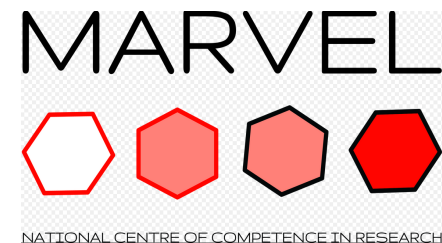


THEOS

THEORY AND SIMULATION  
OF MATERIALS

EPFL



## Hands-on: Functionals

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# Outline

**Exercise 1:** DFT+ $U$  study of FeO

**Exercise 2:** DFT with hybrid functionals: study of Si

**Exercise 3:** DFT with Van der Waals functionals: study of graphite

# Outline

**Exercise 1:** DFT+ $U$  study of FeO

**Exercise 2:** DFT with hybrid functionals: study of Si

**Exercise 3:** DFT with Van der Waals functionals: study of graphite

# DFT+U

The DFT+U total energy:

$$E_{\text{DFT}+U} = E_{\text{DFT}} + E_U$$

The Hubbard correction energy:

$$E_U = \frac{1}{2} \sum_{I,m,m',\sigma} \underbrace{(U^I - J^I)}_{U_{\text{eff}}^I} (\delta_{mm'} - n_{mm'}^{I\sigma}) n_{m'm}^{I\sigma}$$

effective Hubbard  
parameter



The occupation matrix:

$$n_{mm'}^{I\sigma} = \sum_{v,\mathbf{k}} f_{v\mathbf{k}}^{\sigma} \langle \psi_{v\mathbf{k}}^{\sigma} | \varphi_m^I \rangle \langle \varphi_m^I | \psi_{v\mathbf{k}}^{\sigma} \rangle$$

The total occupation of localized states (*d* or *f*) at site *I*:

$$n^I = \sum_{m,\sigma} n_{mm}^{I\sigma}$$

The Kohn-Sham equation:

$$\left[ -\frac{1}{2} \nabla^2 + \hat{V}_{\text{KS}}^{\sigma} + \hat{V}_U^{\sigma} \right] \psi_{v\mathbf{k}}^{\sigma}(\mathbf{r}) = \varepsilon_{v\mathbf{k}}^{\sigma} \psi_{v\mathbf{k}}^{\sigma}(\mathbf{r})$$

# Localized-states manifold

How do we know to what states of a Hubbard atom the  $U_{\text{eff}}$  correction will be applied?



Currently, this is hard-coded (in Quantum ESPRESSO 6.4.1)



Check two subroutines in **quantum-espresso/Modules** :



**set\_hubbard\_n.f90**

principal quantum number " $n$ "



**set\_hubbard\_l.f90**

orbital quantum number " $l$ "

For Fe :  $n = 3$

For Fe :  $l = 2$



Apply the Hubbard  $U_{\text{eff}}$  correction to the  $3d$  electrons of Fe

# Input file pw.FeO.scf.in

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='FeO'
  pseudo_dir = '../..../pseudo'
  outdir='./tmp/'
  verbosity='high'
/
&system
 ibrav = 0,
  celldm(1) = 8.19,
  nat = 4,
  ntyp = 3,
  ecutwfc = 30.0,
  ecutrho = 240.0,
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.02,
  nspin = 2,
  starting_magnetization(1) = 0.5,
  starting_magnetization(2) = -0.5
  lda_plus_u = .true.,
  lda_plus_u_kind = 0,
  U_projection_type = 'atomic',
  Hubbard_U(1) = 1.d-8
  Hubbard_U(2) = 1.d-8
/
&electrons
  conv_thr = 1.d-9
  mixing_beta = 0.3
/
ATOMIC_SPECIES
Fe1 55.845 Fe.pbesol-spn-kjpaw_psl.0.2.1.UPF
Fe2 55.845 Fe.pbesol-spn-kjpaw_psl.0.2.1.UPF
O 16.0 O.pbesol-n-kjpaw_psl.0.1.UPF
CELL_PARAMETERS {alat}
0.50 0.50 1.00
0.50 1.00 0.50
1.00 0.50 0.50
ATOMIC_POSITIONS {crystal}
Fe1 0.00 0.00 0.00
Fe2 0.50 0.50 0.50
O 0.25 0.25 0.25
O 0.75 0.75 0.75
K_POINTS {automatic}
3 3 3 0 0 0
```

SCF calculation

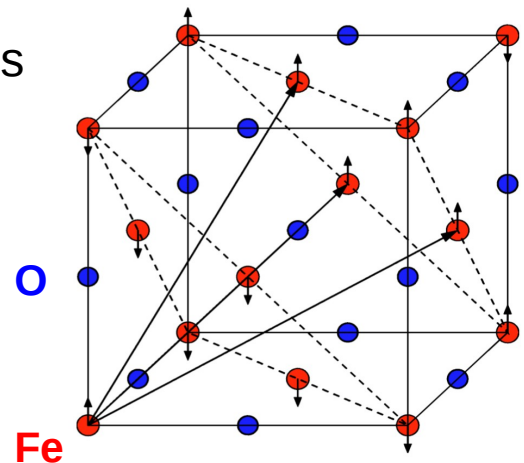
Experimental lattice parameter

'MV' smearing for metals (FeO is metallic @PBEsol)

Spin-polarized (collinear) calculation  
(antiferromagnetic ordering)

Initialize Hubbard parameters for two types of Fe

Two sublattices of Fe atoms



# Input file pw.FeO.nscf.in

