MAX School on Advanced Materials and Molecular Modelling
with QUANTUM ESPRESSO

QE-2021: Hands-on session – Day-4

(Advanced functionals)

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Outline

Example 1: DFT+U study of FeO

Example 2: DFT with hybrid functionals: study of Si

Example 3: DFT with Van der Waals functionals: study of graphite

(We will use HPC for this hands-on, because the examples are quite heavy)   2

Outline

Example 1: DFT+U study of FeO

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Example 3: DFT with Van der Waals functionals: study of graphite

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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:

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

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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 6.7)

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

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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

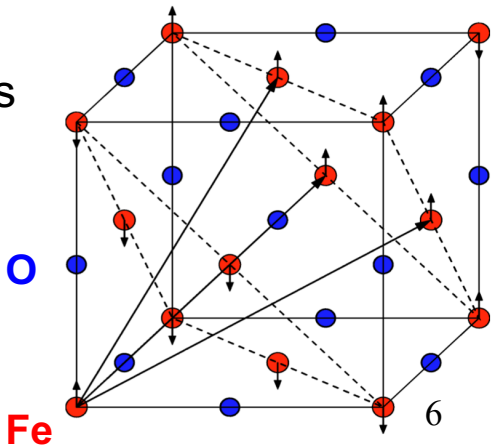ESPRESSO_PSEUDO and ESPRESSO_TMPDIR

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

O

Fe

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QE 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: Choose File   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)[NOTE]
(and smearing (eV) in case of fractional occupations):   fine (0.20 1/Å, 0.2 eV) ⬍

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 library

SSSP Efficiency (version 1.1)

$\Delta_{eff} = 0.44$ meV

[⬇ Cutoffs table] [⬇ Pseudos] [Switch to SSSP Precision]

[Updates v1.1 beta]

H 60(480)																	He 50(200)
Li 40(320)	Be 40(320)											B 35(280)	C 45(360)	N 60(480)	O 50(400)	F 45(360)	Ne 50(200)
Na 40(320)	Mg 30(240)											Al 30(240)	Si 30(240)	P 30(240)	S 35(280)	Cl 40(320)	Ar 60(240)
K 60(480)	Ca 30(240)	Sc 40(160)	Ti 35(280)	V 35(280)	Cr 40(320)	Mn 65(780)	Fe 90(1080)	Co 45(360)	Ni 45(360)	Cu 55(440)	Zn 40(320)	Ga 70(560)	Ge 40(320)	As 35(280)	Se 30(240)	Br 30(240)	Kr 45(180)
Rb 30(120)	Sr 30(240)	Y 35(280)	Zr 30(240)	Nb 40(320)	Mo 35(140)	Tc 30(120)	Ru 35(140)	Rh 35(140)	Pd 45(180)	Ag 50(200)	Cd 60(480)	In 50(400)	Sn 60(480)	Sb 40(320)	Te 30(240)	I 35(280)	Xe 60(240)
Cs 30(240)	Ba 30(240)	*	Hf 50(200)	Ta 45(360)	W 30(240)	Re 30(240)	Os 40(320)	Ir 55(440)	Pt 35(280)	Au 45(180)	Hg 50(200)	Tl 50(400)	Pb 40(320)	Bi 45(360)	Po 75(600)		Rn 120(960)

*	La 40(320)	Ce 40(320)	Pr 40(320)	Nd 40(320)	Pm 40(320)	Sm 40(320)	Eu 40(320)	Gd 40(320)	Tb 40(320)	Dy 40(320)	Ho 40(320)	Er 40(320)	Tm 40(320)	Yb 40(320)	Lu 45(360)

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

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 are 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.

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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!)

