

Tutorial on DFT+ U + V using Quantum ESPRESSO

Iurii Timrov, Fatemeh Haddadi, Edward Linscott, Nicola Marzari

*THEOS and NCCR-MARVEL,
École Polytechnique Fédérale de Lausanne (Switzerland)*



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TRANSITION

Outline

Example 1: Standard DFT calculation for CoO

Example 2: Calculation of Hubbard parameters for CoO

Example 3: DFT+ U + V calculation for CoO

Outline

Example 1: Standard DFT calculation for CoO

Example 2: Calculation of Hubbard parameters for CoO

Example 3: DFT+ U + V calculation for CoO

Input file CoO.scf.in

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='CoO'
  pseudo_dir = '../files/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 0.00000000 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}
0.500380664 0.500380664 1.004818266
0.500380664 1.004818266 0.500380664
1.004818266 0.500380664 0.500380664
K_POINTS {automatic}
3 3 3 0 0 0
```

Self-consistent-field DFT calculation

Specification of the lattice (see CELL_PARAMETERS)

Number of atoms and atomic types

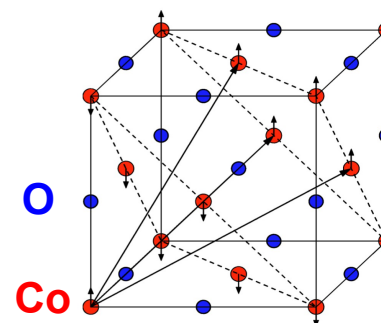
Cutoffs for the wavefunctions and density/potential

Spin-polarized (collinear) calculation (AFM)

Marzari-Vanderbilt smearing (broadening: 0.02 Ry)

Convergence threshold for self-consistency

Pseudopotentials and functional (PBEsol)



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 ($1/\text{\AA}$)^[NOTE]
(and smearing (eV) in case of fractional occupations):

fine (0.20 $1/\text{\AA}$, 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>

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

Input file CoO.nscf.in