```
&control
  calculation='nscf'
  restart_mode='from_scratch',
  prefix='FeO'
  pseudo_dir = '../..../pseudo'
  outdir='./tmp/'
/
&system
 ibrav = 0,
celldm(1) = 8.19,
nat = 4,
ntyp = 3,
ecutwfc = 30.0,
ecutrho = 240.0,
occupations = 'smearing',
smearing = 'mv',
degauss = 0.02,
nspin = 2,
starting_magnetization(1) = 0.5,
starting_magnetization(2) = -0.5
lda_plus_u = .true.,
lda_plus_u_kind = 0,
U_projection_type = 'atomic',
Hubbard_U(1) = 1.d-8
Hubbard_U(2) = 1.d-8
nbnd = 35
/
&electrons
  conv_thr = 1.d-9
  mixing_beta = 0.3
/
ATOMIC_SPECIES
Fe1 55.845 Fe.pbesol-spn-kjpaw_psl.0.2.1.UPF
Fe2 55.845 Fe.pbesol-spn-kjpaw_psl.0.2.1.UPF
O 16.0 0.pbesol-n-kjpaw_psl.0.1.UPF
CELL_PARAMETERS {alat}
0.50 0.50 1.00
0.50 1.00 0.50
1.00 0.50 0.50
ATOMIC_POSITIONS {crystal}
Fe1 0.00 0.00 0.00
Fe2 0.50 0.50 0.50
O 0.25 0.25 0.25
O 0.75 0.75 0.75
K_POINTS {automatic}
6 6 6 0 0 0
```

NSCF calculation

NSCF input is very similar to the SCF input,  
but there a few differences which are  
highlighted here

Number of electronic bands

Projected DOS must be converged with respect to  
the number of **k** points. Also, number of bands must  
be large enough, to have converged projected DOS  
in a specific energy range. All this is controlled here.

**k** points mesh which is denser than in SCF

# Input file projwfc.FeO.in

