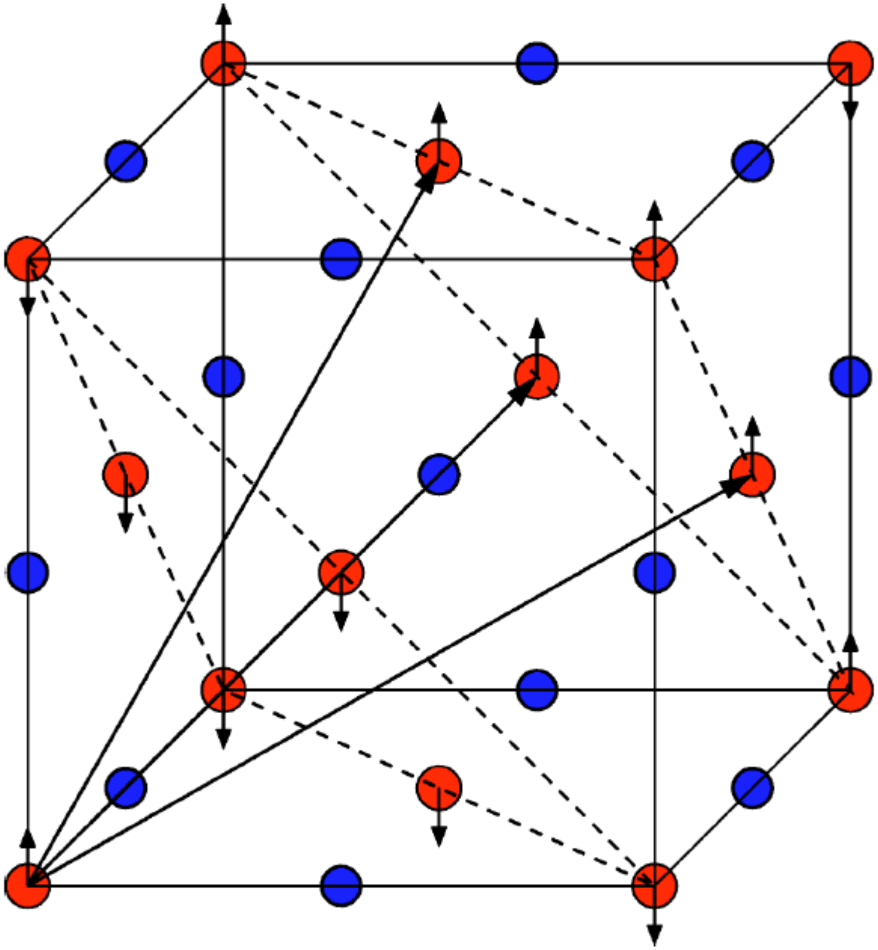
DFT+U practical session

Matteo Cococcioni

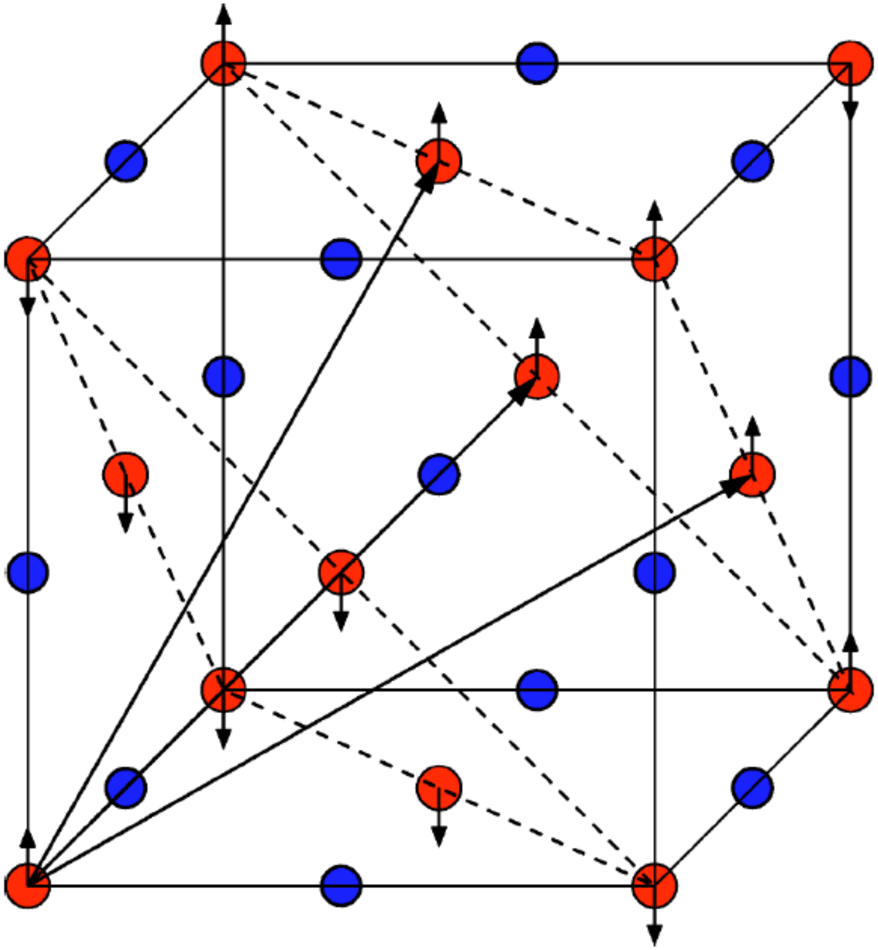
- GGA and GGA+U calculations in FeO
- Calculation of U for bulk Fe
- Calculation of U for NiO
- Exercise I: evaluating U for Cu_2O
- Exercise II: evaluating U for $FePO_4$

FeO-GGA



Rhombohedral
unit cell

FeO-GGA



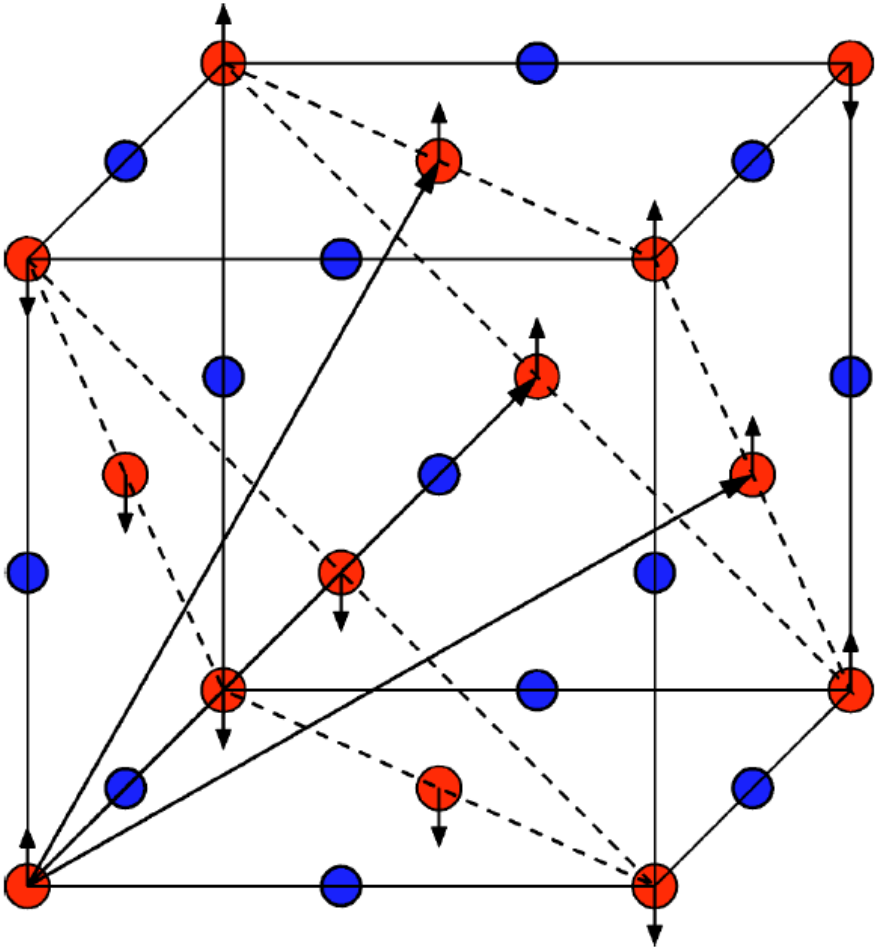
Rhombohedral
unit cell

- **AFM order → 2 types of Fe atoms**

```
ATOMIC_SPECIES
 O    1.  O.pbe-rrkjus.UPF
 Fe1  1.  Fe.pbe-nd-rrkjus.UPF
 Fe2  1.  Fe.pbe-nd-rrkjus.UPF

 starting_magnetization(2)= 0.5
 starting_magnetization(3)=-0.5
```