```
&control
  calculation='nscf'
  restart_mode='from_scratch',
  prefix='CoO'
  pseudo_dir = '../files/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    0.00000000  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}
  0.500380664  0.500380664  1.004818266
  0.500380664  1.004818266  0.500380664
  1.004818266  0.500380664  0.500380664
K_POINTS {automatic}
6 6 6 0 0 0
```

Non-self-consistent-field DFT calculation

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

Number of Kohn-Sham bands/states that are computed

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.

Here we use a denser **k** points mesh (w.r.t SCF)

Input file CoO.projwfc.in

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

Gaussian broadening for PDOS

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

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

Energy grid step

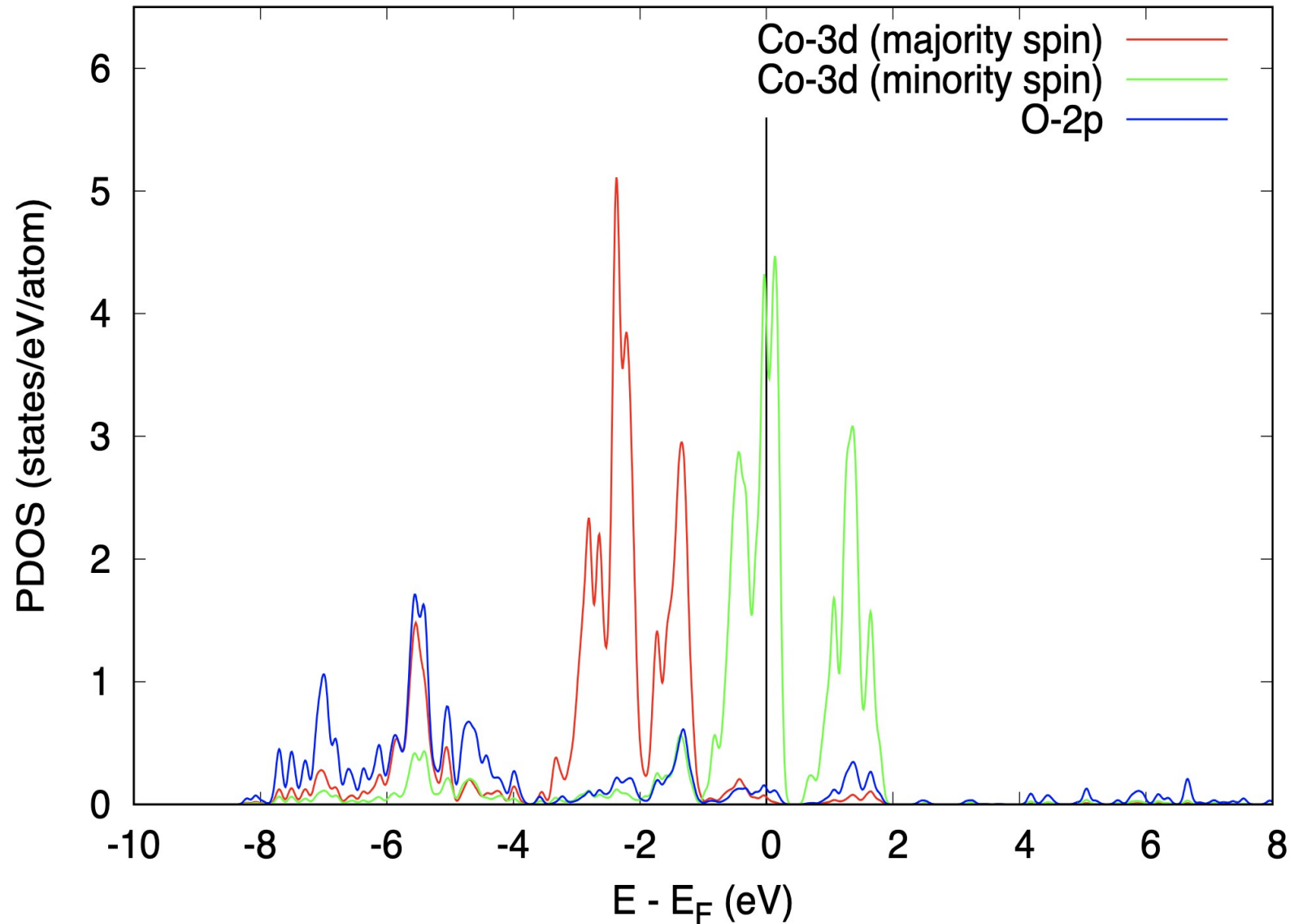
Gnuplot script: plot_pdos.gp

Inspect the script: it aims at plotting Co-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 “**CoO_PDOS.eps**”

PDOS of CoO from a standard DFT calculation



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



Let's try **DFT+U+V**

Experimentally CoO is known to be insulating

Outline

Example 1: Standard DFT calculation for CoO

Example 2: Calculation of Hubbard parameters for CoO

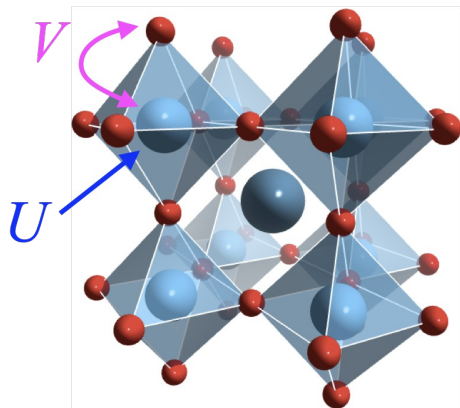
Example 3: DFT+ U + V calculation for CoO

DFT+ U + V

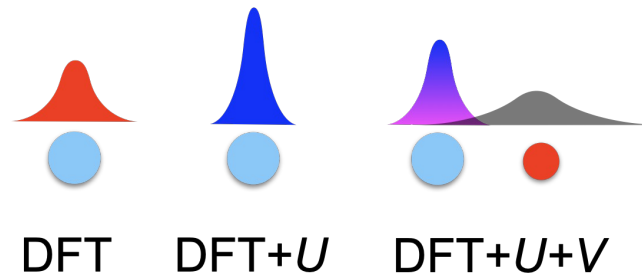
DFT+ U + V is an **extended formulation** that takes into account **inter-site Hubbard interactions**:

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

↑ effective on-site Hubbard interaction ↑ inter-site Hubbard interactions



← **atomic localisation &
inter-atomic hybridisations**



**Both U and V are
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)

Hubbard projectors

$$(\mathbf{n}^{I\sigma})_{m_1 m_2} = \sum_i f_i \langle \psi_{i\sigma} | \varphi_{m_2}^I \rangle \langle \varphi_{m_1}^I | \psi_{i\sigma} \rangle$$

Currently, Hubbard projectors are hard-coded (in Quantum ESPRESSO 6.7)



Check two subroutines in quantum-espresso/Modules :



`set_hubbard_n.f90`

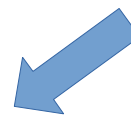
principal quantum number “ n ”

`set_hubbard_l.f90`

orbital quantum number “ l ”

For Co : $n = 3$

For Co : $l = 2$



3d atomic orbitals (orthogonalized) of Co are Hubbard projector functions

Input file CoO.scf.in for DFT+*U*+*V*