```
&projwfc  
  prefix='FeO'  
  outdir='./tmp/'  
  ngauss = 0,  
  degauss = 0.005,  
  Emin = -15.0,  
  Emax = 30.0,  
  DeltaE = 0.01  
/
```

Simple Gaussian broadening of PDOS

Value of Gaussian broadening, in Ry (not eV!)

Minimum and maximum value of energy for the plot, in eV

Energy grid step

## Gnuplot script: plot\_pdos.gnu

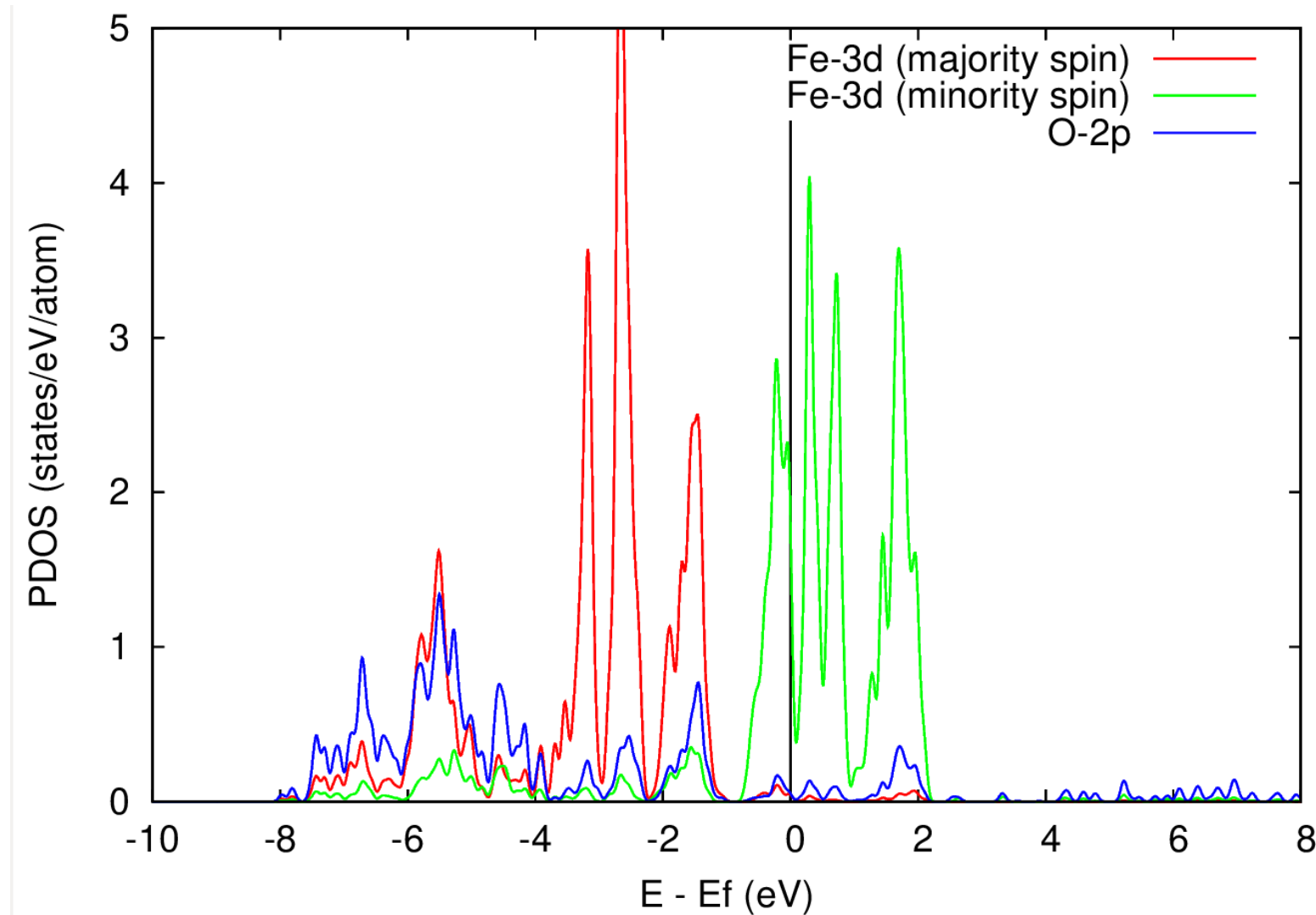
Inspect the script: it aims at plotting Fe-3d state (majority spin and minority spin) and O-2p states.

PDOS is shifted such that the Fermi energy corresponds to the zero of energy.

Visualize the file “[FeO\\_PDOS.eps](#)”



# PDOS of FeO from standard DFT calculation



DFT predicts FeO to be metallic (**but this is wrong!**)



Let's try **DFT+U**

Experimentally FeO is known to be insulating

# Input file pw.FeO.scf.in for DFT+ $U$

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='FeO'
  pseudo_dir = '.././../pseudo'
  outdir='./tmp/'
  verbosity='high'
/
&system
  ibrav = 0,
  celldm(1) = 8.19,
  nat = 4,
  ntyp = 3,
  ecutwfc = 30.0,
  ecutrho = 240.0,
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.02,
  nspin = 2,
  starting_magnetization(1) = 0.5,
  starting_magnetization(2) = -0.5
  lda_plus_u = .true.,
  lda_plus_u_kind = 0,
  U_projection_type = 'atomic',
  Hubbard_U(1) = 5.2
  Hubbard_U(2) = 5.2
/
&electrons
  conv_thr = 1.d-9
  mixing_beta = 0.3
/
ATOMIC_SPECIES
Fe1 55.845 Fe.pbesol-spn-kjpaw_psl.0.2.1.UPF
Fe2 55.845 Fe.pbesol-spn-kjpaw_psl.0.2.1.UPF
O 16.0 O.pbesol-n-kjpaw_psl.0.1.UPF
CELL_PARAMETERS {alat}
0.50 0.50 1.00
0.50 1.00 0.50
1.00 0.50 0.50
ATOMIC_POSITIONS {crystal}
Fe1 0.00 0.00 0.00
Fe2 0.50 0.50 0.50
O 0.25 0.25 0.25
O 0.75 0.75 0.75
K_POINTS {automatic}
3 3 3 0 0 0
```

Here we want to put a Hubbard  $U$  correction for 3d electrons of Fe atoms

Which value of  $U$  to use?

