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)

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     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}
   0.500380664   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)
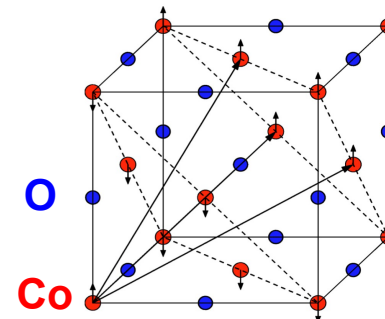
Number of atoms and atomic types

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)

O

Co

https://www.quantum-espresso.org/Doc/INPUT_PW.html

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

Refine cell (using spglib): No ⬍

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 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     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}
   0.500380664    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!)

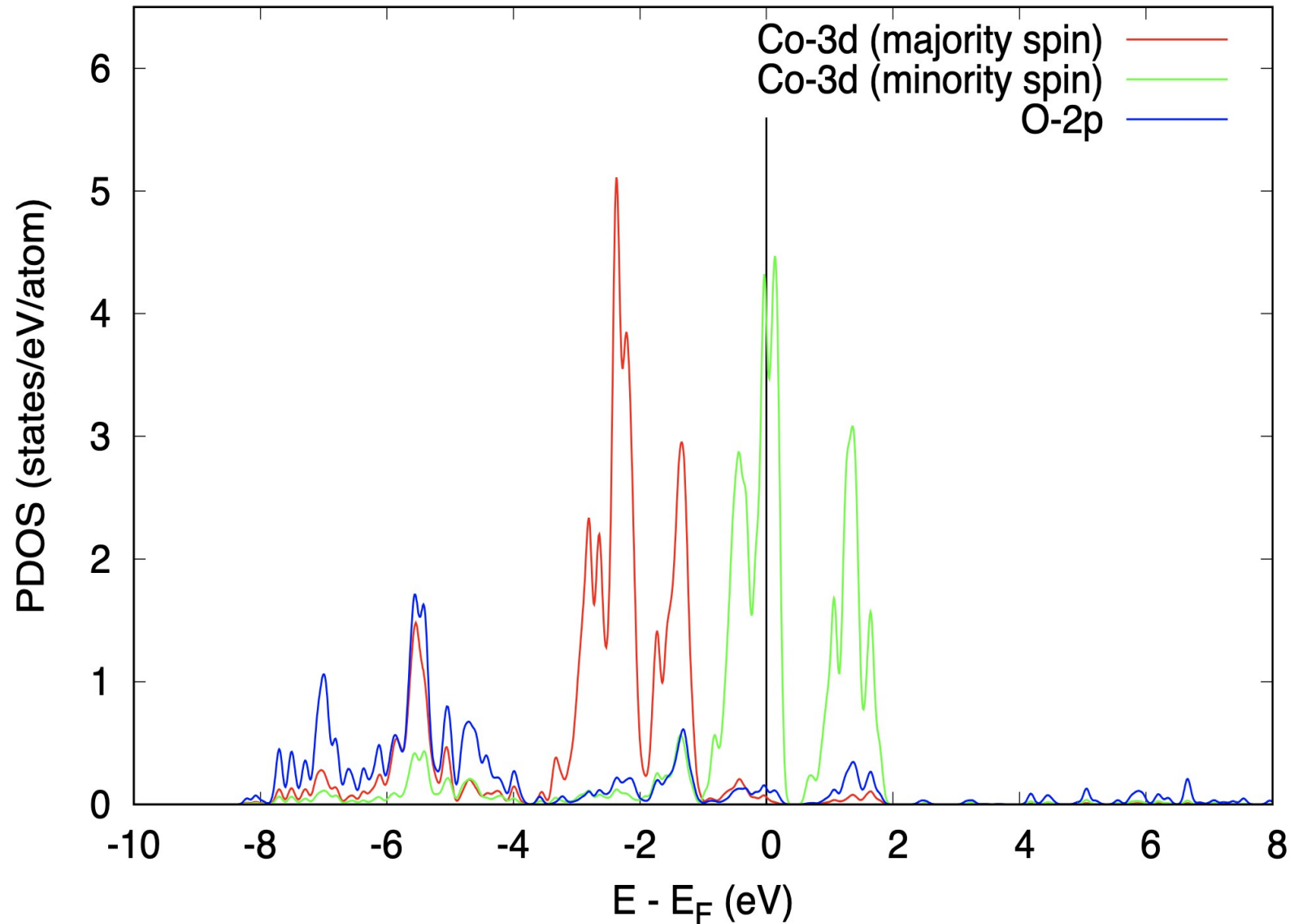Minimum and maximum value of energy for the plot, in eV