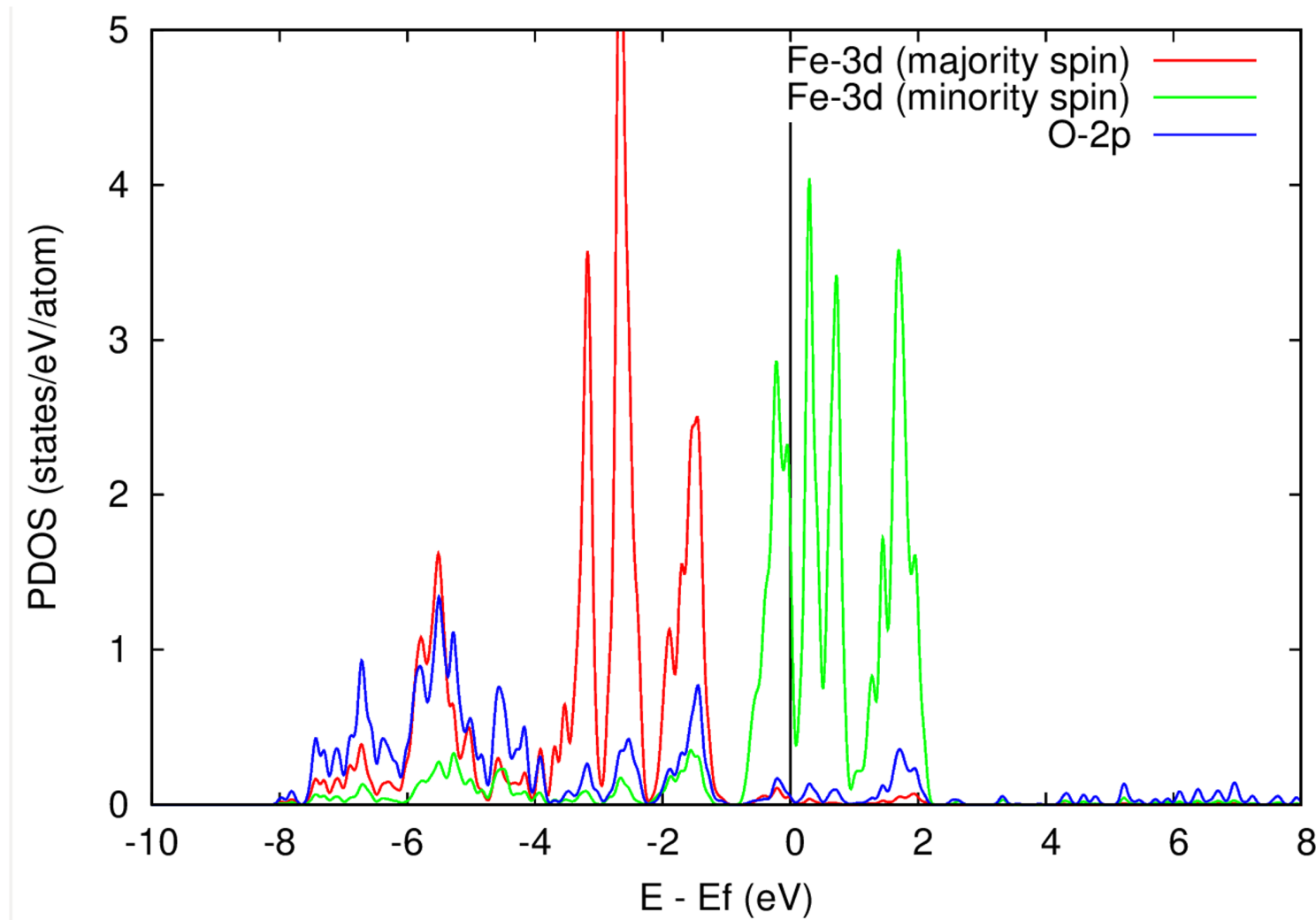Minimum and maximum value of energy for the plot, in eV

Energy grid step

Gnuplot script: plot_pdos.gp

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**"

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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) = 4.6
    Hubbard_U(2) = 4.6
/
&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* = 4.6 eV for Fe-*3d* states (see next slides)