For every material Hubbard  $U$  is different; here we use  $U = 5.2$  eV for Fe-3d states for demonstration purposes

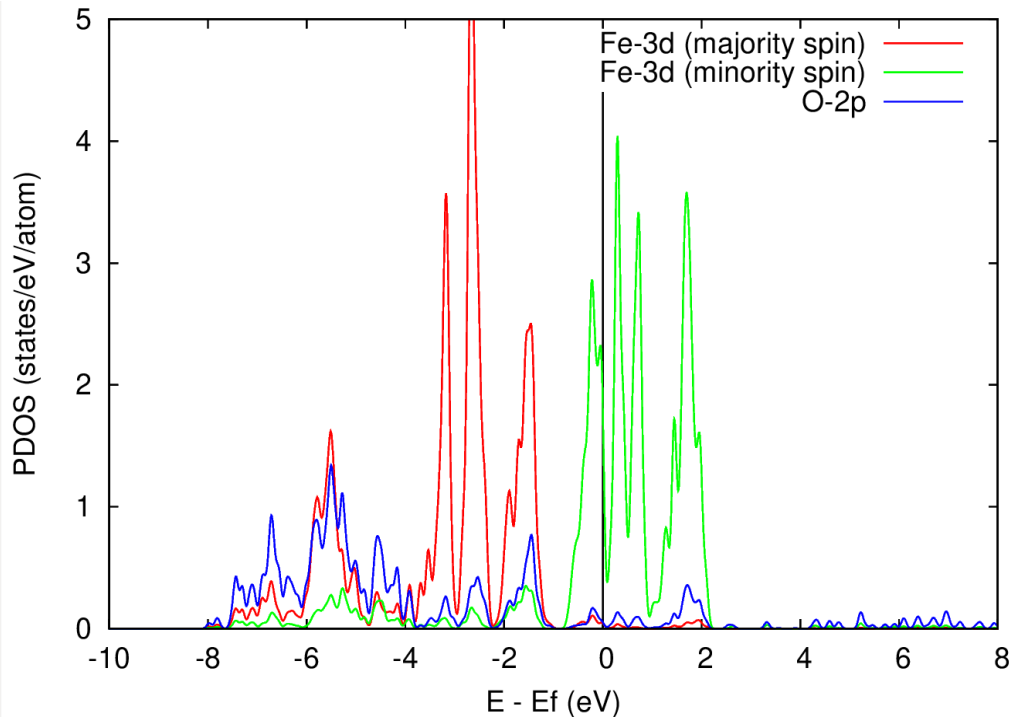
Hubbard  $U$  values (in eV) for atomic type 1 & type 2

Hubbard  $U$  can be computed from first principles:

I. Timrov, N. Marzari, M. Cococcioni, PRB **98**, 085127 (2018)

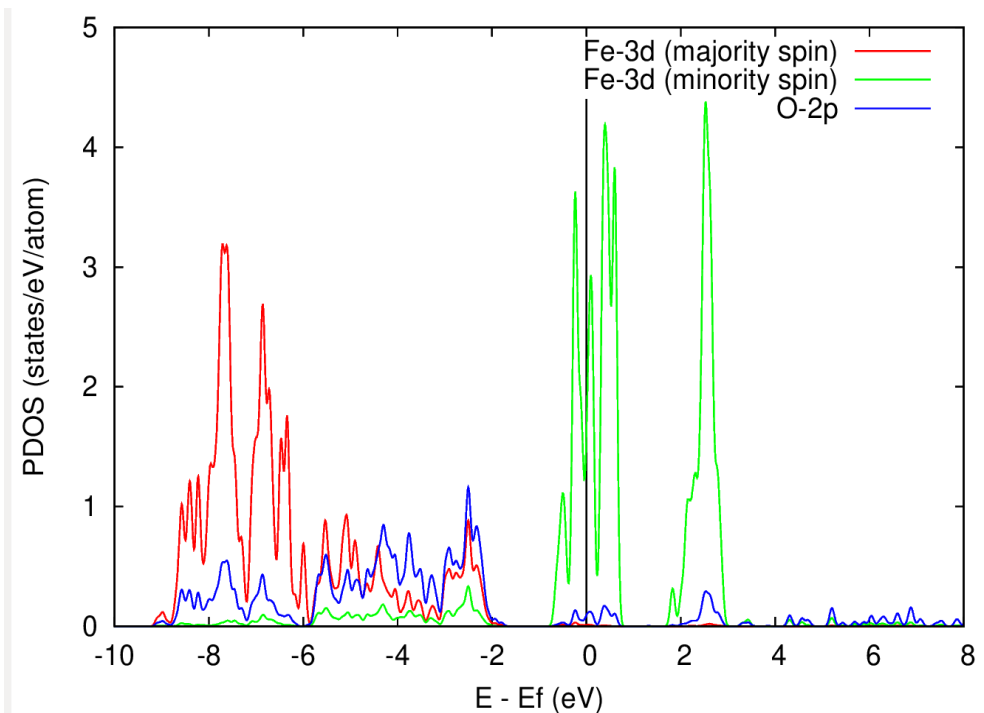
# DFT vs DFT+ $U$

## DFT



The solution with DFT is metallic

## DFT+ $U$



The solution with DFT+ $U$  is also metallic...

