

# Hands-on: Advanced functionals

Presenter: Iurii Timrov

Tutors: Alberto Carta, Musa Hussien, Garu Gebreyesus, and others



# **Exercise 1**

**DFT+*U* for CoO**

Check README.md how to run the calculations

```
pw.x < Co0.scf.in |tee Co0.scf.out
```

```
pw.x < Co0.nscf.in |tee Co0.nscf.out
```

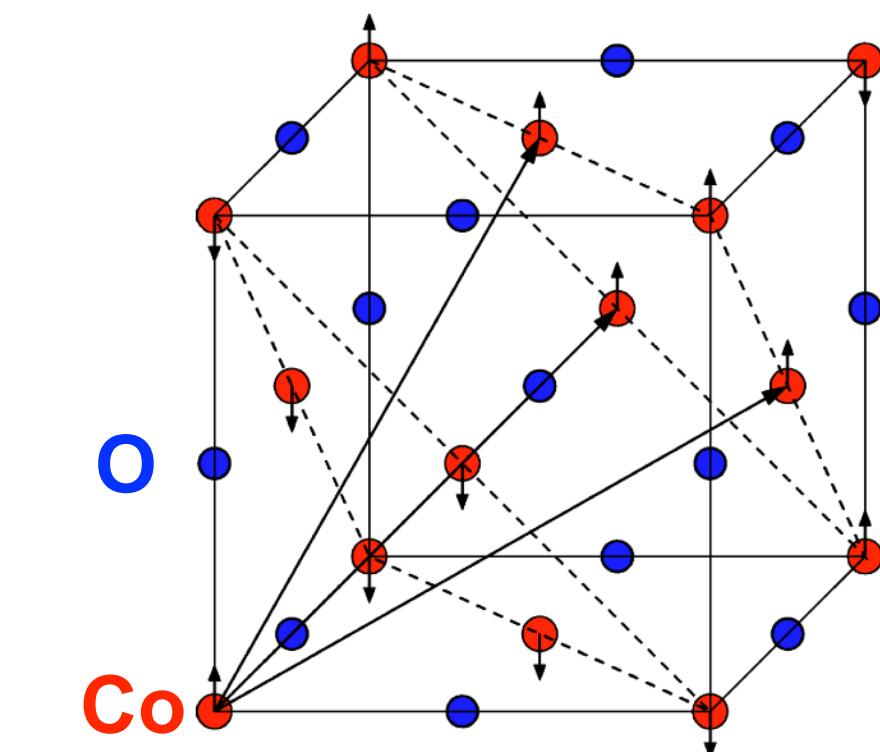
```
projwfc.x < Co0.projwfc.in |tee Co0.projwfc.out
```

```
gnuplot plot_pdos.gp
```

```
evince Co0_PDOS.eps
```

# 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

Quantum ESPRESSO input generator and structure visualizer

- ▶ About the Quantum ESPRESSO input generator and structure visualizer
- ▶ Instructions
- ▶ Acknowledgements

## Upload your structure

Upload a crystal structure:  no file selected

Select here the file format:  Quantum ESPRESSO input [parser: qetools]

Select here the pseudopotential library:  SSSP Efficiency PBEsol (version 1.1)

Select here the magnetism/smearing:  non-magnetic metal (fractional occupations)

Select here the k-points distance (1/Å)  fine (0.20 1/Å, 0.2 eV)

(and smearing (eV) in case of fractional occupations):

Refine cell (using spglib):  No

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

[Generate the PWscf input file](#)

## Otherwise, pick an example

Select here a structure:  Al

Select here the pseudopotential library:  SSSP Efficiency PBEsol (version 1.1)

Select here the magnetism/smearing:  non-magnetic metal (fractional occupations)

Select here the k-points distance (1/Å)  fine (0.20 1/Å, 0.2 eV)

(and smearing (eV) in case of fractional occupations):

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

[Generate the PWscf input file](#)

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

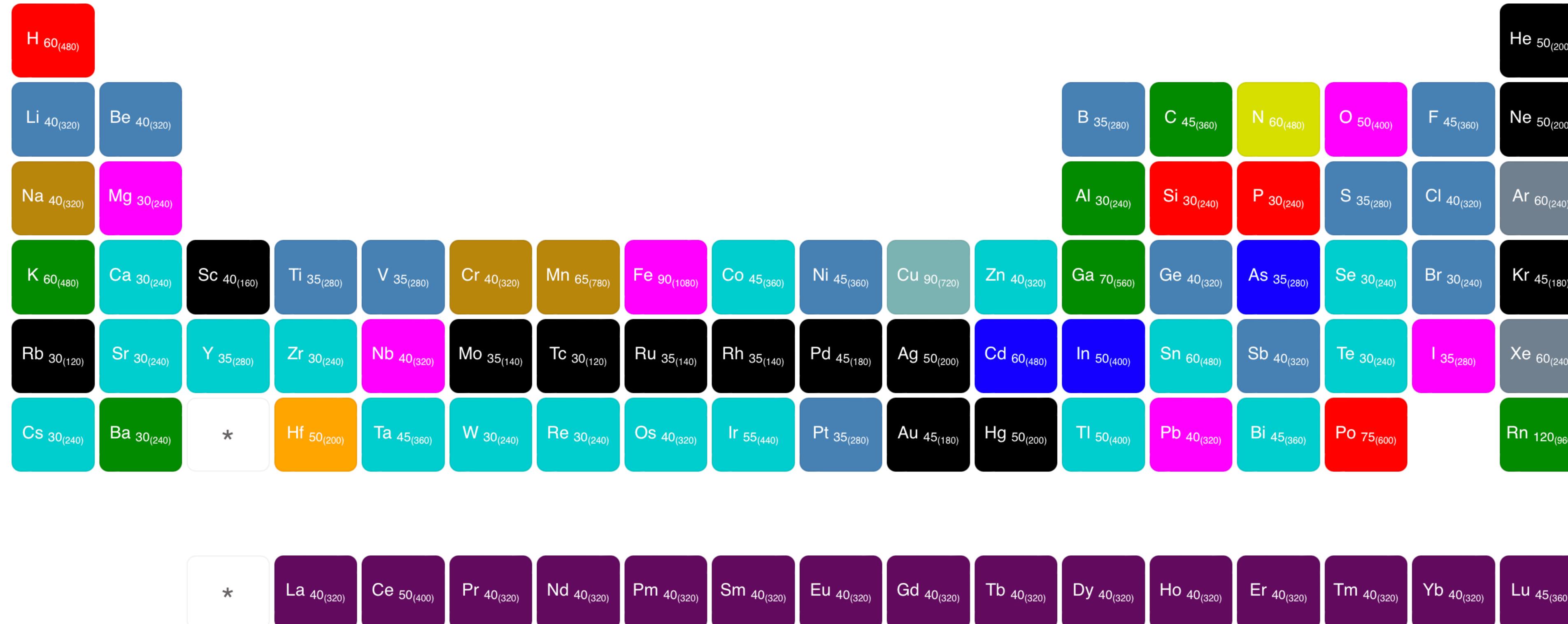
# SSSP pseudopotential library

## SSSP Efficiency (version 1.2.1)

$$\Delta_{\text{eff}} = 0.44 \text{ meV}$$

Note: The Ir (Iridium) pseudopotential of efficiency library has a ghost state at ~10 eV above fermi energy, please use it with caution.

[Cutoffs table](#)  [Pseudos](#) [Switch to SSSP Precision](#)