```
calculation='scf'
restart_mode='from_scratch',
prefix='CoO'
pseudo_dir = '../files/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
lda_plus_u = .true.,
lda_plus_u_kind = 2,
U_projection_type = 'ortho-atomic',
Hubbard_V(1,1,1) = 1.d-10
Hubbard_V(2,2,1) = 1.d-10
Hubbard_V(3,3,1) = 1.d-10
/
&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 0.00000000 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}
0.500380664 0.500380664 1.004818266
0.500380664 1.004818266 0.500380664
1.004818266 0.500380664 0.500380664
K_POINTS {automatic}
3 3 3 0 0 0
```

Hubbard-specific input keywords

lda_plus_u_kind = 0 (DFT+*U*, Dudarev)
lda_plus_u_kind = 1 (DFT+*U*, Lichtenstein)
lda_plus_u_kind = 2 (DFT+*U*+*V*, Dudarev)

U_projection_type = 'atomic'

U_projection_type = 'ortho-atomic'

Hubbard_V(na,nb,k), (na,nb,k) = (1,1,1) ... (natx,27*natx,4)	REAL
Default:	0.D0 for all elements

Hubbard_V(na,nb,k): V parameters (eV) between atoms na and nb, used in DFT+*U*+*V* calculations (only for [lda_plus_u_kind=2](#)). The atomic indices na and nb correspond to the atomic positions in the [ATOMIC_POSITIONS](#) card (this is not the same as Hubbard_U which is specified for [ATOMIC_SPECIES](#)). When na=nb, then Hubbard_V(na,na,k) is the on-site Hubbard_U for the atom na. natx=50 (if needed it can be changed in /Modules/parameters.f90) The index k controls the "interaction type" (k=1 is used for the simplest DFT+*U*+*V* calculation):
k=1 - interaction between standard orbitals (both on na and nb);
k=2 - interaction between standard (on na) and background (on nb) orbitals;
k=3 - interaction between background orbitals (both on na and nb);
k=4 - interaction between background (on na) and standard (on nb) orbitals. Standard orbitals correspond to the main Hubbard channel (e.g. d electrons in transition metals) and background orbitals correspond to the secondary Hubbard channel (e.g. p electrons in transition metals).

How to compute the Hubbard U and V parameters?

Linear response theory



Density-functional perturbation theory (DFPT)

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



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



Sum over \mathbf{q} points (each \mathbf{q} point corresponds to a different perturbation of electronic occupations)

How to compute the Hubbard U and V parameters?

Using the **HP** (Hubbard Parameters) code of Quantum ESPRESSO

Input file “CoO.hp.in”:

```
&inputhp  
  prefix = 'CoO'  
  outdir = './tmp'  
  nq1 = 2, nq2 = 2, nq3 = 2  
  conv_thr_chi = 1.d-6  
/
```

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

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

Convergence threshold for χ



parameters.out (file with Hubbard parameters U and V)

Warning: These Hubbard parameters are not converged with respect to **k** and **q**!
You need to perform careful convergence tests!

Documentation: [quantum-espresso/HP/Doc/INPUT_HP.txt](https://www.quantum-espresso.org/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)

File parameters.out

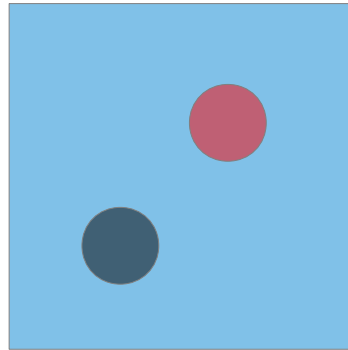
#	Atom 1	Atom 2	Hubbard V (eV)	
1	1	1	6.6421	U for Co1(3d)
1	55		0.4917	
1	47		0.4917	
1	23		0.4917	
1	12		0.4917	
1	44		0.4917	
1	20		0.4917	
2	2	2	6.6421	U for Co2(3d)
2	67		0.4917	