The 3d states of Fe are fully occupied for the majority spin, while for the minority spin they are still partially occupied.

The reason of this failure of DFT+ $U$  is that it gets stuck in a **local minimum** (which corresponds to a metallic state) and it needs a “hint” to reach the correct (insulating) ground state.

# How to “push” DFT+ $U$ to the global minimum?

Check the output file pw.FeO.scf.out from the DFT+ $U$  calculation

After the 1-st iteration we have:

**Fe1** atom 1 Tr[ns(na)] (up, down, total) = 5.00634 1.09448 6.10082

spin 1

eigenvalues:

1.000 1.000 1.002 1.002 1.002

spin 2

eigenvalues:

0.129 0.129 0.270 0.270 0.296

**Fe2** atom 2 Tr[ns(na)] (up, down, total) = 1.09429 5.00635 6.10063

spin 1

eigenvalues:

0.129 0.129 0.270 0.270 0.296

spin 2

eigenvalues:

1.000 1.000 1.002 1.002 1.002

# How to “push” DFT+*U* to the global minimum?

Check the output file pw.FeO.scf.out from the DFT+*U* calculation

After the 1-st iteration we have:

**Fe1**

```
atom 1 Tr[ns(na)] (up, down, total) = 5.00634 1.09448 6.10082
  spin 1
    eigenvalues:
    1.000 1.000 1.002 1.002 1.002
  spin 2
    eigenvalues:
    0.129 0.129 0.270 0.270 0.296
```

*starting\_ns\_eigenvalue(5,2,1) = 1.0*

**Fe2**

```
atom 2 Tr[ns(na)] (up, down, total) = 1.09429 5.00635 6.10063
  spin 1
    eigenvalues:
    0.129 0.129 0.270 0.270 0.296
  spin 2
    eigenvalues:
    1.000 1.000 1.002 1.002 1.002
```

*starting\_ns\_eigenvalue(5,1,2) = 1.0*

Let's try to force/suggest the occupancy of the 5-th state to be 1.0 instead of 0.296 !

Why 5-th state? Because it is the one which is non-degenerate and if occupied fully could lead to an insulating result.

# A “hint” for DFT+*U* where to look for a correct solution

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='FeO'
  pseudo_dir = './pseudopotentials/'
  outdir='./tmp/'
/
&system
  ibrav = 0,
  celldm(1) = 8.19,
  nat = 4,
  ntyp = 3,
  ecutwfc = 30.0,
  ecutrho = 240.0,
  occupations = 'smearing',
  smearing = 'mv',
  degauss = 0.02,
  nspin = 2,
  starting_magnetization(1) = 0.5,
  starting_magnetization(2) = -0.5
  lda_plus_u = .true.,
  lda_plus_u_kind = 0,
  U_projection_type = 'atomic',
  Hubbard_U(1) = 5.2
  Hubbard_U(2) = 5.2
  starting_ns_eigenvalue(5,2,1) = 1.0
  starting_ns_eigenvalue(5,1,2) = 1.0
/
&electrons
  conv_thr = 1.d-9
  mixing_beta = 0.3
/
ATOMIC_SPECIES
Fe1 55.845 Fe.pbesol-spn-kjpaw_psl.0.2.1.UPF
Fe2 55.845 Fe.pbesol-spn-kjpaw_psl.0.2.1.UPF
O 16.0 O.pbesol-n-kjpaw_psl.0.1.UPF
CELL_PARAMETERS {alat}
0.50 0.50 1.00
0.50 1.00 0.50
1.00 0.50 0.50
ATOMIC_POSITIONS {crystal}
Fe1 0.00 0.00 0.00
Fe2 0.50 0.50 0.50
O 0.25 0.25 0.25
O 0.75 0.75 0.75
K_POINTS {automatic}
3 3 3 0 0 0
```

**starting\_ns\_eigenvalue(m,ispin,ityp)**

In the first iteration of a DFT+*U* run it overwrites the **m**-th eigenvalue of the **ns** occupation matrix for the **ispin** spin-component of atomic species of type **ityp**.

Why? This is useful to suggest the desired orbital occupations when the default choice takes another path.

5-th eigenvalue spin 2 (down) type 1: Fe1 fully occupied

**starting\_ns\_eigenvalue(5,2,1) = 1.0**

5-th eigenvalue spin 1 (up) type 2: Fe2 fully occupied

**starting\_ns\_eigenvalue(5,1,2) = 1.0**

# Understanding the setup of starting\_ns\_eigenvalue

Check the output file pw.FeO.scf.out from the DFT+ $U$  calculation (with starting\_ns\_eigenvalue):

After the 1-st iteration (i.e. when we forced the 1.0 occupancy of the 5-th state) we have:

Modify starting ns matrices according to input values

