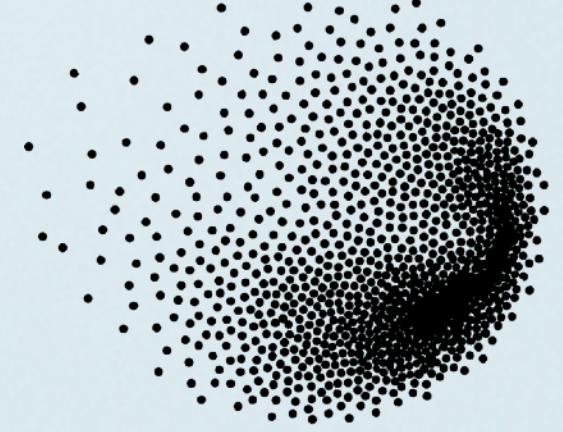


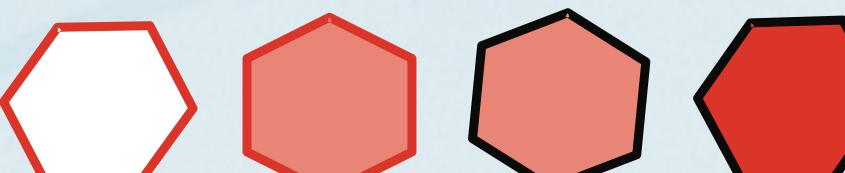
# Hands-on: Advanced functionals

Presenter: Iurii Timrov (PSI)

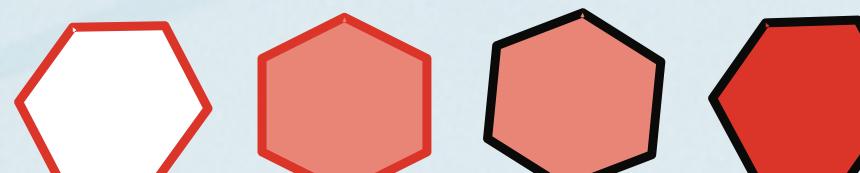
Tutors: Alberto Carta (PSI) and Garu Gebreyesus (Uni. Ghana)



**PSI**



MARVEL

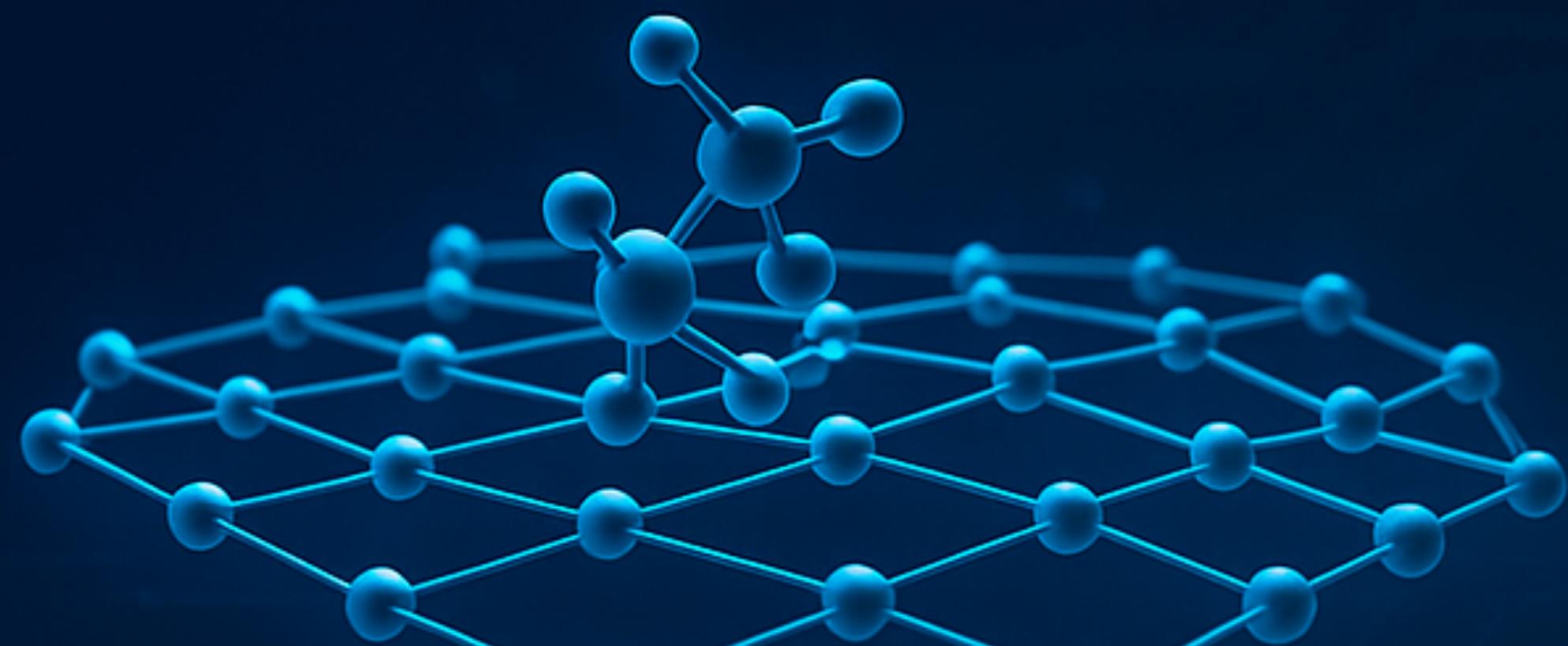


NATIONAL CENTRE OF COMPETENCE IN RESEARCH

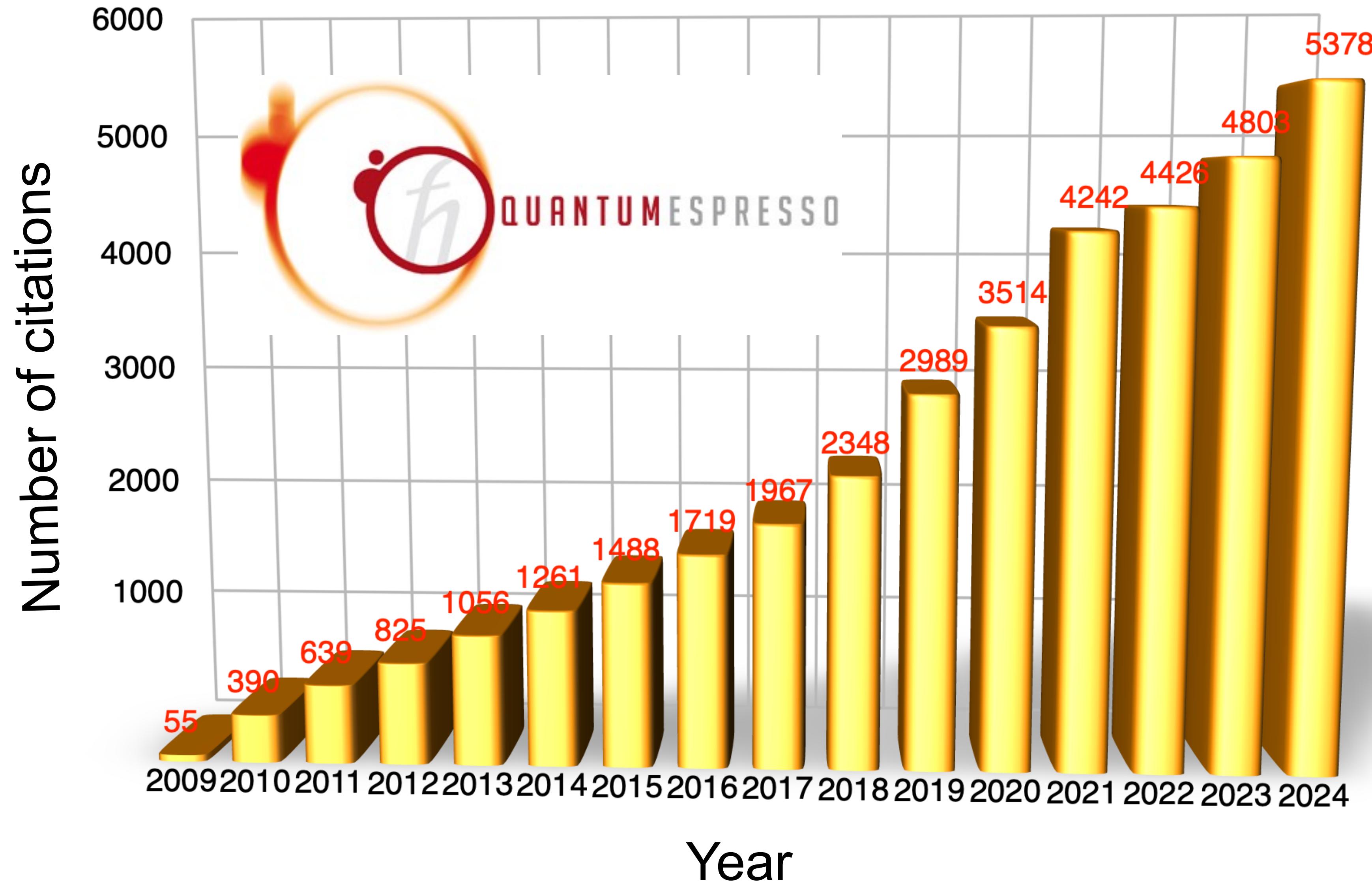




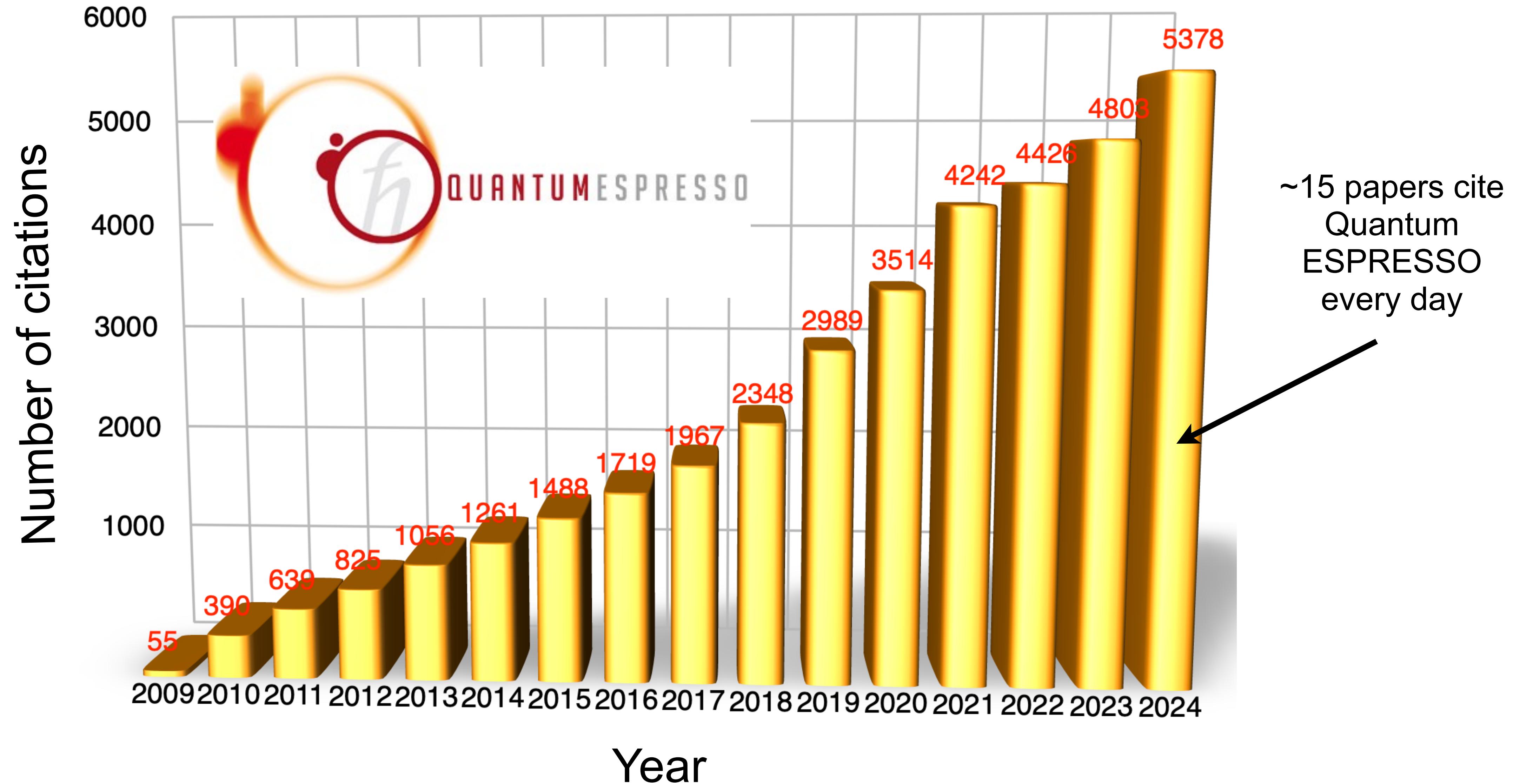
open-source  
**QUANTUM ESPRESSO**  
ELECTRONIC-STRUCTURE CODE  
FOR MATERIALS SCIENCE APPLICATIONS



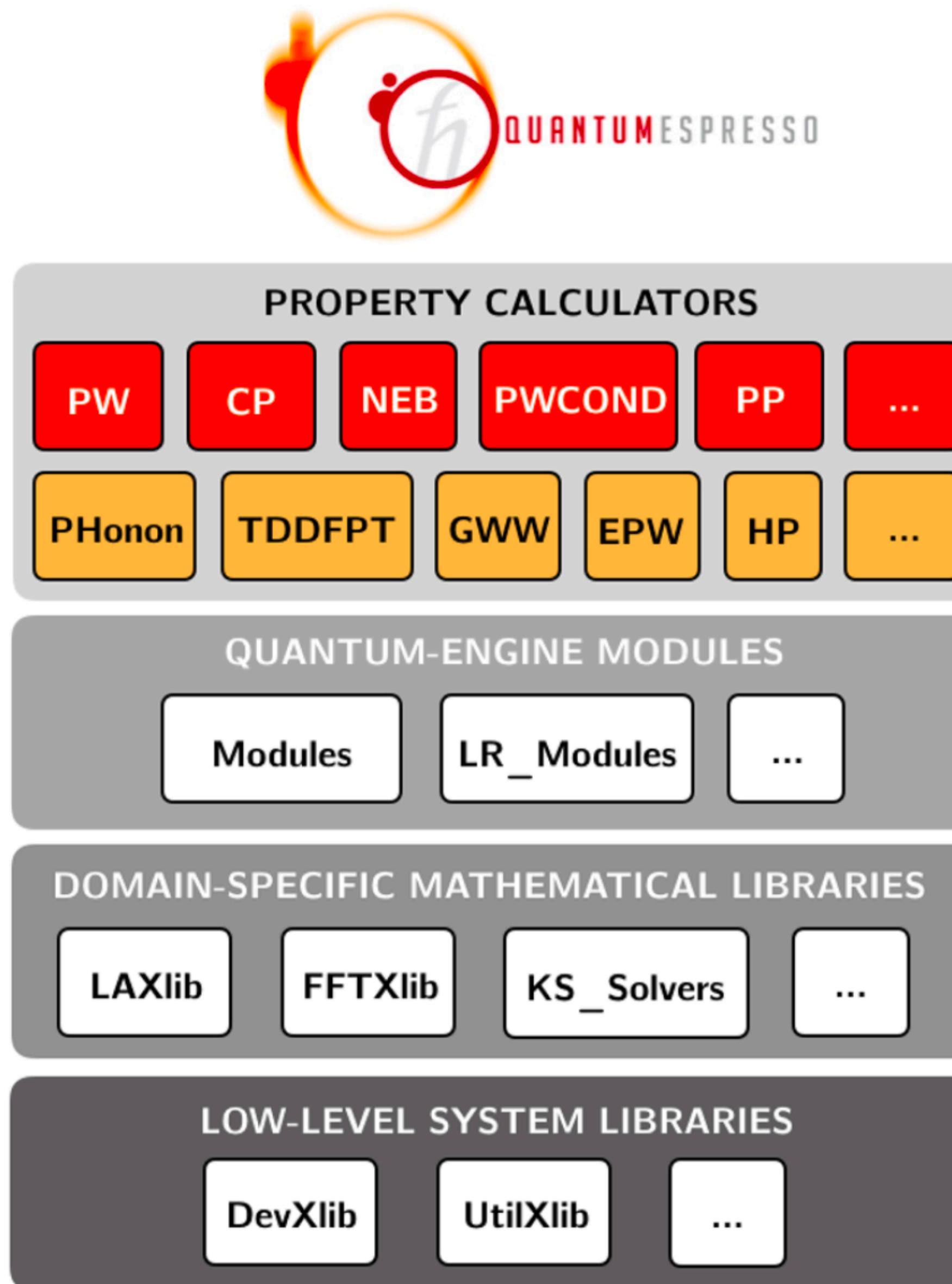
# Quantum ESPRESSO



# Quantum ESPRESSO



# Quantum ESPRESSO is a suite of codes



Quantum ESPRESSO is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.