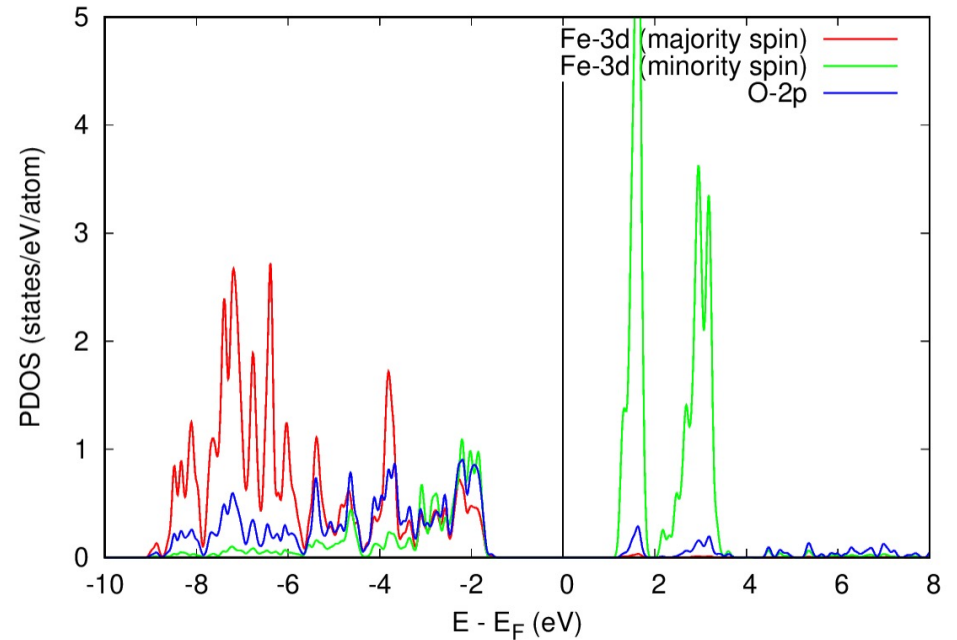Hubbard U values (in eV) for atomic type 1 & type 2

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DFT vs DFT+*U*

DFT
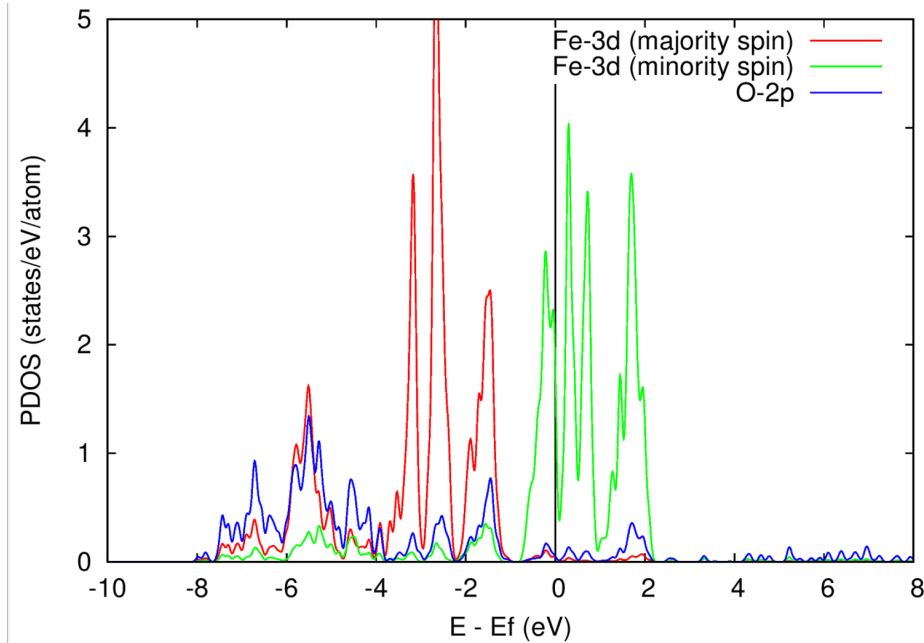
The solution with DFT+*U* is metallic

If DFT+*U* does not give the insulating solution, use **starting_ns_eigenvalue**. Check for more details this paper: PRB 71, 035105 (2005).

DFT+*U*

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

Agreement with the experiement!

How to compute the Hubbard *U* parameter?