```
Fe1 atom 1 Tr[ns(na)] (up, down, total) = 5.00634 1.79838 6.80472
    spin 1
    eigenvalues:
    1.000 1.000 1.002 1.002 1.002

    spin 2
    eigenvalues:
    0.129 0.129 0.270 0.270 1.000

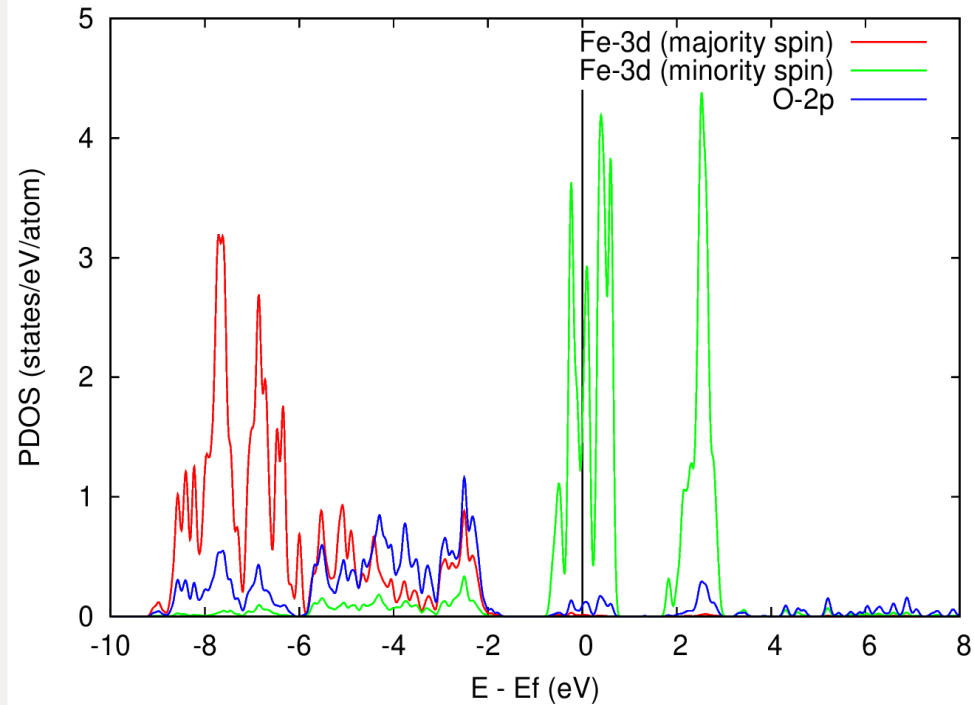
atom 2 Tr[ns(na)] (up, down, total) = 1.79825 5.00635 6.80460
    spin 1
    eigenvalues:
    0.129 0.129 0.270 0.270 1.000

    spin 2
    eigenvalues:
    1.000 1.000 1.002 1.002 1.002
```

After this the DFT+ $U$  calculation converges to an insulating ground state with lower energy than the previous one.

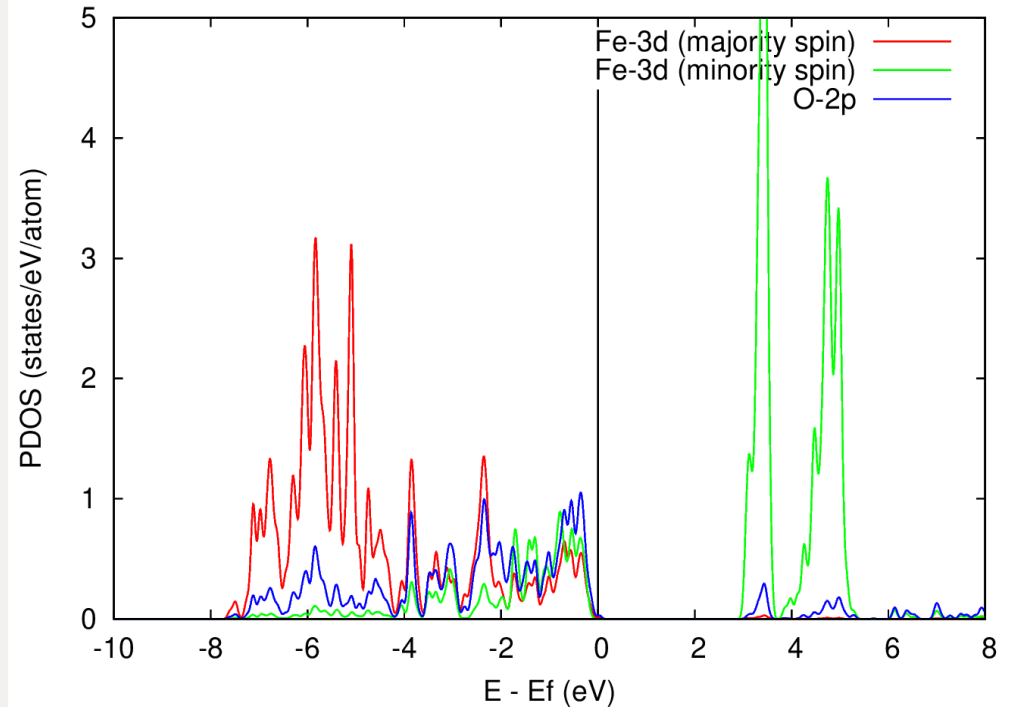
# Comparison of DFT+ $U$ results w/o and w/ starting\_ns\_eigenvalue

## DFT+ $U$



The solution with DFT+ $U$  is metallic

## DFT+ $U$ (with starting\_ns\_eigenvalue)



The solution with DFT+ $U$  is **insulating**



**Agreement with the experiment!**



# Outline

**Exercise 1:** DFT+ $U$  study of FeO

**Exercise 2:** DFT with hybrid functionals: study of Si

**Exercise 3:** DFT with Van der Waals functionals: study of graphite

# Input file pw.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
```