PW - DFT, DFT+U, ...

CP - Car-Parrinello molecular dynamics

NEB - Nudged Elastic Bands

PP - Postprocessing tools

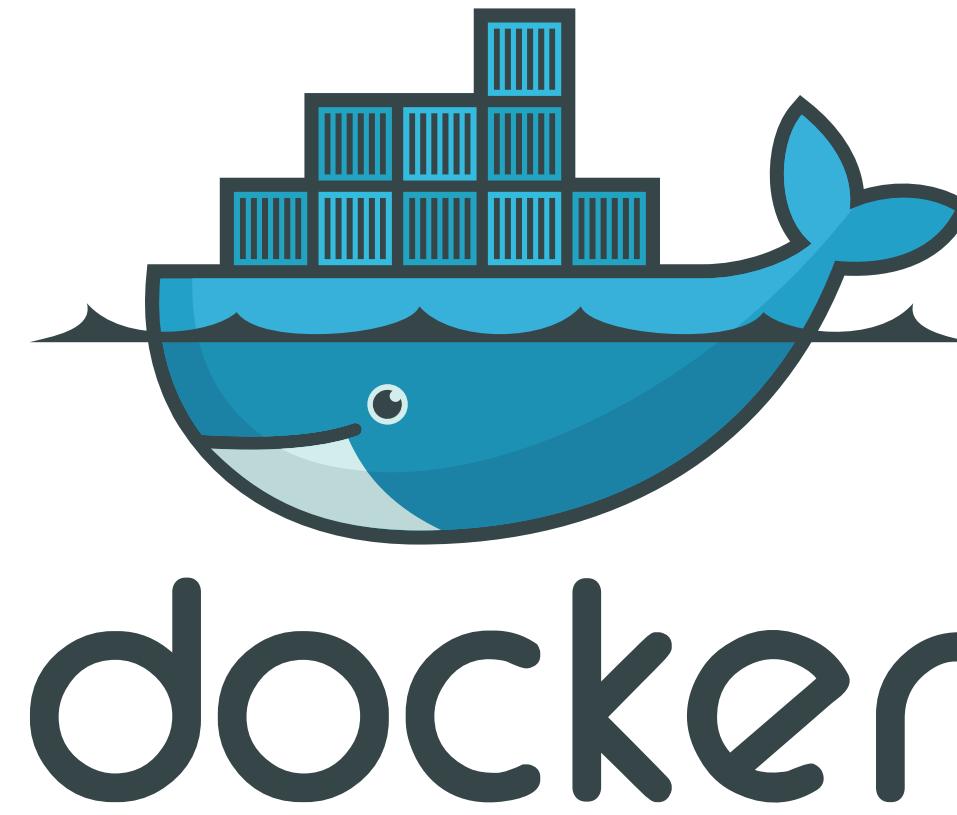
Phonon - Phonon calculations

TDDFPT - Spectroscopy

HP - Calculation of Hubbard parameters

...

# Docker



## What is Docker?

Docker is a tool for packaging and running applications in isolated environments called “containers”

## Why use Docker?

It makes software portable, reproducible, and easy to share

## Ideal for schools:

Perfect for scientific codes like Quantum ESPRESSO:  
install once, run anywhere

## In practice:

One command sets up a full working environment for simulations, tutorials, or workshops.

To start the Docker container for this school, type in the terminal:

`asesma_qe`

# **Exercise 1**

**DFT+*U* for CoO**

Check README.md how to run the calculations

```
mpirun -n 2 pw.x < Co0.scf.in |tee Co0.scf.out
```

```
mpirun -n 2 pw.x < Co0.nscf.in |tee Co0.nscf.out
```

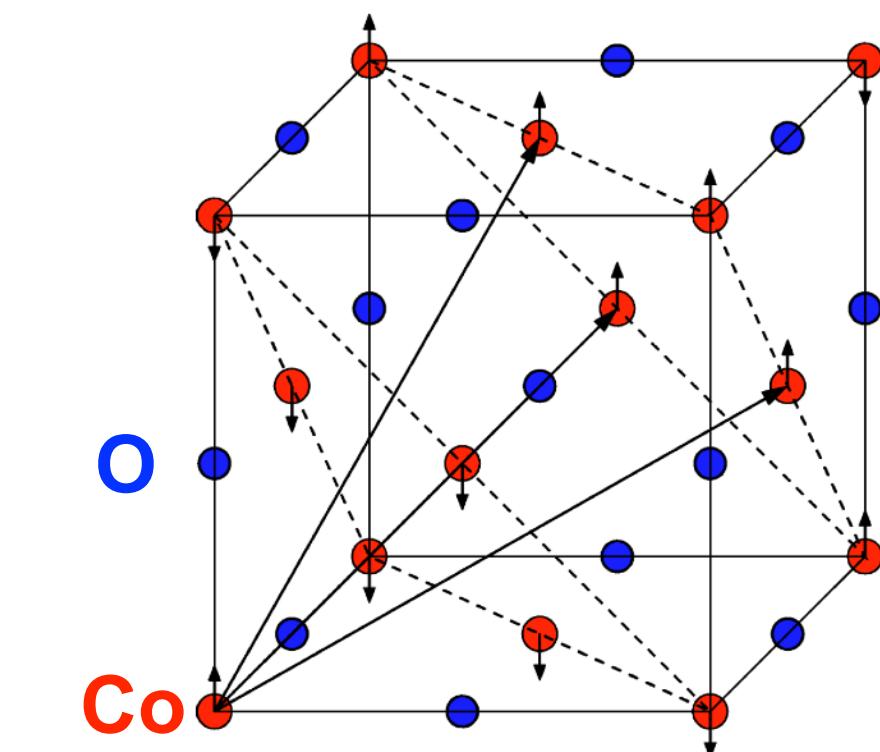
```
mpirun -n 2 projwfc.x < Co0.projwfc.in |tee Co0.projwfc.out
```

```
python3 plot_pdos.py
```

```
Visualize the file Co0_PDOS.pdf
```

# Input file CoO.scf.in

```
&control
  calculation='scf'           ← Self-consistent-field (SCF) calculation
  restart_mode='from_scratch',
  prefix='CoO'
  pseudo_dir = '../pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 0,                  ← Specification of the lattice (see CELL_PARAMETERS)
  celldm(1) = 8.00,
  nat = 4,                    ← Number of atoms and atomic types
  ntyp = 3,
  ecutwfc = 35.0             ← Kinetic-energy cutoff for the wavefunctions and density/potential
  ecutrho = 280.0
  nspin = 2
  starting_magnetization(1) = 0.5,
  starting_magnetization(2) = -0.5,
  occupations = 'smearing',   ← Spin-polarized collinear calculation (AFM)
  smearing = 'mv',
  degauss = 0.02
/
&electrons
  conv_thr = 1.d-10          ← Convergence threshold for self-consistency
/
ATOMIC_SPECIES
  Co1 58.933194 co_pbesol_v1.2.uspp.F.UPF
  Co2 58.933194 co_pbesol_v1.2.uspp.F.UPF
  O   15.999   O.pbesol-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS {crystal}
  Co1    0.0000000   0.0000000   0.0000000
  Co2    0.5000000   0.5000000   0.5000000
  O     0.2500000   0.2500000   0.2500000
  O     0.7500000   0.7500000   0.7500000
CELL_PARAMETERS {alat}
  0.570726115  0.570726115  1.031099100
  0.570726115  1.031099100  0.570726115
  1.031099100  0.570726115  0.570726115
K_POINTS {automatic}
  3 3 3 0 0 0
```



# Quantum ESPRESSO input generator and structure visualizer

► About the Quantum ESPRESSO input generator and structure visualizer

► Instructions

► Acknowledgements

Upload a crystal structure

Pick an example structure

Upload a file:

**Choose file** No file chosen

Select the file format:

Quantum ESPRESSO input [parser: qetools] ▾

Select the protocol:[?]

balanced ▾

Select the XC functional:

PBESol ▾

Select the magnetism/smearing:[?]

non-magnetic metal (fractional occupations) ▾

Refine cell (using spglib):

No ▾

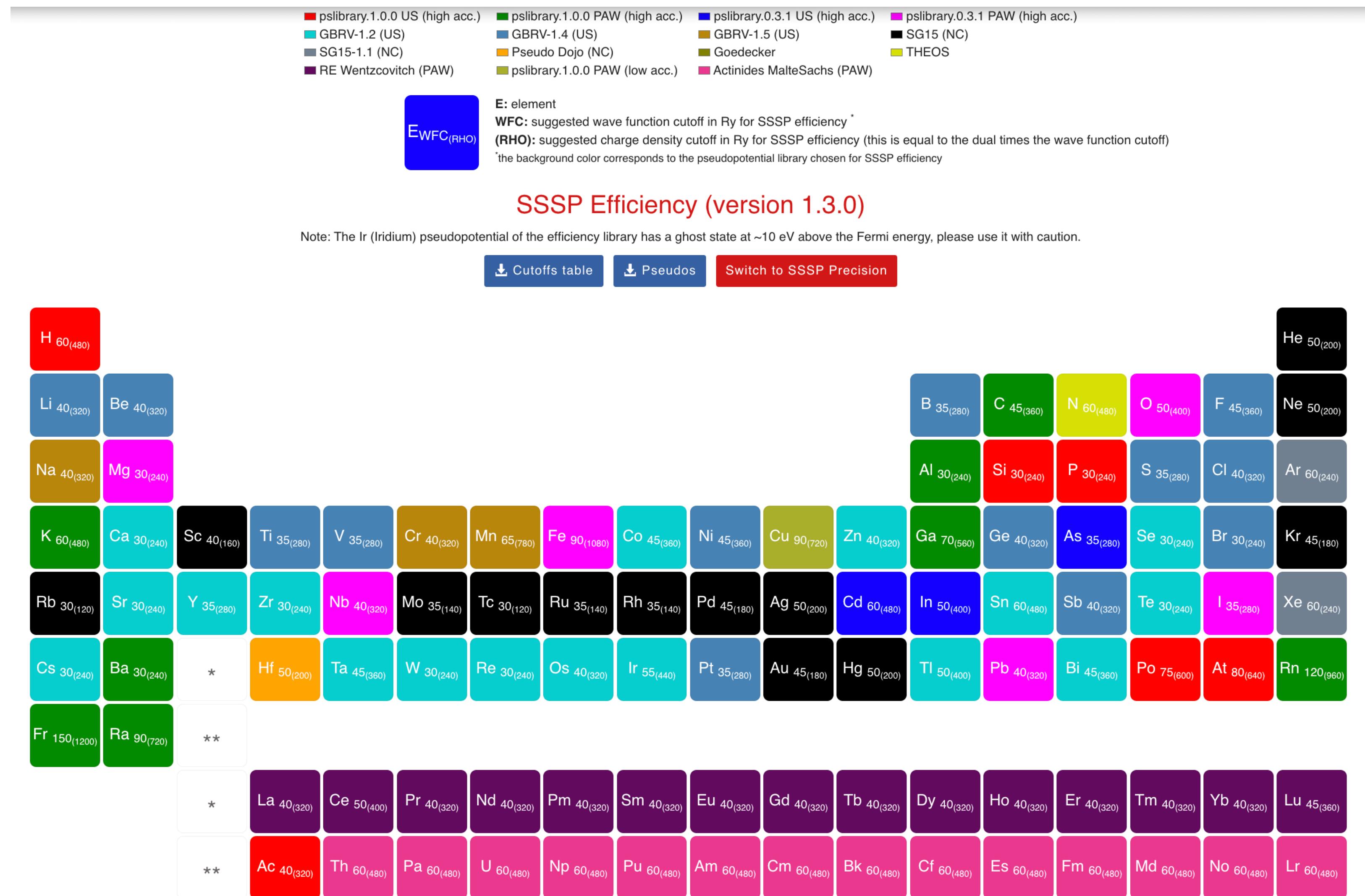
► Advanced settings[?]

By continuing, you agree with the [terms of use](#) of this service.

Generate the PWscf input file

<https://www.materialscloud.org/work/tools/qeinputgenerator>

# SSSP pseudopotential library



<https://www.materialscloud.org/discover/sssp/table/efficiency>

# Input file CoO.scf.in

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='CoO'
  pseudo_dir = '../..../pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 0,
  celldm(1) = 8.00,
  nat = 4,
  ntyp = 3,
  ecutwfc = 35.0
  ecutrho = 280.0
  nspin = 2
  starting_magnetization(1) = 0.5,
  starting_magnetization(2) = -0.5,
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.02
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Co1 58.933194 co_pbessol_v1.2.uspp.F.UPF
Co2 58.933194 co_pbessol_v1.2.uspp.F.UPF
O 15.999 O.pbesol-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS {crystal}
Co1 0.00000000 0.00000000 0.00000000
Co2 0.50000000 0.50000000 0.50000000
O 0.25000000 0.25000000 0.25000000
O 0.75000000 0.75000000 0.75000000
CELL_PARAMETERS {alat}
  0.570726115 0.570726115 1.031099100
  0.570726115 1.031099100 0.570726115
  1.031099100 0.570726115 0.570726115
K_POINTS {automatic}
  3 3 3 0 0 0
```

# Input file CoO.nscf.in

```
&control
  calculation='nscf'
  restart_mode='from_scratch',
  prefix='CoO'
  pseudo_dir = '../..../pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 0,
  celldm(1) = 8.00,
  nat = 4,
  ntyp = 3,
  ecutwfc = 35.0
  ecutrho = 280.0
  nspin = 2
  starting_magnetization(1) = 0.5,
  starting_magnetization(2) = -0.5,
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.02
  nbnd = 40
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Co1 58.933194 co_pbessol_v1.2.uspp.F.UPF
Co2 58.933194 co_pbessol_v1.2.uspp.F.UPF
O 15.999 O.pbesol-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS {crystal}
Co1 0.00000000 0.00000000 0.00000000
Co2 0.50000000 0.50000000 0.50000000
O 0.25000000 0.25000000 0.25000000
O 0.75000000 0.75000000 0.75000000
CELL_PARAMETERS {alat}
  0.570726115 0.570726115 1.031099100
  0.570726115 1.031099100 0.570726115
  1.031099100 0.570726115 0.570726115
K_POINTS {automatic}
  6 6 6 0 0 0
```

## Input file CoO.projwfc.in