FeO–GGA



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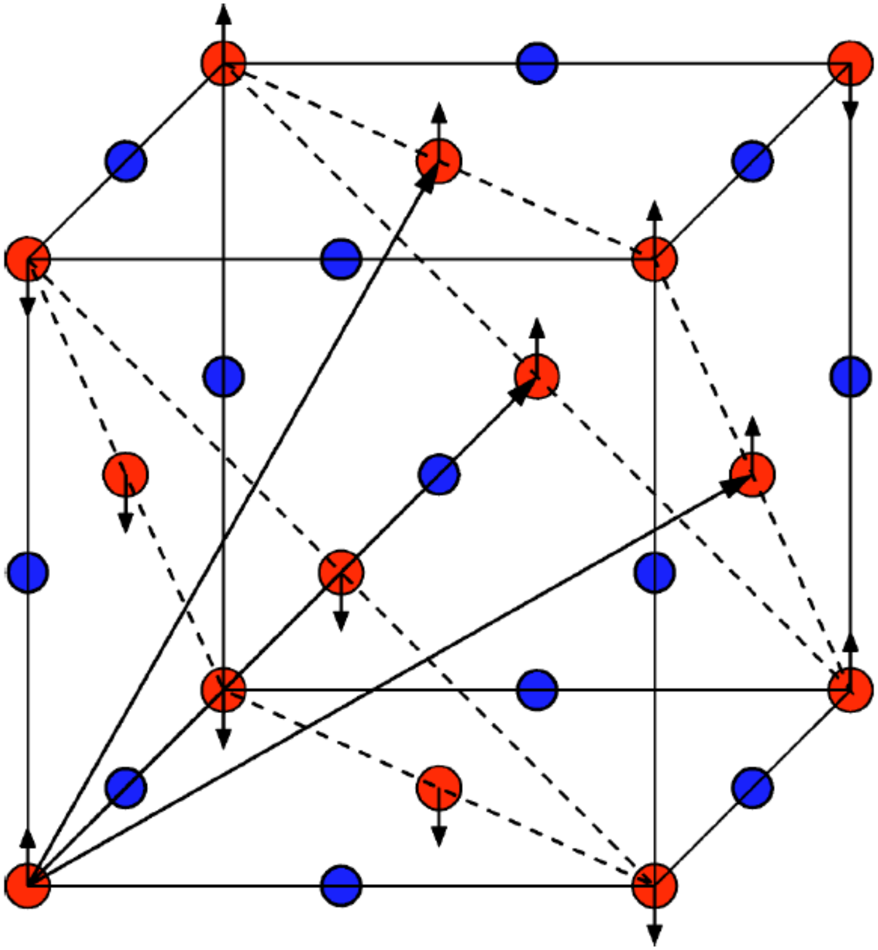
- **Rhombohedral unit cell:**

```
CELL_PARAMETERS
0.50 0.50 1.00
0.50 1.00 0.50
1.00 0.50 0.50
```

FeO–GGA



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- **Rhombohedral unit cell:**

```
CELL_PARAMETERS
0.50 0.50 1.00
0.50 1.00 0.50
1.00 0.50 0.50
```

- **No Hubbard correction**

```
lda_plus_u = .true.,
Hubbard_U(1) = 1.d-10,
Hubbard_U(2) = 1.d-10,
Hubbard_U(3) = 1.d-10,
```

FeO-GGA

- Check the output file: feo.scf.out

```
LDA+U parameters:
U( 2)     =  0.00000000
alpha( 2) =  0.00000000
U( 3)     =  0.00000000
Alpha( 3) =  0.00000000
```

← Hubbard correction on atom 2 (Fe1)

← Hubbard_alpha perturbation on atom 2 (Fe1)

Total occupations:

$n^{I\uparrow}$ $n^{I\downarrow}$ n^{I}

```
atom    1   Tr[ns(na)] (up, down, total) =   2.78796  2.78796  5.57592
atom    3   Tr[ns(na)] (up, down, total) =   4.97463  1.85925  6.83388
atom    4   Tr[ns(na)] (up, down, total) =   1.85931  4.97463  6.83394
```

- Oxygen atoms non-magnetic, $n^{up} = n^{down}$
- Iron atoms ordered anti-ferromagnetically

FeO-GGA

Eigenvalues and eigenvectors of occupation matrices $n^{I\sigma}_{m_1 m_2}$ **(5x5 matrices):**

basis set: z^2, xz, yz, x^2–y^2, xy $\longrightarrow \mathbf{v}_i = c^i_{z^2} d_{z^2} + c^i_{xz} d_{xz} + c^i_{yz} d_{yz} + c^i_{x^2-y^2} d_{x^2-y^2} + c^i_{xy} d_{xy}$

spin 1

eigenvalues:

0.991 0.991 0.998 0.998 0.998

eigenvectors:

$$\begin{array}{ccccccc}
|c^1_{z^2}|^2 & \leftarrow & 0.523 & 0.438 & 0.035 & 0.004 & 0.000 \\
|c^1_{xz}|^2 & \leftarrow & 0.024 & 0.002 & 0.022 & 0.619 & 0.333 \\
|c^1_{yz}|^2 & \leftarrow & 0.001 & 0.025 & 0.368 & 0.272 & 0.333 \\
|c^1_{x^2-y^2}|^2 & \leftarrow & 0.438 & 0.523 & 0.004 & 0.035 & 0.000 \\
|c^1_{xy}|^2 & \leftarrow & 0.014 & 0.012 & 0.571 & 0.070 & 0.333 \\
 & & \mathbf{c^1} & \mathbf{c^2} & \mathbf{c^3} & \mathbf{c^4} & \mathbf{c^5}
\end{array}$$

Caution:

In previous versions of QE, the eigenvectors are printed as row vectors and the coefficients are not squared.

occupations:

```
 0.991 -0.001 -0.001  0.000 -0.001
-0.001  0.998  0.000 -0.001  0.000
-0.001  0.000  0.998  0.001  0.000
 0.000 -0.001  0.001  0.991  0.000
-0.001  0.000  0.000  0.000  0.998
```

$\longleftarrow$ **5x5** $n^{I\sigma}_{m_1 m_2}$ **matrix**

$$n^I_{lm} = \sum_{kv} f_{kv} \langle \psi_{kv} | \phi^I_m \rangle \langle \phi^I_l | \psi_{kv} \rangle$$

FeO–GGA

Level splittings:

```
atom    3
spin  1 eigenvalues: 0.991  0.991  0.998  0.998  0.998
spin  2 eigenvalues: 0.281  0.281  0.282  0.508  0.508

atom    4
spin  1 eigenvalues: 0.281  0.281  0.282  0.508  0.508
spin  2 eigenvalues: 0.991  0.991  0.998  0.998  0.998
```

FeO-GGA

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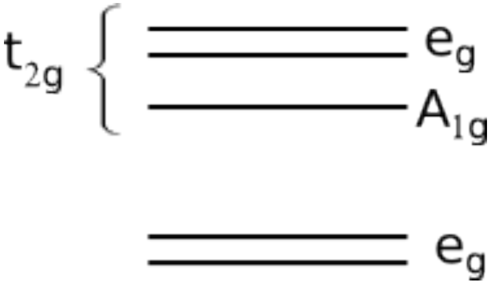

Split by rhombohedral symmetry (magnetic order)

Partial occupations of atomic orbitals

↓

metallic bands

FeO–GGA

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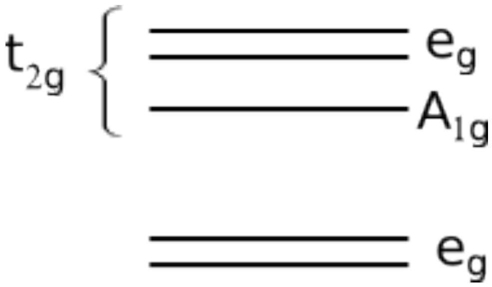


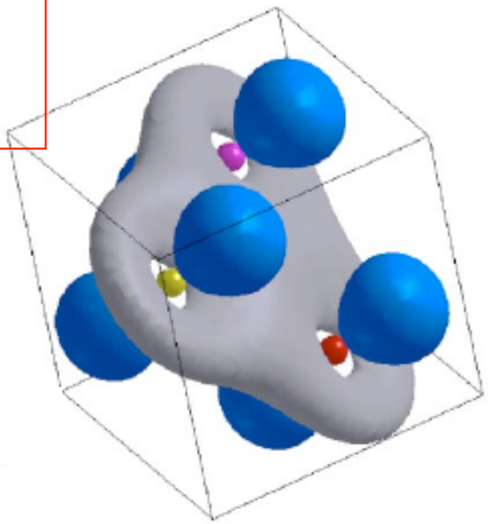
Split by rhombohedral symmetry (magnetic order)