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

PDOS (states/eV/atom) vs $E - E_F$ (eV). Legend: Co-3d (majority spin) in red, Co-3d (minority spin) in green, O-2p in blue.

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

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

Experimentally CoO is know 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:**

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

↑   ↑

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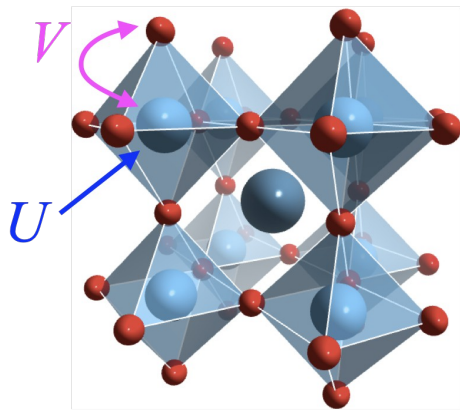
atomic localisation &
inter-atomic hybridisations

DFT   DFT+*U*   DFT+*U+V*
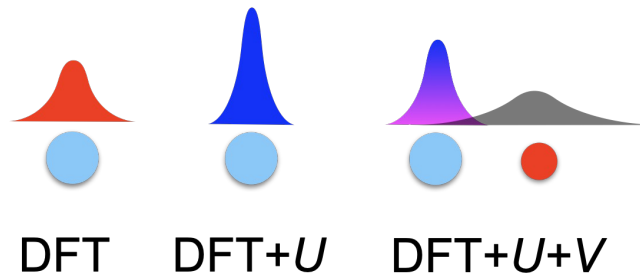
Both *U* and *V* are computed using the HP code

[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

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

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

Check two subroutines in quantum-espresso/Modules :
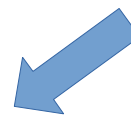
set_hubbard_n.f90

principal quantum number "n"

For Co : $n = 3$

set_hubbard_l.f90

orbital quantum number "l"

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      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}
   0.500380664   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).
Wnen 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 orbitlas (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

$\updownarrow$

Density-functional perturbation theory (DFPT)

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

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

Sum over **q** points (each **q** point corresponds to a different perturbation of electronic occupations)

How to compute the Hubbard *U* and *V* parameters?

Using the **HP** (**H**ubbard **P**arameters**)** 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

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	6.6421
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	6.6421
2	67	0.4917
2	56	0.4917
2	24	0.4917
2	48	0.4917
2	91	0.4917
2	59	0.4917

U for Co1(3d)

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

U for Co2(3d)

