THEOS
THEORY AND SIMULATION OF MATERIALS

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Hands-on: Advanced 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

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Exercise 1: DFT+*U* study of FeO

Exercise 2: DFT with hybrid functionals: study of Si

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DFT+*U*

The DFT+*U* total energy: $E_{\mathrm{DFT}+U} = E_{\mathrm{DFT}} + E_U$

The Hubbard correction energy: $E_U = \frac{1}{2} \sum_{I,m,m',\sigma} \underbrace{\left(U^I - J^I\right)}_{U^I_{\mathrm{eff}}} \left(\delta_{mm'} - n^{I\sigma}_{mm'}\right) n^{I\sigma}_{m'm}$

effective Hubbard parameter

The occupation matrix: $n^{I\sigma}_{mm'} = \sum_{v,\mathbf{k}} f^{\sigma}_{v\mathbf{k}} \langle \psi^{\sigma}_{v\mathbf{k}} | \varphi^{I}_{m'} \rangle \langle \varphi^{I}_{m} | \psi^{\sigma}_{v\mathbf{k}} \rangle$

The total occupation of localized states (*d* or *f*) at site *I* : $n^I = \sum_{m,\sigma} n^{I\sigma}_{mm}$

The Kohn-Sham equation: $\left[-\frac{1}{2}\nabla^2 + \hat{V}^{\sigma}_{\mathrm{KS}} + \hat{V}^{\sigma}_{U}\right] \psi^{\sigma}_{v\mathbf{k}}(\mathbf{r}) = \varepsilon^{\sigma}_{v\mathbf{k}}\, \psi^{\sigma}_{v\mathbf{k}}(\mathbf{r})$

Localized-states manifold

How do we know to what states of a Hubbard atom the U_{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*"

For Fe : *n* = 3

`set_hubbard_l.f90`

orbital quantum number "*l*"