Partial occupations of atomic orbitals

↓

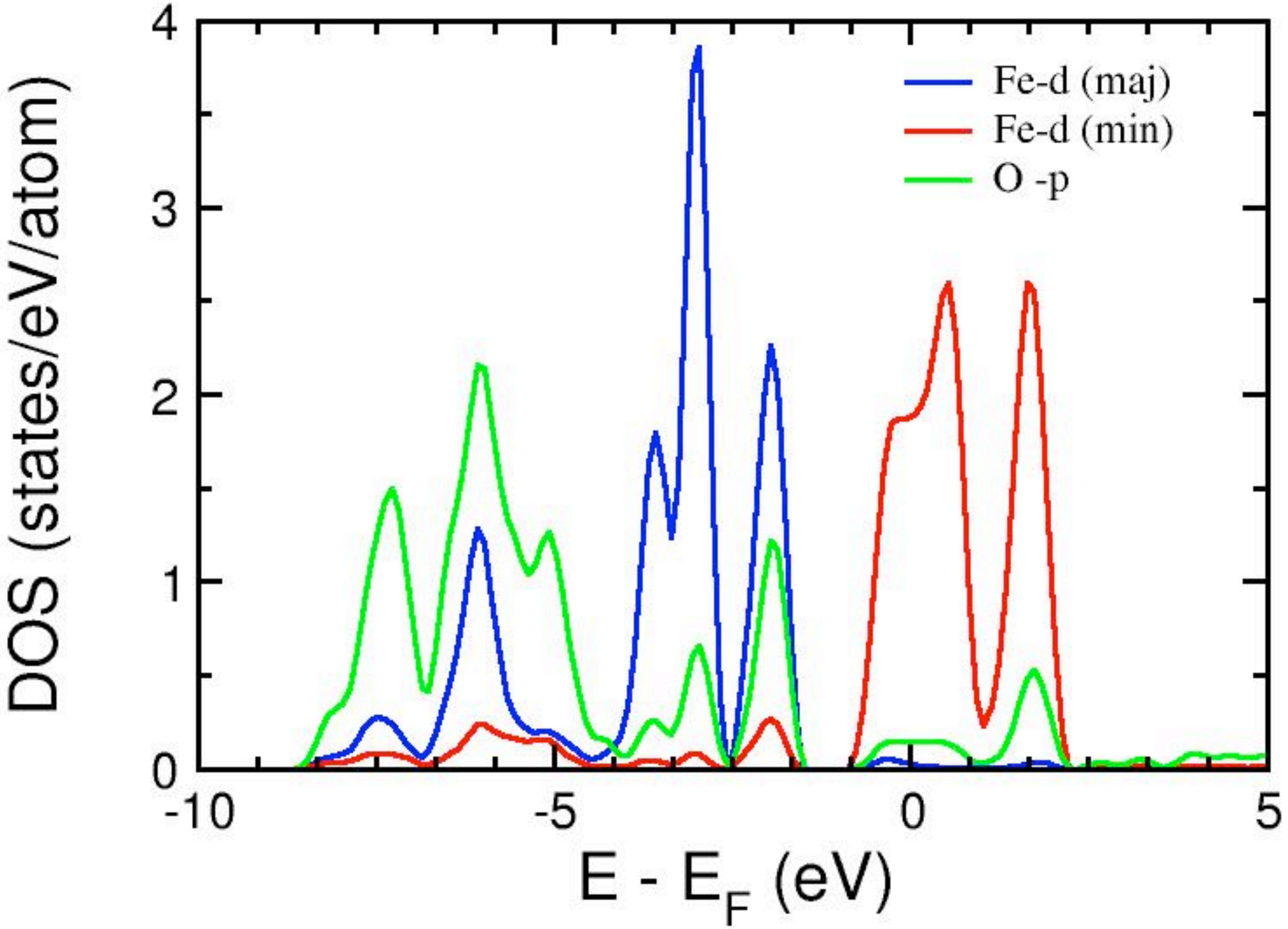
metallic bands

Eigenvector corresponding to A_{1g}: $\begin{pmatrix} 0.000 \\ 0.333 \\ 0.333 \\ 0.000 \\ 0.333 \end{pmatrix}$ →



FeO–GGA density of states

Density of states:



- **Majority spin states are almost full, they are below E_F**
- **Minority spin states are partially occupied at E_F → metallic behavior**

FeO−GGA+U

FeO-GGA+U

Hubbard U correction of Fe d-states:

```
Hubbard_U(1)=1.d-10,
Hubbard_U(2)=4.3,
Hubbard_U(3)=4.3
```

FeO−GGA+U

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```

Total occupations:

$n^{I\uparrow}$ $n^{I\downarrow}$ n^{I}

```
atom    1   Tr[ns(na)] (up, down, total) =   2.80479  2.80492  5.60971
atom    3   Tr[ns(na)] (up, down, total) =   4.99045  1.73174  6.72219
atom    4   Tr[ns(na)] (up, down, total) =   1.73173  4.99046  6.72219
```

FeO-GGA+U

Hubbard U correction of Fe d-states:

```
Hubbard_U(1)=1.d-10,
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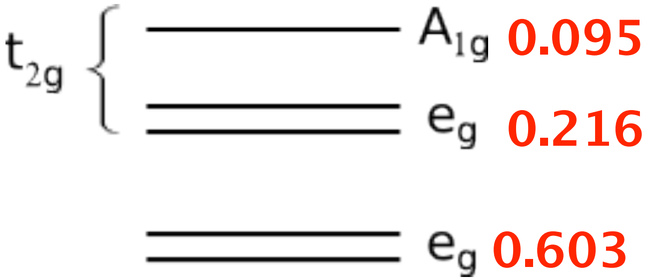
atom    4   Tr[ns(na)] (up, down, total) =   1.73173  4.99046  6.72219
```

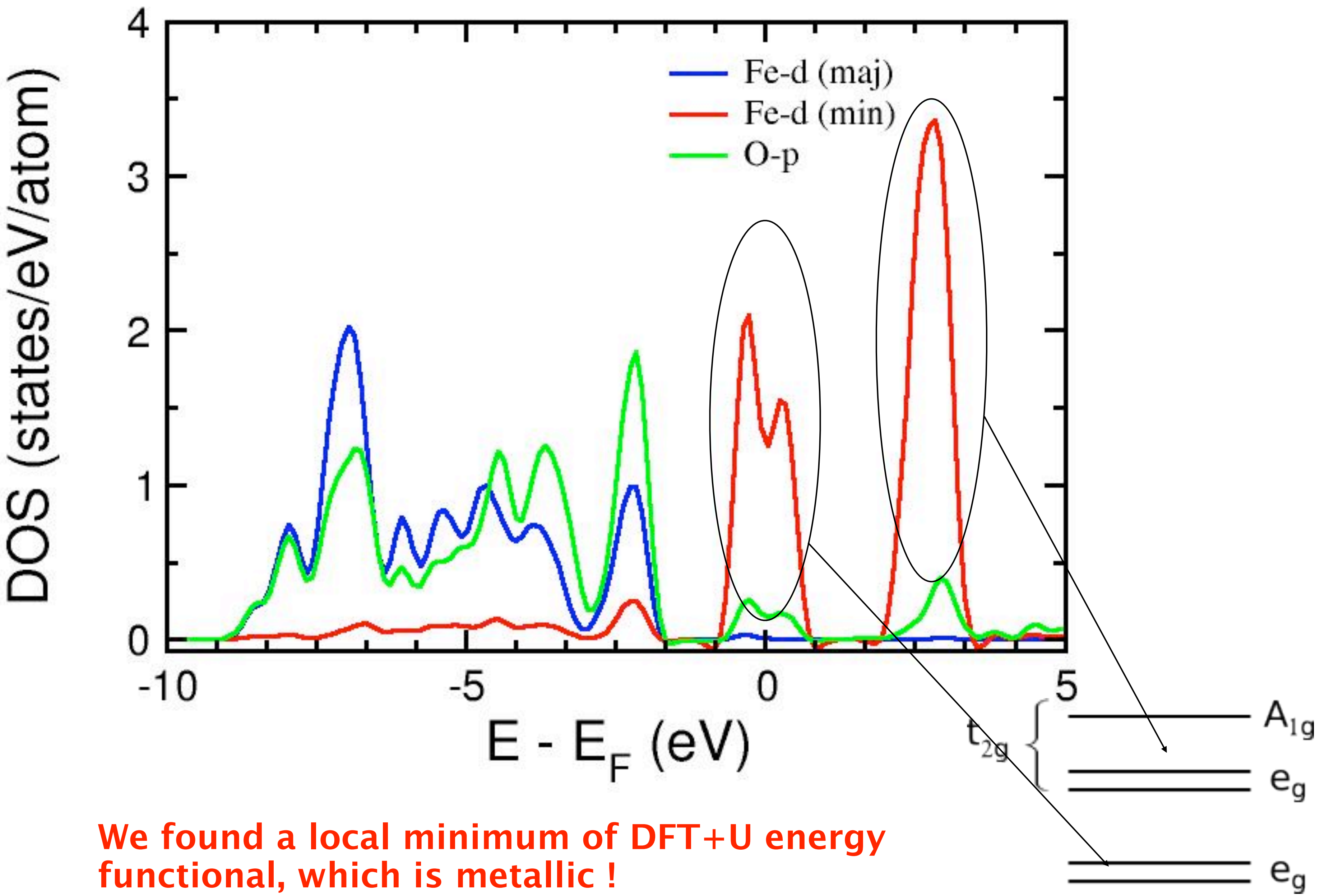
Check minority spin occupations of either Fe atom:

```
atom    4 spin  1
   eigenvalues:
 0.095  0.216  0.216  0.603  0.603
   eigenvectors:
 0.000  0.848  0.030  0.085  0.037
 0.333  0.034  0.047  0.002  0.584
 0.333  0.009  0.072  0.467  0.119
 0.000  0.030  0.848  0.037  0.085
 0.333  0.078  0.003  0.410  0.176
```

Still partial occupations!
METALLIC



FeO-GGA+U density of states



We found a local minimum of DFT+U energy functional, which is metallic !

FeO−GGA+U

FeO-GGA+U

Let us try to suggest a different possible electronic configuration to the system:

Check minority spin occupations of either Fe atom after the 1st iteration:

```
atom   4  spin  1
  eigenvalues:
 0.164  0.164  0.202  0.252  0.252
  eigenvectors:
 0.043  0.940  0.000  0.013  0.004
 0.006  0.005  0.333  0.000  0.655
 0.011  0.001  0.333  0.492  0.163
 0.940  0.043  0.000  0.004  0.013
 0.001  0.011  0.333  0.491  0.164
```

FeO–GGA+U

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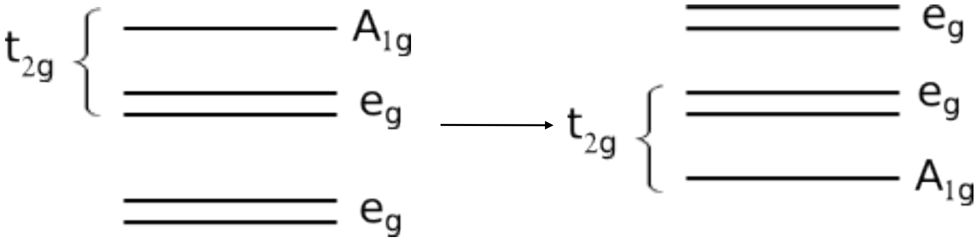
```



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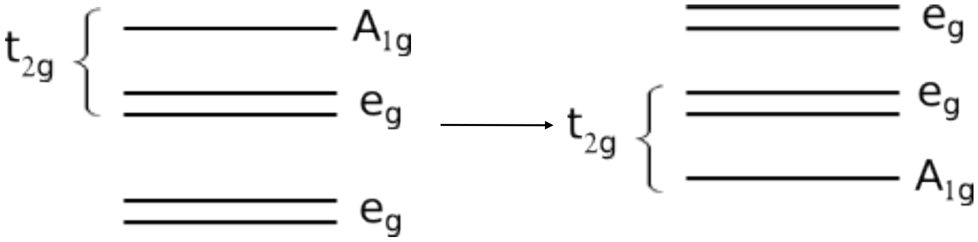
```