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

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

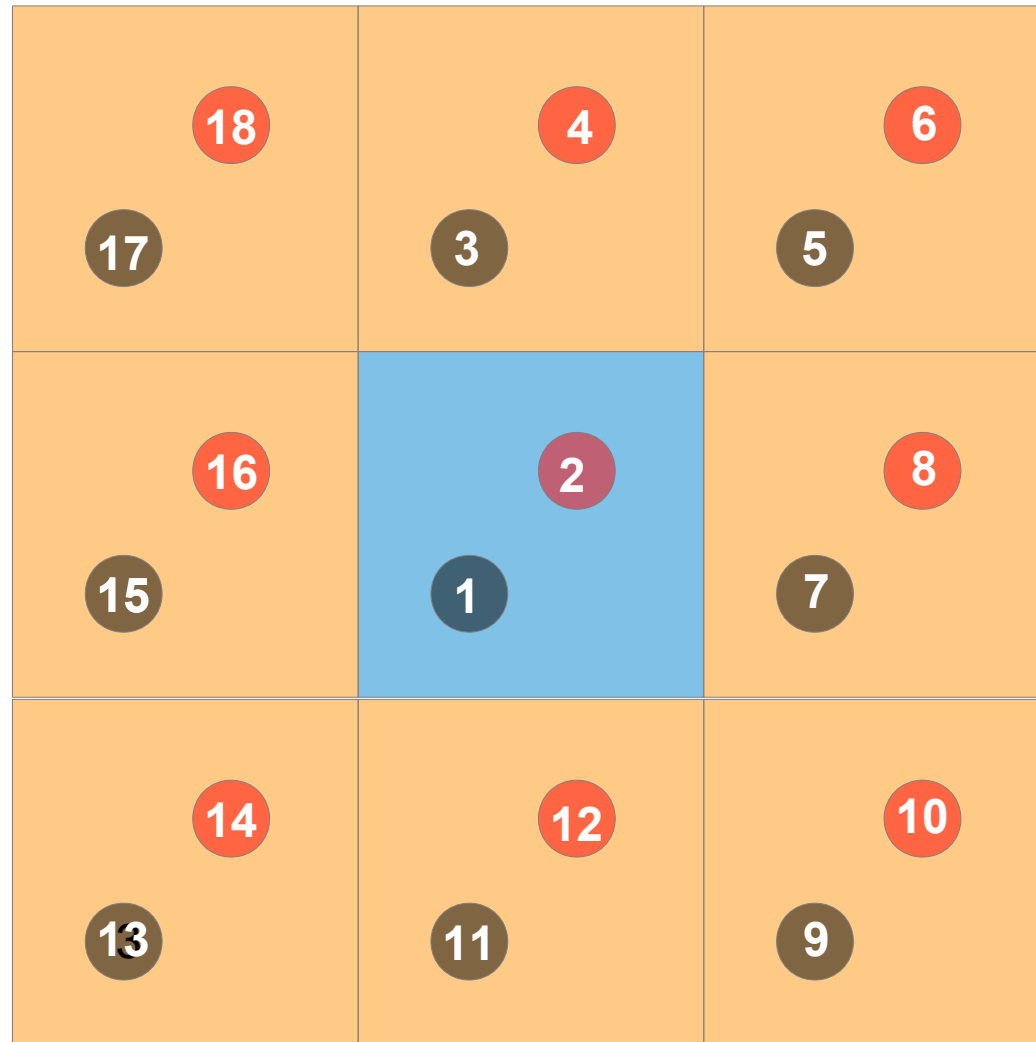# Neighbors in periodic boundary conditions
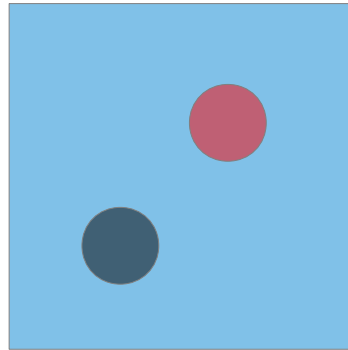