2	56		0.4917	
2	24		0.4917	
2	48		0.4917	
2	91		0.4917	
2	59		0.4917	

V between Co1(3d) and its 6 nearest neighbors O(2p)

V between Co2(3d) and its 6 nearest neighbors O(2p)

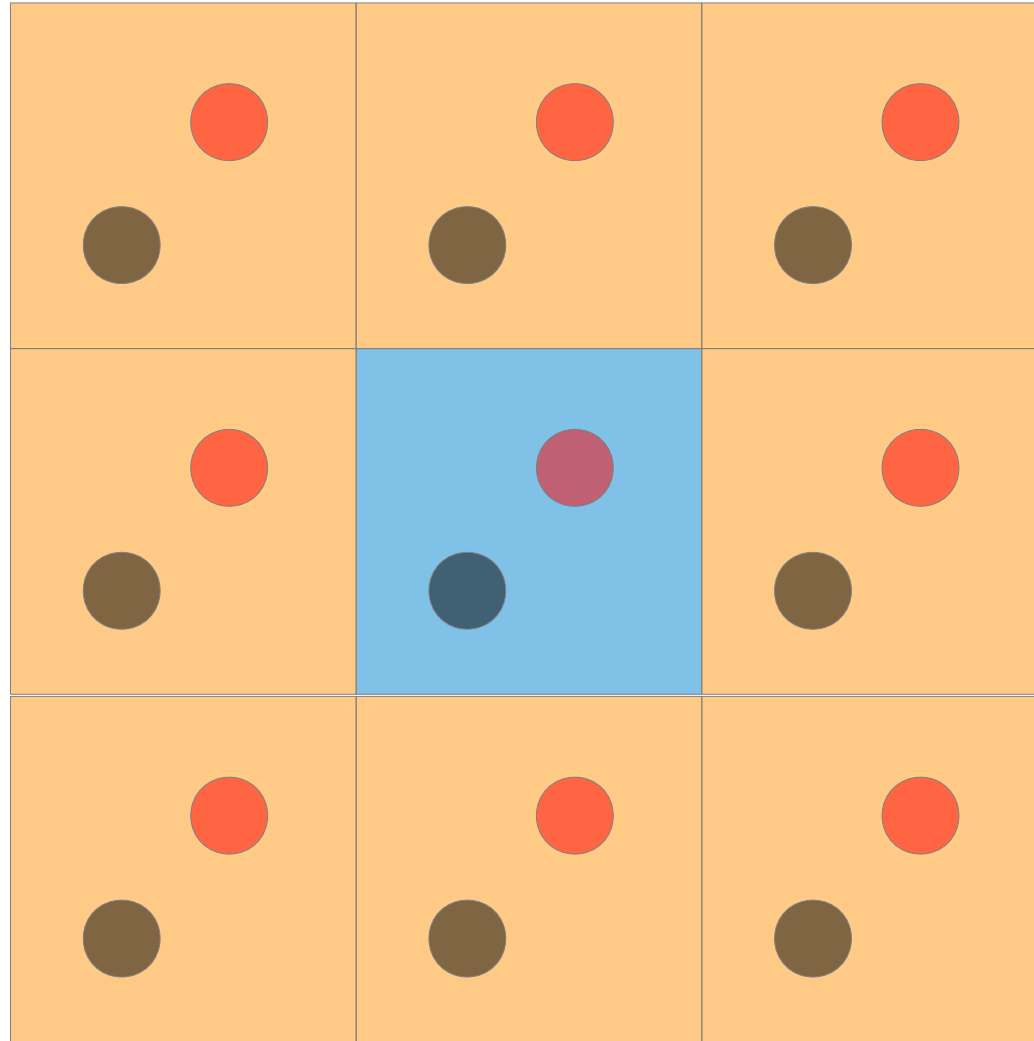
What is the meaning of these indices for Atom 1 and Atom 2? (see next slides)

Neighbors in periodic boundary conditions



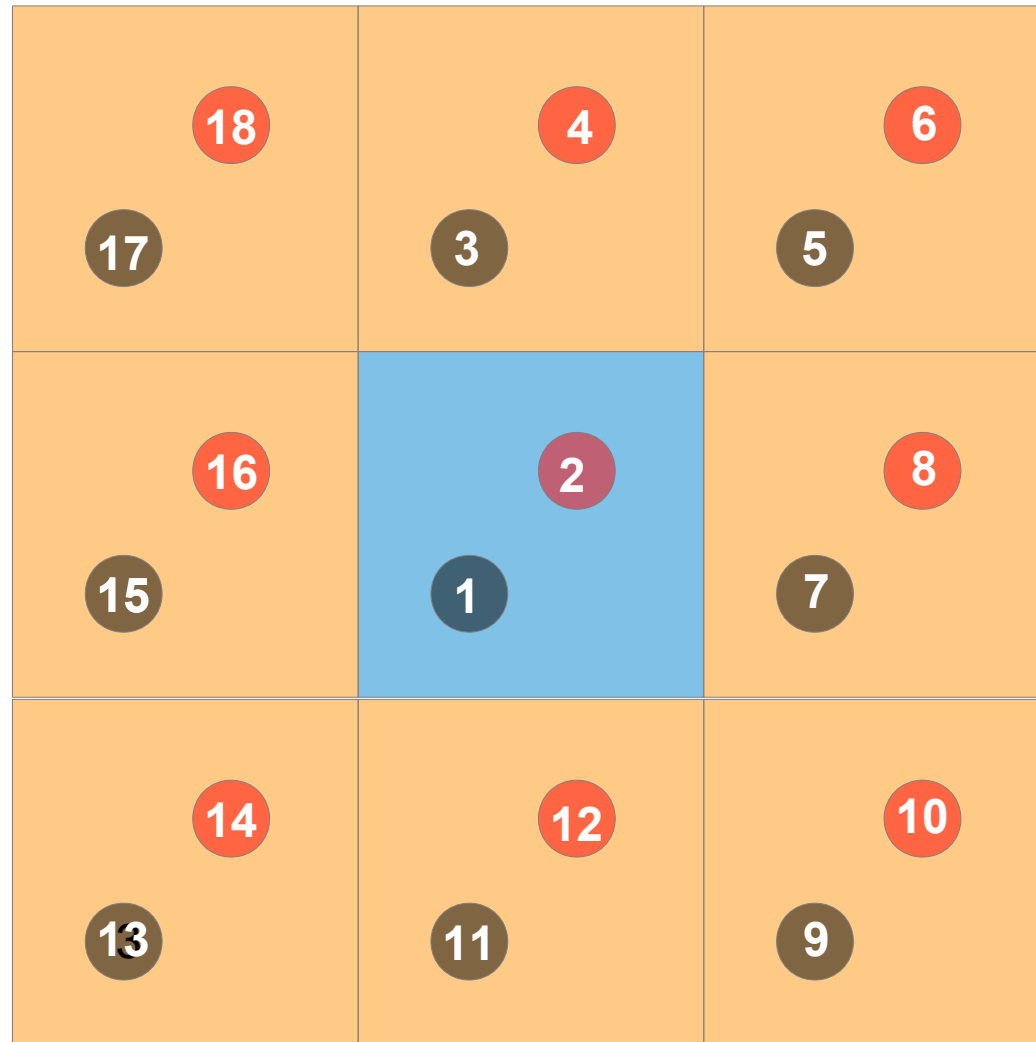
Let us consider a 2D case with 2 atoms in the primitive unit cell

Neighbors in periodic boundary conditions



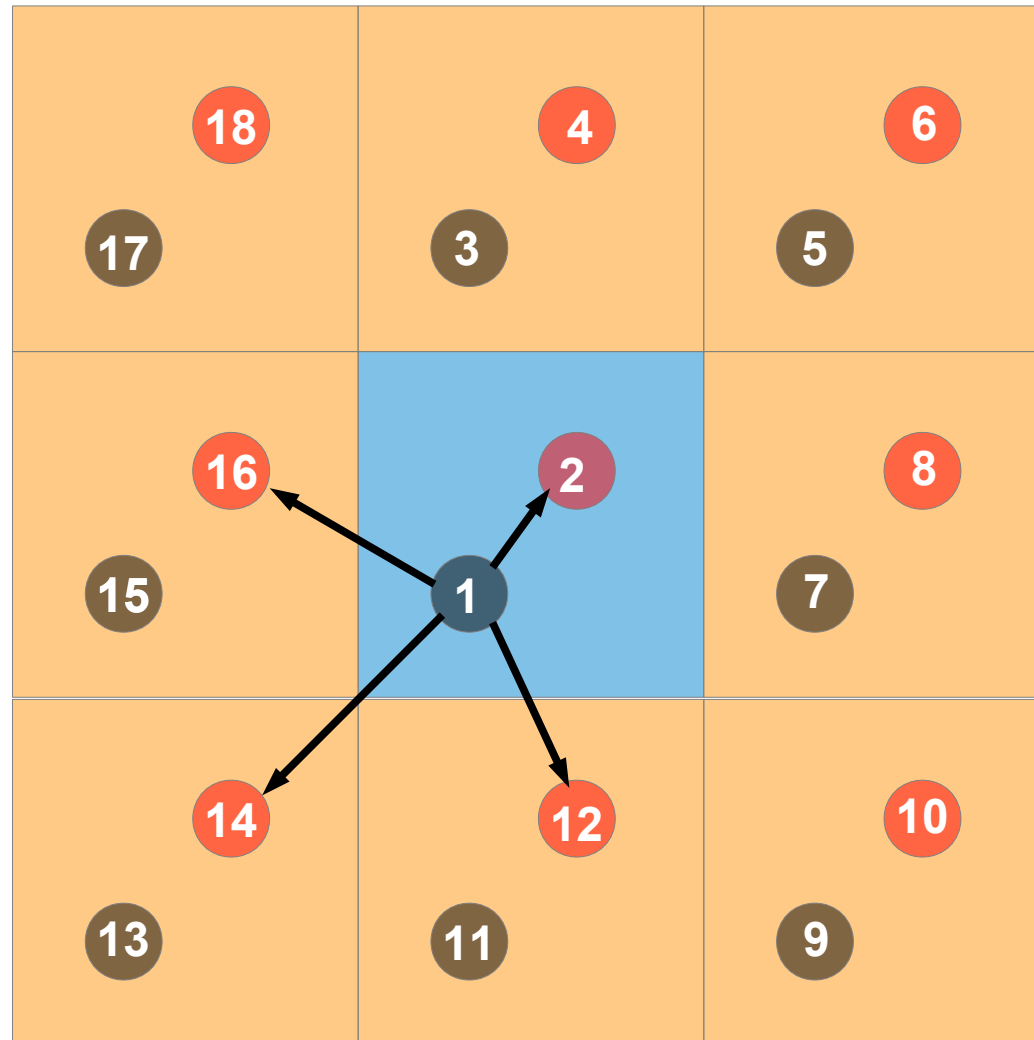
Let us periodically repeat our cell along all directions (virtual 3x3 supercell in 2D)

Neighbors in periodic boundary conditions



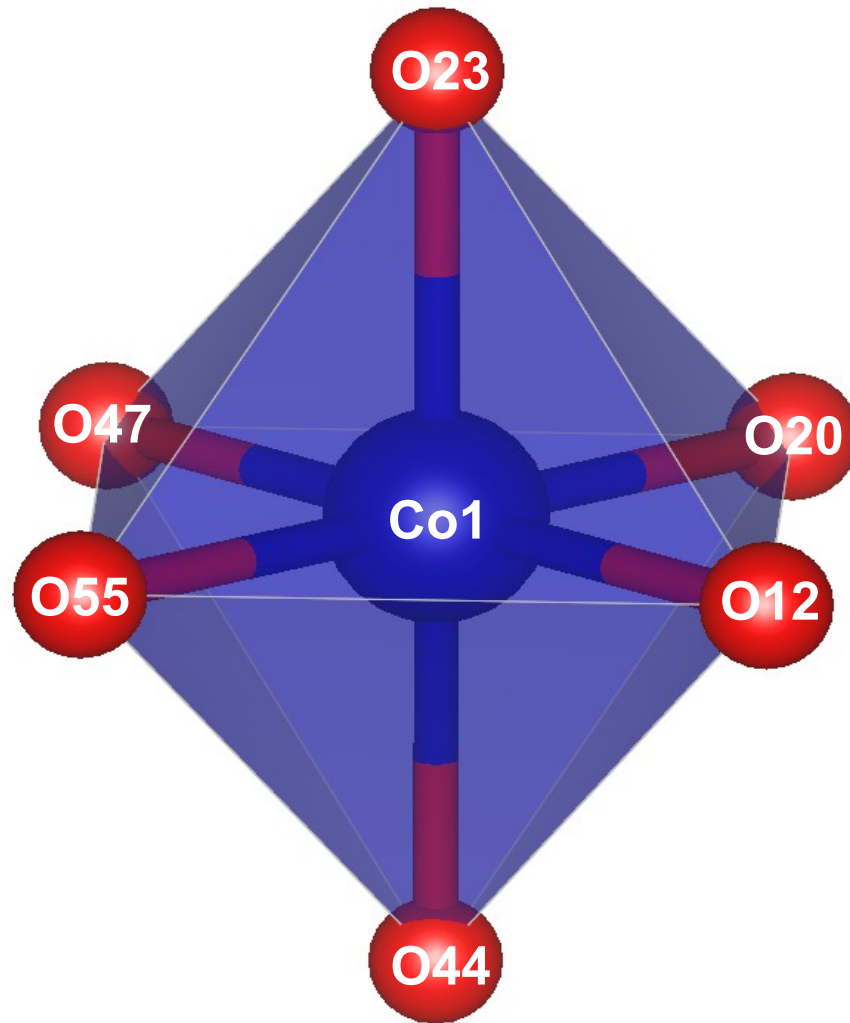
Let us number/label all the atoms

Neighbors in periodic boundary conditions



Now we can determine nearest neighbors for each transition-metal atom

The 3D case of CoO: 3x3x3 virtual supercell



Co1 and Co2 both have 6 nearest neighbors which are O atoms

Outline

Example 1: Standard DFT calculation for CoO

Example 2: Calculation of Hubbard parameters for CoO

Example 3: DFT+ U + V calculation for CoO

Input file CoO.scf.in

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='CoO'
  pseudo_dir = './files/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
  lda_plus_u = .true.,
  lda_plus_u_kind = 2,
  U_projection_type = 'ortho-atomic',
  Hubbard_parameters = 'file'
/
&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 0.00000000 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}
0.500380664 0.500380664 1.004818266
0.500380664 1.004818266 0.500380664
1.004818266 0.500380664 0.500380664
K_POINTS {automatic}
3 3 3 0 0 0
```