For Fe : *l* = 2

Apply the Hubbard U_{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

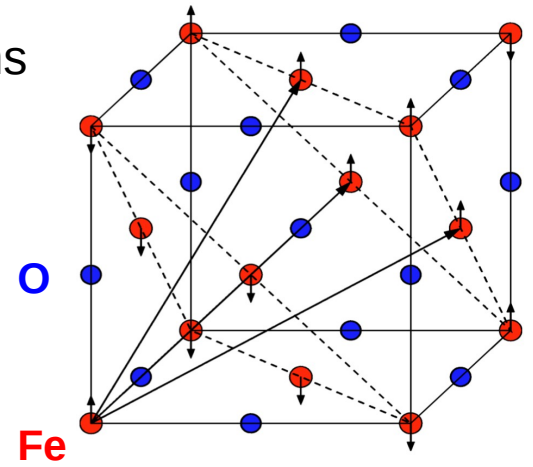
Experimental lattice parameter

'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   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}
 6 6 6 0 0 0
```

NSCF calculation

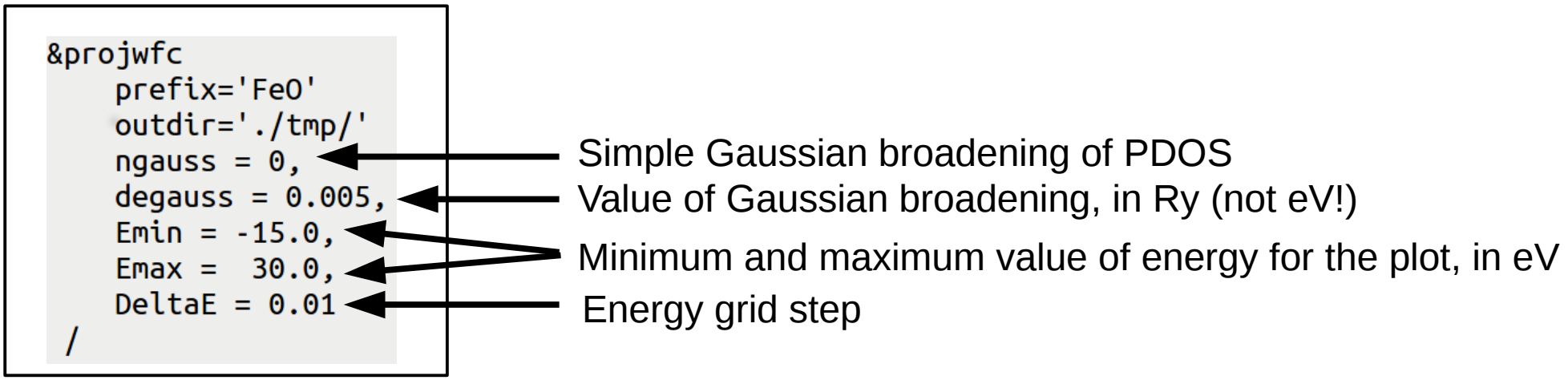
NSCF input is very similar to the SCF input, but there a few differences which are highlighted here