```
&projwfc
    prefix='CoO'
    outdir='./tmp'
    ngauss = 0, ← Gaussian broadening for PDOS
    degauss = 0.005, ← Value of the Gaussian broadening (in Ry)
    Emin = -15.0,
    Emax = 30.0, ← Minimum and maximum energy for the plot (in eV)
    DeltaE = 0.01 ← Energy grid step
/

```

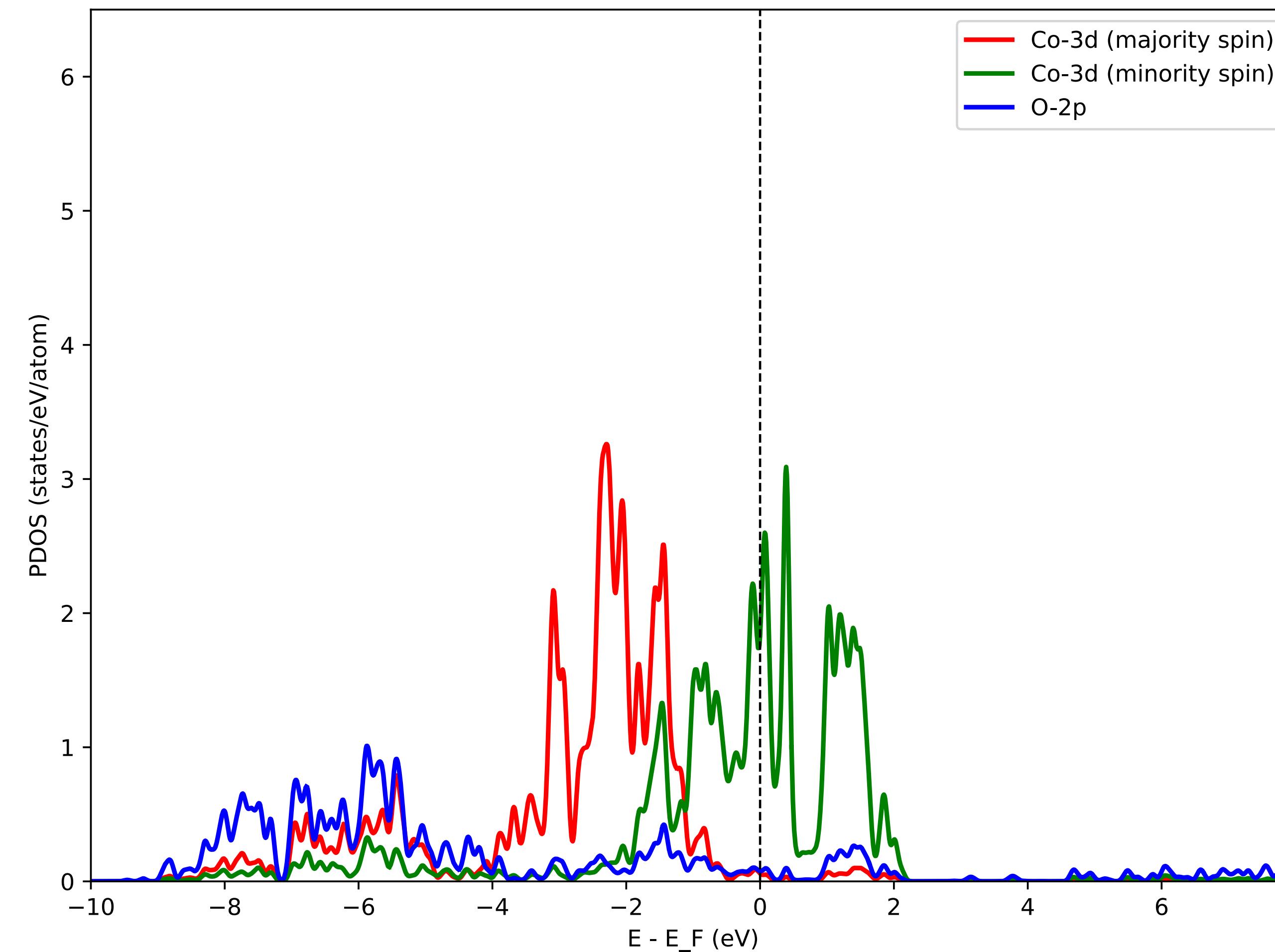
## Python3 script: plot\_pdos.py

Inspect the script. It aims at plotting Co-3d states (majority spin and minority spin) and O-2p states.

PDOS is shifted such that the Fermi energy corresponds to zero of energy. Use the Fermi energy from the file CoO.scf.out

After running the script, visualize the file CoO\_PDOS.pdf

# PDOS using DFT (PBEsol)



DFT predicts CoO to be metallic (**this is wrong**)

Experimentally CoO is insulating

Let's try DFT+*U*

# Input file CoO.scf.in

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='CoO'
  pseudo_dir = '../pseudo'
  outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 0,
  celldm(1) = 8.00,
  nat = 4,
  ntyp = 3,
  ecutwfc = 35.0
  ecutrho = 280.0
  nspin = 2
  starting_magnetization(1) = 0.5,
  starting_magnetization(2) = -0.5,
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.02
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
  Co1 58.933194 co_pbesol_v1.2.uspp.F.UPF
  Co2 58.933194 co_pbesol_v1.2.uspp.F.UPF
  O 15.999 O.pbesol-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS {crystal}
  Co1    0.00000000    0.00000000    0.00000000
  Co2    0.50000000    0.50000000    0.50000000
  O     0.25000000    0.25000000    0.25000000
  O     0.75000000    0.75000000    0.75000000
CELL_PARAMETERS {alat}
  0.570726115  0.570726115  1.031099100
  0.570726115  1.031099100  0.570726115
  1.031099100  0.570726115  0.570726115
K_POINTS {automatic}
  3 3 3 0 0 0
HUBBARD {ortho-atomic}
  U Co1-3d 0.0001
  U Co2-3d 0.0001
```

HUBBARD card

Name of the card

Type of the Hubbard projectors

HUBBARD {ortho-atomic}		
U	Co1-3d	0.0001
U	Co2-3d	0.0001

Name of the Hubbard parameter

Atomic type of the chemical element  
to which we want to apply  
the Hubbard correction

Detailed description of the new Hubbard input syntax (since v7.1):  
See Hubbard\_input.pdf

We set some small initial value  
just to activate the Hubbard machinery in the code

Value of the Hubbard  
parameter (in eV)

# Input file CoO.hp.in

```
&inputhp
```

```
prefix = 'CoO'
```

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

```
nq1 = 2, nq2 = 2, nq3 = 2
```

```
conv_thr_chi = 1.d-6
```

```
/
```



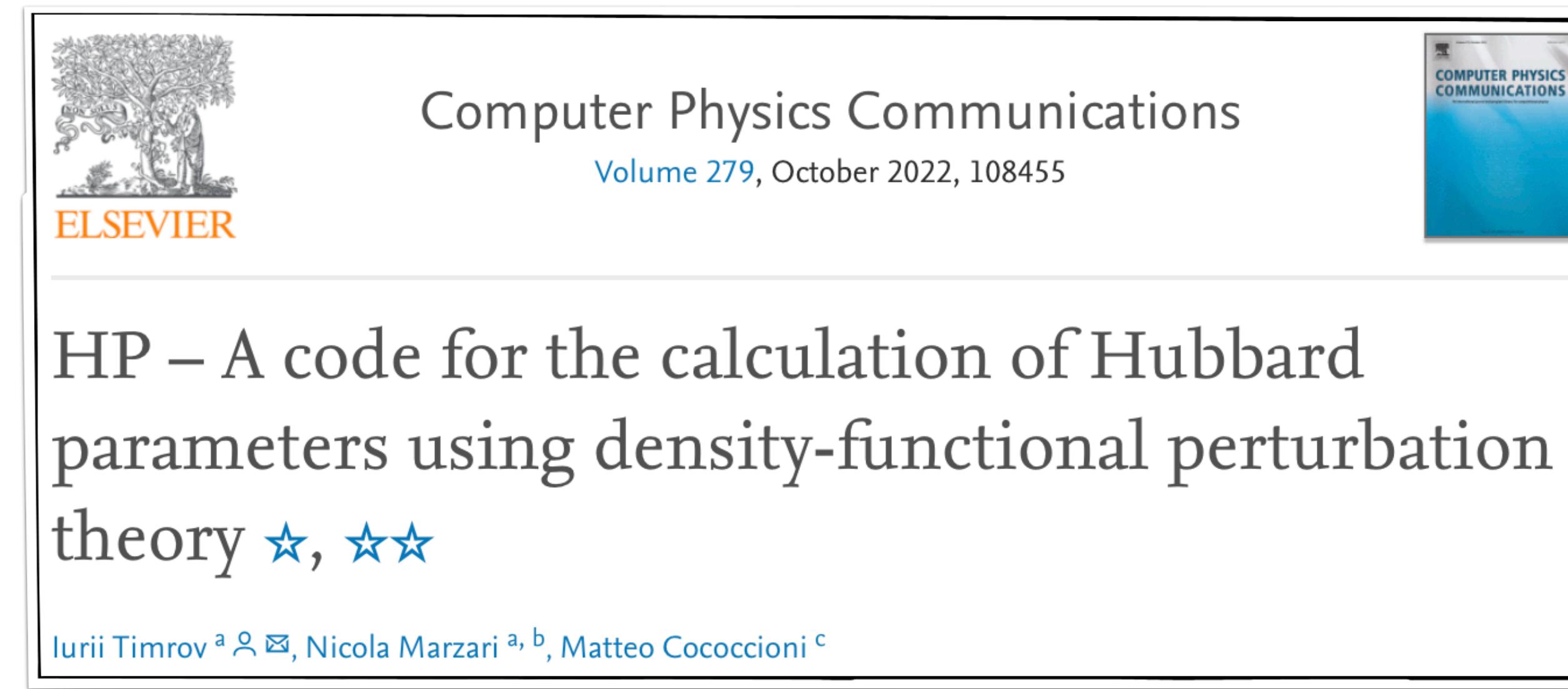
The same as in the CoO.scf.in input



Size of the **q** points mesh



Convergence threshold for computing the self-consistent response matrix  $\chi$  (in eV<sup>-1</sup>)



**Important notice:** The calculation of the Hubbard  $U$  parameter must be converged (as any other quantity of interest)!

Hubbard  $U$  must be converged with respect to the kinetic-energy cutoff (ecutwfc and ecutrho), **k** points mesh, and **q** points mesh.

For more details see: *I. Timrov, N. Marzari, M. Cococcioni, Phys. Rev. B 98, 085127 (2018)*.

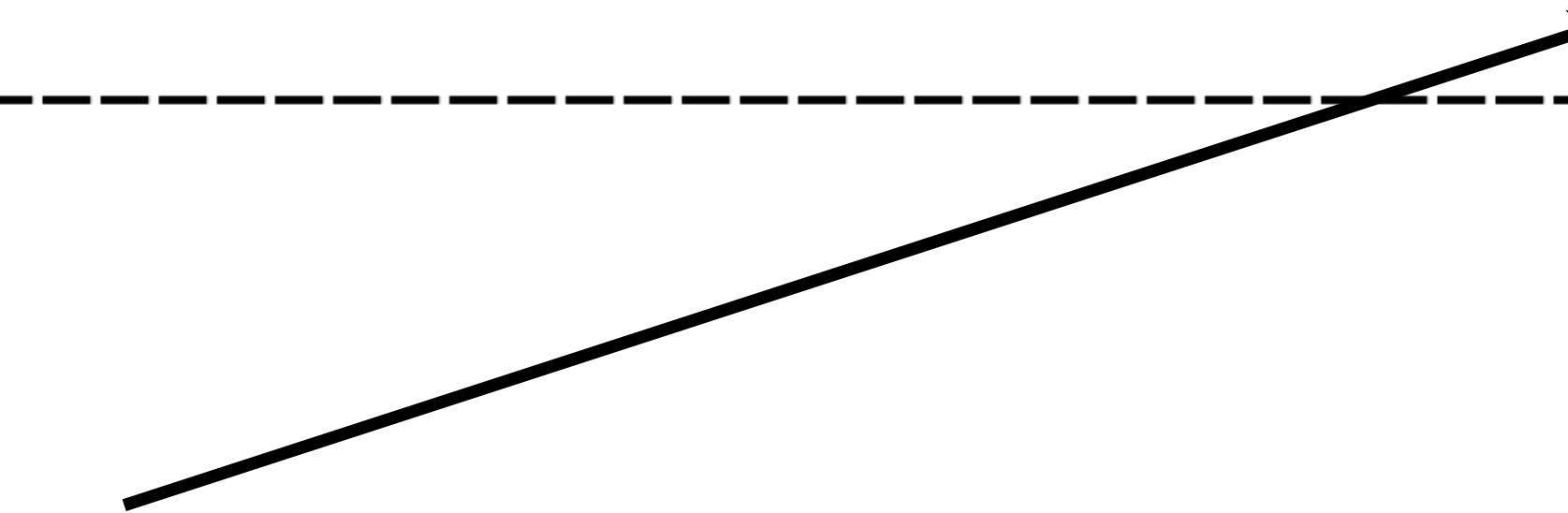
# Output file CoO.Hubbard\_parameters.dat

=====

## Hubbard U parameters:

site	n.	type	label	spin	new_type	new_label	Hubbard U (eV)
1	1	1	Co1	1	1	Co1	6.7553
2	2	2	Co2	-1	1	Co1	6.7553

=====



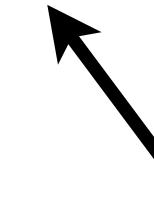
These are the output Hubbard  $U$  parameters for Co1-3d and Co2-3d states

These parameters are computed in a “one-shot” fashion (i.e. from the DFT-PBEsol ground state)

# Input file CoO.scf.in

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='CoO'
  pseudo_dir = '../pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 0,
  celldm(1) = 8.00,
  nat = 4,
  ntyp = 3,
  ecutwfc = 35.0
  ecutrho = 280.0
  nspin = 2
  starting_magnetization(1) = 0.5,
  starting_magnetization(2) = -0.5,
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.02
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Co1 58.933194 co_pbesol_v1.2.uspp.F.UPF
Co2 58.933194 co_pbesol_v1.2.uspp.F.UPF
O 15.999 O.pbesol-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS {crystal}
Co1    0.0000000    0.0000000    0.0000000
Co2    0.5000000    0.5000000    0.5000000
O     0.2500000    0.2500000    0.2500000
O     0.7500000    0.7500000    0.7500000
CELL_PARAMETERS {alat}
  0.570726115  0.570726115  1.031099100
  0.570726115  1.031099100  0.570726115
  1.031099100  0.570726115  0.570726115
K_POINTS {automatic}
  3 3 3 0 0 0
HUBBARD {ortho-atomic}
U Co1-3d 6.8
U Co2-3d 6.8
```

HUBBARD {ortho-atomic}  
U Co1-3d 6.8  
U Co2-3d 6.8



This is the value of the Hubbard  $U$  parameter (in eV)  
that we computed using the HP code

We need to specify the same Hubbard  $U$  in the CoO.nscf.in file

← HUBBARD card

# Input file CoO.scf.in

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='CoO'
  pseudo_dir = '../..../pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 0,
  celldm(1) = 8.00,
  nat = 4,
  ntyp = 3,
  ecutwfc = 35.0
  ecutrho = 280.0
  nspin = 2
  starting_magnetization(1) = 0.5,
  starting_magnetization(2) = -0.5,
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.02
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
  Co1 58.933194 co_pbesol_v1.2.uspp.F.UPF
  Co2 58.933194 co_pbesol_v1.2.uspp.F.UPF
  O 15.999 0.pbesol-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS {crystal}
  Co1    0.0000000    0.0000000    0.0000000
  Co2    0.5000000    0.5000000    0.5000000
  O     0.2500000    0.2500000    0.2500000
  O     0.7500000    0.7500000    0.7500000
CELL_PARAMETERS {alat}
  0.570726115  0.570726115  1.031099100
  0.570726115  1.031099100  0.570726115
  1.031099100  0.570726115  0.570726115
K_POINTS {automatic}
  3 3 3 0 0 0
HUBBARD {ortho-atomic}
U Co1-3d 6.8
U Co2-3d 6.8
```