SCF calculation

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

Grid for the  $\mathbf{q}$  points  
1x1x1 0s the minimal grid ( $\mathbf{q}=0$ ), it is fast  
but not very accurate

If .true. Use extrapolation for the  $\mathbf{q} \rightarrow 0$  limit

Specifies that the singularity at  $\mathbf{q} \rightarrow 0$  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"`

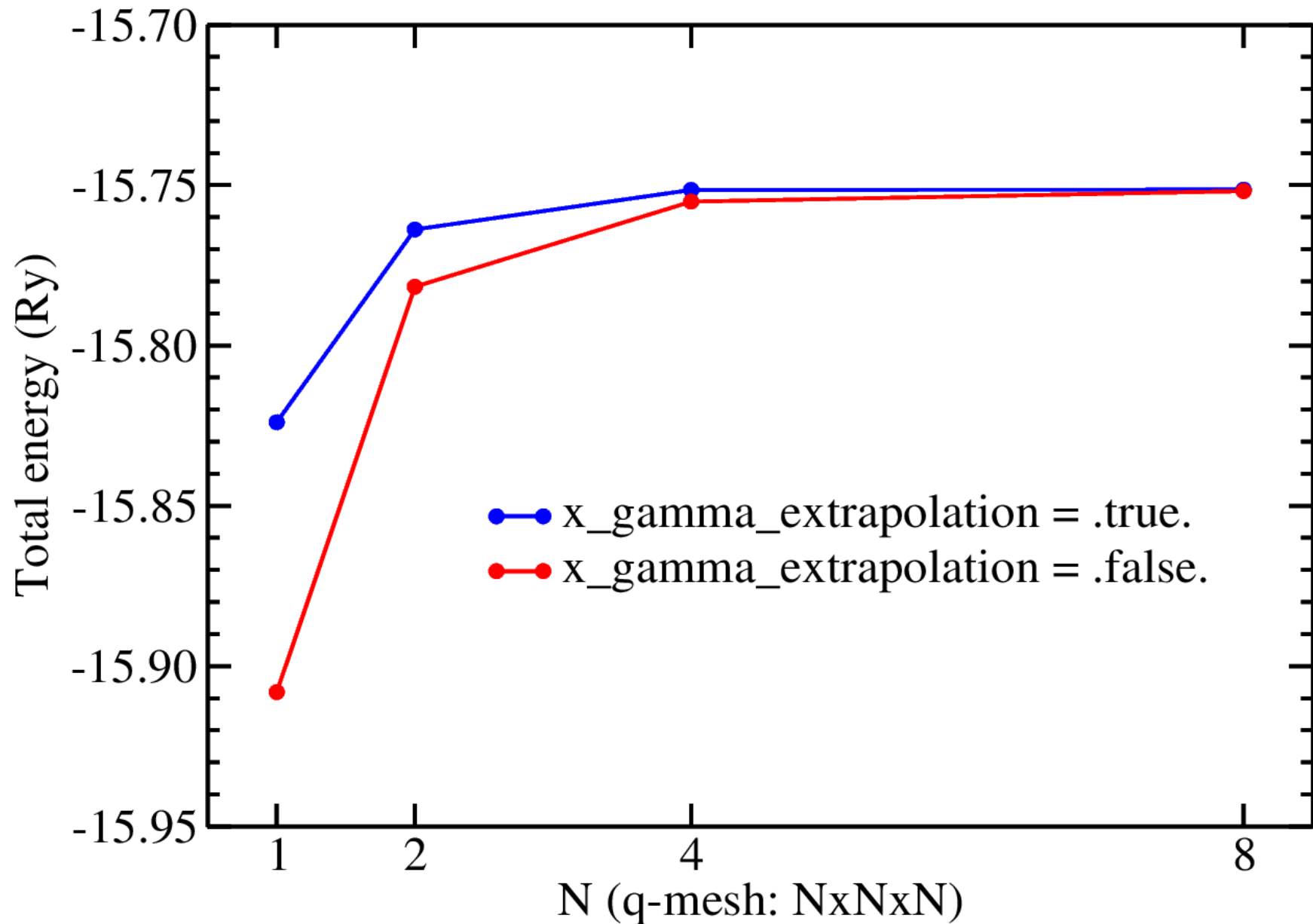
Heyd, Scuseria, Ernzerhof, J. Chem. Phys. 118, 8207 (2003)