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



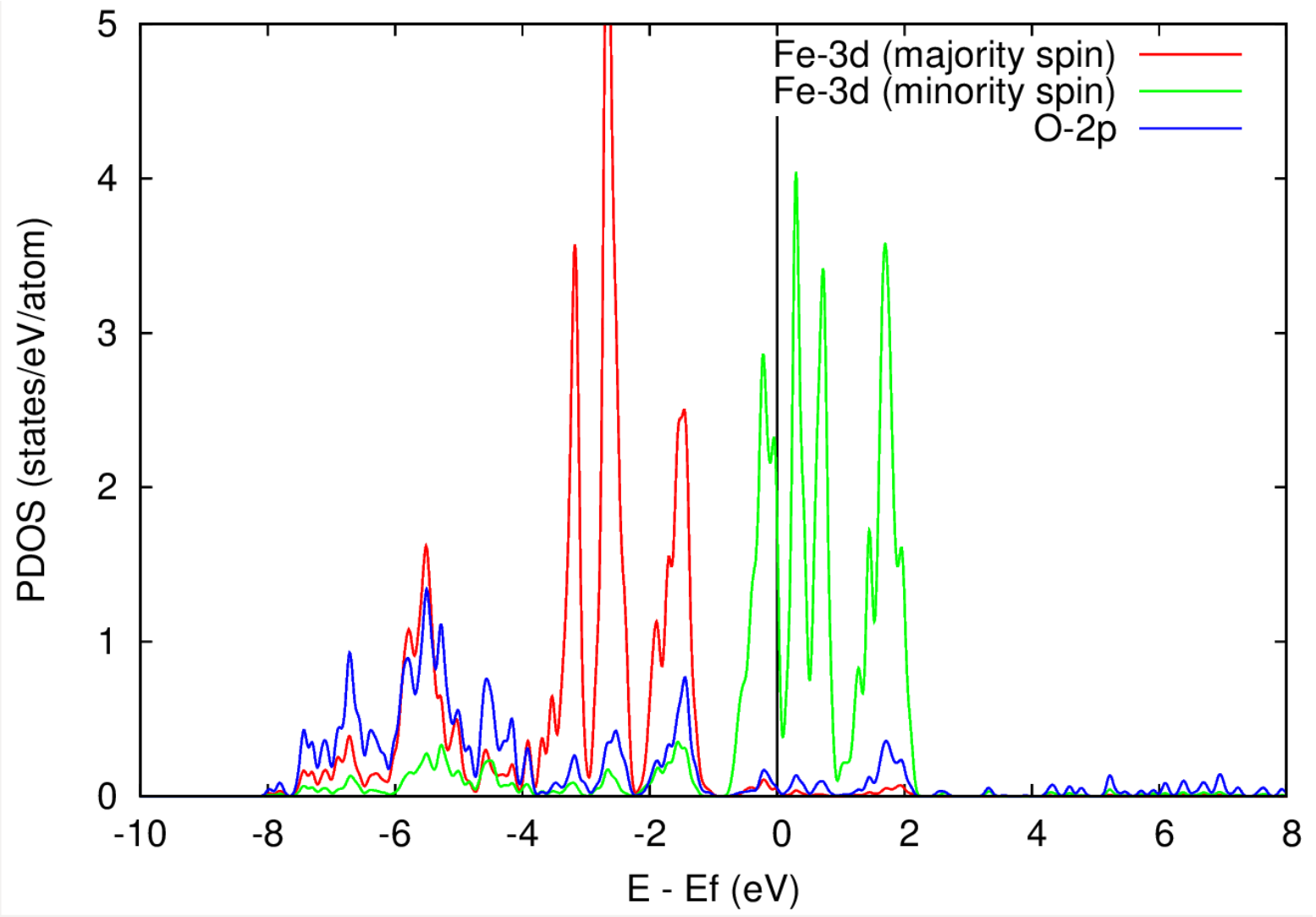
Gnuplot script: plot_pdos.gnu

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 know 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

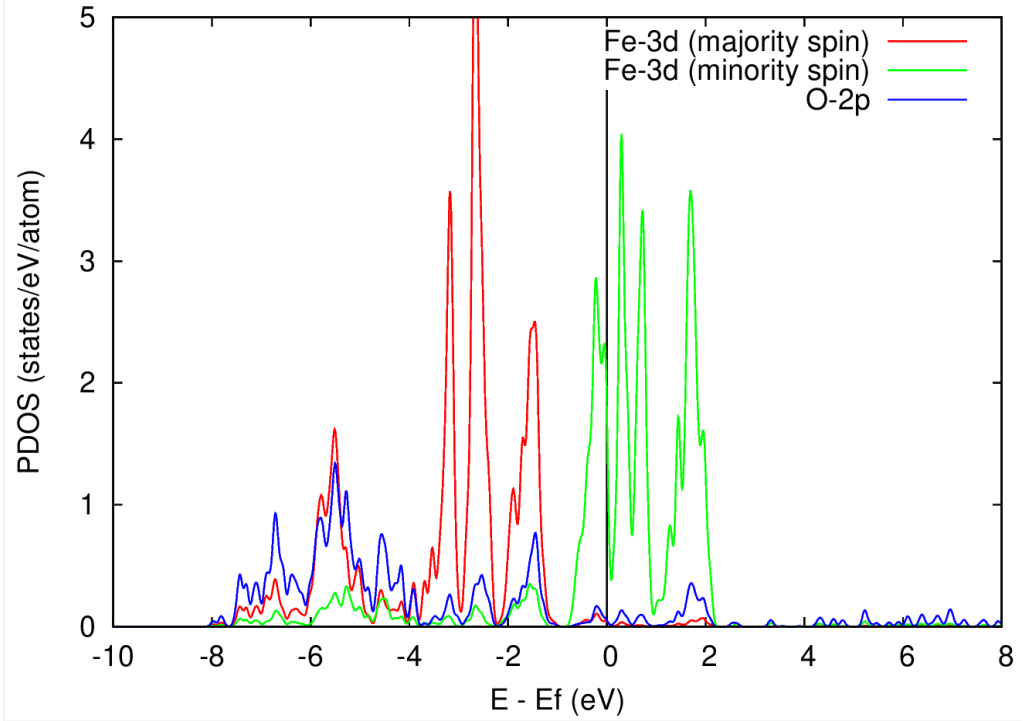
Hubbard U values (in eV) for atomic type 1 & type 2

Hubbard *U* can be computed from first principles:

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

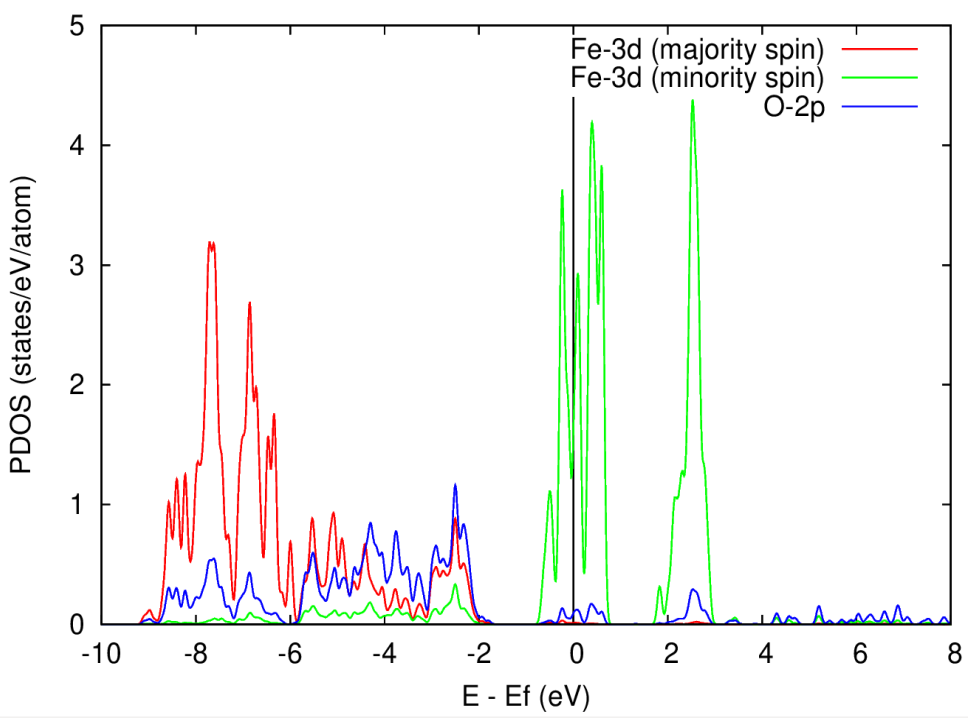
DFT vs DFT+*U*

DFT



The solution with DFT is metallic

DFT+*U*



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

The 3*d* states of Fe a 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.

非简并

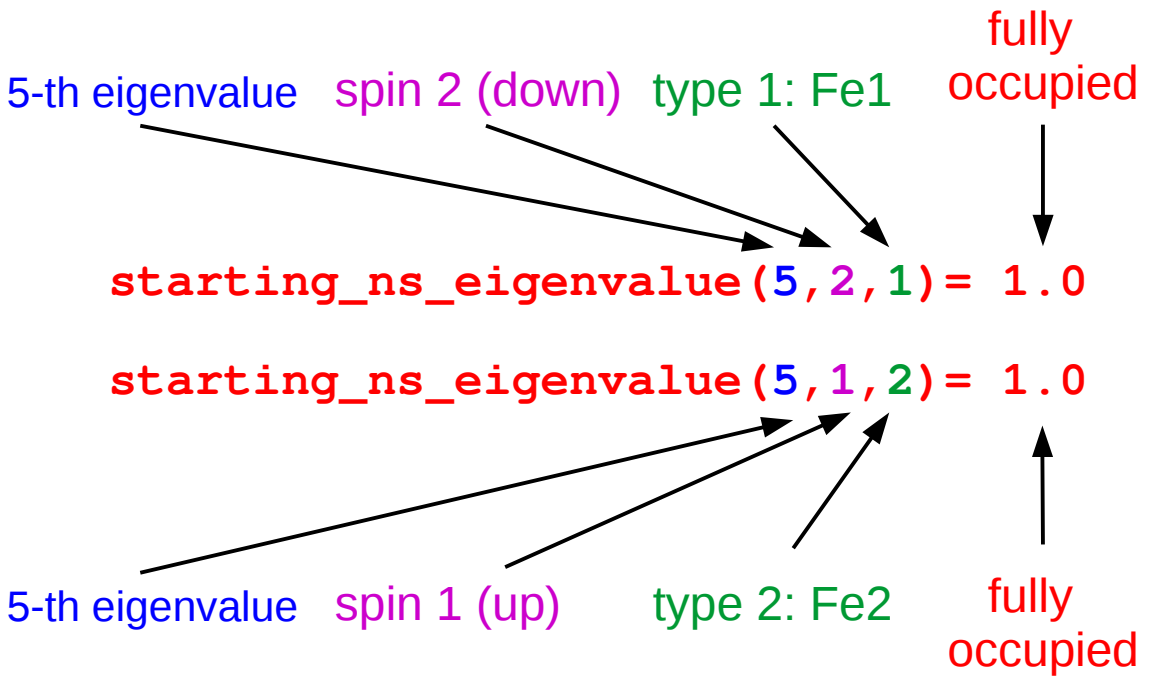
A “hint” for DFT+*U* where to look for a correct solution