# Input file CoO.nscf.in

```
&control
  calculation='nscf'
  restart_mode='from_scratch',
  prefix='CoO'
  pseudo_dir = '../..../pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 0,
  celldm(1) = 8.00,
  nat = 4,
  ntyp = 3,
  ecutwfc = 35.0
  ecutrho = 280.0
  nspin = 2
  starting_magnetization(1) = 0.5,
  starting_magnetization(2) = -0.5,
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.02
  nbnd = 40
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
  Co1 58.933194 co_pbesol_v1.2.uspp.F.UPF
  Co2 58.933194 co_pbesol_v1.2.uspp.F.UPF
  O 15.999 0.pbesol-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS {crystal}
  Co1    0.0000000    0.0000000    0.0000000
  Co2    0.5000000    0.5000000    0.5000000
  O     0.2500000    0.2500000    0.2500000
  O     0.7500000    0.7500000    0.7500000
CELL_PARAMETERS {alat}
  0.570726115  0.570726115  1.031099100
  0.570726115  1.031099100  0.570726115
  1.031099100  0.570726115  0.570726115
K_POINTS {automatic}
  6 6 6 0 0 0
HUBBARD {ortho-atomic}
U Co1-3d 6.8
U Co2-3d 6.8
```

## Input file CoO.projwfc.in

This is exactly the same as before

```
&projwfc
    prefix='CoO'
    outdir='./tmp'
    ngauss = 0, ← Gaussian broadening for PDOS
    degauss = 0.005, ← Value of the Gaussian broadening (in Ry)
    Emin = -15.0, ← Minimum and maximum energy for the plot (in eV)
    Emax = 30.0, ←
    DeltaE = 0.01 ← Energy grid step
/

```

## Python3 script: plot\_pdos.py

Plot the PDOS using the gnuplot and the plot\_pdos.py script

PDOS is shifted such that the Fermi energy corresponds to zero of energy. Use the Fermi energy from the file CoO.scf.out

After running the script, visualize the file CoO\_PDOS.pdf

## Run the calculations

```
mpirun -n 2 pw.x < Co0.scf.in |tee Co0.scf.out
```

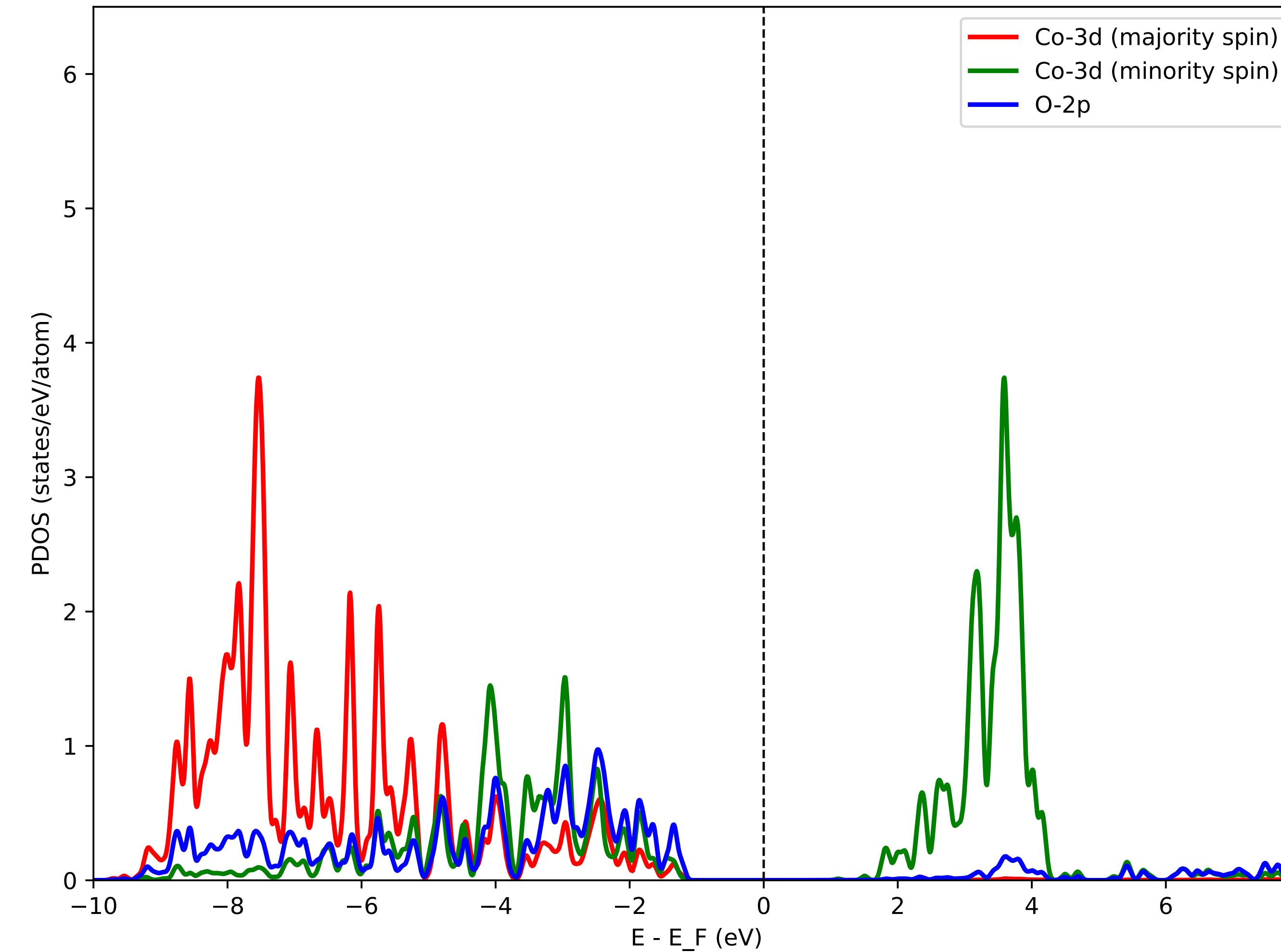
```
mpirun -n 2 pw.x < Co0.nscf.in |tee Co0.nscf.out
```

```
mpirun -n 2 projwfc.x < Co0.projwfc.in |tee Co0.projwfc.out
```

```
python3 plot_pdos.py
```

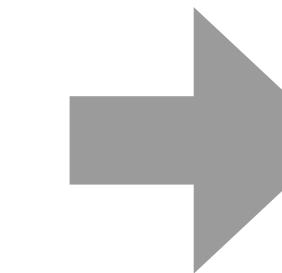
```
Visualize the file Co0_PDOS.pdf
```

# PDOS using DFT+ $U$



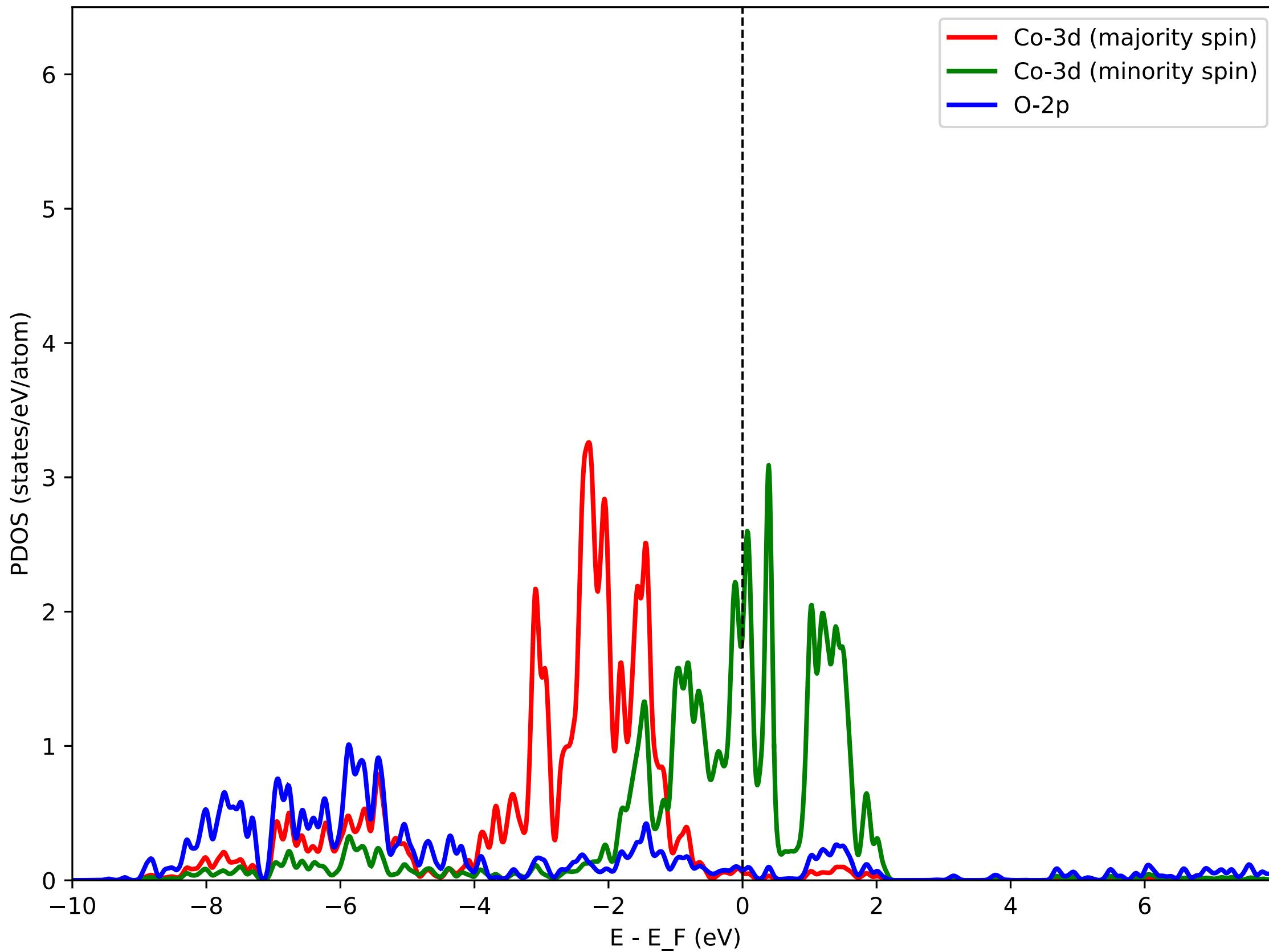
DFT+ $U$  predicts CoO to be insulating (this is correct)

Experimentally CoO is insulating

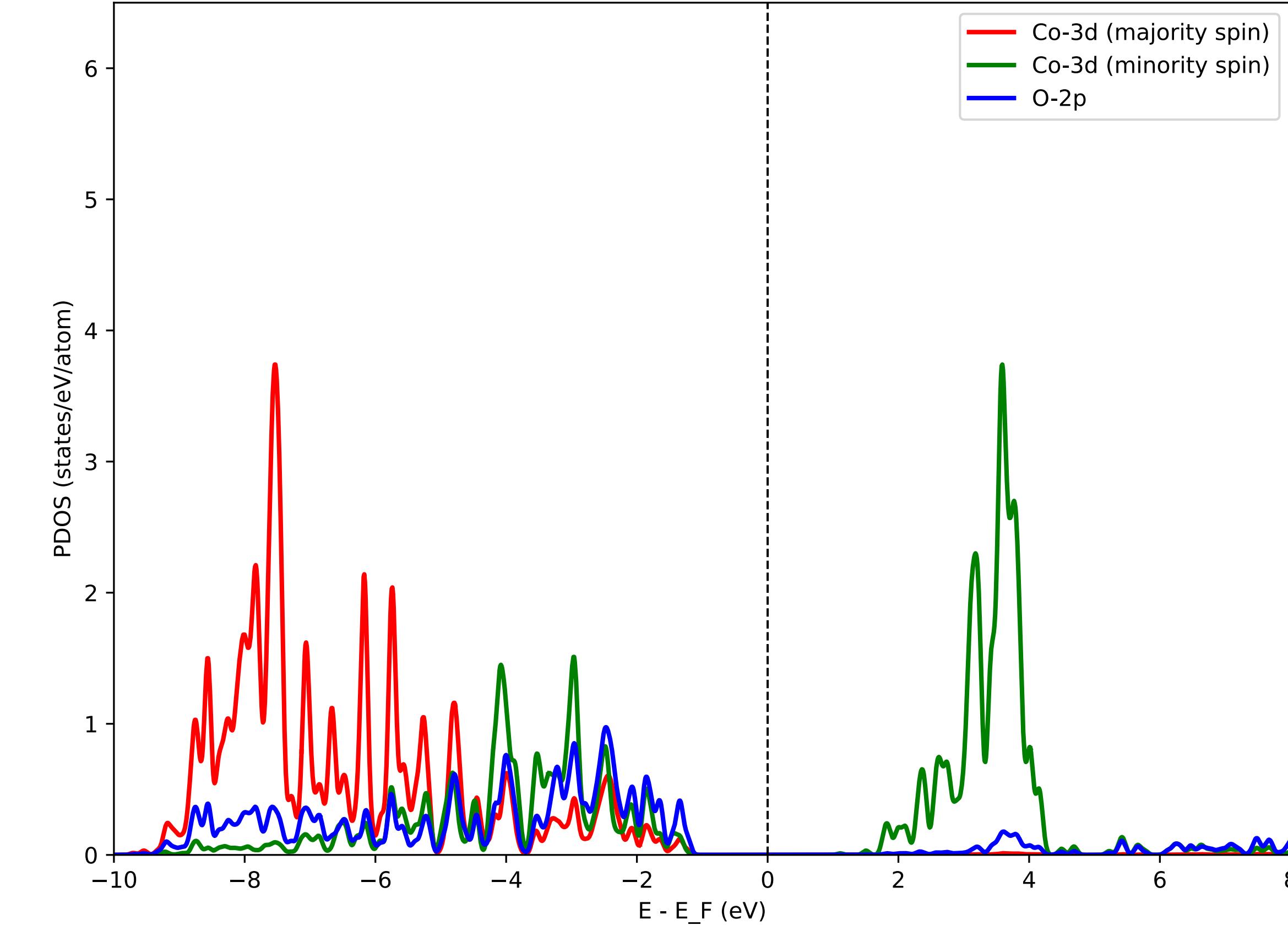


Agreement with experiment

## PDOS using DFT



## PDOS using DFT+ $U$



Co-3d (minority spin) states are split

Co-3d (majority spin) states are shifted to lower energies

DFT+ $U$  band gap: 2.4 eV

Experimental gap:  $2.5 \pm 0.3$  eV

## **Exercise 2**

**Hybrid functional PBE0 for Si**

## The $\mathbf{q} + \mathbf{G} = 0$ divergence

In periodic systems, the exact exchange contains a divergence when  $\mathbf{q} + \mathbf{G} = 0$ :

$$E_x = -\frac{4\pi}{2\Omega} \times \frac{\Omega}{(2\pi)^3} \int d\mathbf{q} \sum_{\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{q} + \mathbf{G}|^2}$$

where

We need to setup the  $\mathbf{q}$  mesh

We need to setup the  $\mathbf{k}$  mesh

$$A(\mathbf{q} + \mathbf{G}) = \frac{\Omega}{(2\pi)^3} \int d\mathbf{k} |\rho_{\mathbf{k},v}^{\mathbf{k}-\mathbf{q},v'}(\mathbf{q} + \mathbf{G})|^2 \equiv \frac{1}{N_k} \sum_{\mathbf{k}} |\rho_{\mathbf{k},v}^{\mathbf{k}-\mathbf{q},v'}(\mathbf{q} + \mathbf{G})|^2$$

(the finite sum over  $N_k$   $\mathbf{k}$ -points is what we actually compute) and

$$\rho_{\mathbf{k},v}^{\mathbf{k}-\mathbf{q},v'}(\mathbf{r}) = \psi_{\mathbf{k}-\mathbf{q},v'}^*(\mathbf{r}) \psi_{\mathbf{k},v}(\mathbf{r}).$$

