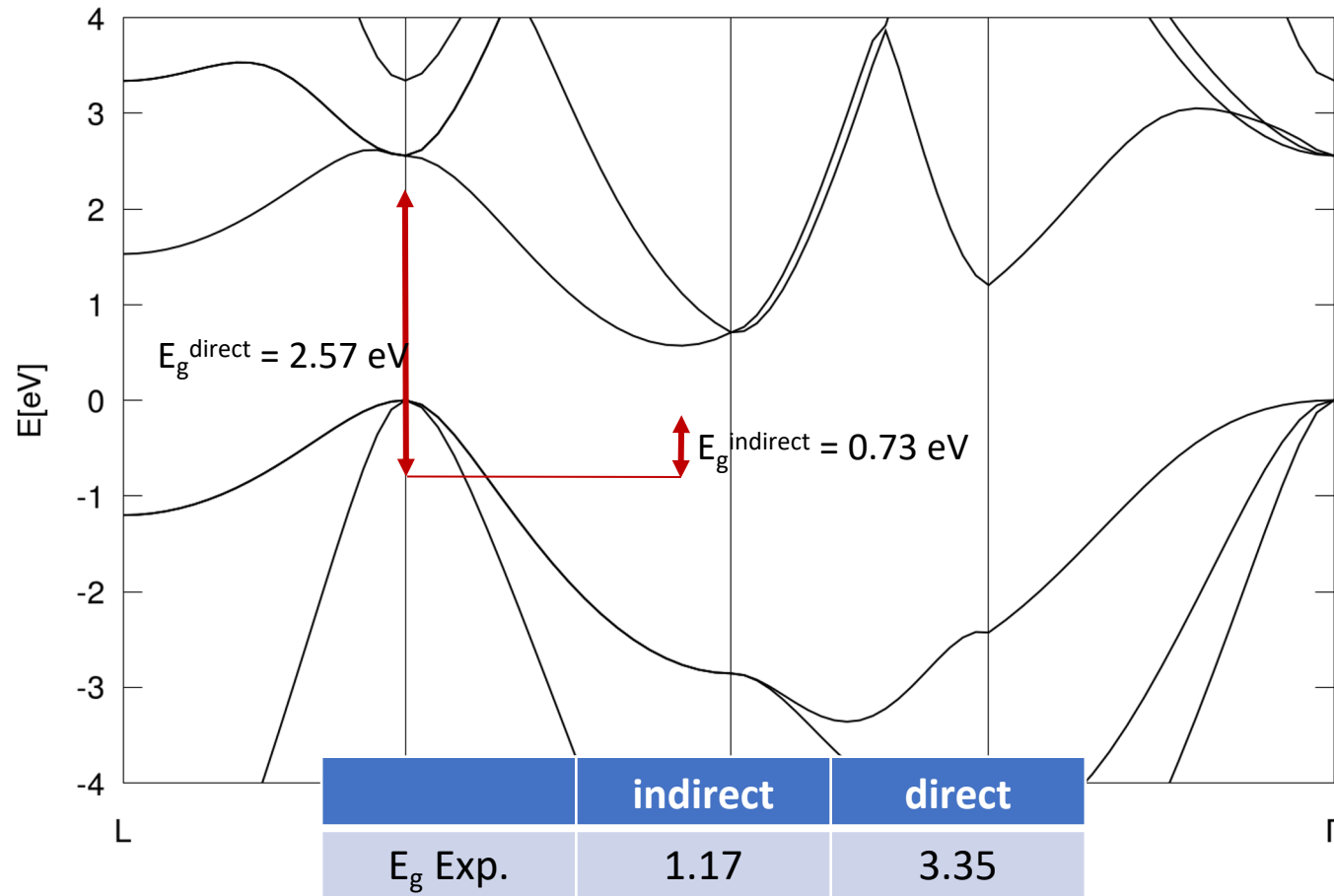
Goal of exercise3



LDA Silicon band structure



GGA Silicon band structure



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

Thank you!

Questions?