<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, ← Minimum and maximum energy for the plot (in eV)
    Emax = 30.0, ←
    DeltaE = 0.01 ← Energy grid step
/

```

## Gnuplot script: plot\_pdos.gp

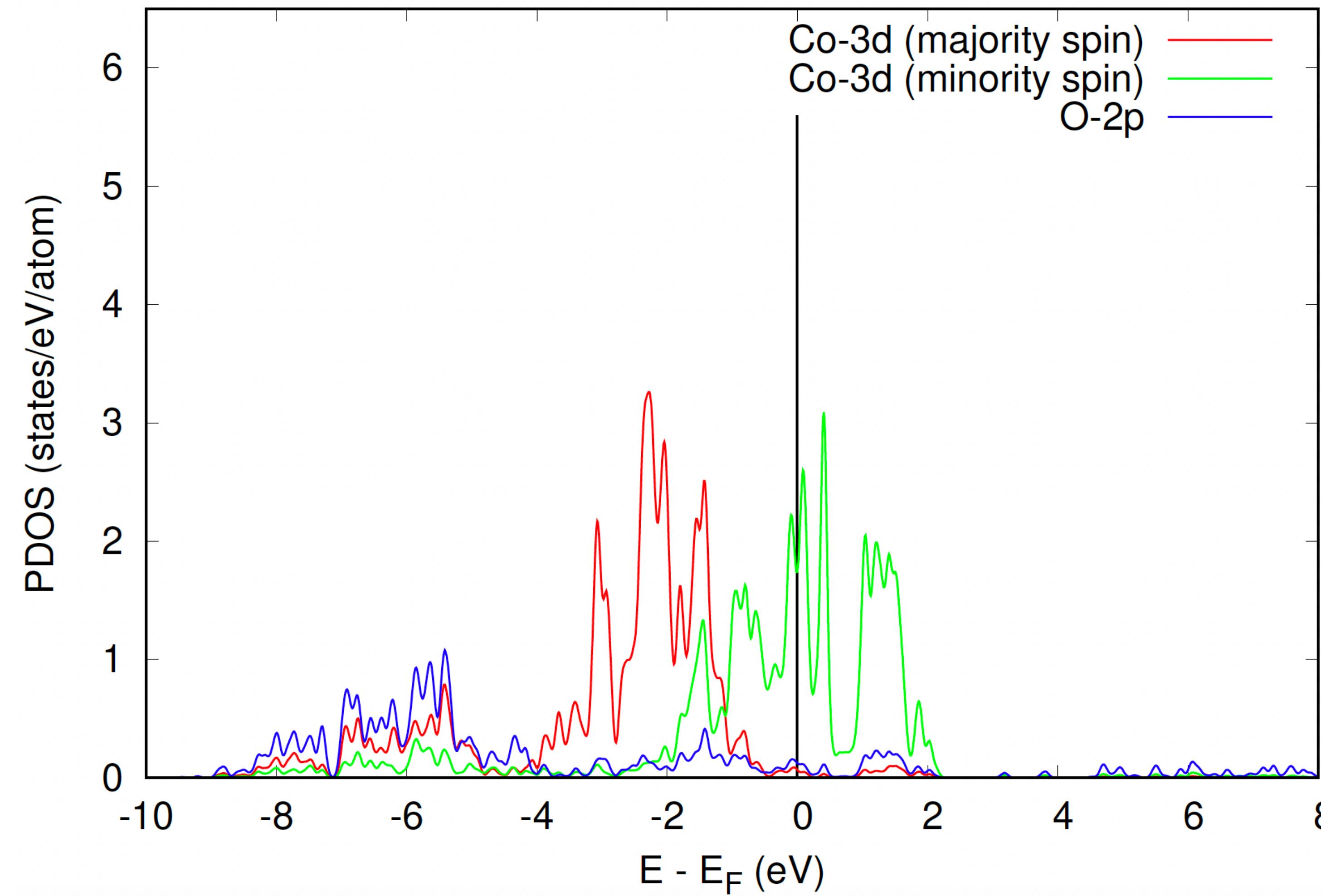
Inspect the script. It aims at plotting Co-3d states (majority spin and minority spin) and O-2p states.

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

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

Try to use xFroggie to plot the PDOS: <https://xfroggie.com/>

# 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

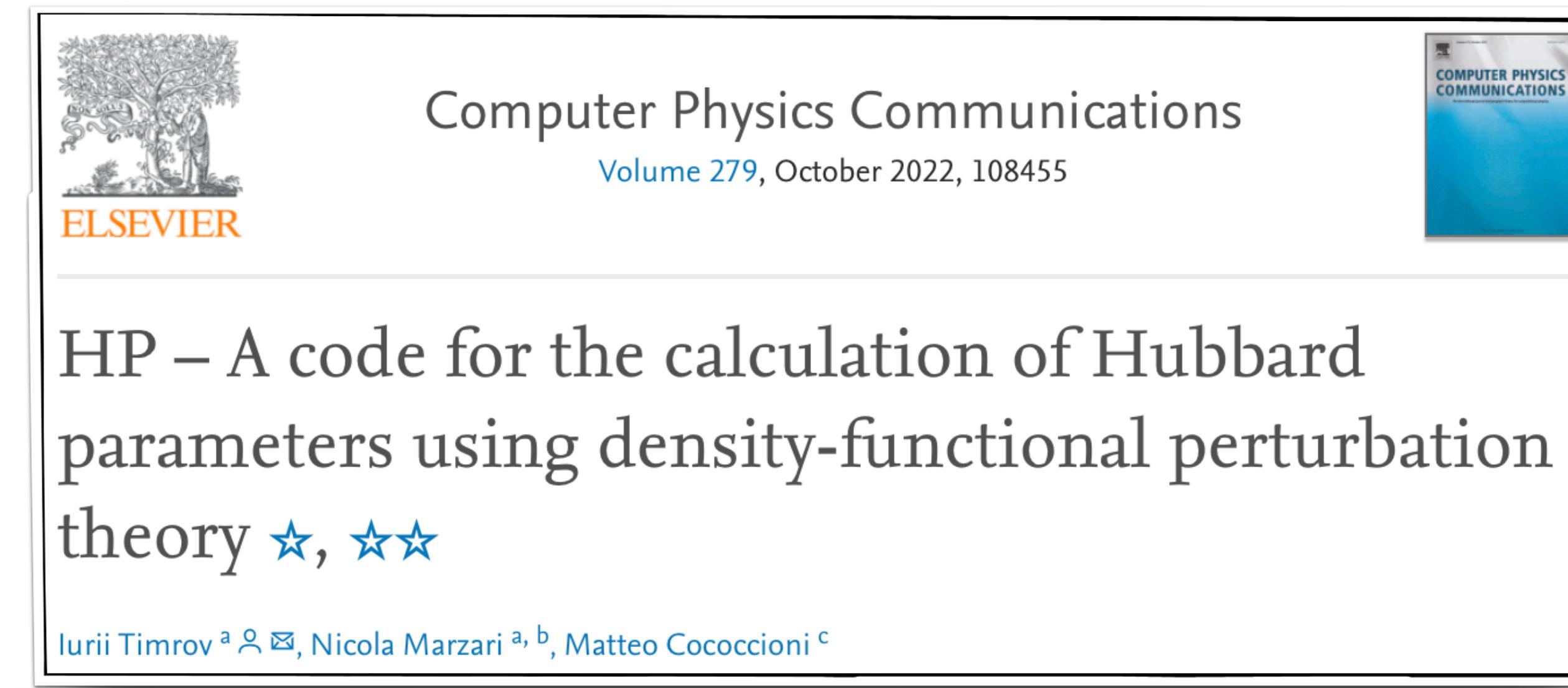
We set some small initial value  
just to activate the Hubbard machinery in the code

Value of the Hubbard  
parameter (in eV)

# Input file CoO.hp.in

```
&inputhp
```

```
prefix = 'CoO'  
outdir = './tmp' ← The same as in the CoO.scf.in input  
nq1 = 2, nq2 = 2, nq3 = 2 ← Size of the q points mesh  
conv_thr_chi = 1.d-6 ← Convergence threshold for computing the self-consistent  
/ response matrix  $\chi$  (in eV-1)
```



**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)*.

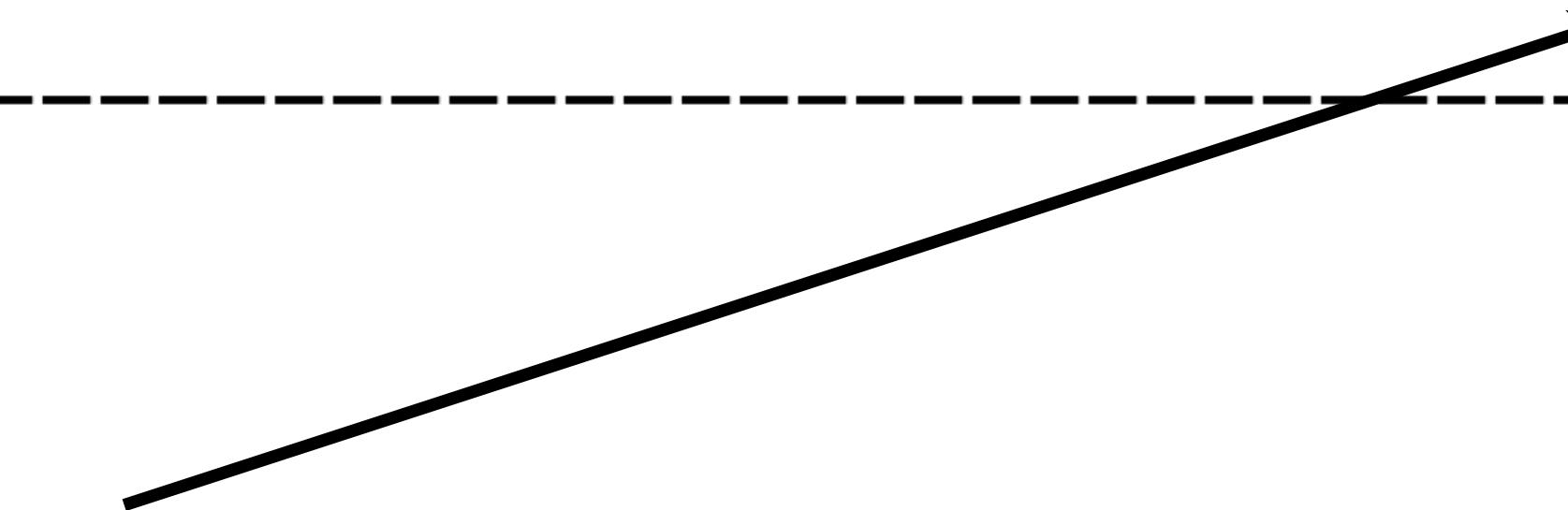
# Output file CoO.Hubbard\_parameters.dat

=====

## 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

=====



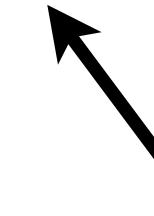
These are the output Hubbard  $U$  parameters for Co1-3d and Co2-3d states

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
/