Linear response theory

$\Updownarrow$

Density-functional perturbation theory (DFPT)

$$U^I = (\chi_0^{-1} - \chi^{-1})_{II}$$

$$\chi_{IJ} = \sum_{\sigma,m} \frac{dn_{mm}^{I\sigma}}{d\lambda^J} \quad \Longleftrightarrow \quad \frac{dn_{m_1 m_2}^{sl\sigma}}{d\lambda^{s'l'}} = \frac{1}{N_\mathbf{q}} \sum_\mathbf{q}^{N_\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})} \Delta_\mathbf{q}^{s'} \bar{n}_{m_1 m_2}^{s\,\sigma}$$

Sum over all **q** points in a **q** mesh

How to compute the Hubbard *U* parameter?

Using the **HP** (**H**ubbard **P**arameters**)** code of Quantum ESPRESSO

Input file "hp.FeO.in":

```
&inputhp
   prefix = 'FeO'
  !outdir = './tmp/'
   nq1 = 1, nq2 = 1, nq3 = 1
/
```

Prefix and **outdir** must be exactly the same as in the input file pw.FeO.scf.in

Size of the **q** point mesh: 1x1x1 in this case

U = 4.6 eV

Warning: This *U* value is not converged with respect to the **k** and **q** meshes!!!

Documentation: quantum-espresso/HP/Doc/INPUT_HP.txt

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

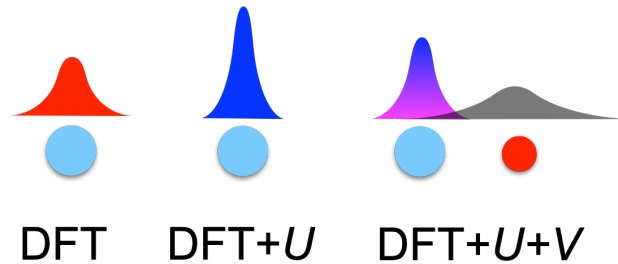I. Timrov, N. Marzari, M. Cococcioni, PRB **103**, 045141 (2021)

DFT+*U*+*V*

DFT+*U*+*V* is an extended formulation that takes into account inter-site Hubbard interactions:

$$E = E_{\mathrm{DFT}} + \frac{1}{2} \sum_{I,\sigma} U^{I} \operatorname{Tr}\left[\left(\mathbf{1} - \mathbf{n}^{I\sigma}\right) \mathbf{n}^{I\sigma}\right] - \frac{1}{2} \sum_{I,J,\sigma} V^{IJ} \operatorname{Tr}\left[\mathbf{n}^{IJ\sigma} \mathbf{n}^{JI\sigma}\right]$$

↑ effective on-site Hubbard interaction   ↑ inter-site Hubbard interactions
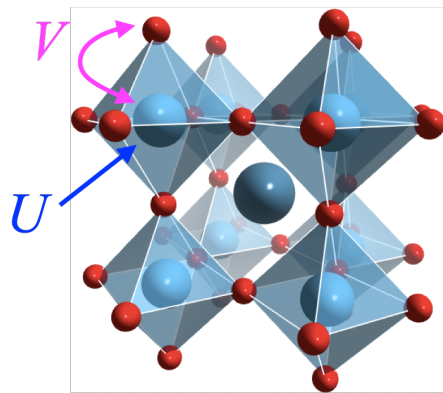
atomic localisation &
inter-atomic hybridisations

DFT   DFT+*U*   DFT+*U*+*V*

Both *U* and *V* can be computed using the HP code

[1] *V.L. Campo Jr and M. Cococcioni, JPCM 22, 055602 (2010).*

Theory: V.L. Campo Jr and M. Cococcioni, JPCM 22, 055602 (2010)

I. Timrov, N. Marzari, M. Cococcioni, PRB **103**, 045141 (2021)

Outline

Example 1: DFT+U study of FeO

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Example 3: DFT with Van der Waals functionals: study of graphite

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

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

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

We need to setup the q mesh

where

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

(the finite sum over N_k **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 pw.Si.scf.in