This divergence is integrable, see: F.Gygi and A.Baldereschi, PRB 34, 4405 (1986)

# Input file Si.scf.in

```
&control
    calculation='scf'
    restart_mode='from_scratch',
    prefix='Si'
    pseudo_dir = ' ../../pseudo'
   outdir='./tmp'
    verbosity='high'
/
&system
    ibrav = 2,
    celldm(1) = 10.20,
    nat = 2,
    ntyp = 1,
    ecutwfc = 20.0,
    input_dft = 'pbe0',
    nqx1 = 1, nqx2 = 1, nqx3 = 1,
    x_gamma_extrapolation = .true.
    exxdiv_treatment = 'gygi-baldereschi'
/
&electrons
    conv_thr = 1.d-9
    mixing_beta = 0.3
/
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}
8 8 8 1 1 1
```

Type of the hybrid functional (PBE0 in this case)

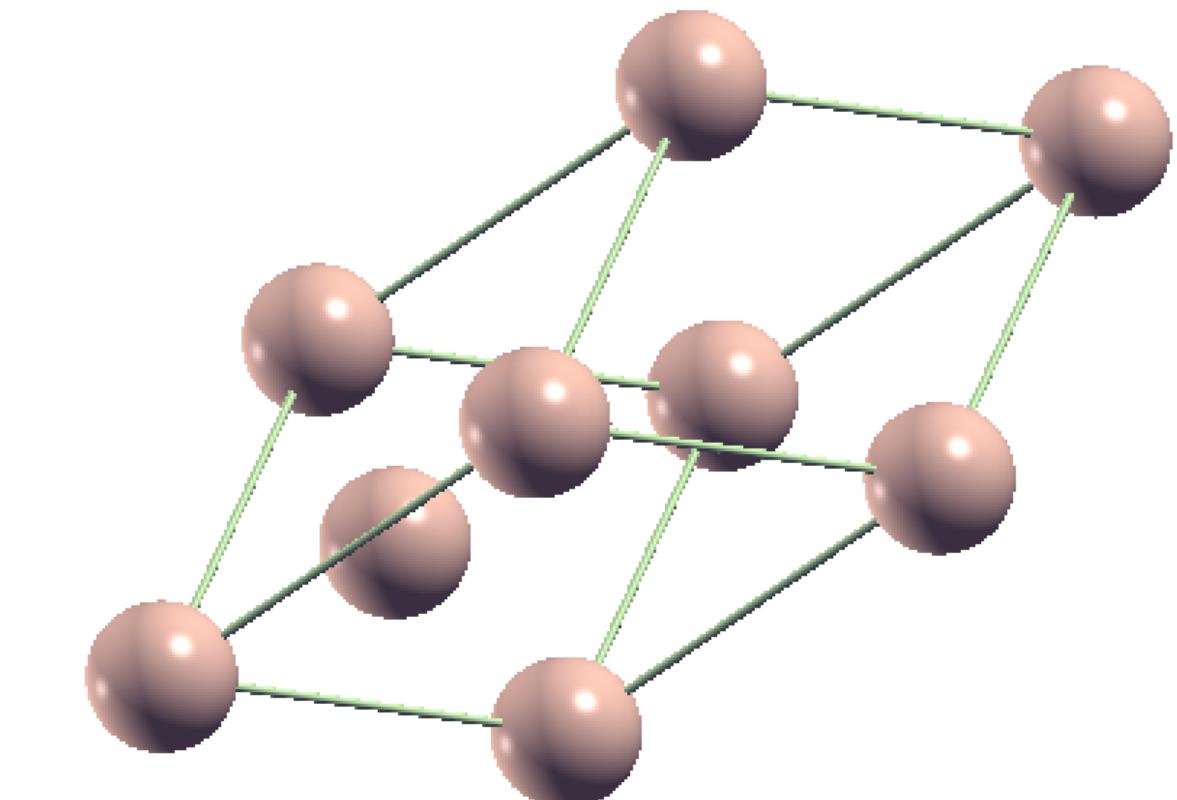
Override the functional written in the pseudopotential (PP) file.  
**Important:** use a PP for the closest GGA (PBE in this case),  
there are no PP's for hybrids.

q-point mesh

1x1x1 is the minimal mesh ( $\mathbf{q}=0$ ), it is fast but not accurate

Treatment of the  $\mathbf{q} + \mathbf{G} = 0$  divergence

Singularity is analytically integrated



## Popular hybrid functionals

input\_dft = "PBE0"

J.P.Perdew, M. Ernzerhof, K.Burke, JCP 105, 9982 (1996)

C. Adamo, V. Barone, JCP 110, 6158 (1999)

input\_dft = "B3LYP"

P.J. Stephens,F.J. Devlin,C.F. Chabalowski,M.J. Frisch, J.Phys.Chem 98, 11623 (1994)

input\_dft = "HSE"

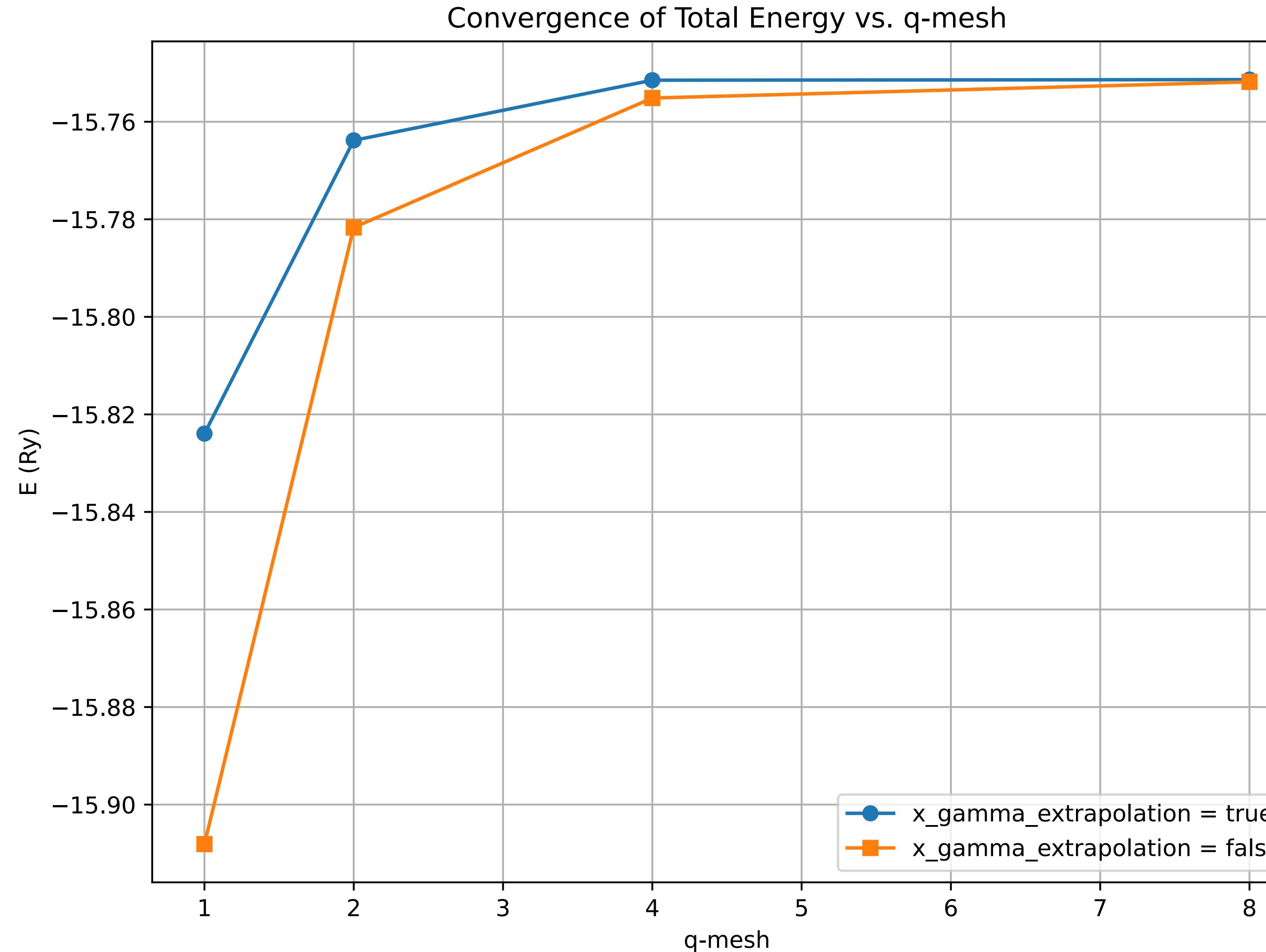
Heyd, Scuseria, Ernzerhof, J. Chem. Phys. 118, 8207 (2003)

Heyd, Scuseria, Ernzerhof, J. Chem. Phys. 124, 219906 (2006)

# Types of treatment of the $\mathbf{q} + \mathbf{G} = 0$ divergence

<b>exxdiv_treatment</b>	CHARACTER
	<i>Default:</i> 'gygi-baldereschi'
Specific for EXX. It selects the kind of approach to be used for treating the Coulomb potential divergencies at small $\mathbf{q}$ vectors.	
' <b>gygi-baldereschi</b> ' :	appropriate for cubic and quasi-cubic supercells
' <b>vcut_spherical</b> ' :	appropriate for cubic and quasi-cubic supercells
' <b>vcut_ws</b> ' :	appropriate for strongly anisotropic supercells, see also <a href="#"><u>ecutvcut</u></a> .
' <b>none</b> ' :	sets Coulomb potential at $\mathbf{G}, \mathbf{q}=0$ to 0.0 (required for GAU-PBE)

# Convergence of the total energy with respect to the q-point mesh

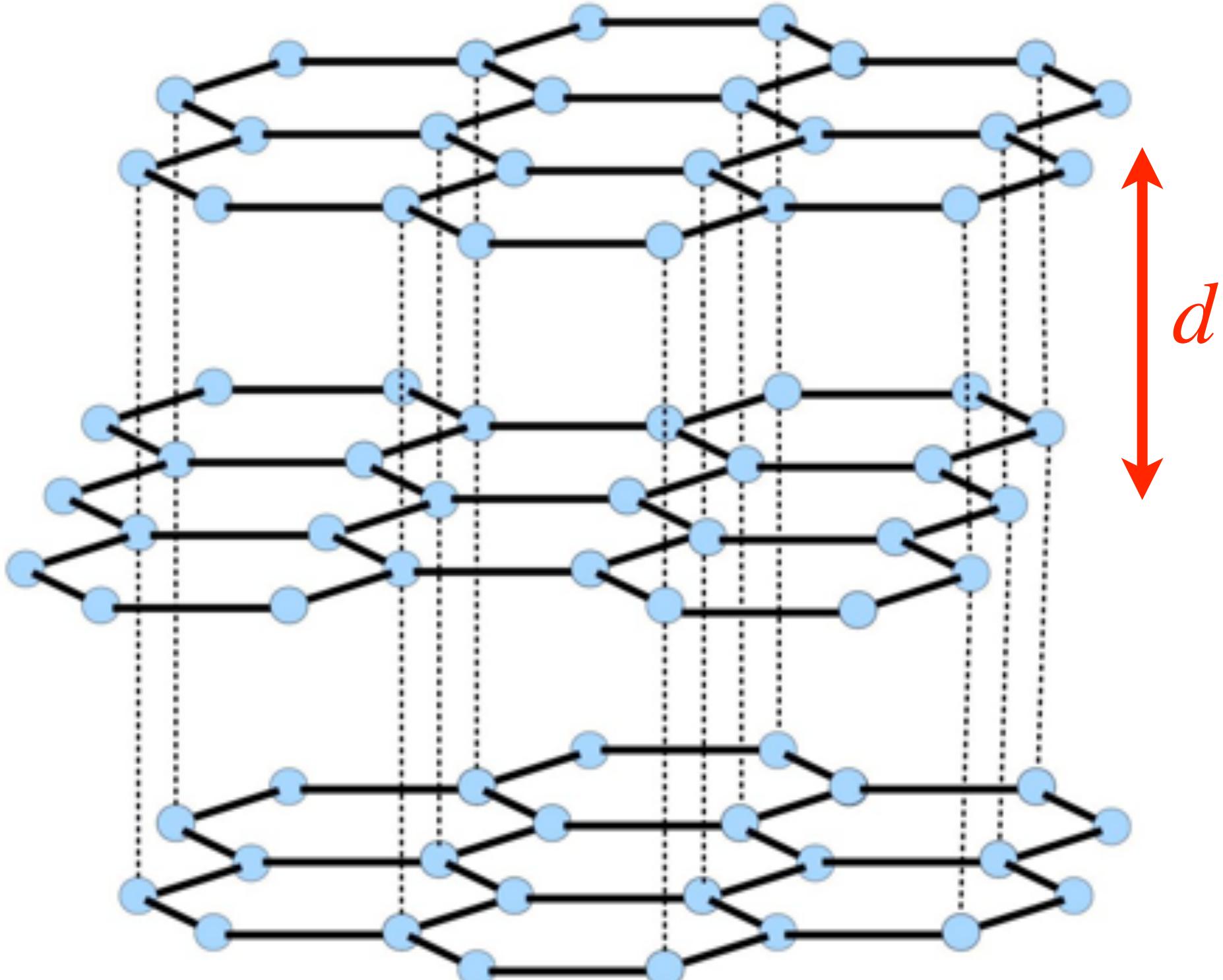


Convergence is faster when `x_gamma_extrapolation = .true.`

## **Exercise 3**

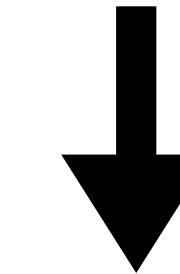
**Van der Waals functionals for graphite**

# Graphite



There are van der Waals (dispersive) interactions between layers in graphite.

The equilibrium inter-layer distance  $d$  is too small within LDA and too large within GGA with respect to the experimental value (3.336 Å).



Van der Waals interactions must be taken into account!

# Input file graphite.vc-relax.in

```
&control
  calculation='vc-relax' ← Variable-cell optimization
  restart_mode='from_scratch',
  prefix='graphite'
  pseudo_dir = '.../.../pseudo'
 outdir='./tmp/'
  verbosity='high'
  etot_conv_thr = 1.0D-5
  forc_conv_thr = 1.0D-4
/
```

```
&system
  ibrav = 4, ← Hexagonal lattice, a and c are in Angstrom!
  a = 2.466,
  c = 6.411,
  nat = 4,
  ntyp = 1,
  ecutwfc = 30.0,
  ecutrho = 240.0,
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.02,
  input_dft = 'vdw-DF' ← Type of the van Der Waals functional (vdw-DF in this case)
/
```

```
&electrons
  conv_thr = 1.d-9
  mixing_beta = 0.3
/
```

```
&ions
/
```

```
&cell
/
```

```
ATOMIC_SPECIES
```

```
  C 12.011 C.pbe-rrkjus.UPF
```

```
ATOMIC_POSITIONS {crystal}
```

C	0.000000	1.000000	0.75000
C	0.666667	0.333333	0.75000
C	0.000000	1.000000	0.25000
C	0.333333	0.666667	0.25000

```
K_POINTS {automatic}
```

```
  4 4 2 1 1 1
```

Variable-cell optimization

Hexagonal lattice, a and c are in Angstrom!

Type of the van Der Waals functional (vdw-DF in this case)

Override the functional written in the PP file.