```

## Gnuplot script: plot\_pdos.gp

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

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

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

Try to use xFroggie to plot the PDOS: <https://xfroggie.com/>

## Run the calculations

```
pw.x < Co0.scf.in |tee Co0.scf.out
```

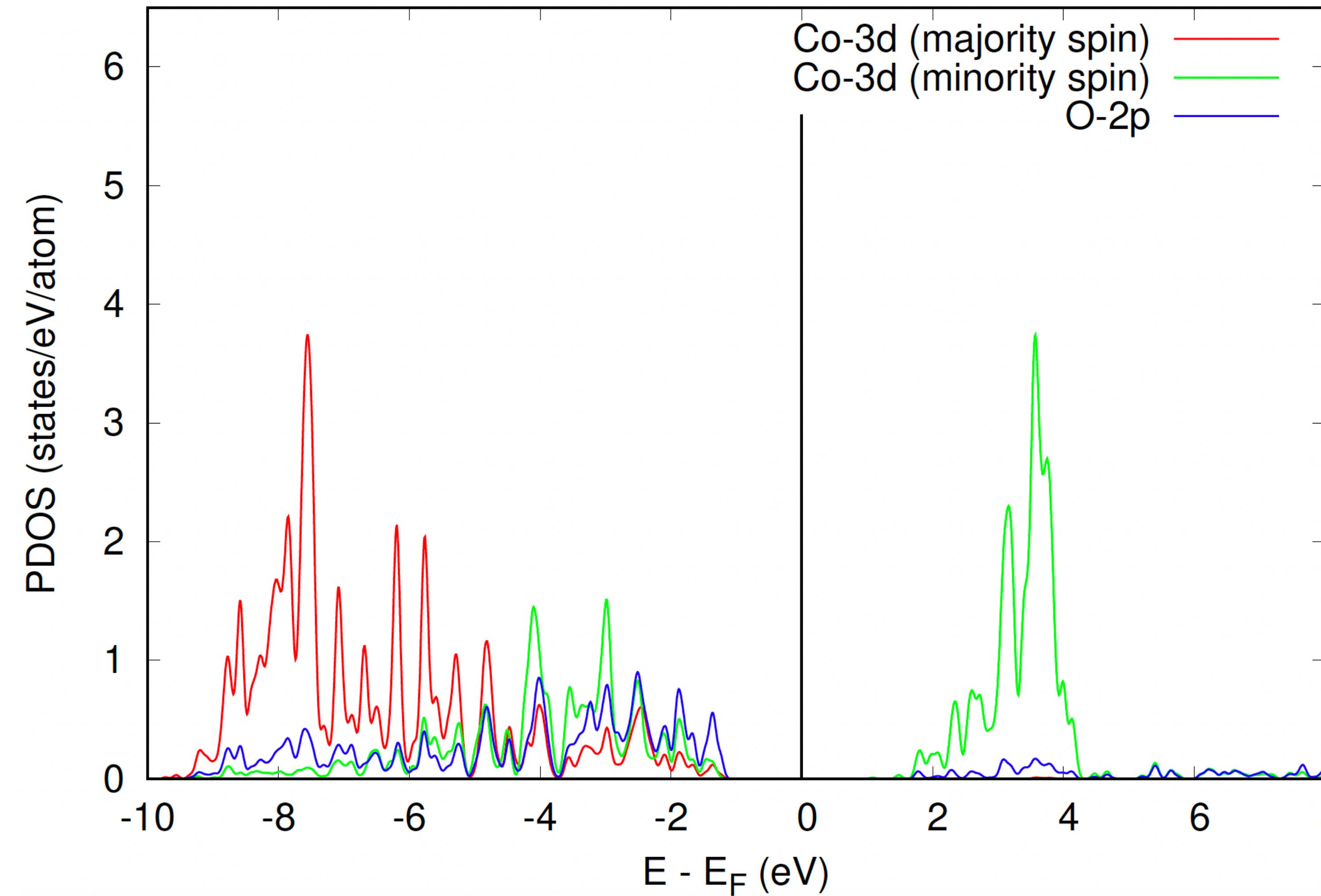
```
pw.x < Co0.nscf.in |tee Co0.nscf.out
```

```
projwfc.x < Co0.projwfc.in |tee Co0.projwfc.out
```

```
gnuplot plot_pdos.gp
```

```
evince Co0_PDOS.eps
```

# PDOS using DFT+ $U$

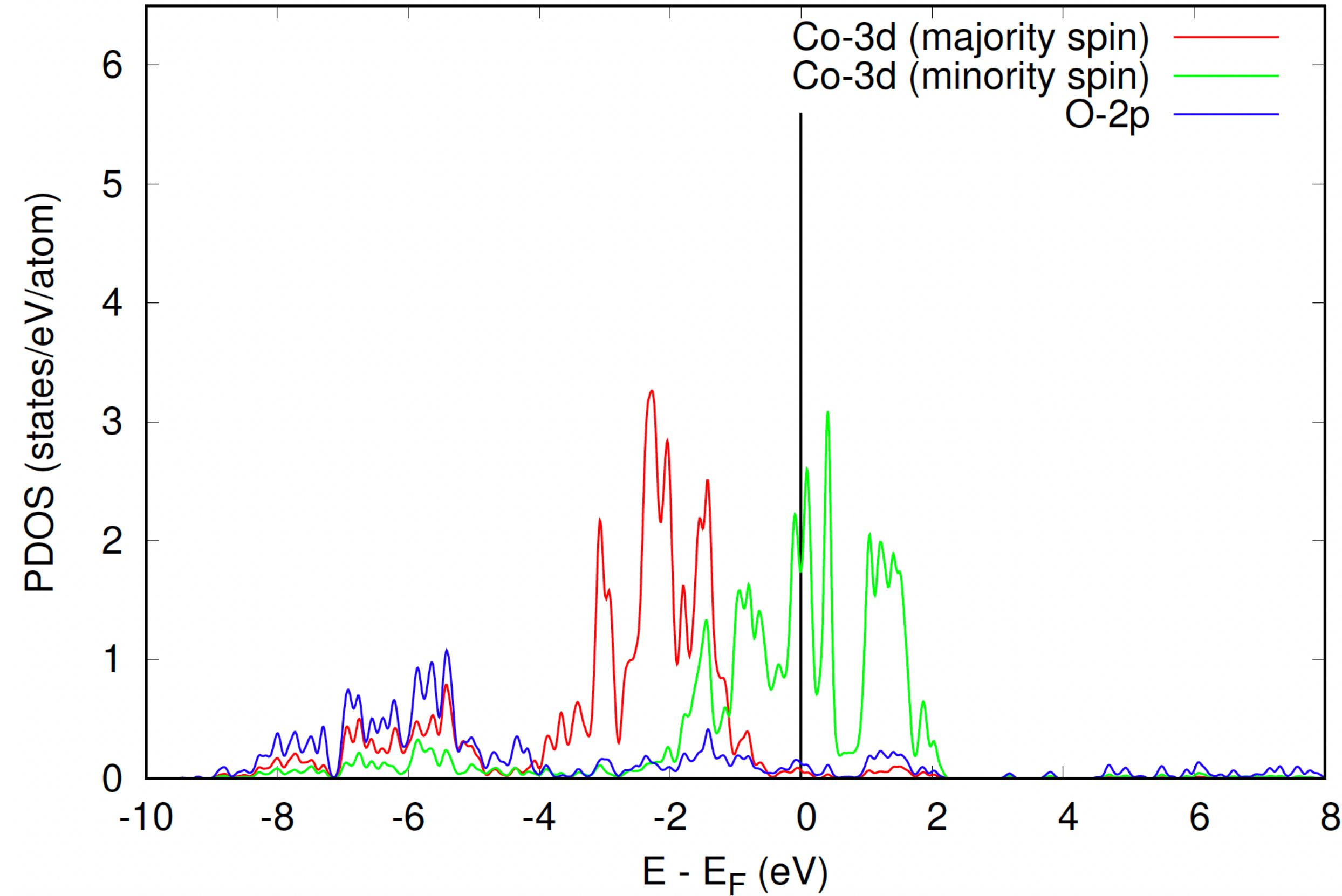


DFT+ $U$  predicts CoO to be insulating (this is correct)

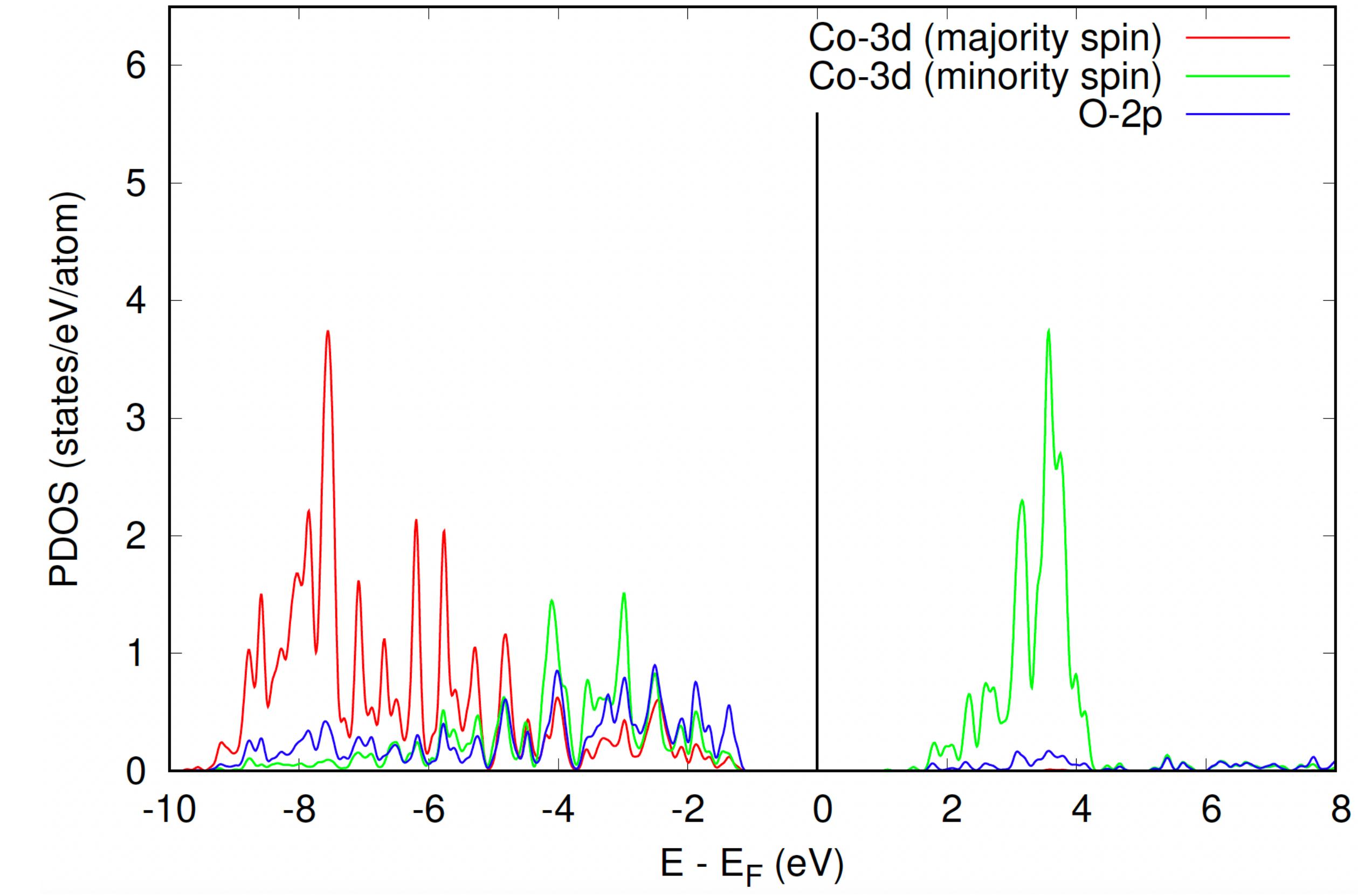
Experimentally CoO is insulating

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)