Self-consistent-field DFT+ U + V calculation

Hubbard keywords as before

Read Hubbard U and V from file [parameters.in](#)

Note: you need to rename the previously obtained file from parameters.out to parameters.in and use it in exercise “3_DFT+ U + V ”

Input file CoO.nscf.in

```
&control
  calculation='nscf'
  restart_mode='from_scratch',
  prefix='CoO'
  pseudo_dir = '../files/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
  lda_plus_u = .true.,
  lda_plus_u_kind = 2,
  U_projection_type = 'ortho-atomic',
  Hubbard_parameters = 'file'
/
&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      0.00000000      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}
  0.500380664  0.500380664  1.004818266
  0.500380664  1.004818266  0.500380664
  1.004818266  0.500380664  0.500380664
K_POINTS {automatic}
6 6 6 0 0 0
```

Non-self-consistent-field DFT+ U + V calculation

Hubbard keywords as before

Read Hubbard U and V from file [parameters.in](#)

Input file CoO.projwfc.in

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

Gaussian broadening for PDOS

Value of the 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

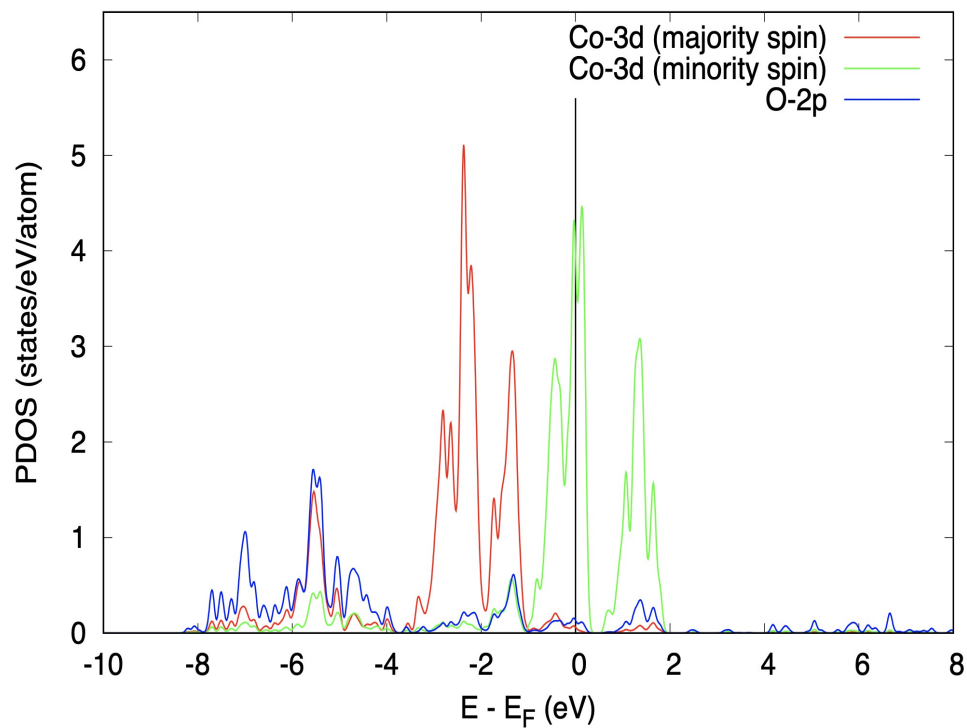
Inspect the script: it aims at plotting Co-3d state (majority spin and minority spin) and O-2p states.

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

Visualize the file “**CoO_PDOS.eps**”