Important: use PP for the closest GGA (PBE in this case),  
because there are no PP for non-local functionals

The **k** point mesh is denser along X and Y than along Z (in reciprocal space), reflecting shorter periodicity in the XY plane

# Types of the Van der Waals corrections

vdw_corr	CHARACTER
<i>Default:</i>	'none'
<i>See:</i>	<a href="#">london_s6</a> , <a href="#">london_rcut</a> , <a href="#">london_c6</a> , <a href="#">london_rvdw</a> , <a href="#">dftd3_version</a> , <a href="#">dftd3_threebody</a> , <a href="#">ts_vdw_econv_thr</a> , <a href="#">ts_vdw_isolated</a> , <a href="#">xdm_a1</a> , <a href="#">xdm_a2</a>
Type of Van der Waals correction. Allowed values:	
'grimme-d2', 'Grimme-D2', 'DFT-D', 'dft-d' : Semiempirical Grimme's DFT-D2. Optional variables: <a href="#">london_s6</a> , <a href="#">london_rcut</a> , <a href="#">london_c6</a> , <a href="#">london_rvdw</a> S. Grimme, J. Comp. Chem. 27, 1787 (2006), <a href="https://doi.org/10.1002/jcc.20495">doi:10.1002/jcc.20495</a> V. Barone et al., J. Comp. Chem. 30, 934 (2009), <a href="https://doi.org/10.1002/jcc.21112">doi:10.1002/jcc.21112</a>	
'grimme-d3', 'Grimme-D3', 'DFT-D3', 'dft-d3' : Semiempirical Grimme's DFT-D3. Optional variables: <a href="#">dftd3_version</a> , <a href="#">dftd3_threebody</a> S. Grimme et al, J. Chem. Phys 132, 154104 (2010), <a href="https://doi.org/10.1063/1.3382344">doi:10.1063/1.3382344</a>	
'TS', 'ts', 'ts-vdw', 'ts-vdW', 'tkatchenko-scheffler' : Tkatchenko-Scheffler dispersion corrections with first-principle derived C6 coefficients. Optional variables: <a href="#">ts_vdw_econv_thr</a> , <a href="#">ts_vdw_isolated</a> See A. Tkatchenko and M. Scheffler, <a href="#">PRL 102, 073005 (2009)</a> .	
'MBD', 'mbd', 'many-body-dispersion', 'mbd_vdw' : Many-body dipersion (MBD) correction to long-range interactions. Optional variables: <a href="#">ts_vdw_isolated</a> A. Ambrosetti, A. M. Reilly, R. A. DiStasio, A. Tkatchenko, J. Chem. Phys. 140 18A508 (2014).	
'XDM', 'xdm' : Exchange-hole dipole-moment model. Optional variables: <a href="#">xdm_a1</a> , <a href="#">xdm_a2</a> A. D. Becke et al., J. Chem. Phys. 127, 154108 (2007), <a href="https://doi.org/10.1063/1.2795701">doi:10.1063/1.2795701</a> A. Otero de la Roza et al., J. Chem. Phys. 136, 174109 (2012), <a href="https://doi.org/10.1063/1.4705760">doi:10.1063/1.4705760</a>	
Note that non-local functionals (eg vdw-DF) are NOT specified here but in <a href="#">input_dft</a>	

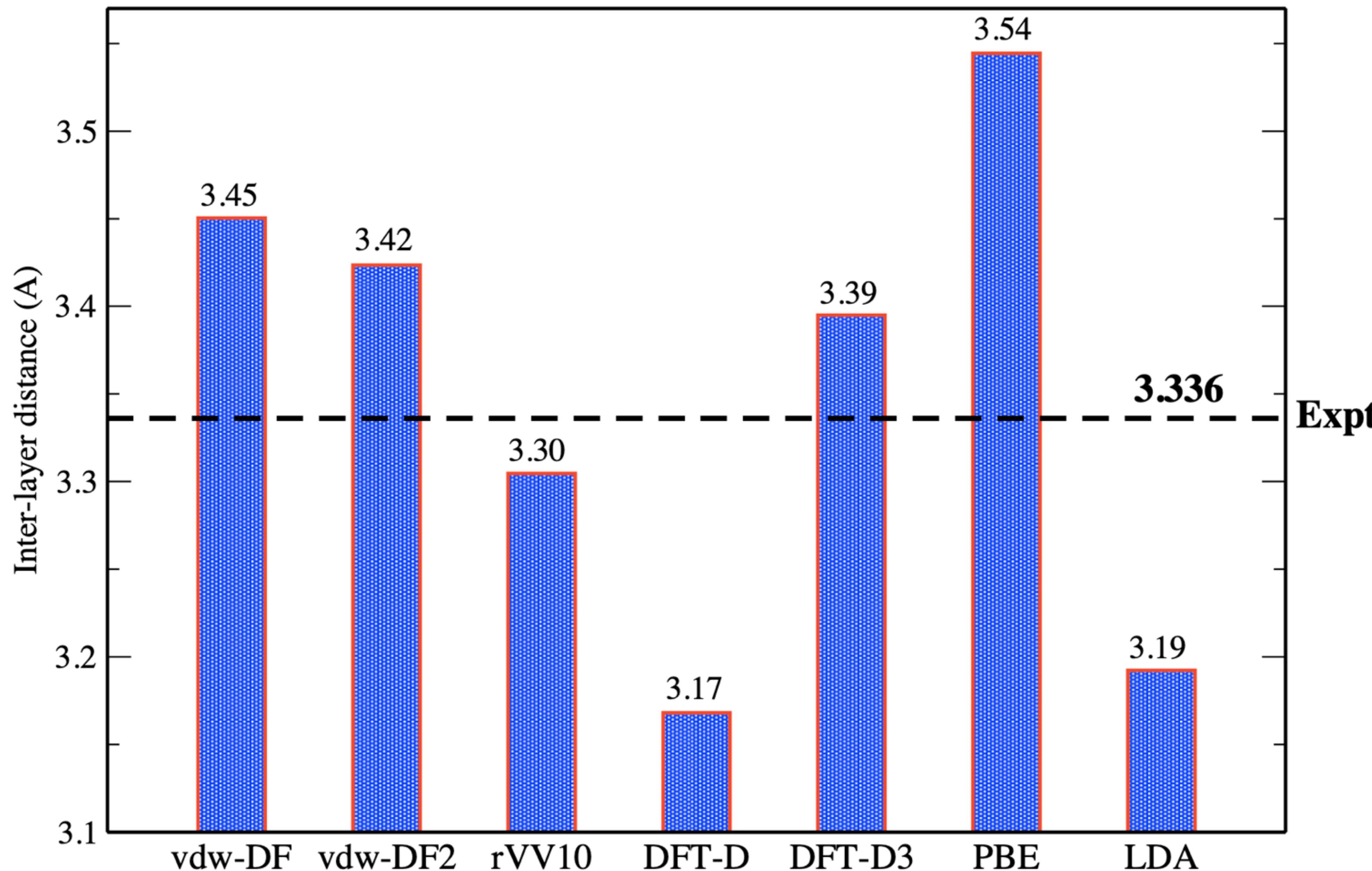
# Structural optimization of graphite

Study different cases:

1. input_dft = 'vdw-DF'	@PBE pseudo (non-local)	C.pbe-rrkjus.UPF
2. input_dft = 'vdw-DF2'	@PBE pseudo (non-local)	C.pbe-rrkjus.UPF
3. input_dft = 'rVV10'	@PBE pseudo (non-local)	C.pbe-rrkjus.UPF
4. vdw_corr = 'DFT-D'	@PBE pseudo (semi-empirical)	C.pbe-rrkjus.UPF
5. vdw_corr = 'DFT-D3'	@PBE pseudo (semi-empirical)	C.pbe-rrkjus.UPF
6. Normal PBE calculation	@PBE pseudo	C.pbe-rrkjus.UPF
7. Normal LDA calculation	@LDA pseudo	C.pz-rrkjus.UPF

Use XCrySDen (outside the Docker) to determine the inter-layer distances after the optimization

# Inter-layer distance in graphite



**Note:** these results must be carefully converged (cutoff, k points, etc.)

## **Exercise 4**

**meta-GGA for Si and Fe**

# Input file

```
&control
  calculation='scf'
  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 = 40.0, ←
  input_dft = 'SCAN' ←
  nbnd = 5
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Si 28.086 Si.SCAN.UPF ←
ATOMIC_POSITIONS {alat}
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25
K_POINTS {automatic}
12 12 12 0 0 0
```

Experimental lattice parameter

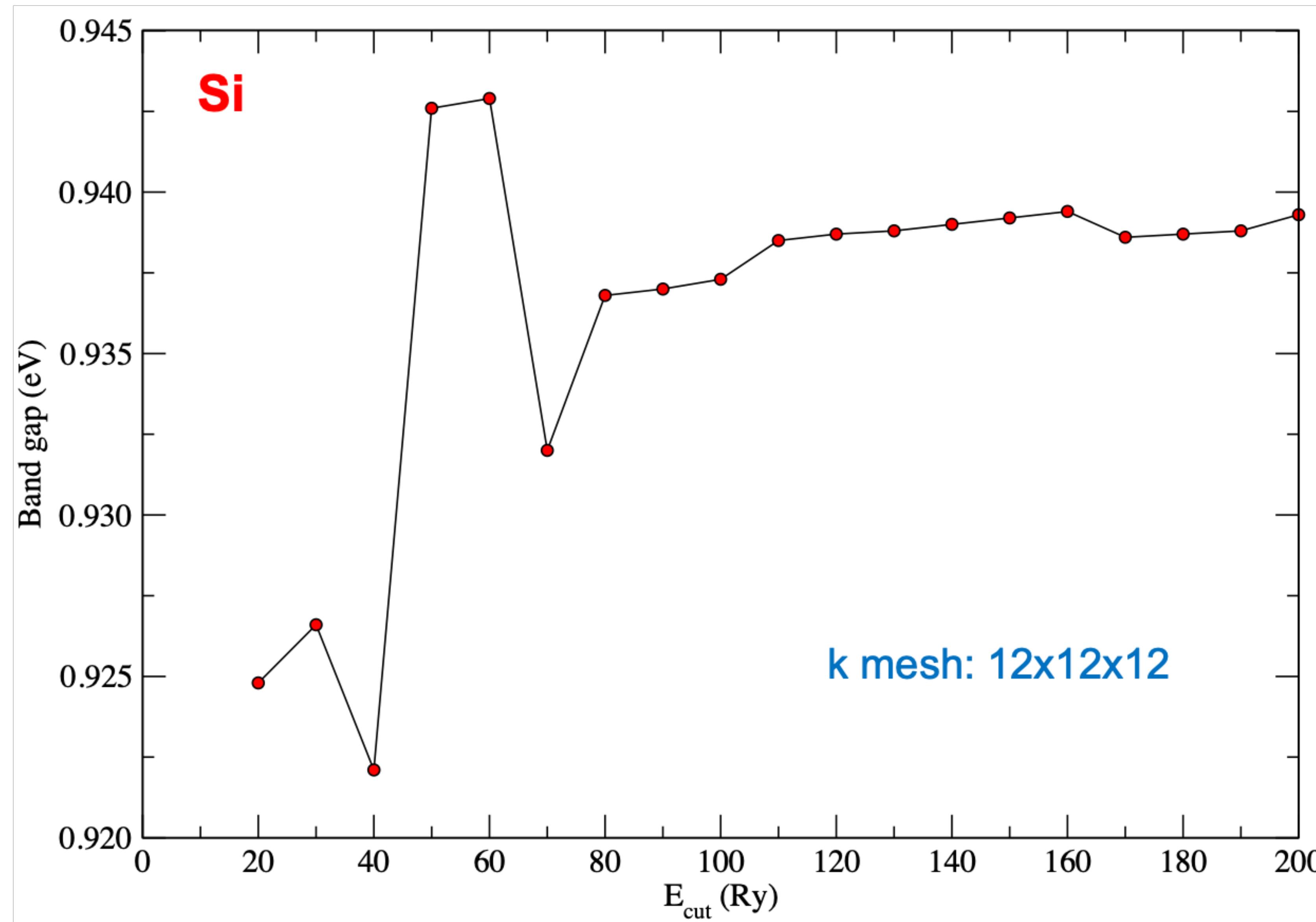
It is necessary to perform convergence tests w.r.t ecutwfc

Set up the SCAN functional from the input  
Quantum ESPRESSO must be compiled with Libxc

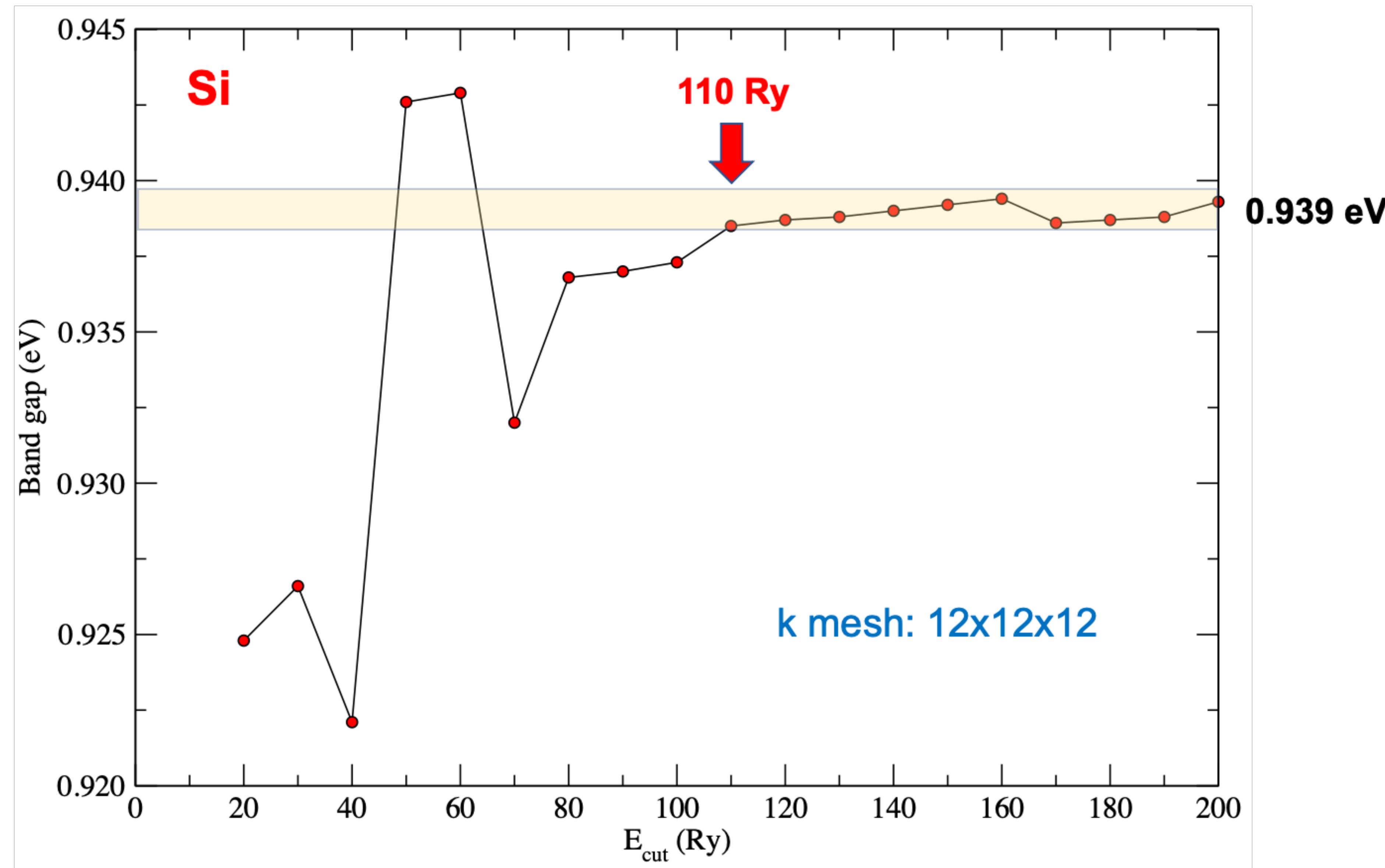
Pseudopotential generated using the SCAN functional