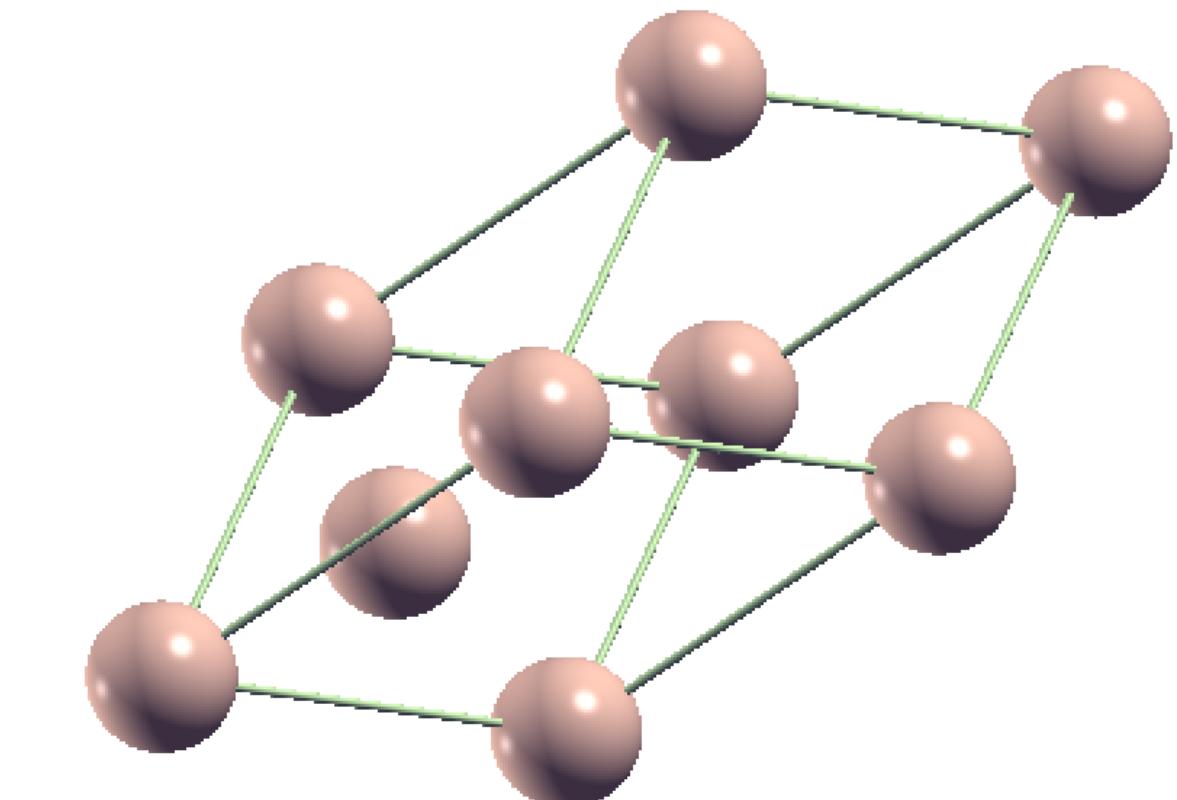
Override the functional written in the pseudopotential (PP) file.  
**Important:** use a PP for the closest GGA (PBE in this case),  
there are no PP's for hybrids.

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"

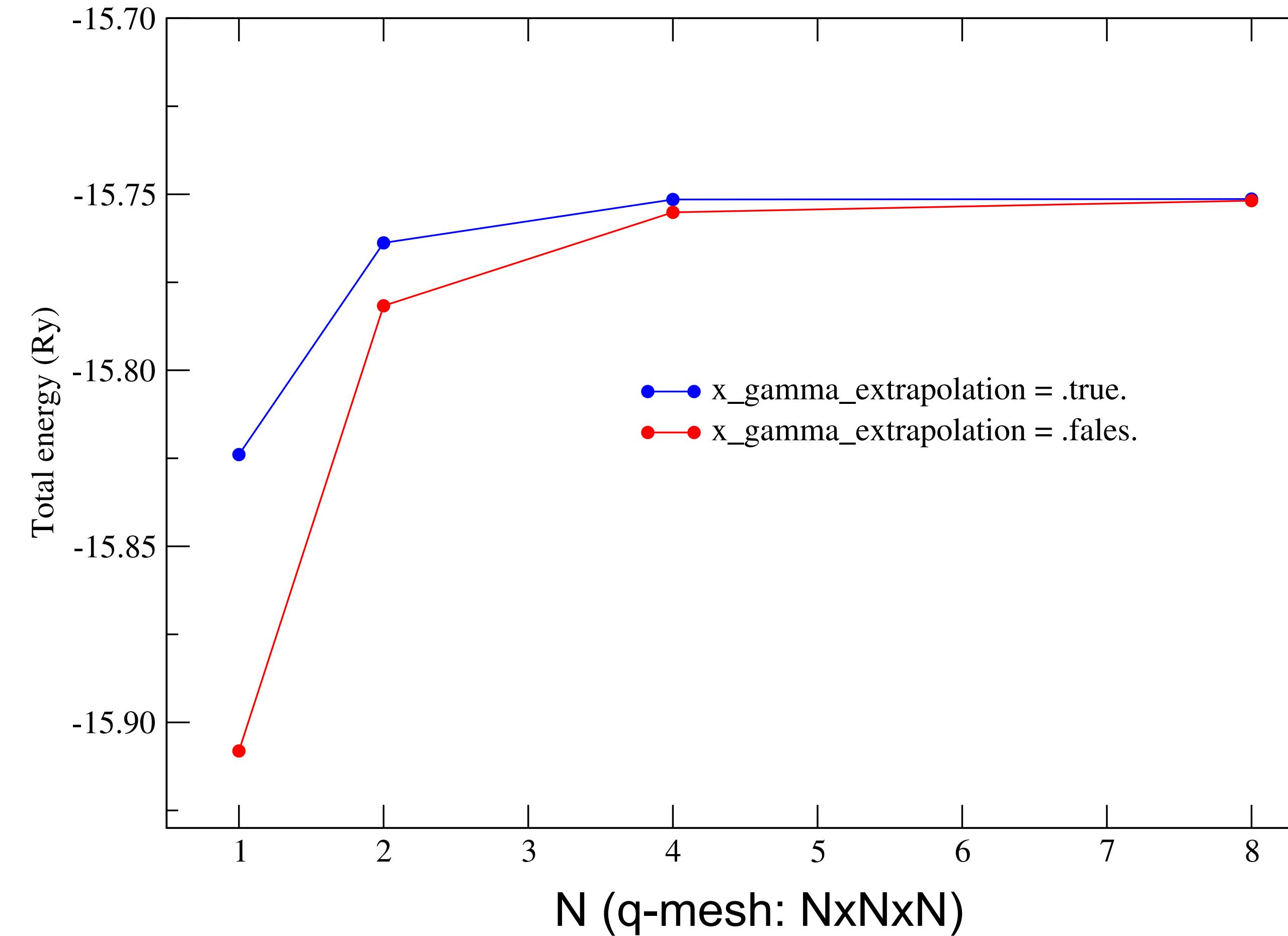
Heyd, Scuseria, Ernzerhof, J. Chem. Phys. 118, 8207 (2003)