Hybrid functionals are very computationally expensive!

```
&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 pseudo-potential (PP) file.
Important: use a PP for the closest GGA (PBE in this case), there are no PP's for hybrids.

Mesh for the **q** points 1x1x1 is 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

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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

Slow calculations ➡ do for scarce **q** meshes and check the "reference" folder
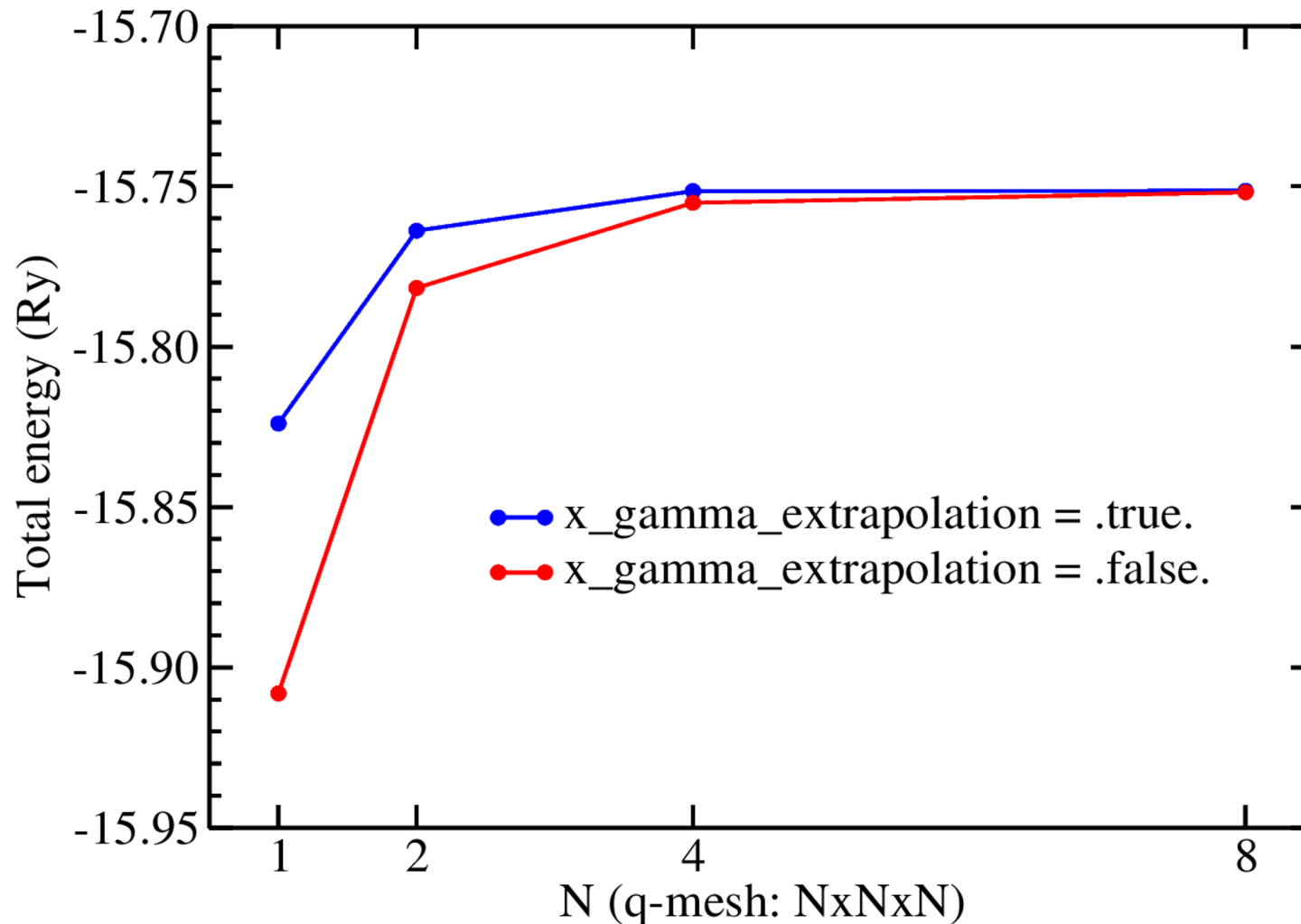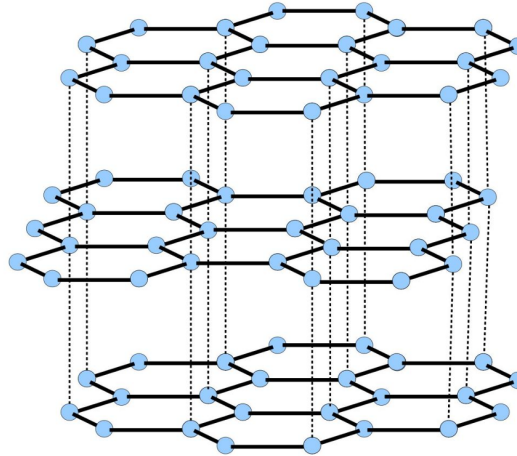
Outline

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Example 2: DFT with hybrid functionals: study of Si

Example 3: DFT with Van der Waals functionals: study of graphite
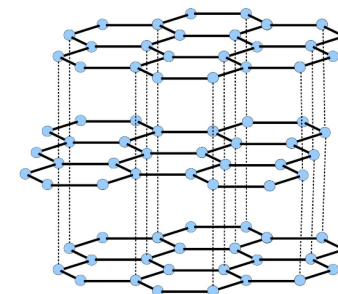
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Graphite

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.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

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

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

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

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Types of the van der Waals correction

vdw_corr	CHARACTER
Default:	'none'
See:	london_s6, london_rcut, london_c6, london_rvdw, dftd3_version, dftd3_threebody, ts_vdw_econv_thr, ts_vdw_isolated, xdm_a1, xdm_a2