```
&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.



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
```

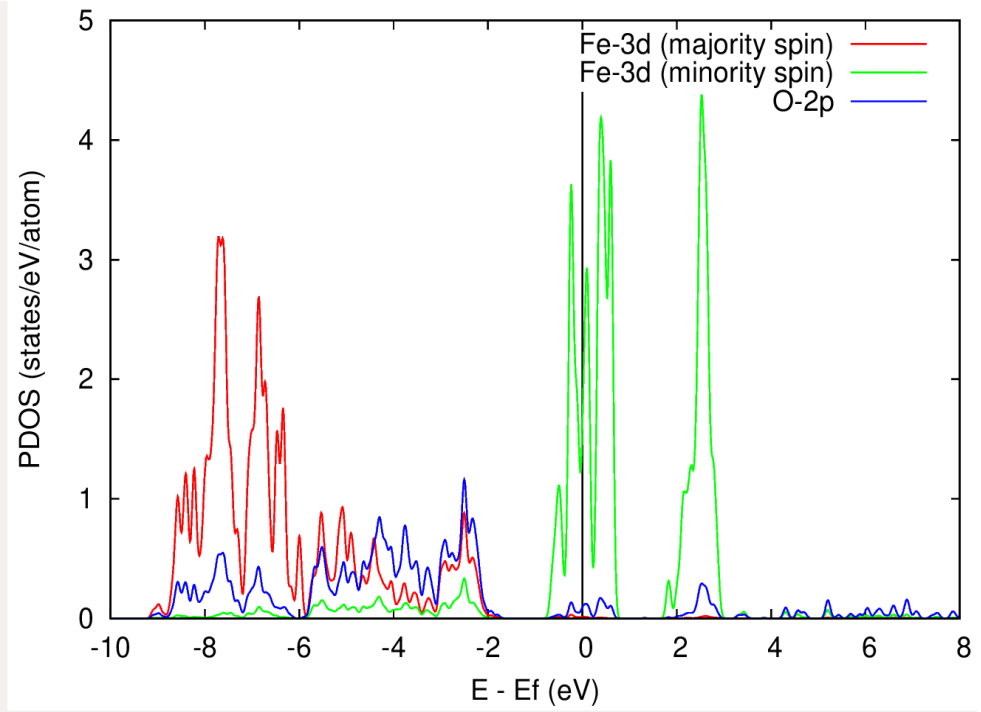
Fe1

```
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.

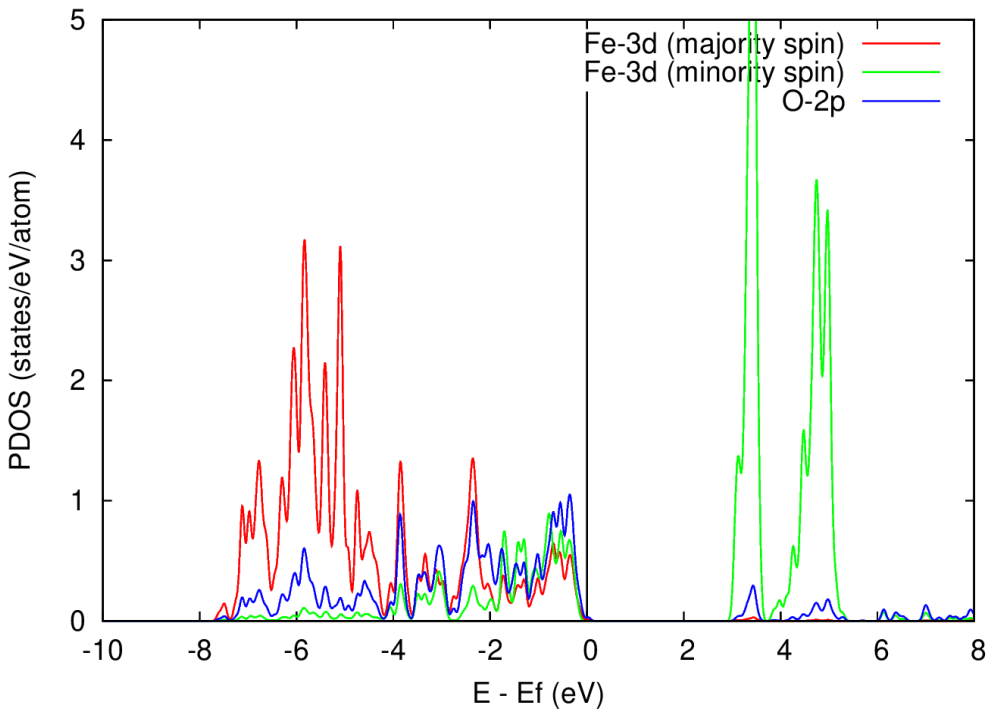
Comparison of DFT+*U* results w/o and w/ starting_ns_eigenvalue