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

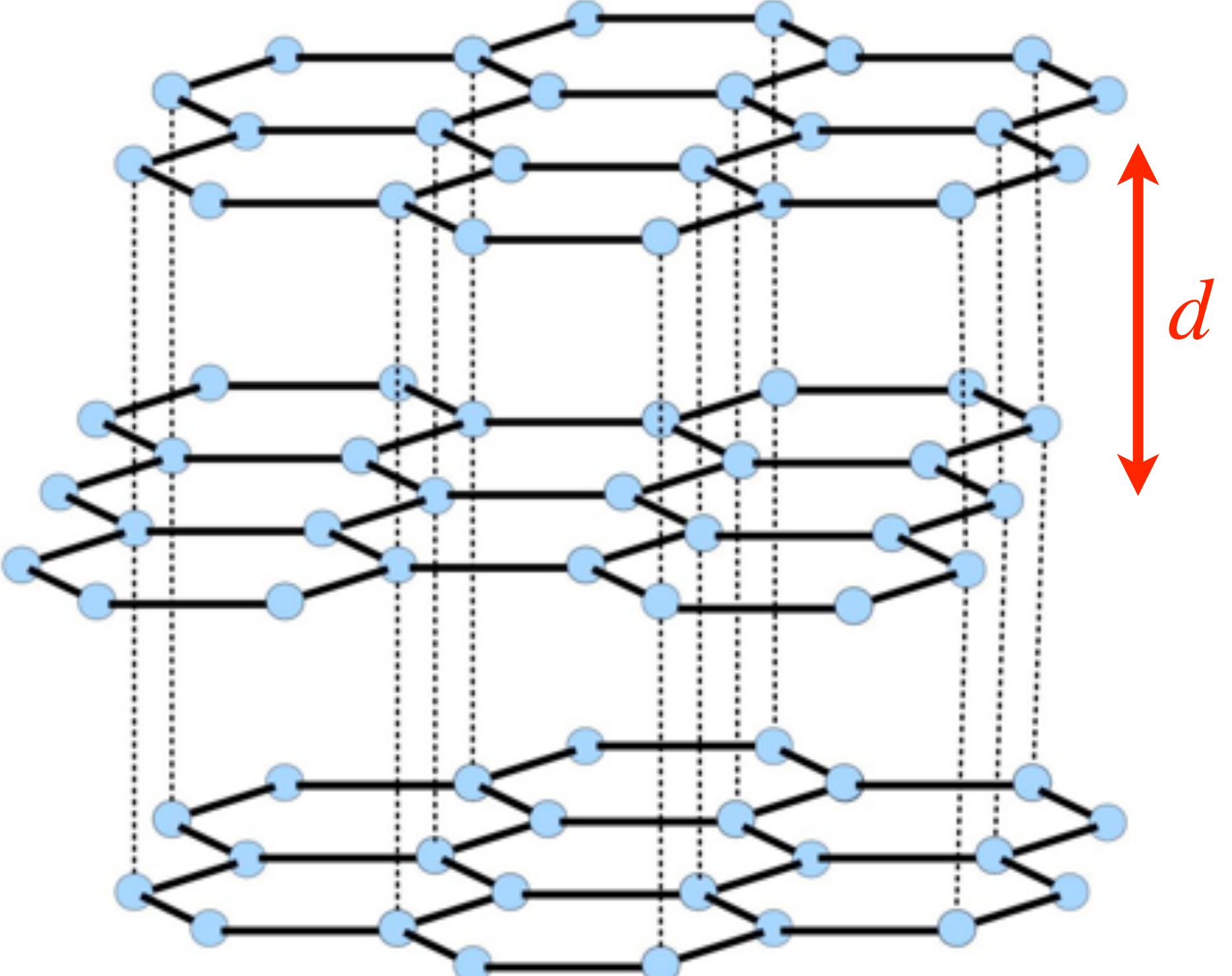


Convergence is faster when `x_gamma_extrapolation = .true.`.

## **Exercise 3**

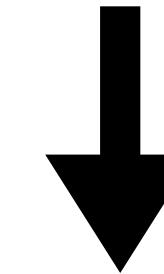
**Van der Waals functionals for graphite**

# 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>	

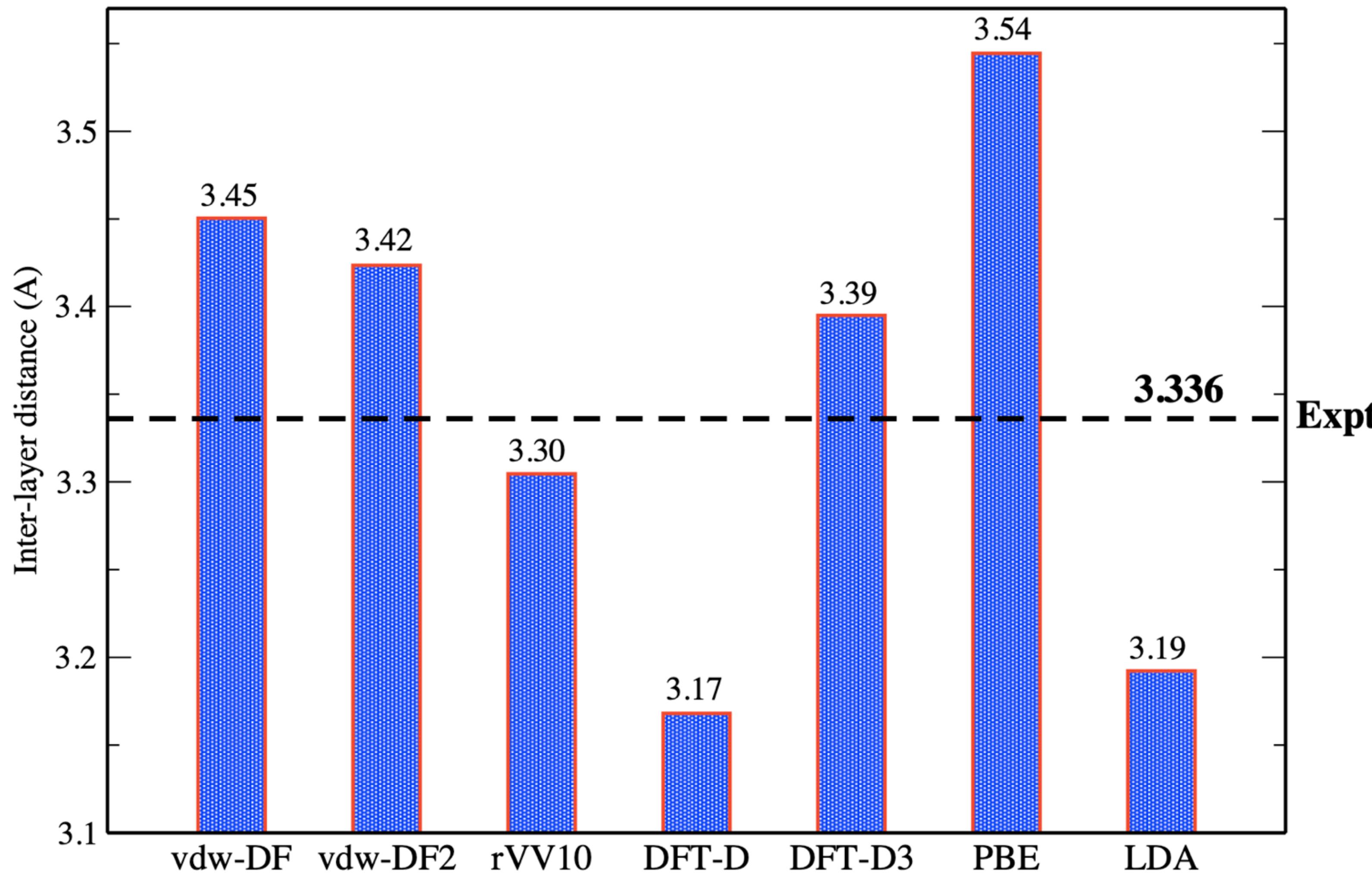
# Structural optimization of graphite

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 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

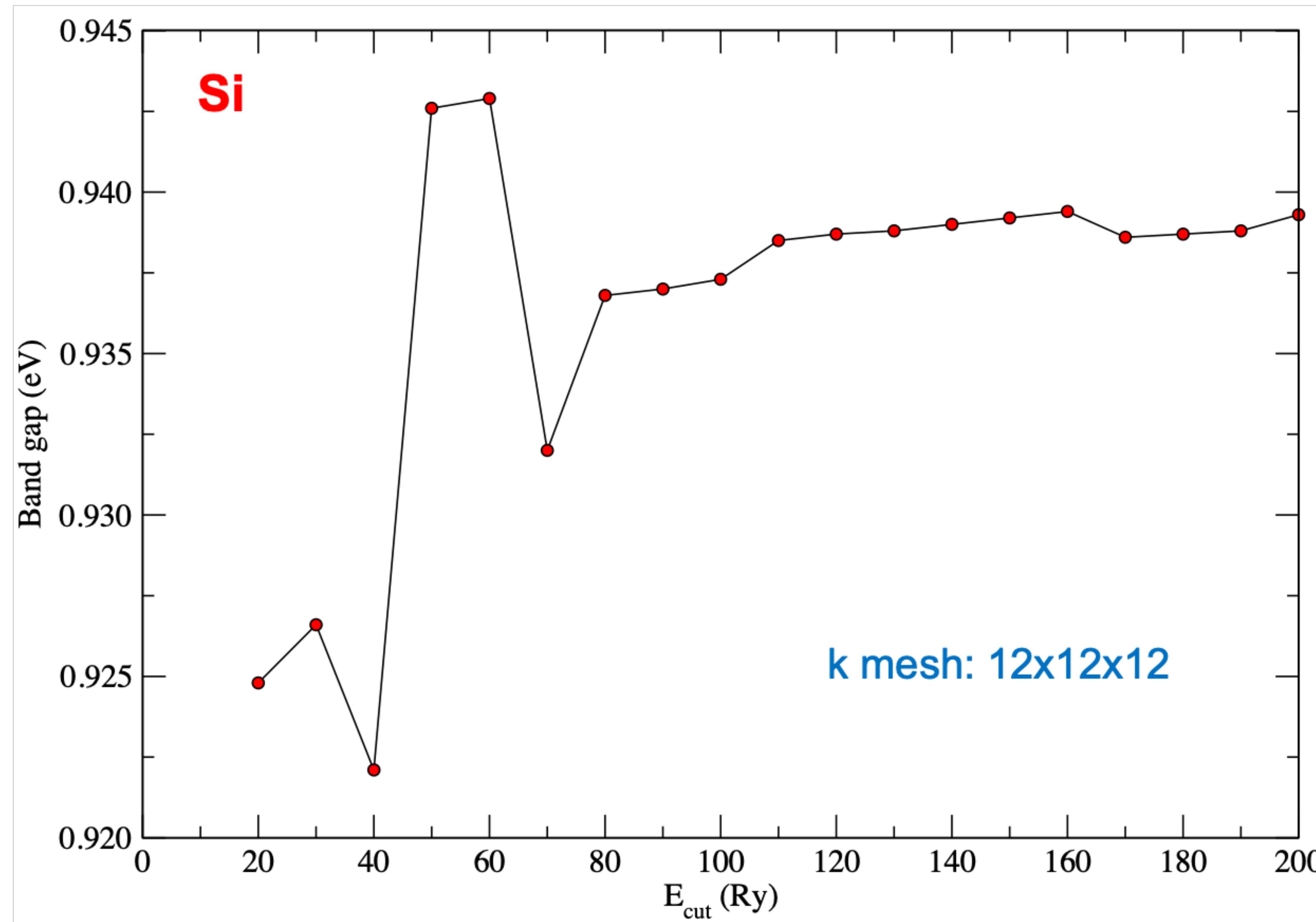
It is necessary to perform convergence tests w.r.t ecutwfc