```
Type of Van der Waals correction. Allowed values:

    'grimme-d2', 'Grimme-D2', 'DFT-D', 'dft-d' :
        Semiempirical Grimme's DFT-D2. Optional variables:
        london_s6, london_rcut, london_c6, london_rvdw
        S. Grimme, J. Comp. Chem. 27, 1787 (2006), doi:10.1002/jcc.20495
        V. Barone et al., J. Comp. Chem. 30, 934 (2009), doi:10.1002/jcc.21112

    'grimme-d3', 'Grimme-D3', 'DFT-D3', 'dft-d3' :
        Semiempirical Grimme's DFT-D3. Optional variables:
        dftd3_version, dftd3_threebody
        S. Grimme et al, J. Chem. Phys 132, 154104 (2010), doi:10.1002/jcc.20495

    'TS', 'ts', 'ts-vdw', 'ts-vdW', 'tkatchenko-scheffler' :
        Tkatchenko-Scheffler dispersion corrections with first-principle derived
        C6 coefficients.
        Optional variables: ts_vdw_econv_thr, ts_vdw_isolated
        See A. Tkatchenko and M. Scheffler, PRL 102, 073005 (2009).

    'XDM', 'xdm' :
        Exchange-hole dipole-moment model. Optional variables: xdm_a1, xdm_a2
        A. D. Becke et al., J. Chem. Phys. 127, 154108 (2007), doi:10.1063/1.2795701
        A. Otero de la Roza et al., J. Chem. Phys. 136, 174109 (2012),
        doi:10.1063/1.4705760

Note that non-local functionals (eg vdw-DF) are NOT specified here but in input_dft
```

# Structural optimization in graphite

```
Perform a variable-cell optimization : `pw.x < pw.graphite.vc-relax.in > pw.graphite.vc-relax.out`

Study different cases:
1.  `input_dft = 'vdw-DF'`     @PBE pseudo (non-local)
2.  `input_dft = 'vdw-DF2'`    @PBE pseudo (non-local)
3.  `input_dft = 'rVV10'`      @PBE pseudo (non-local)
4.  `vdw_corr  = 'DFT-D'`      @PBE pseudo (semi-empirical)
5.  `vdw_corr  = 'DFT-D3'`     @PBE pseudo (semi-empirical)
6.   Normal PBE calculation    @PBE pseudo
7.   Normal LDA calculation    @LDA pseudo