Let us consider a 2D case with 2 atoms in the primitive unit cell
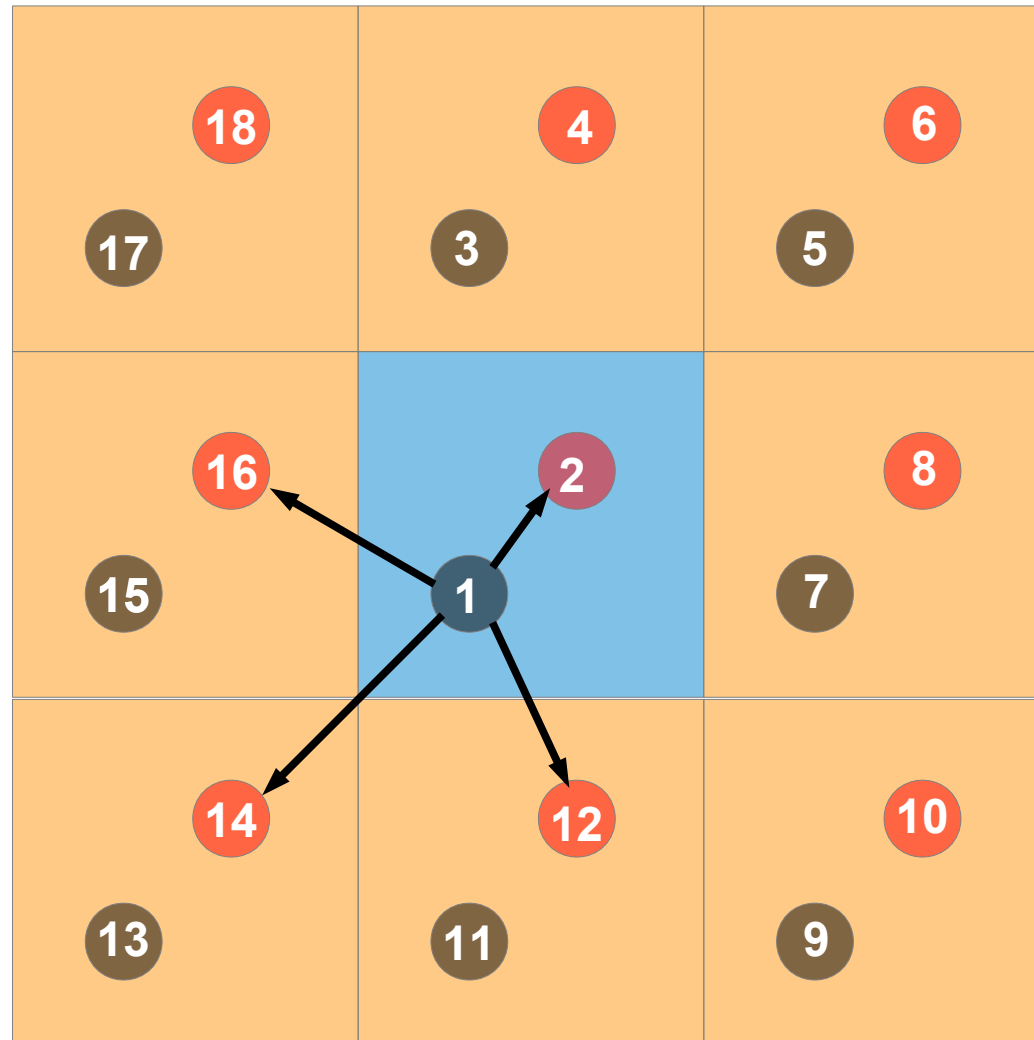
Neighbors in periodic boundary conditions
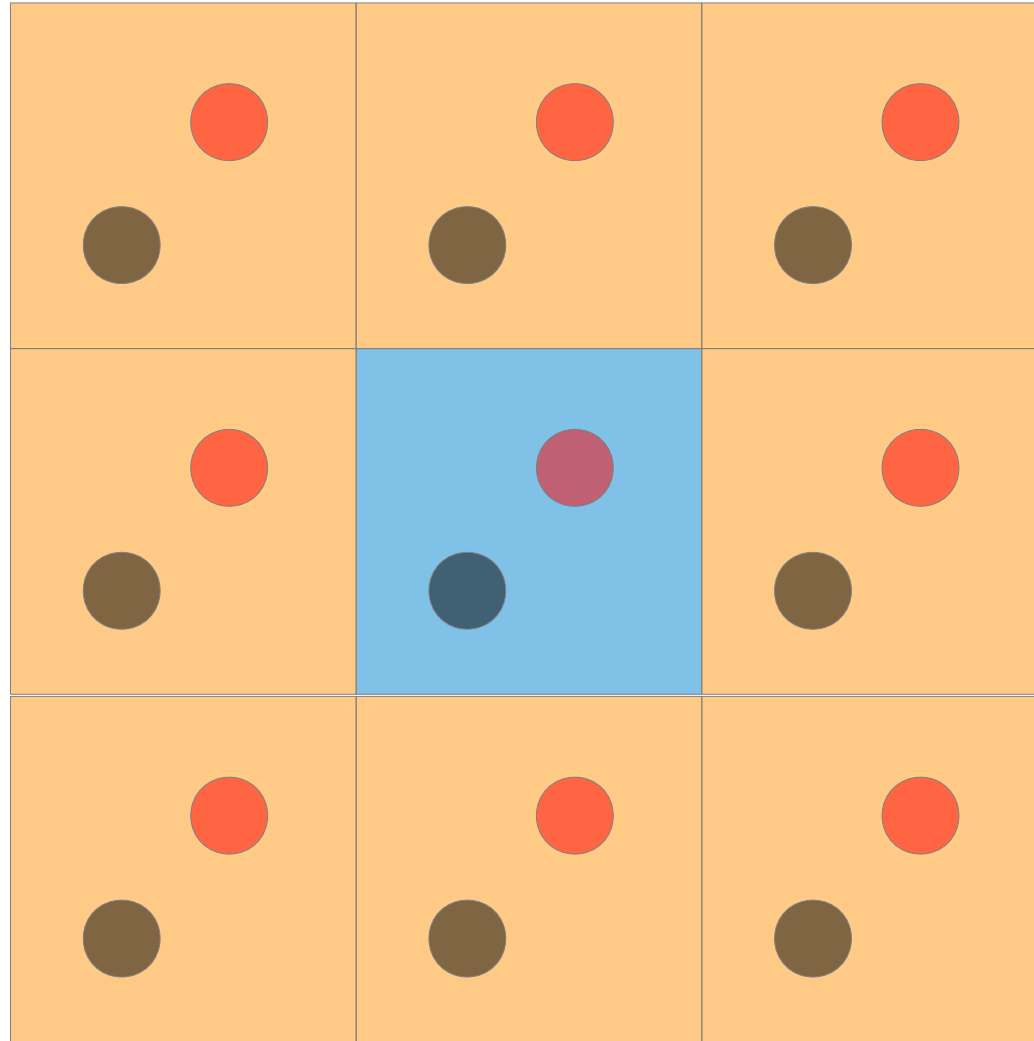
Let us periodically repeat our cell along all directions (virtual 3x3 supercell in 2D)