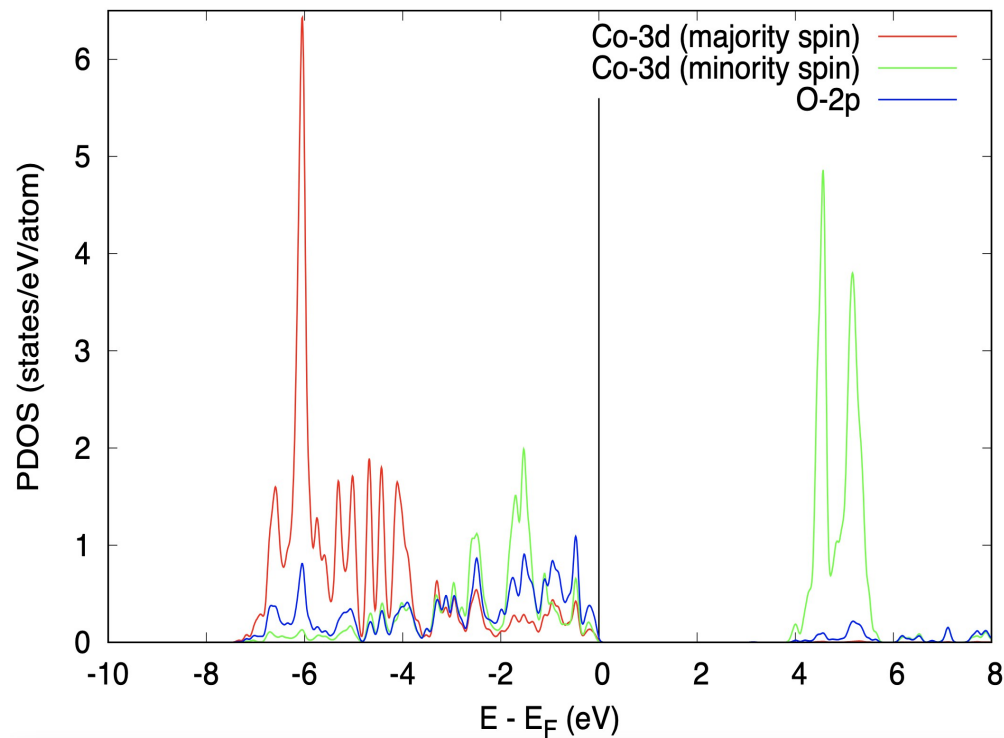
DFT vs DFT+ $U+V$

DFT



The solution with DFT is metallic

DFT+ $U+V$

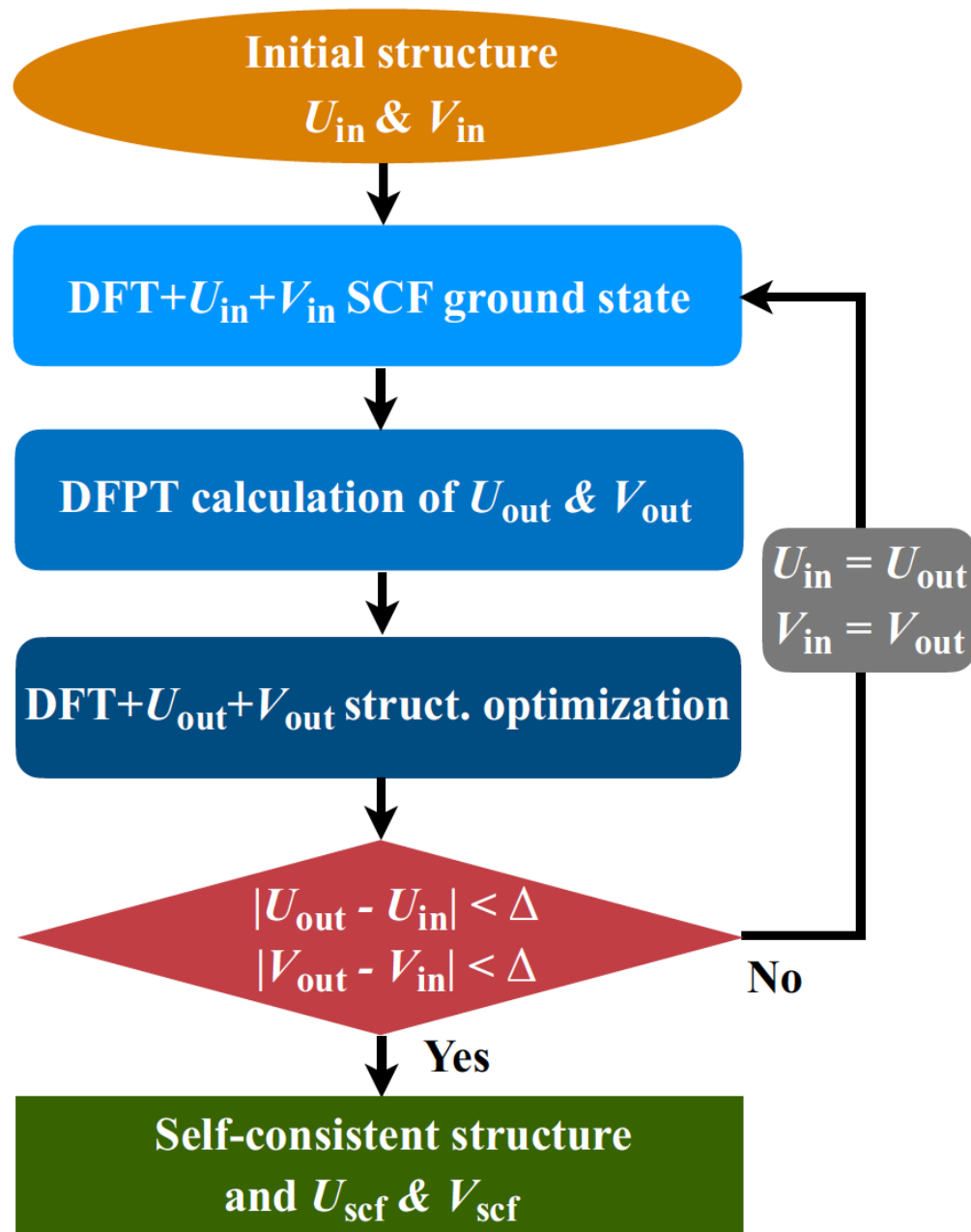


The solution with DFT+ $U+V$ is **insulating**



Agreement with the experiment!

Self-consistent calculation of Hubbard parameters



Some examples where intersite Hubbard V is important

- Structural properties and energetics of molecular complexes: J. Chem. Phys. 134, 094103 (2011)
- Voltages in Li-ion batteries: Phys. Rev. Materials 3, 033801 (2019)
- Formation energies of oxygen vacancies: Phys. Rev. Research 2, 023313 (2020)
- Energetics of complex magnetic systems: arXiv: 2106.00520 (2021)