Compare the optimized inter-layer distances with the experimental value of 3.336 A.
```

Inter-layer distance in graphite
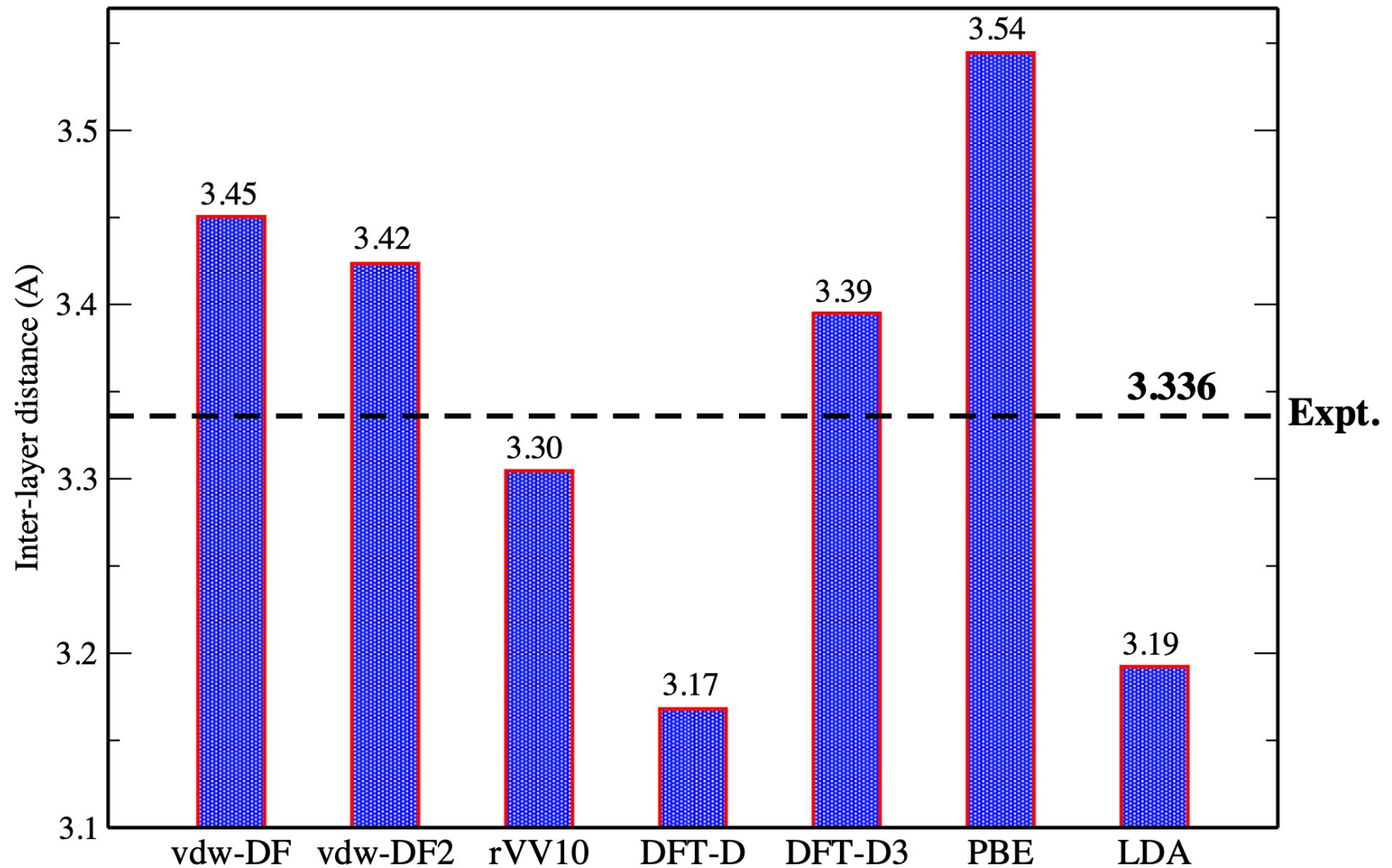
Note: these results must be carefully converged (cutoff, k points, etc.)