<https://yaoyi92.github.io/scan-tm-pseudopotentials.html>

# SCAN functional & SCAN pseudopotential



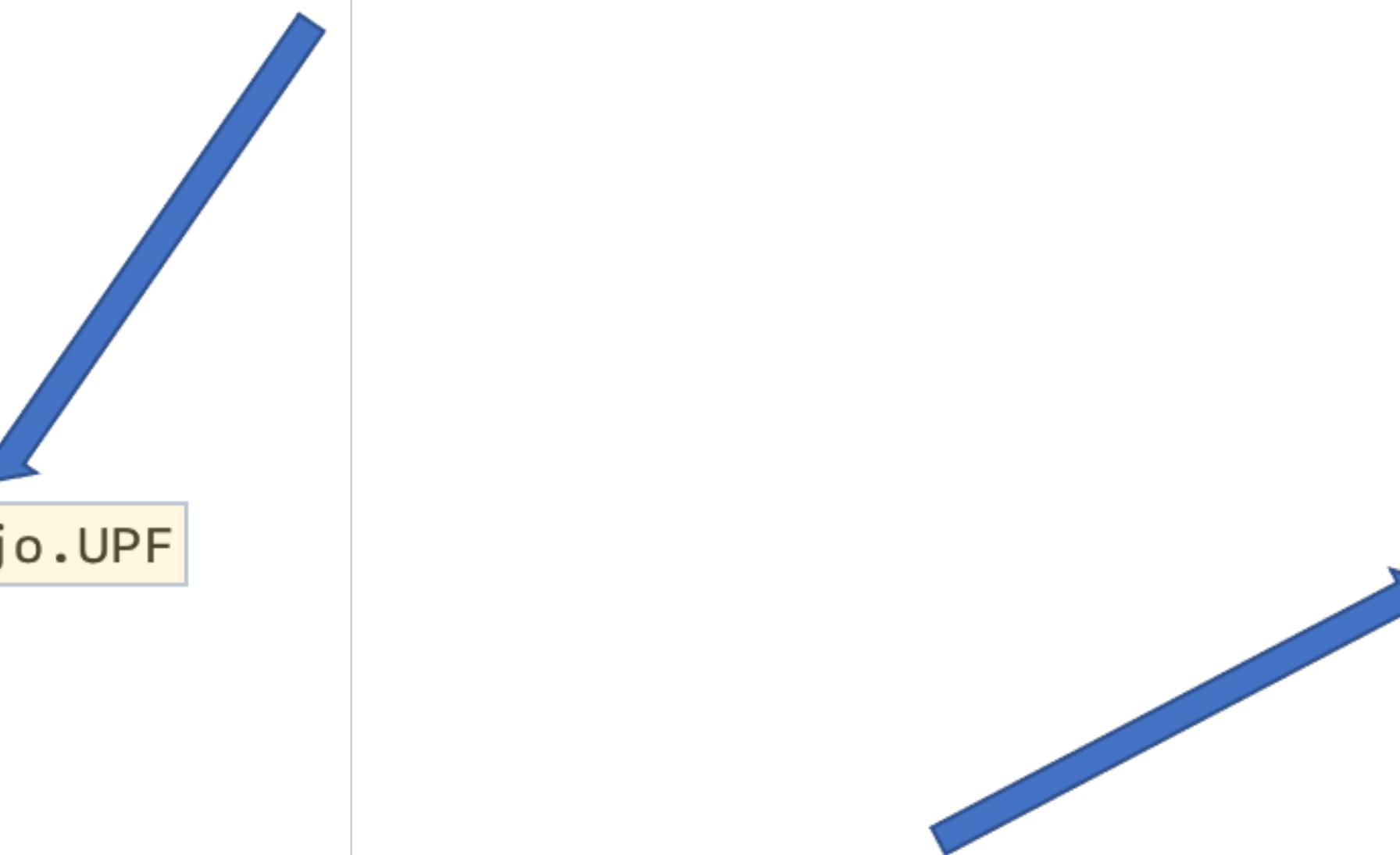
# SCAN functional & SCAN pseudopotential



# SCAN functional & PBE pseudopotential

```
&control
  calculation='scf'
  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 = 110.0,
  input_dft = 'SCAN'
  nbnd = 5
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Si 28.086 Si.pbe_PseudoDojo.UPF
ATOMIC_POSITIONS {alat}
  Si 0.00 0.00 0.00
  Si 0.25 0.25 0.25
K_POINTS {automatic}
  12 12 12 0 0 0
```

Pseudo Dojo library  
<http://www.pseudo-dojo.org>



SG15 library

[http://www.quantum-simulation.org/potentials/sg15\\_oncv/](http://www.quantum-simulation.org/potentials/sg15_oncv/)

```
&control
  calculation='scf'
  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 = 110.0,
  input_dft = 'SCAN'
  nbnd = 5
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Si 28.086 Si_ONCV_PBE-1.2.upf
ATOMIC_POSITIONS {alat}
  Si 0.00 0.00 0.00
  Si 0.25 0.25 0.25
K_POINTS {automatic}
  12 12 12 0 0 0
```

## SCAN functional with different pseudopotentials

Ecut = 110 (Ry), k mesh: 12x12x12

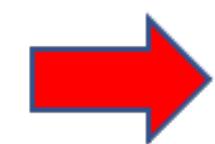
Functional	Pseudopotential	Library	Gap (eV)
SCAN	SCAN	Yi Yao's library	0.94
SCAN	PBE	SG15 ONCV	0.83
SCAN	PBE	Pseudo Dojo	0.64

Gap<sub>expt</sub> = 1.17 (eV)

## SCAN functional with different pseudopotentials

Ecut = 110 (Ry), k mesh: 12x12x12

Functional	Pseudopotential	Library	Gap (eV)
SCAN	SCAN	Yi Yao's library	0.94
SCAN	PBE	SG15 ONCV	0.83
SCAN	PBE	Pseudo Dojo	0.64



Gap<sub>expt</sub> = 1.17 (eV)

Currently, nonlinear core correction (NLCC) is not implemented for meta-GGA in Quantum ESPRESSO!

Pseudopotentials that have NLCC=.true. introduce some inconsistency for meta-GGA calculations.

NLCC=.false.  
NLCC=.false.  
NLCC=.true.

# SCAN functional with different pseudopotentials

Ecut = 110 (Ry), k mesh: 12x12x12

Functional	Pseudopotential	Library	Gap (eV)
SCAN	SCAN	Yi Yao's library	0.94
SCAN	PBE	SG15 ONCV	0.83
SCAN	PBE	Pseudo Dojo	0.64
PBE	PBE	SG15 ONCV	0.56
PBE	PBE	Pseudo Dojo	0.57

Gap<sub>expt</sub> = 1.17 (eV)

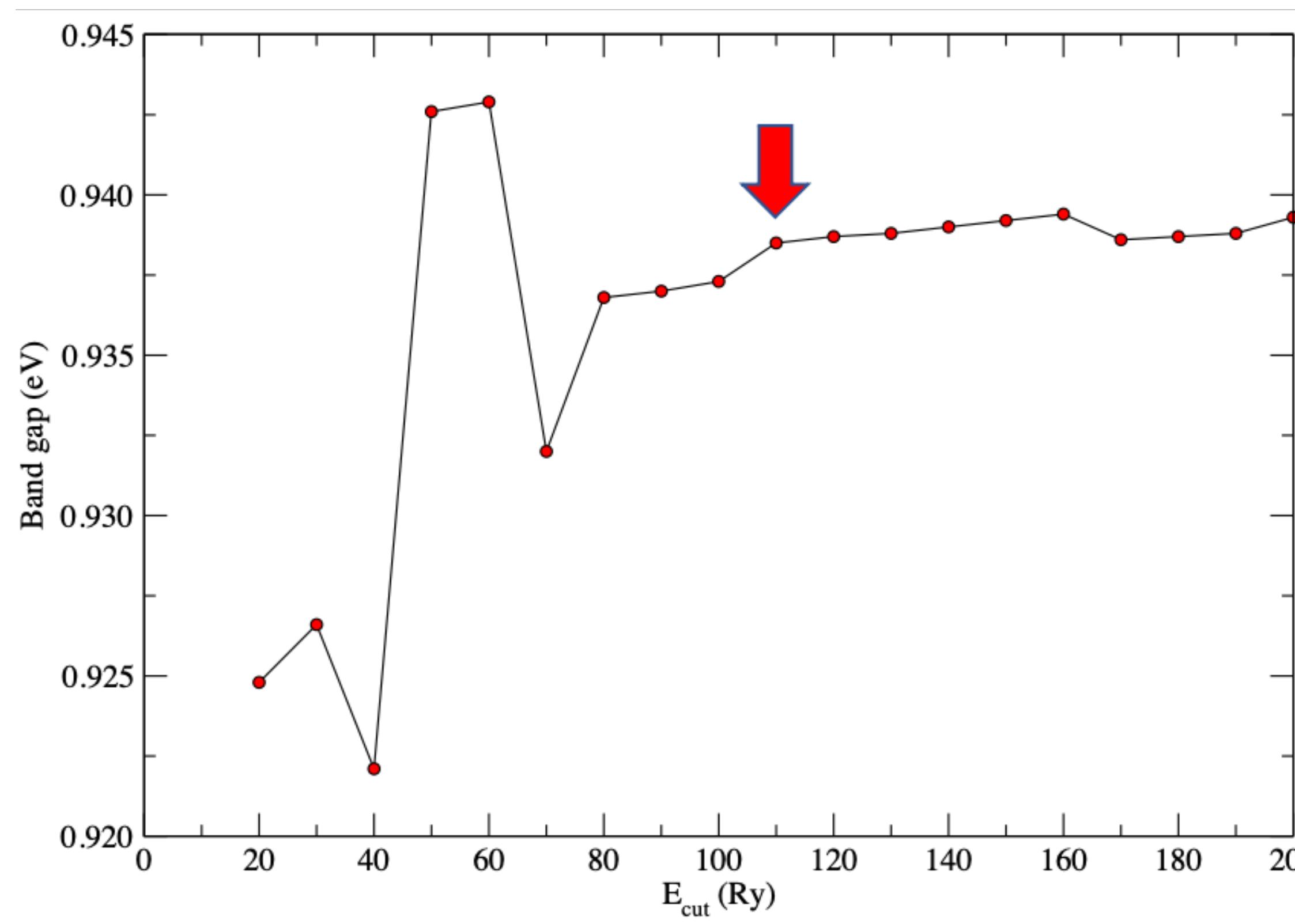
SCAN calculation with the SCAN pseudopotential gives the most accurate results

Y. Yao and Y. Kanai, J. Chem. Phys. **146**, 224105 (2017).

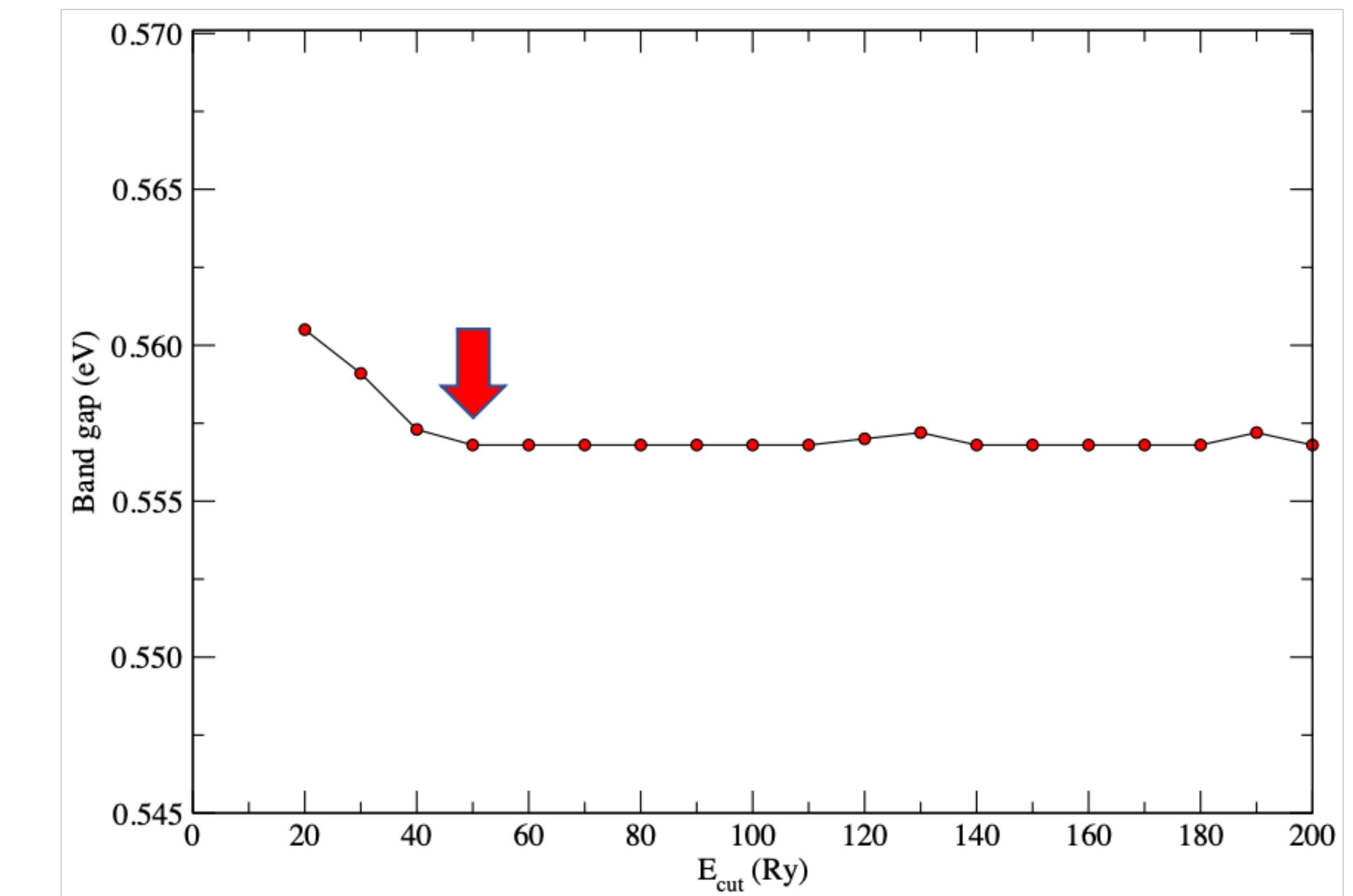
# Convergence with respect to $E_{\text{cut}}$

k mesh: 12x12x12

SCAN with SCAN pseudopotential



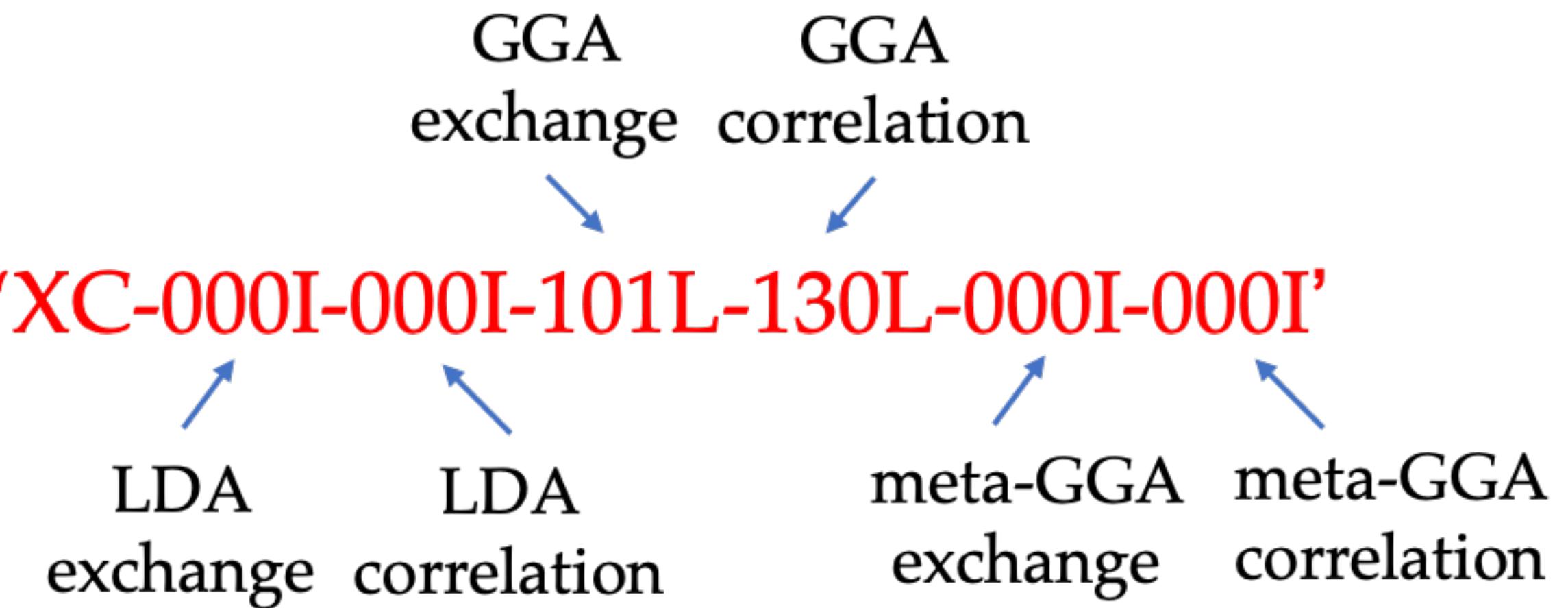
PBE with PBE pseudopotential (SG15)