We want to drive the system to a configuration where the A1g state is fully occupied:

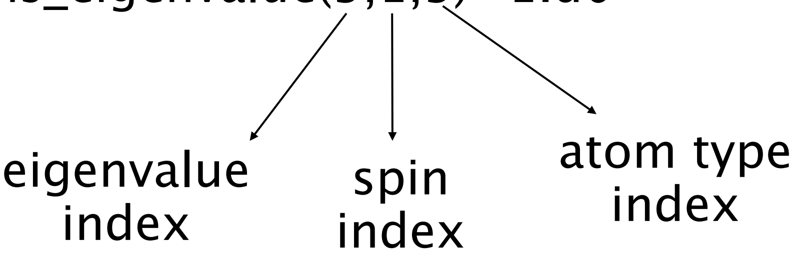
- This state is **singlet** → filling it **completely** will lead to an insulator
- Physically, it points along the [111] direction, perpendicular to (111) AFM planes

FeO-GGA+U2

FeO-GGA+U2

Override the **3rd eigenvalue** of the **spin 2 of atom 2** and **spin 1 of atom 3** with 1.d0:

```
starting_ns_eigenvalue(3,2,2)=1.d0,
starting_ns_eigenvalue(3,1,3)=1.d0
```



eigenvalue index

spin index

atom type index

FeO-GGA+U2

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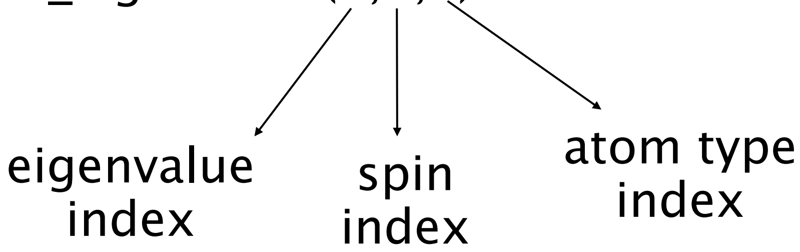


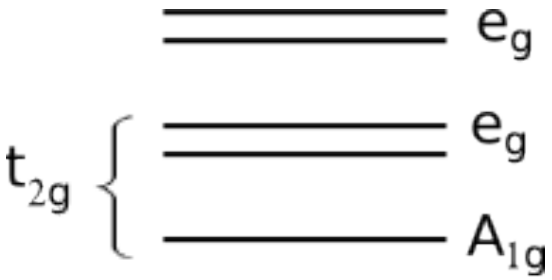
eigenvalue index

spin index

atom type index

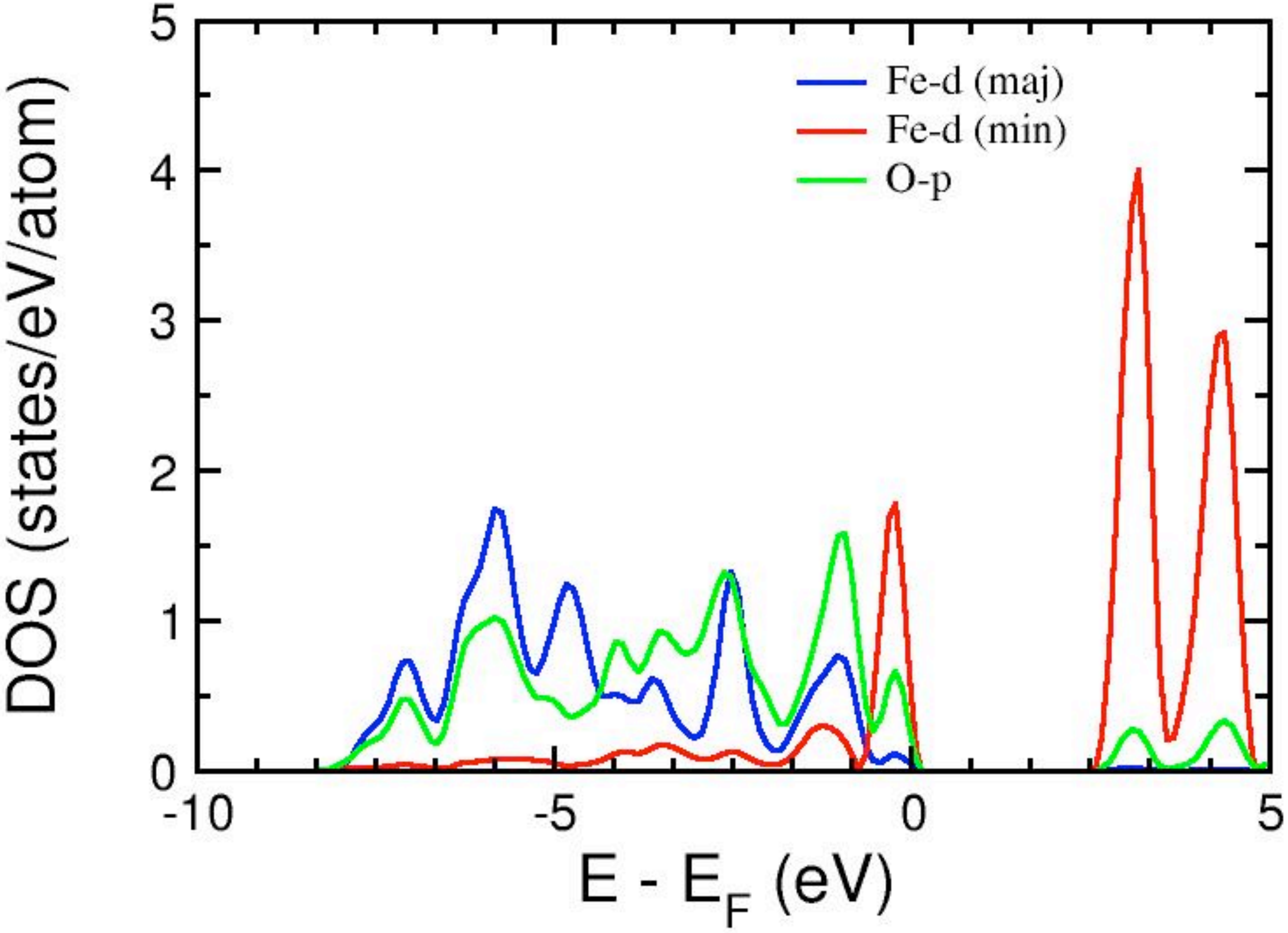
Check the resulting minority spin occupations of either Fe atom:

```
atom    4   spin  1
  eigenvalues:
 0.091  0.091  0.240  0.240  0.996
  eigenvectors:
 0.009  0.002  0.617  0.372  0.000
 0.010  0.650  0.000  0.007  0.333
 0.419  0.241  0.006  0.001  0.333
 0.002  0.009  0.372  0.617  0.000
 0.561  0.099  0.004  0.003  0.333
```



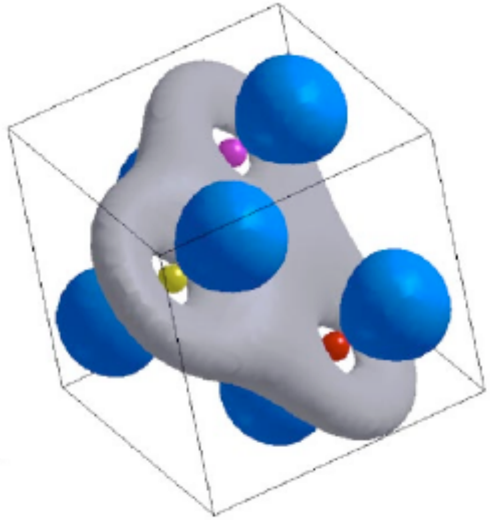
- **A1g state is fully occupied**
- **Other are almost empty.**

FeO–GGA+U2 density of states



The insulating state is found !

- A1g is completely full.
- No partial occupations.