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

# Types of treatment of divergences at $q \rightarrow 0$

<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 $q$ 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="#">ecutvcut</a> .	
<b>'none'</b> : sets Coulomb potential at $G, q=0$ to 0.0 (required for GAU-PBE)	

# Convergence of the total energy wrt q point grid



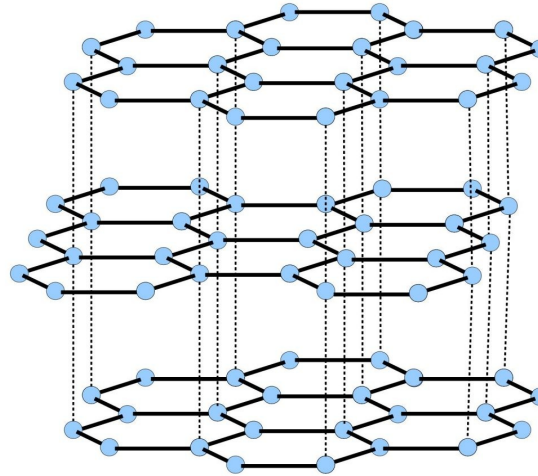
# Outline

**Exercise 1:** DFT+ $U$  study of FeO

**Exercise 2:** DFT with hybrid functionals: study of Si

**Exercise 3:** DFT with Van der Waals functionals: study of graphite

# Graphite



Graphite has Van der Waals (dispersive) interactions between layers.

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



Van der Waals interactions must be taken into account.

# Input file pw.graphite.scf.in

```
&control  
  calculation='scf'  
  restart_mode='from_scratch',  
  prefix='graphite'  
  pseudo_dir = '../..../pseudo'  
  outdir='./tmp/'  
  verbosity='high'  
  tprnfor = .true.  
  tstress = .true.
```

SCF calculation

Calculation of forces and stress

```
/  
&system  
 ibrav = 4,  
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'
```

Hexagonal lattice, a and c are in Angstrom!

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

Remember to generate and store the kernel table!  
vdW\_kernel\_table

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

```
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
```

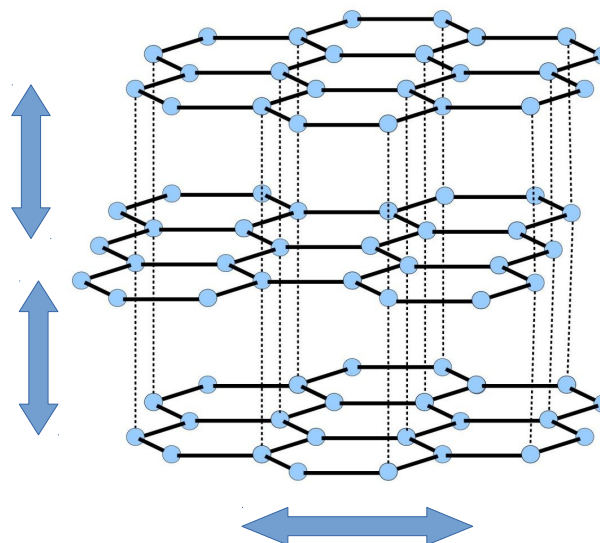
The **k** point grid is denser along xy than along z, reflecting shorter periodicity in the xy plane



# Input file pw.graphite.vc-relax.in

```
&control  
  calculation='vc-relax'  
  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,  
  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'  
/  
&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



If we do not specify anything inside these namelists, then the default values will be used for various control parameters

# Structural optimization in graphite

Can you find your equilibrium state? What do you get if you

- set `input_dft='vdW-DF2'`?
- set `input_dft='PZ'` (LDA, but with a PBE pseudopotential)?
- remove `input_dft`, in which case PBE is assumed (the XC functional is read from the PP file)?
- remove `input_dft`, set variable `vdw_corr='Grimme-D2'` in `namelist &system`?  
This performs a DFT-D calculation
- remove `input_dft`, `vdw_corr`, replace the PP with a LDA one, e.g. `C.pz-rrkjus.UPF`?