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 experiement!

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 **q** points
1x1x1 0s the minimal grid (**q**=0), it is fast but not very accurate

If .true. Use extrapolation for the **q**->0 limit

Specifies that the singularity at **q**->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 treatement of divergences at q->0

exxdiv_treatment	CHARACTER
Default:	'gygi-baldereschi'

Specific for EXX. It selects the kind of approach to be used
for treating the Coulomb potential divergencies at small q vectors.

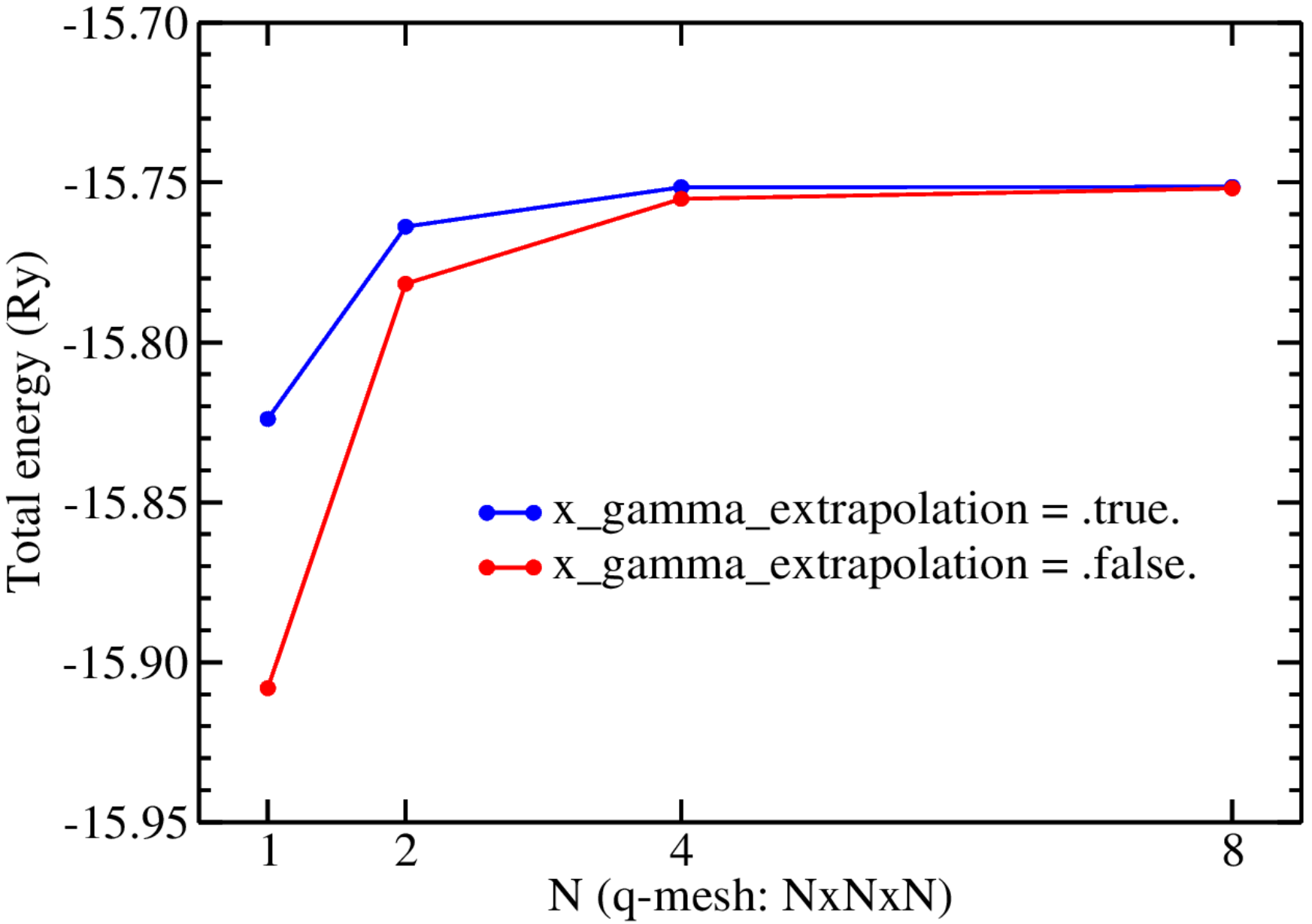
'gygi-baldereschi' :
appropriate for cubic and quasi-cubic supercells