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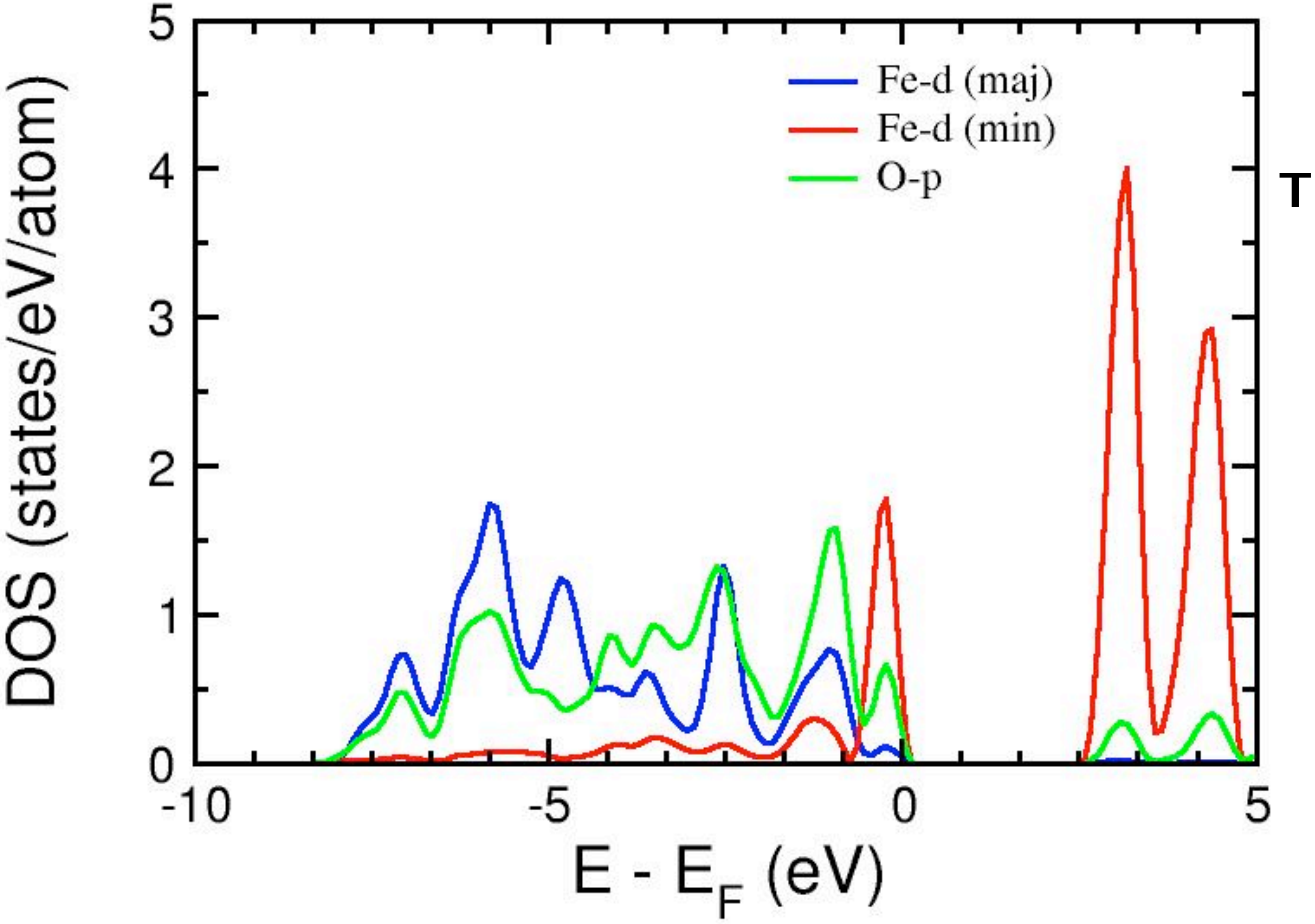

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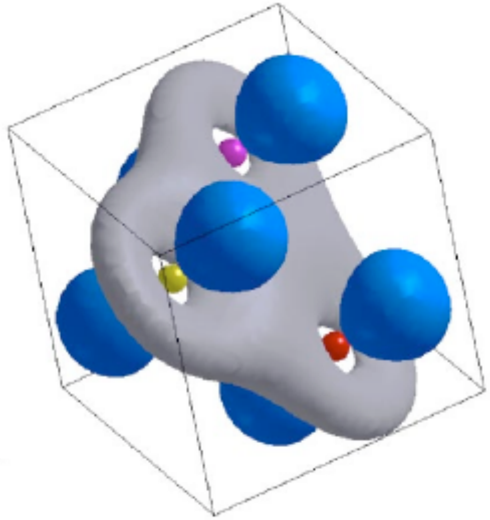


Which of these local minima has lower energy?

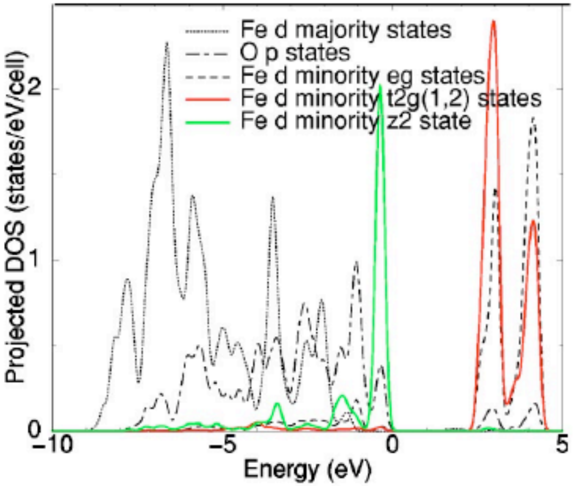
DFT+U metallic → total energy = −175.07464368 Ry

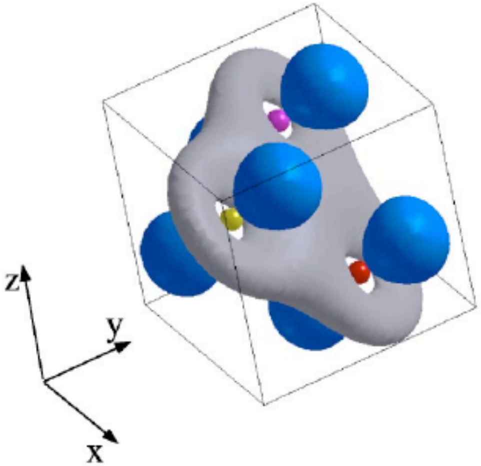
DFT+U insulating → total energy = −175.16678519 Ry

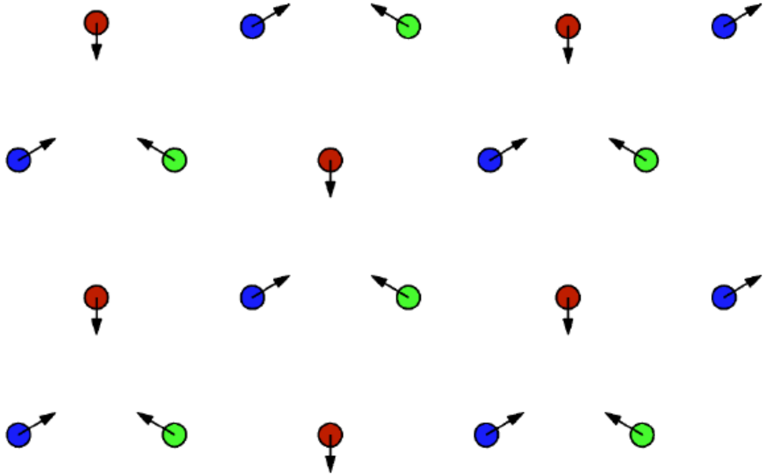
FeO–GGA+U2

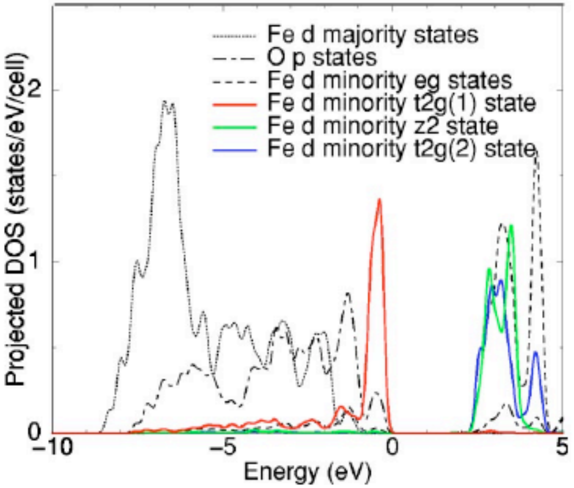
What about other local energy minima?

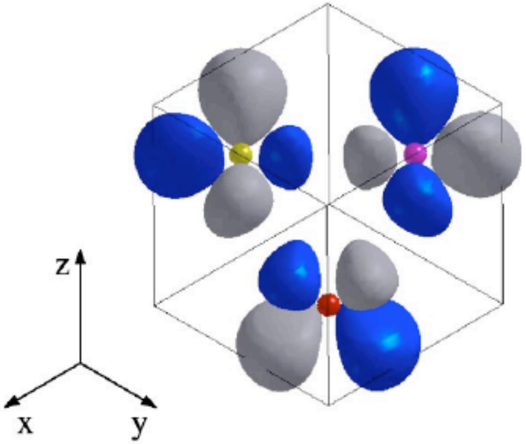
- Are there other minima with lower energy?
- How to find them? → Physical intuition (and breaking of symmetry)!









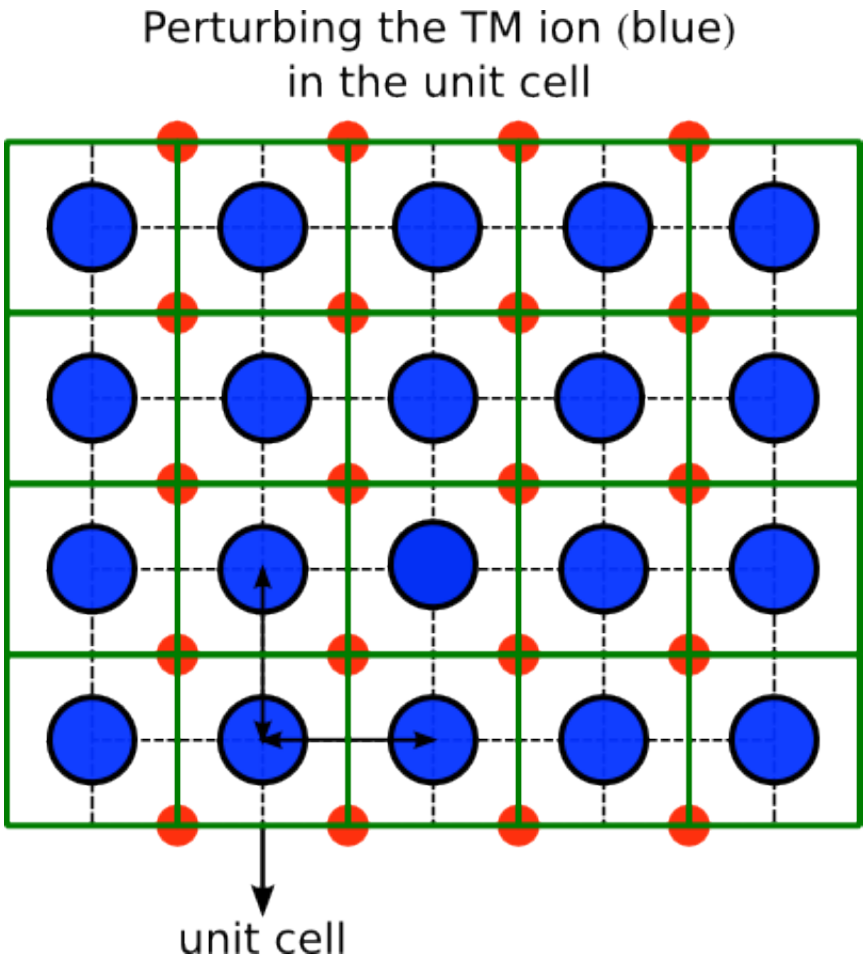


Cococcioni and de Gironcoli, PRB 71, 035105 (2005)

Calculation of U (bulk Fe)

If we use the unit cell, perturbing an atom will perturb all the atoms of the same type in the crystal.