Convergence is achieved much faster with PBE than with SCAN

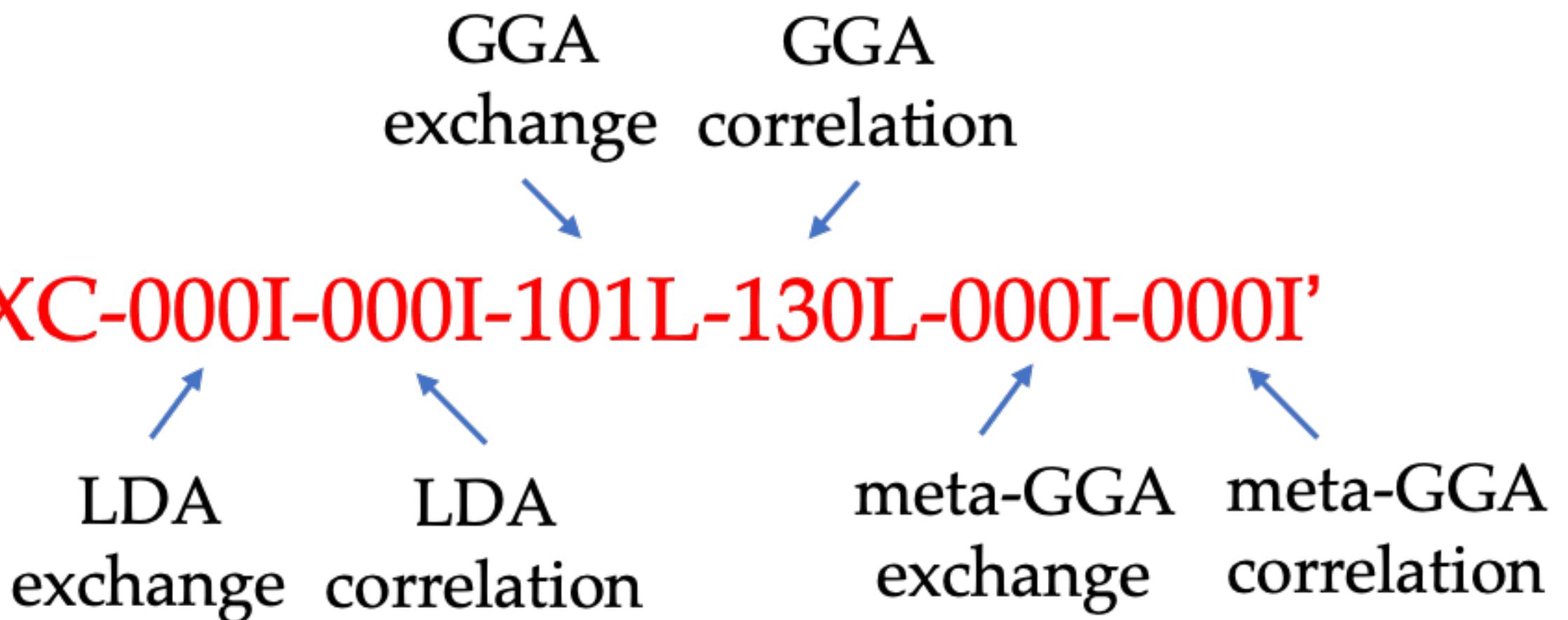
## Setting up the XC functional

`input_dft = 'PBE'` or `input_dft='XC-000I-000I-101L-130L-000I-000I'`



## Setting up the XC functional

`input_dft = 'PBE'` or `input_dft='XC-000I-000I-101L-130L-000I-000I'`



`input_dft = 'SCAN'` or `input_dft='XC-000I-000I-000I-000I-263L-267L'`

no short  
name  
in QE

~~`input_dft = 'rSCAN'` or `input_dft='XC-000I-000I-000I-000I-493L-494L'`~~

`input_dft = 'r2SCAN'` or `input_dft='XC-000I-000I-000I-000I-497L-498L'`

Read more about this here: [https://www.quantum-espresso.org/Doc/user\\_guide/node13.html](https://www.quantum-espresso.org/Doc/user_guide/node13.html)

Libxc with IDs: <https://libxc.gitlab.io/>

# Different flavors of SCAN

Functional	Pseudopotential	Library	Gap (eV)
SCAN	PBE	SG15 ONCV	0.83
rSCAN	PBE	SG15 ONCV	0.71
$r^2$ SCAN	PBE	SG15 ONCV	0.70

$$\text{Gap}_{\text{expt}} = 1.17 \text{ (eV)}$$

SCAN is more accurate than rSCAN and  $r^2$ SCAN for predicting the band gap of bulk Si  
(at least when using the PBE pseudopotential)

# Input file

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='Fe'
  pseudo_dir = ' ../../pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 3,
  celldm(1) = 5.418,                                ← Experimental lattice parameter
  nat = 1,
  ntyp = 1,
  ecutwfc = 50.0,                                     ← It is necessary to perform convergence tests w.r.t ecutwfc
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.02,
  nspin = 2,
  starting_magnetization(1) = 0.5,
  input_dft = 'SCAN'                                   ← Set up the SCAN functional from the input
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Fe 55.845 Fe_ONCV_PBE-1.2.upf                    ← Pseudopotential generated using the PBE functional
ATOMIC_POSITIONS {crystal}
Fe 0.000000 0.000000 0.000000
K_POINTS {automatic}
20 20 20 0 0 0
```

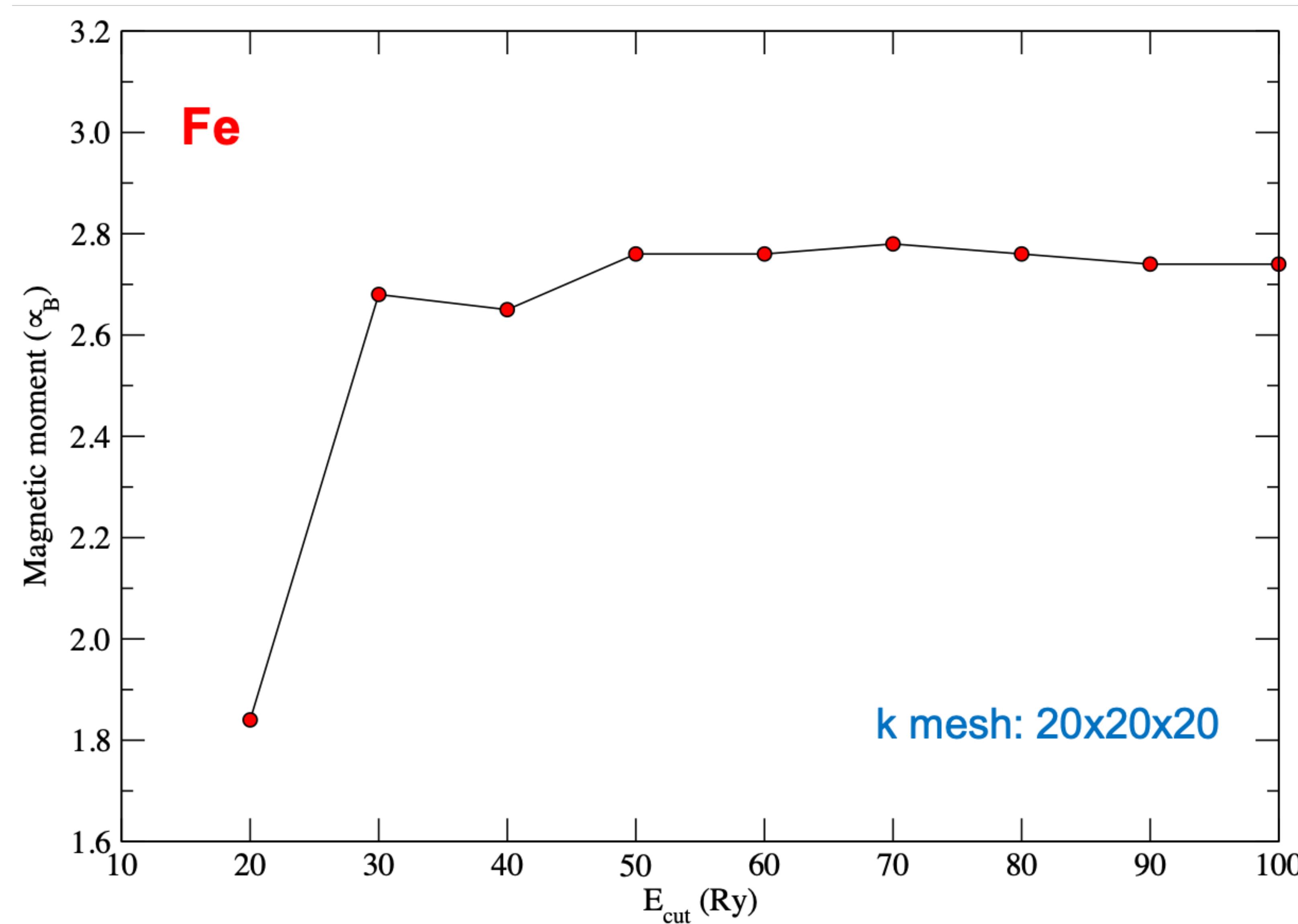
Experimental lattice parameter

It is necessary to perform convergence tests w.r.t ecutwfc

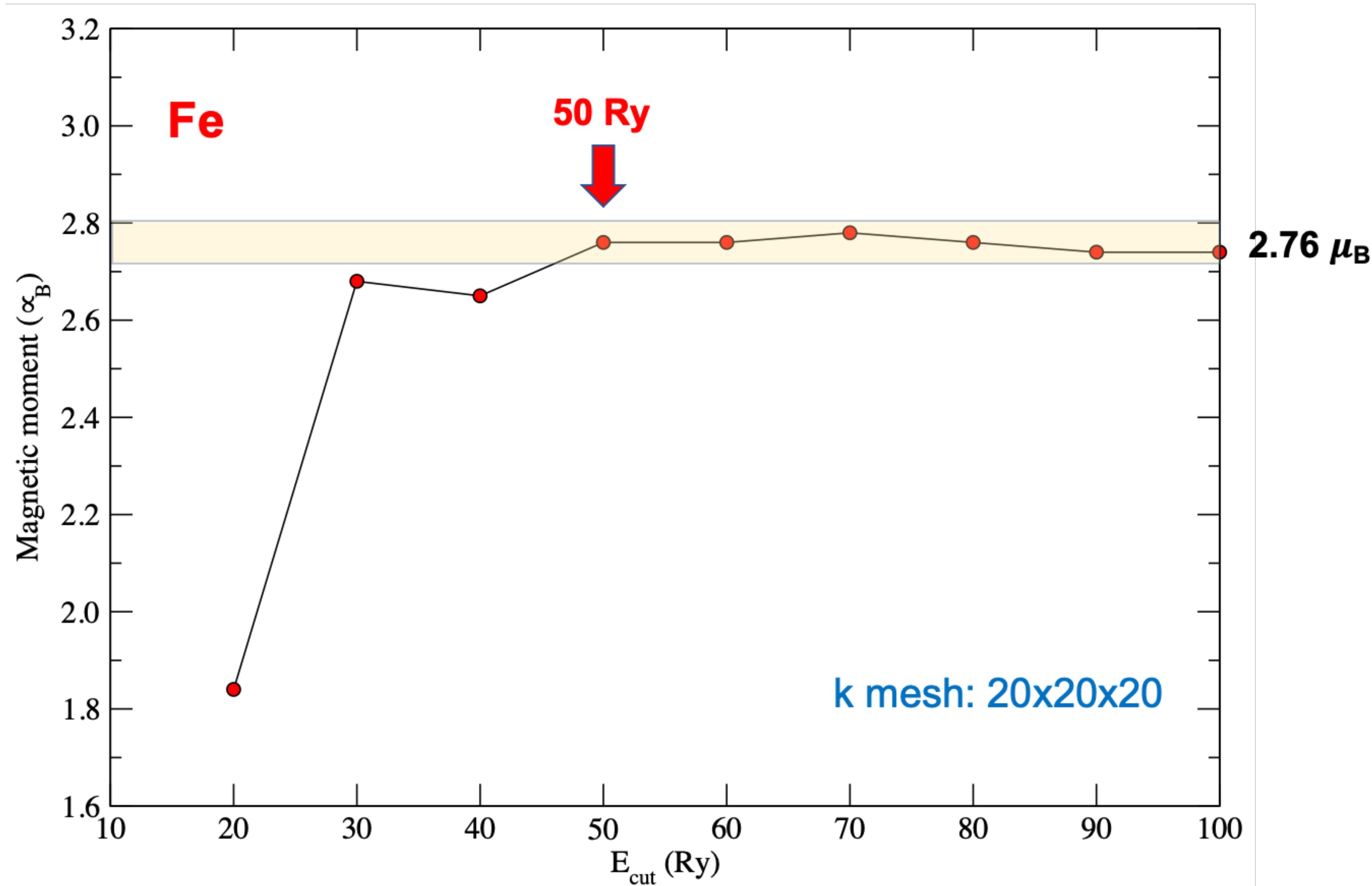
Set up the SCAN functional from the input  
Quantum ESPRESSO must be compiled with Libxc

Pseudopotential generated using the PBE functional  
SG15 ONCV library (there is no SCAN pseudo for Fe)

# SCAN functional & PBE pseudopotential (SG15)



# SCAN functional & PBE pseudopotential (SG15)



# SCAN functional with different pseudopotentials

Ecut = 50 (Ry), k mesh: 20x20x20

WARNING →

Functional	Pseudopotential	Library	$m (\mu_B)$	
SCAN	PBE	SG15 ONCV	2.76	NLCC=.false.
SCAN	PBE	Pseudo Dojo	2.67	NLCC=.true.
PBE	PBE	SG15 ONCV	2.28	
PBE	PBE	Pseudo Dojo	2.26	

$$m_{\text{expt}} = 1.98 - 2.13 (\mu_B)$$

SCAN overestimates magnetic moments in itinerant ferromagnets

PBE is in closer agreement with experiments than SCAN for magnetic moments of itinerant ferromagnets

## Different flavors of SCAN

Functional	Pseudopotential	Library	$m (\mu_B)$
SCAN	PBE	SG15 ONCV	2.76
rSCAN	PBE	SG15 ONCV	2.73
$r^2$ SCAN	PBE	SG15 ONCV	2.73

$$m_{\text{expt}} = 1.98 - 2.13 (\mu_B)$$

Different flavors of SCAN give very similar magnetic moments for bulk Fe