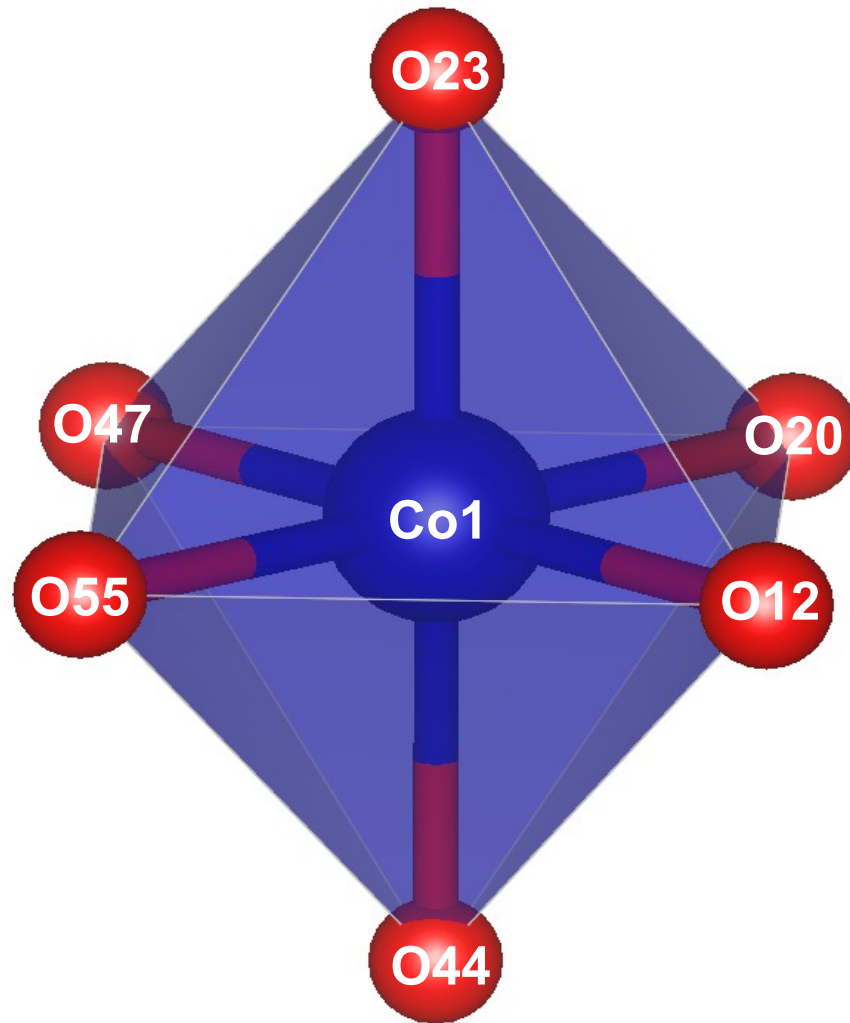# Neighbors in periodic boundary conditions