- Perturbations can not be isolated
- Interactions between periodic images will interfere with each other.



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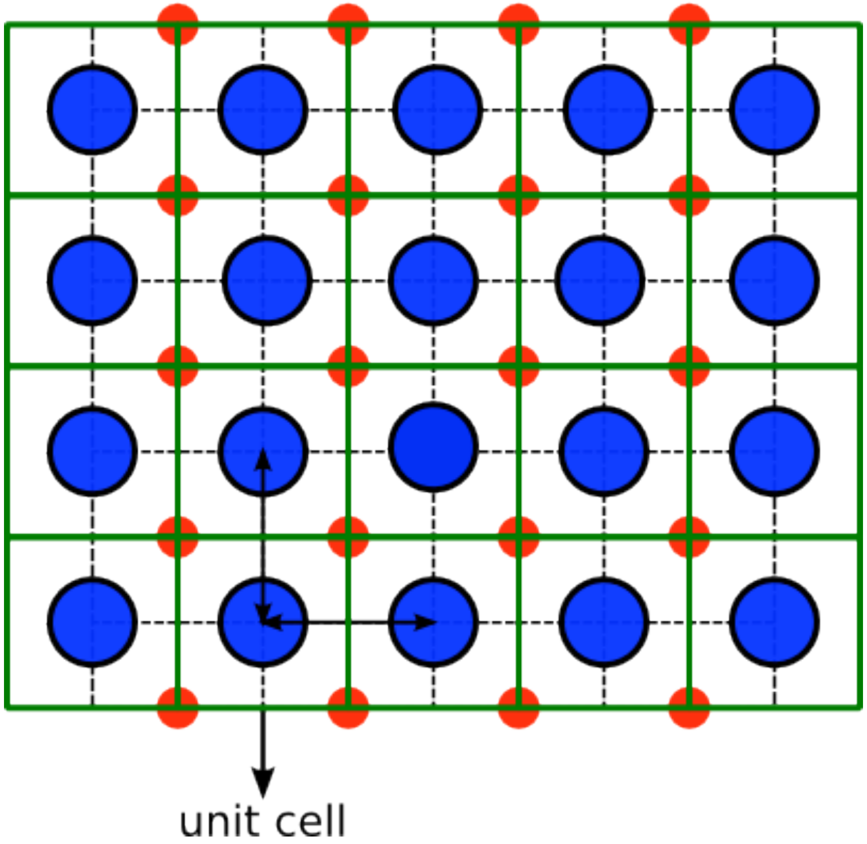
We need a super cell to compute U

Perturbing the TM ion (blue) in the unit cell



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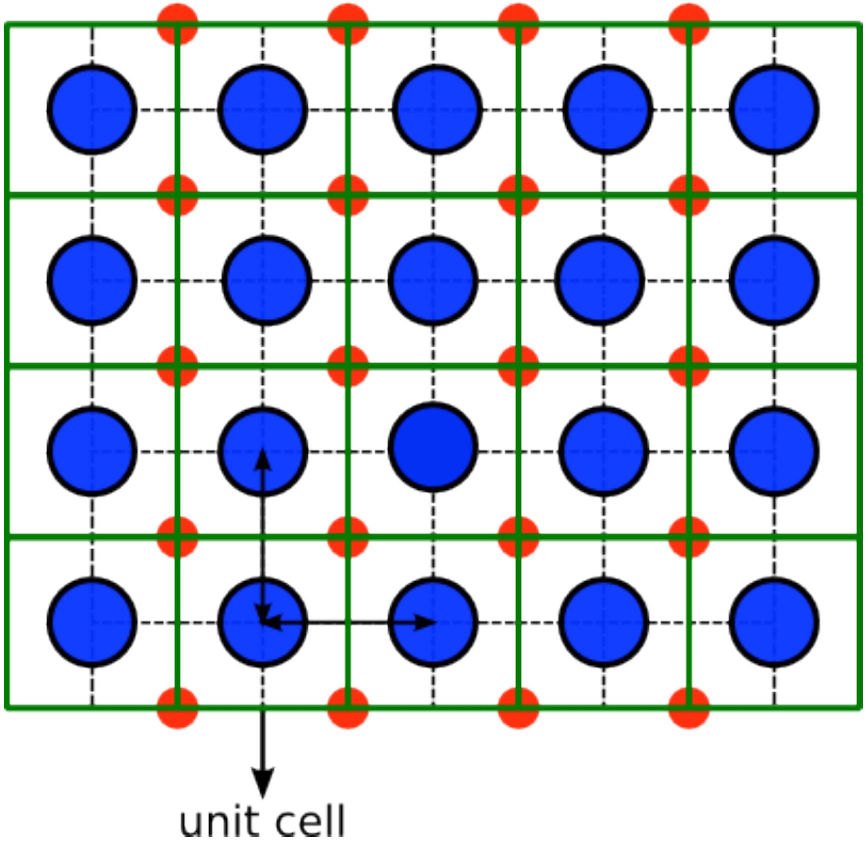

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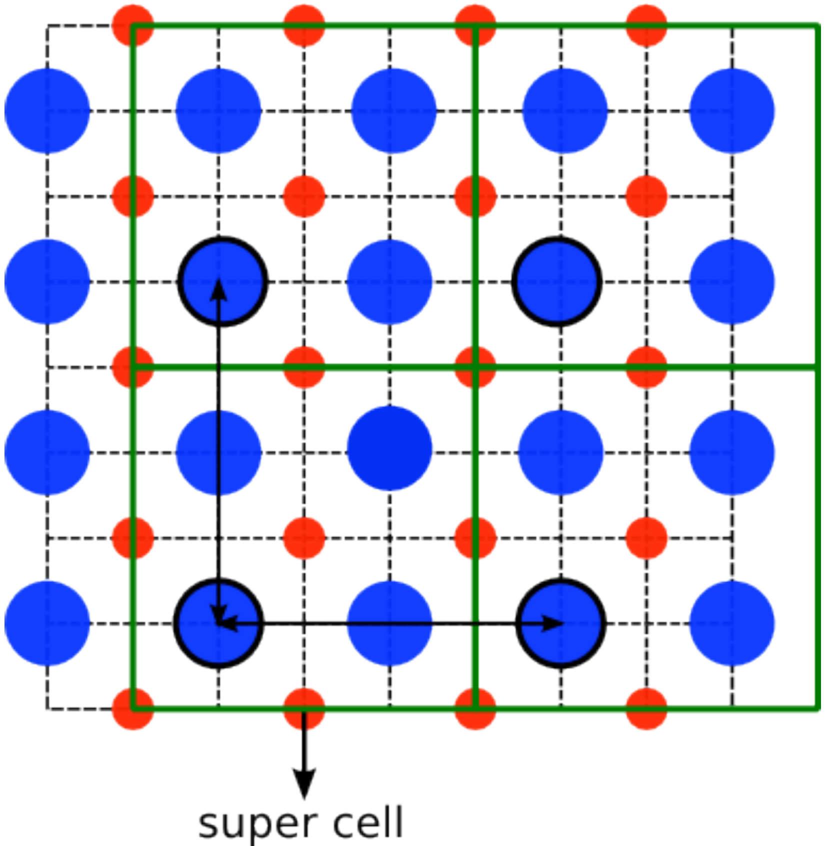
in the super cell