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

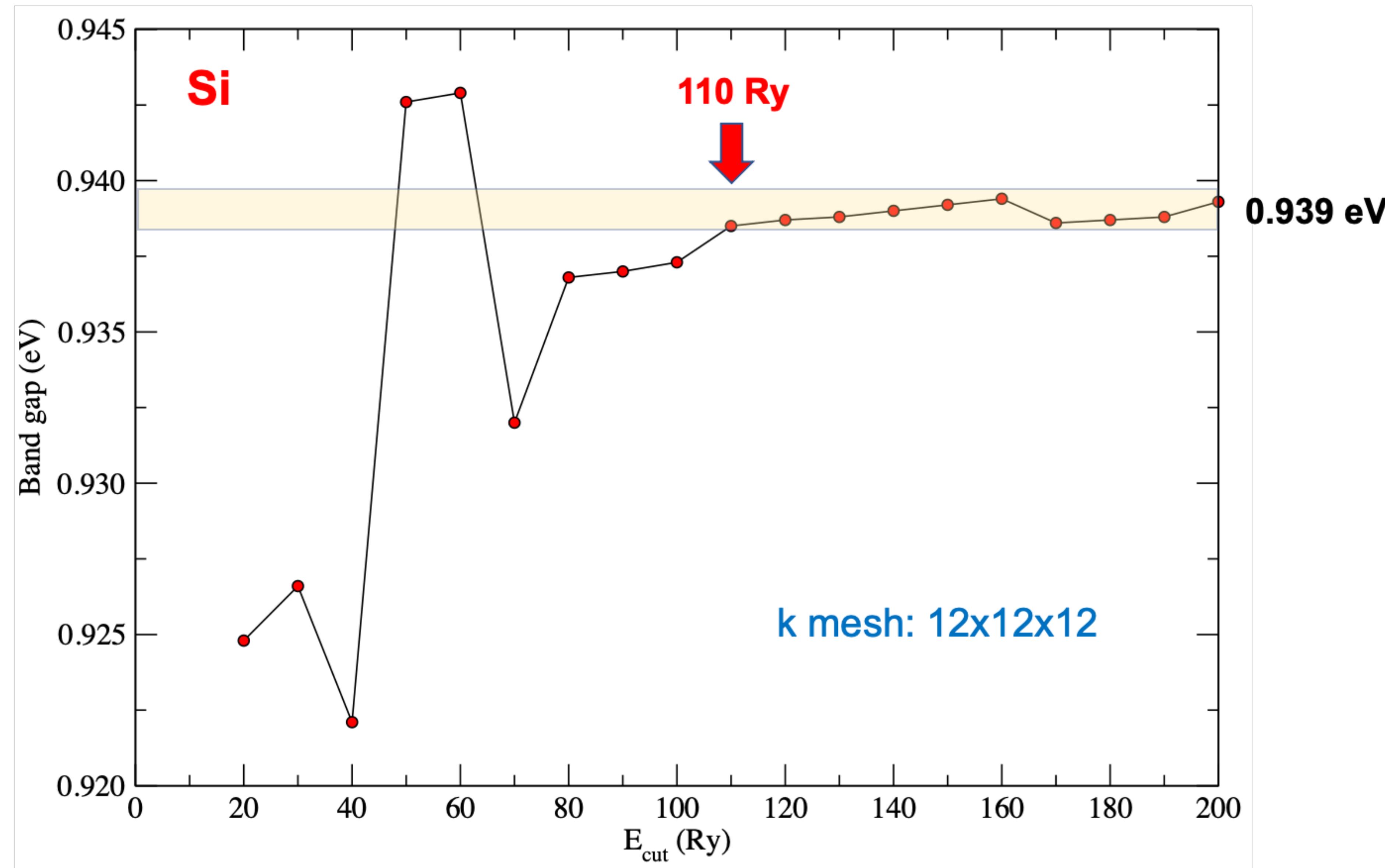
Pseudopotential generated using the SCAN functional

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

# SCAN functional & SCAN pseudopotential



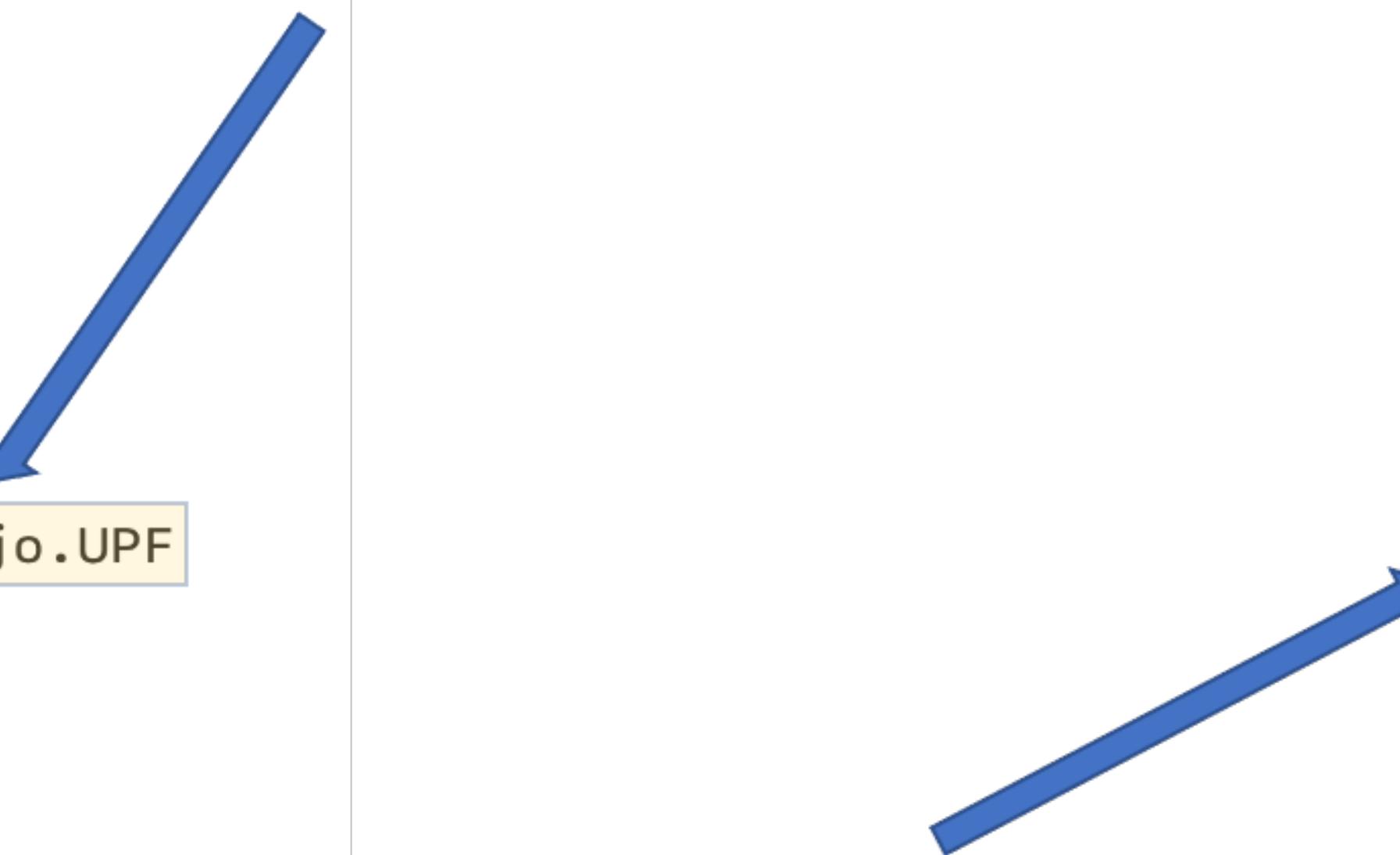
# SCAN functional & SCAN pseudopotential



# 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

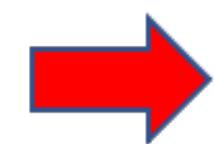
Functional	Pseudopotential	Library	Gap (eV)
SCAN	SCAN	Yi Yao's library	0.94
SCAN	PBE	SG15 ONCV	0.83
SCAN	PBE	Pseudo Dojo	0.64

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.

# 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)

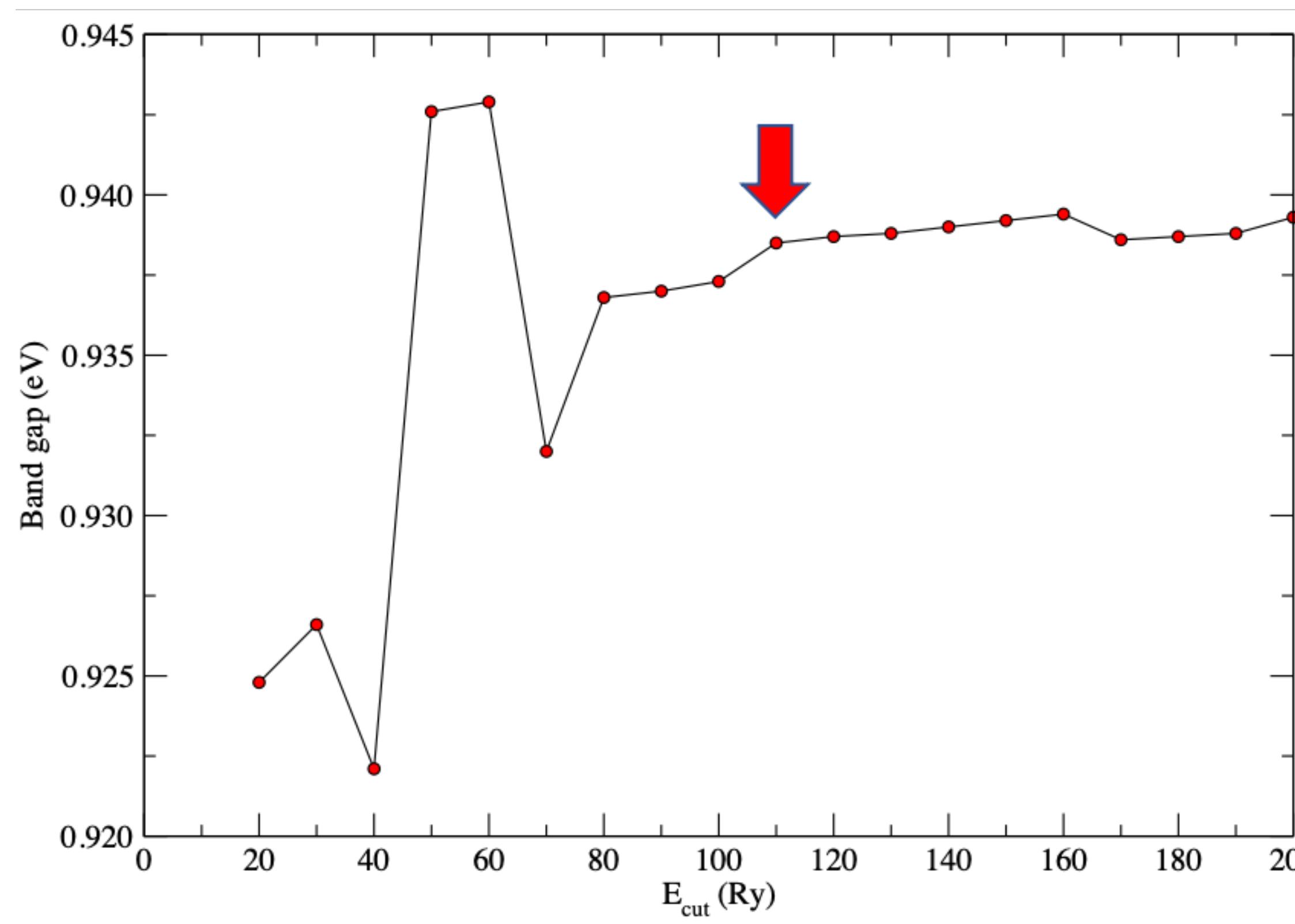
SCAN calculation with the SCAN pseudopotential gives the most accurate results