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     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}
   0.500380664    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     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}
   0.500380664   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,          ← Gaussian broadening for PDOS
    degauss = 0.005,     ← Value of the Gaussian broadening, in Ry (not eV!)
    Emin = -15.0,
    Emax =  30.0,        ← Minimum and maximum value of energy for the plot, in eV
    DeltaE = 0.01        ← 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.
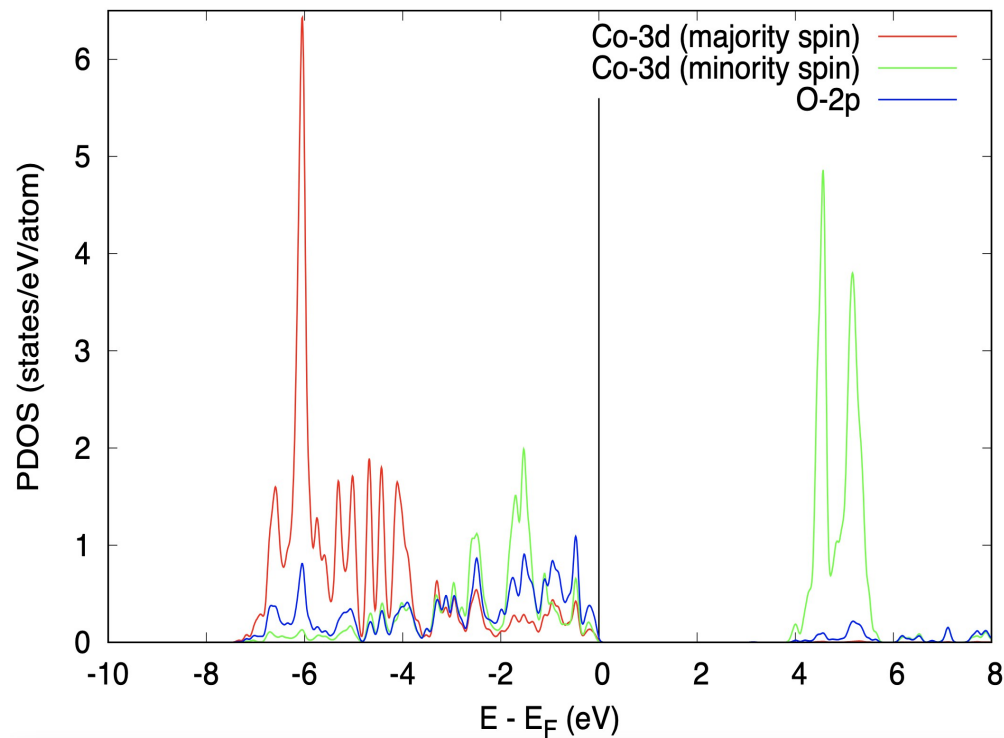
Visualize the file "**CoO_PDOS.eps**"