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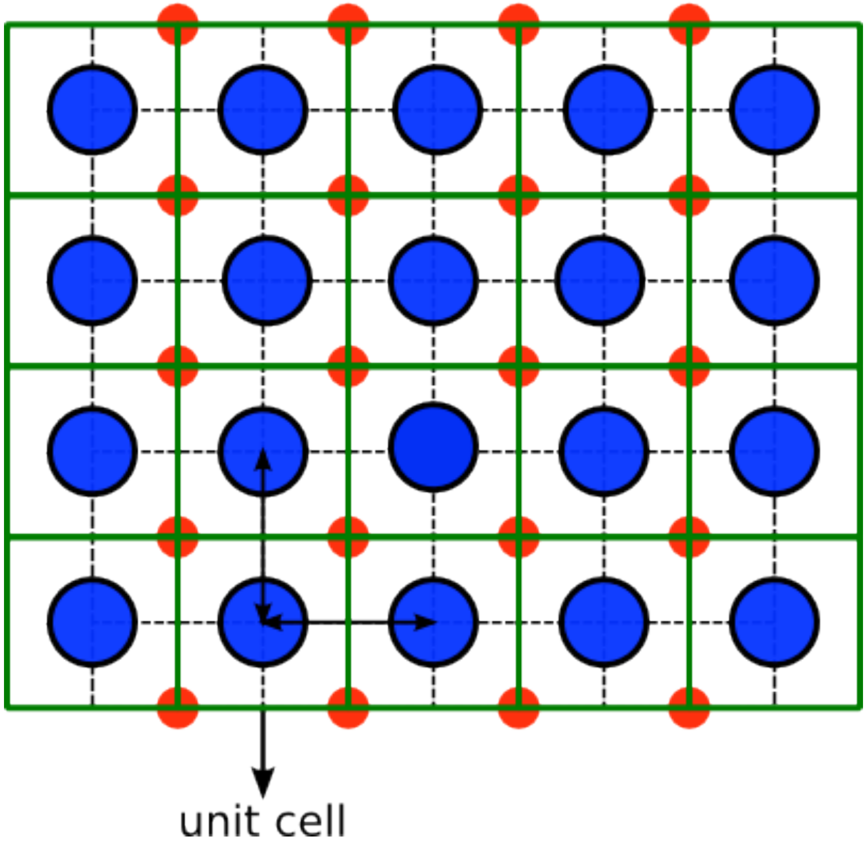
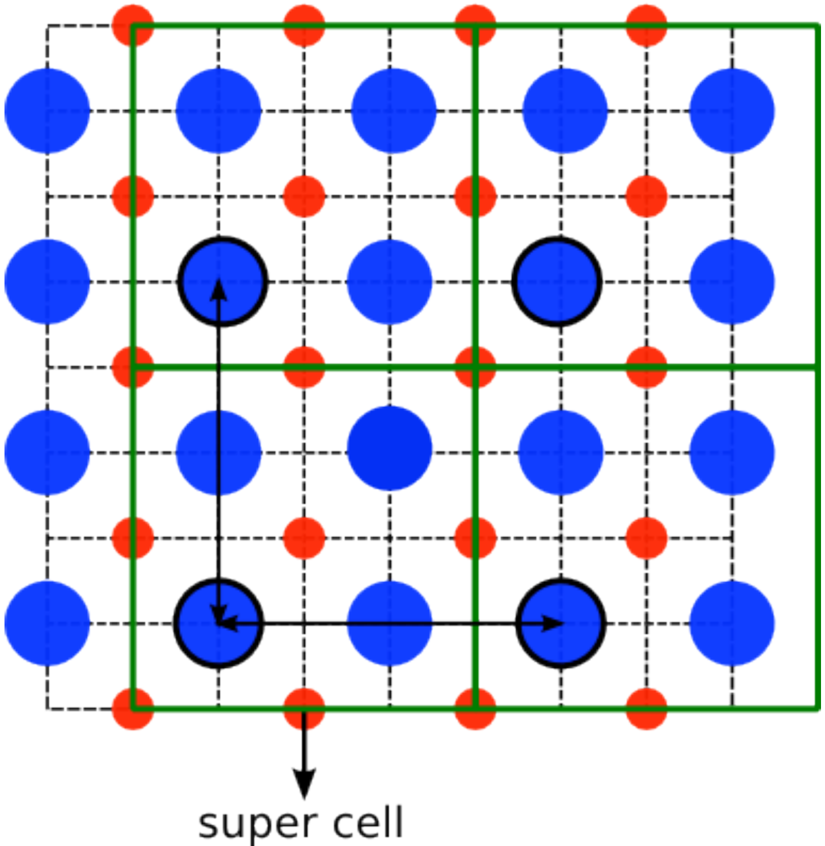
We need a super cell to compute U

Calculated value of U will converge with increasing super cell size.

Perturbing the TM ion (blue) in the unit cell



Perturbing the TM ion (blue) in the super cell



Convergence of U with cell size

The U parameter should be converged with cell size

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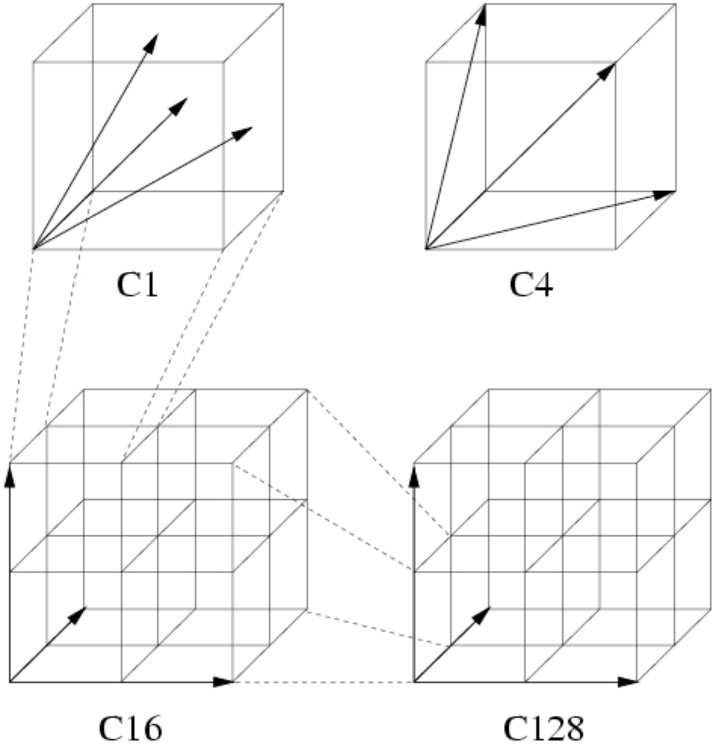
Bulk Fe



Convergence of U with cell size

The U parameter should be converged with cell size

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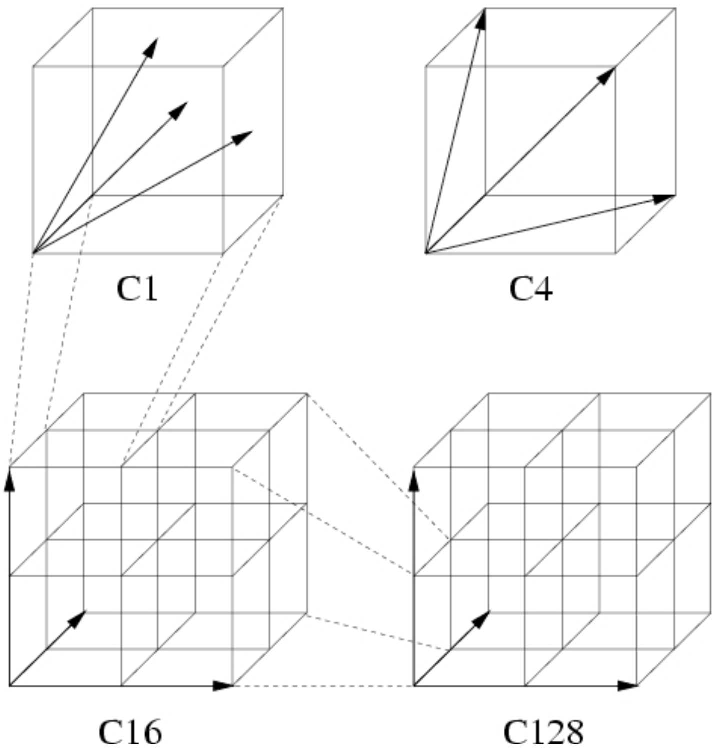
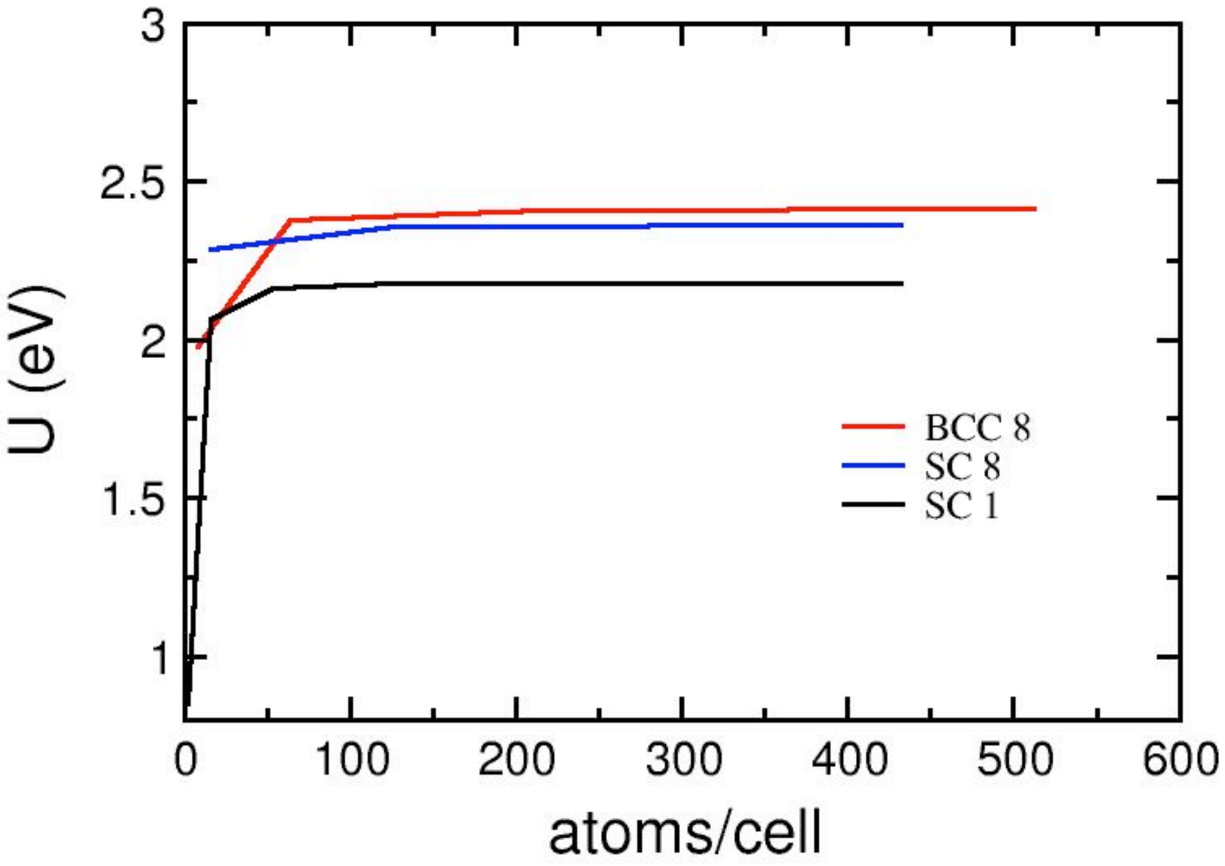
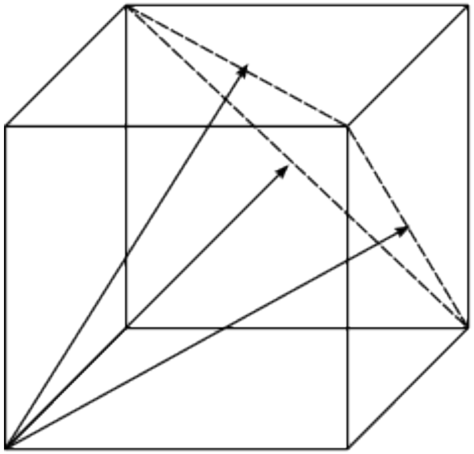