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

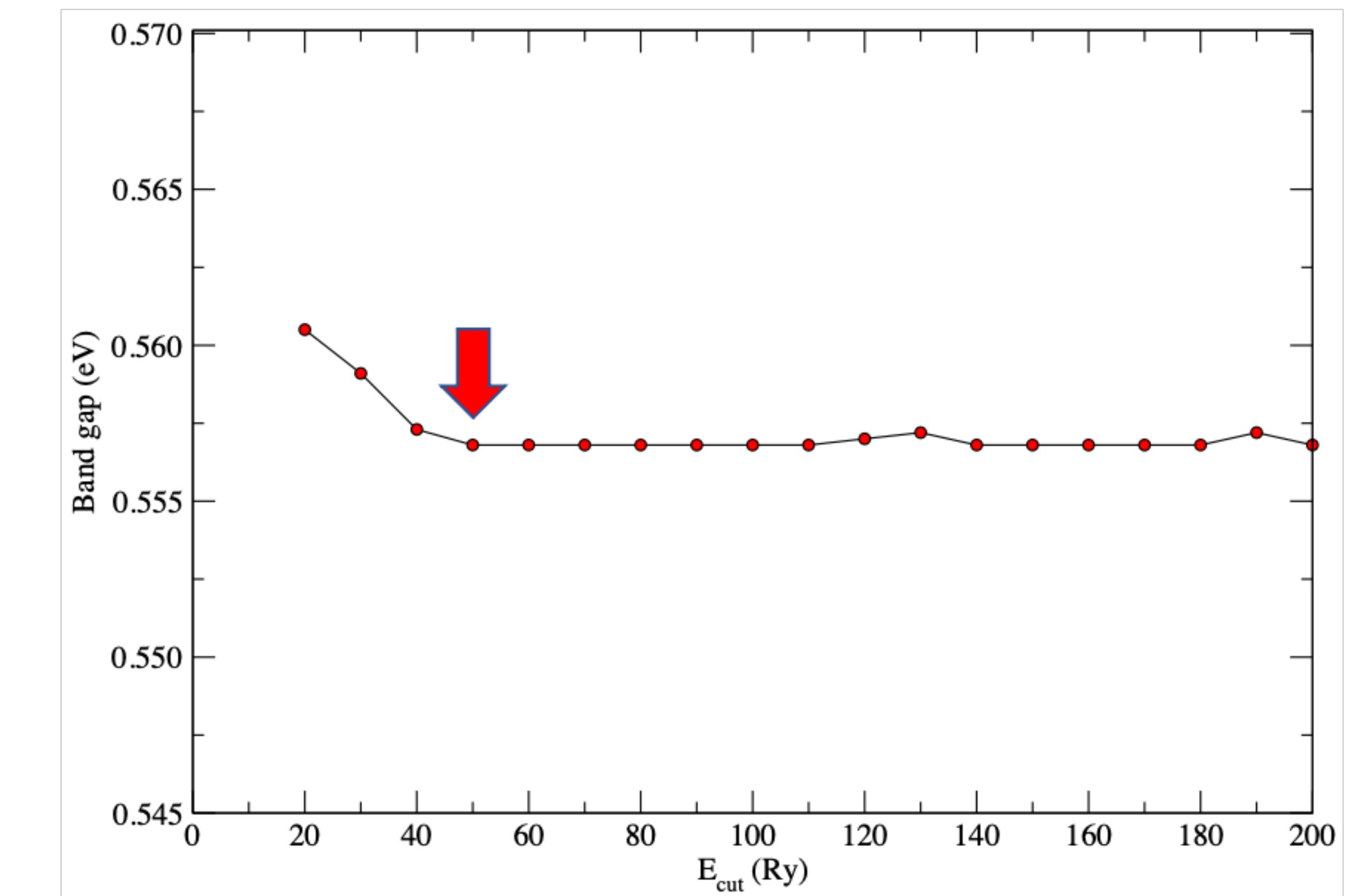
# Convergence with respect to $E_{\text{cut}}$

k mesh: 12x12x12

SCAN with SCAN pseudopotential



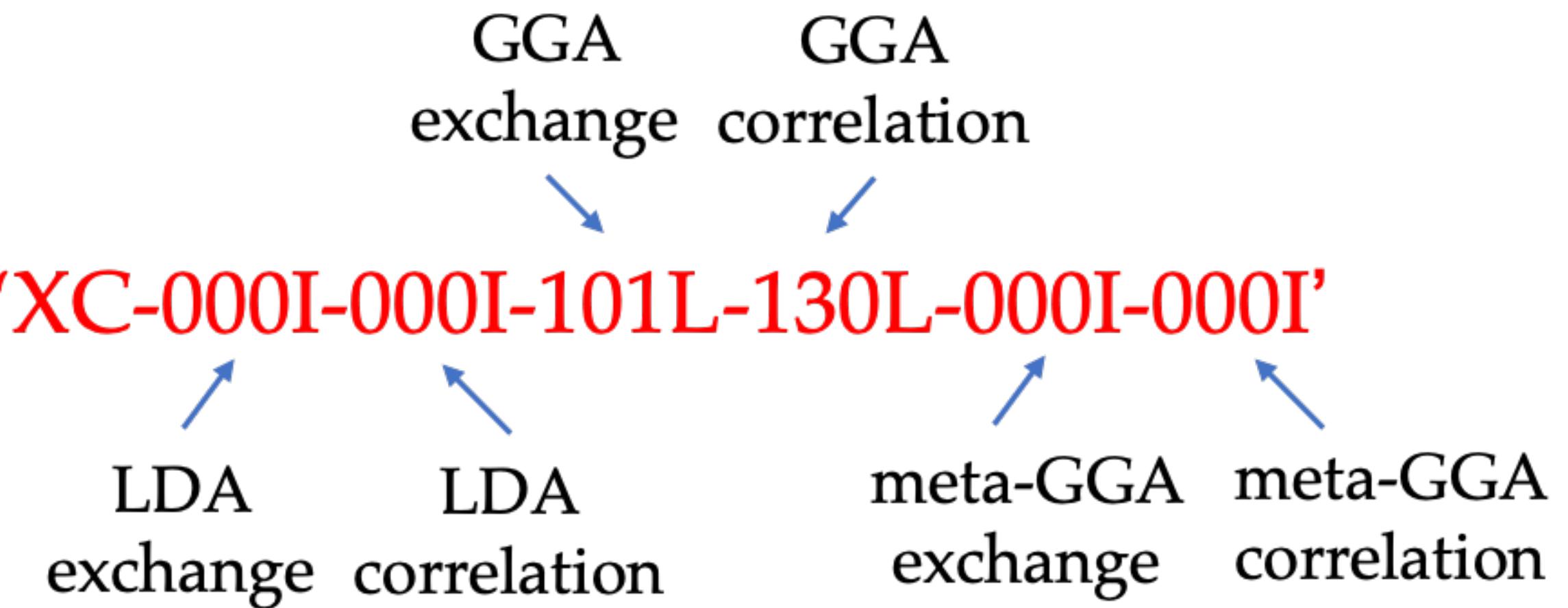
PBE with PBE pseudopotential (SG15)