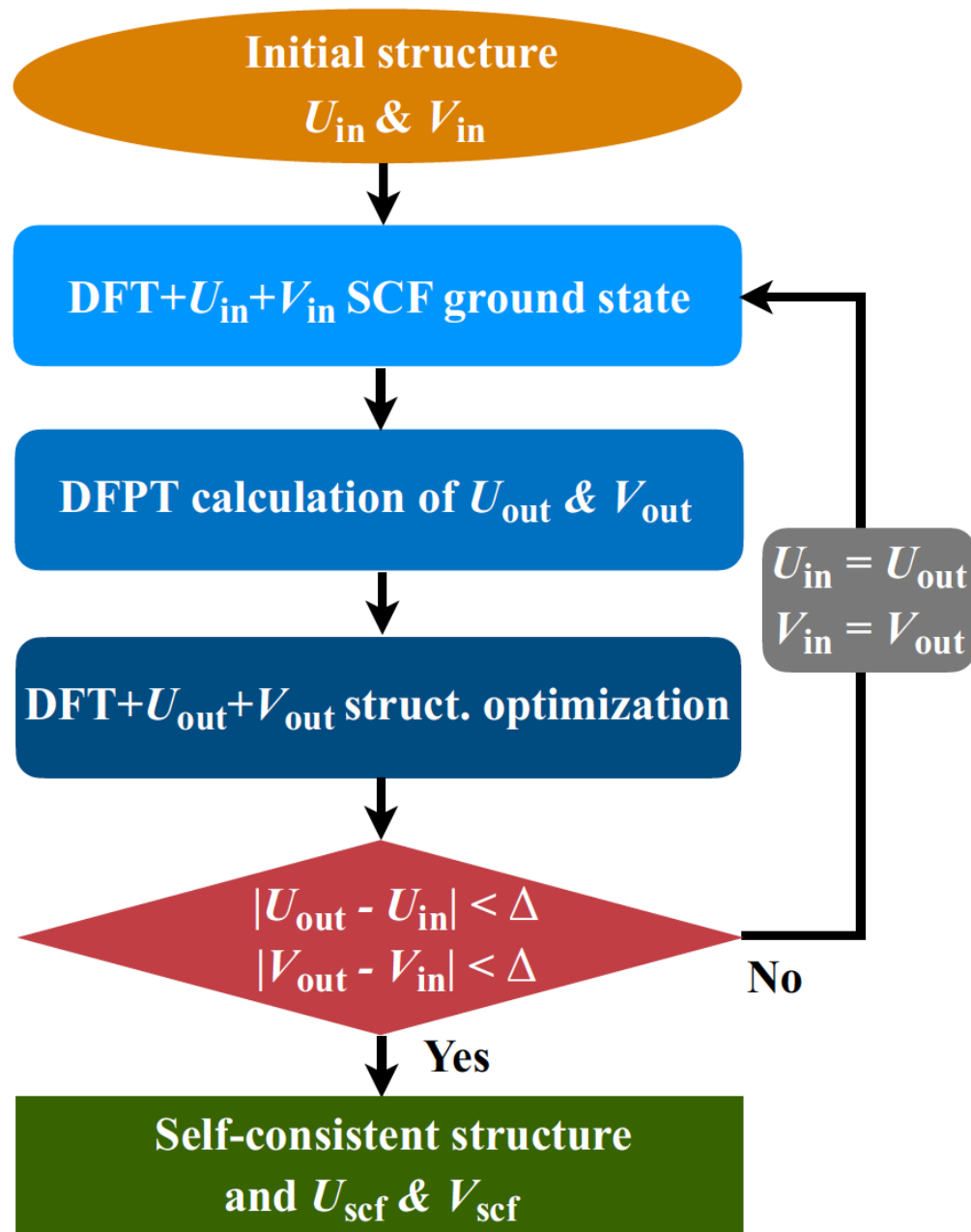# DFT vs DFT+*U*+*V*

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

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

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)