'vcut_spherical' :
appropriate for cubic and quasi-cubic supercells

'vcut_ws' :
appropriate for strongly anisotropic supercells, see also ecutvcut.

'none' :
sets Coulomb potential at G,q=0 to 0.0 (required for GAU-PBE)

Convergence of the total energy wrt q point grid



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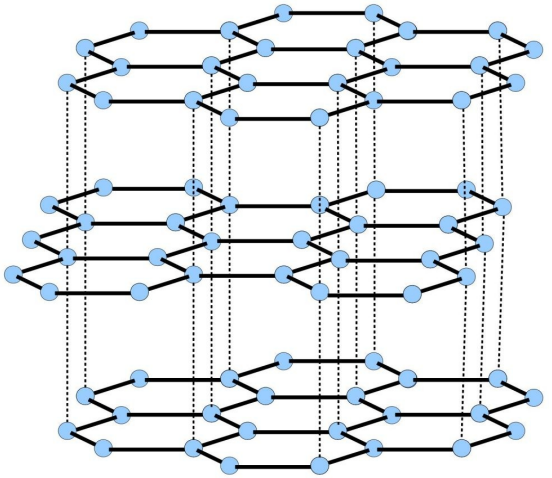
Graphite



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 A).

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.
/
&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
/
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
```

SCF calculation

Calculation of forces and stress

Hexagonal lattice, a and c are in Angtrom!

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

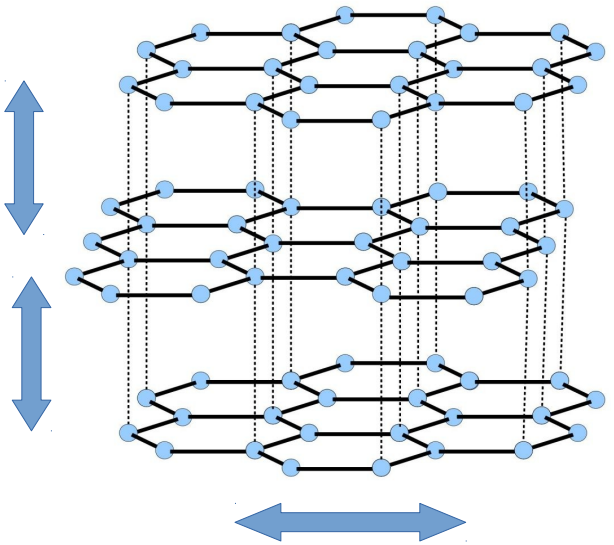
Remember to generate and store the kernel table!
vdW_kernel_table

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`?