Convergence is achieved much faster with PBE than with SCAN

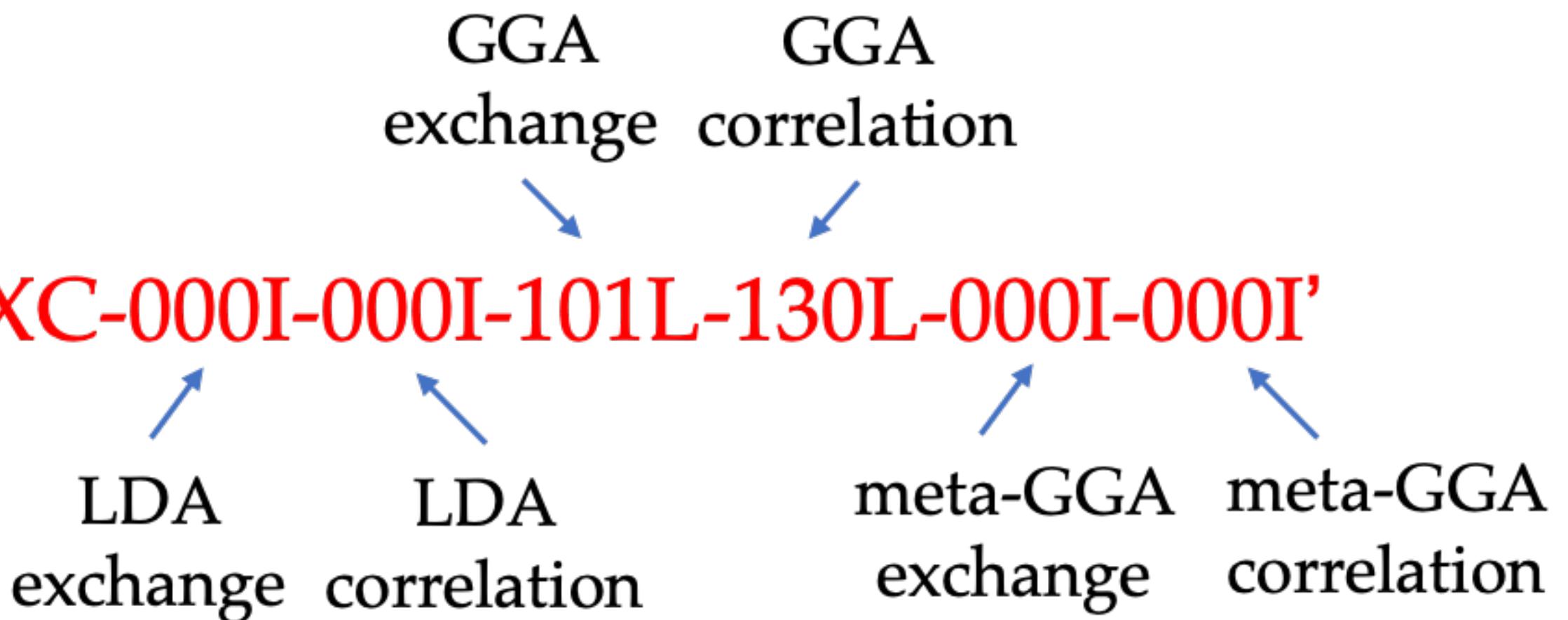
## Setting up the XC functional

`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://tddft.org/programs/libxc/functionals/libxc-6.1.0/>

# 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
```

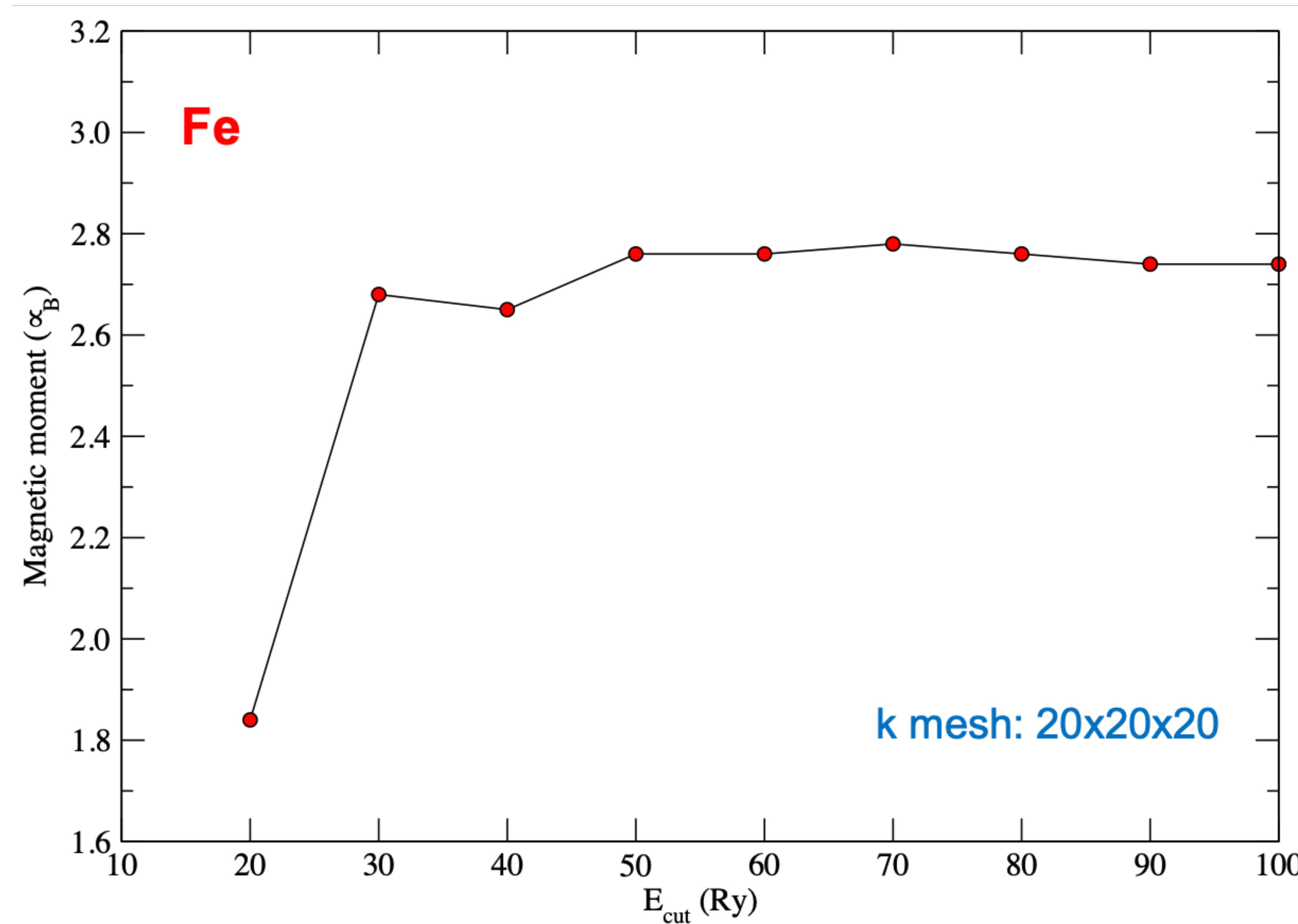
Experimental lattice parameter

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

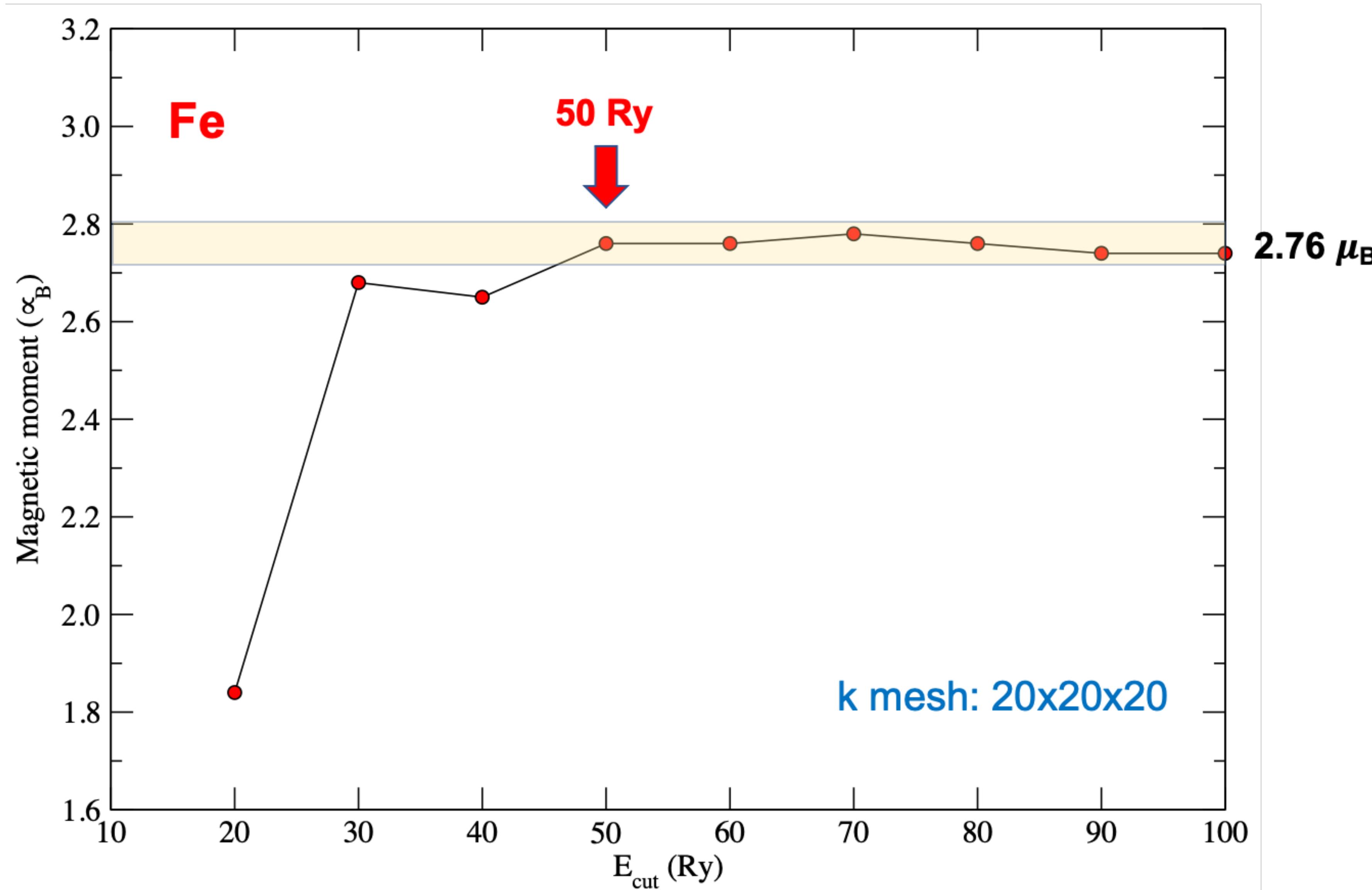
Set up the SCAN functional from the input  
Quantum ESPRESSO must be compiled with Libxc

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