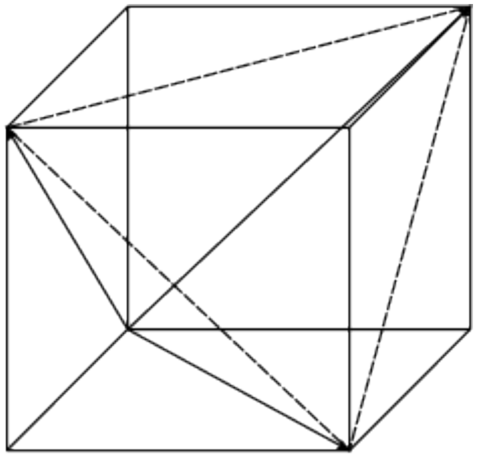


Calculation of U-NiO



unit cell

4 atoms



super cell

16 atoms

```
CELL_PARAMETERS
1.0 1.0 0.0
1.0 0.0 1.0
0.0 1.0 1.0
```

```
ATOMIC_POSITIONS {crystal}
Ni1  0.d0  0.d0  0.d0
Ni2  0.5d0 0.5d0 0.d0
Ni2  0.5d0 0.d0  0.5d0
Ni2  0.d0  0.5d0 0.5d0
Ni3  0.5d0 0.d0  0.d0
Ni3  0.d0  0.5d0 0.d0
Ni3  0.d0  0.d0  0.5d0
Ni3  0.5d0 0.5d0 0.5d0
O1   -0.25d0  0.25d0  0.25d0
O1    0.25d0  0.25d0  0.25d0
O1   -0.25d0  0.25d0  0.75d0
O1   -0.25d0  0.75d0  0.25d0
O1    0.25d0  0.75d0  0.25d0
O1    0.25d0  0.25d0  0.75d0
O1   -0.25d0  0.75d0  0.75d0
O1    0.25d0  0.75d0  0.75d0
```

3 types of Ni atoms:

1. Ni1 perturbed spin up (always put the perturbed atom at the origin)
2. Ni2 unperturbed spin up
3. Ni3 unperturbed spin down

Calculation of U-NiO

Steps:

After perturbing all Hubbard atoms we can now construct response matrices

Calculation of U–NiO

Steps:

1. Perform the unperturbed scf run → nio_1.scf.out
2. Save the wavefunctions and potential in temp1
3. Reading the initial conditions from temp1, perturb the Ni–d orbitals by Hubbard_alpha → ni.–0.15.out, ni.0.0.out, ni.0.15.out

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This step concludes the perturbation of Ni-d states. Now we perturb O-p states

To do so, first shift the coordinates such that one O atom is at the origin

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To do so, first shift the coordinates such that one O atom is at the origin

1. Perform the unperturbed scf run → nio_2.scf.out
2. Save the wavefunctions and potential in temp1
3. Reading the initial conditions from temp1, perturb the Ni-d orbitals by Hubbard_alpha → o.-0.15.out, o.0.0.out, o.0.15.out

After perturbing all Hubbard atoms we can now construct response matrices

Calculation of U-NiO

Response matrices by numerical derivative: $\chi_{IJ} = \frac{\partial n^I}{\partial \alpha_J} \approx \frac{n^I(\alpha = +0.15) - n^I(\alpha = -0.15)}{0.30}$

This step is performed for all the atoms by the program **resp_mat.f90** in the folder Ucalc. This program reads the files dn.I.da.J.dat that contain the occupation of atom I as a function of the perturbation on atom J

$$\chi_{IJ}$$

Calculation of U-NiO

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These quantities are extracted from the output files by the script **grepnalfa_nio_r16**

For example:

```
grep 'Tr' ni.$con.out |tail -16| head -$at |tail -1| awk '{print $10}'
```

extracts the **scf** response of the occupation of atom ``$at'' when a perturbation of intensity ``$con'' is applied to the Ni d-states. This quantity is used to construct χ_{IJ}

Calculation of U-NiO

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likewise;

```
grep 'Tr' ni.$con.out |head -32|tail -16|head -$at|tail -1 | awk '{print $10}'
```

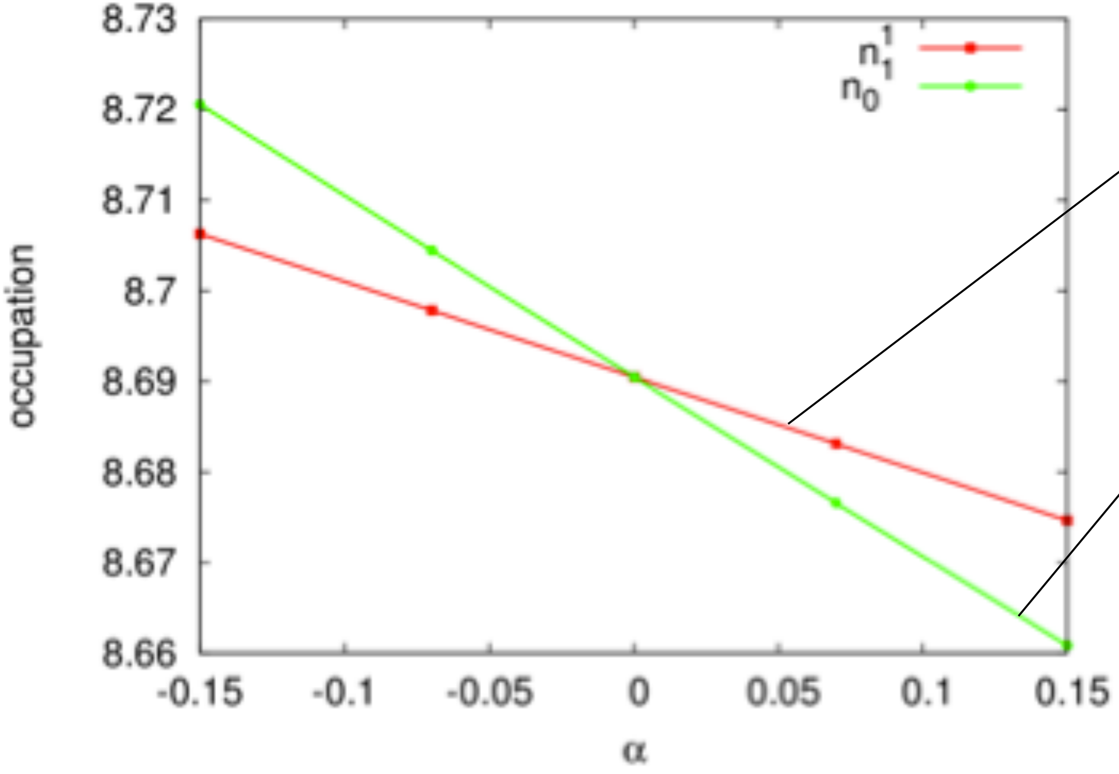
extracts the **bare** response of the occupation of atom ``$at" when a perturbation of intensity ``$con" is applied to the Ni d-states. This quantity is used to construct χ^0_{IJ}

Calculation of U-NiO

Important checks:

- The response must be linear.
- Screened (scf converged) and Kohn-Sham (at fixed potential) responses must coincide at zero perturbation.

e.g.



$$\chi_{11} = \frac{\partial n^1}{\partial \alpha^1}$$

$$\chi^0_{11} = \frac{\partial n^1_0}{\partial \alpha^1}$$

Calculation of U-NiO

Description of the input format for resp_mat.f90

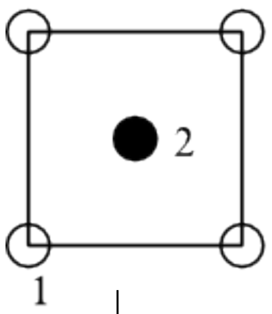
```
&input_mat
 ntyp = 2      # Number of types of atoms
 na(1) = 8     # Number of atoms of type 1
 na(2) = 8     # Number of atoms of type 2
 nalfa = 3     # Number of perturbations
 magn = .true. # .true. for magnetic systems,.false. otherwise.
 filepos = 'pos_nio_r16' # file containing atomic positions
 back = 'no' # to add neutralizing background, see PRB-71 35105 (05)
 filednda = 'file.nio.r16' # file containing the names of dn*dat
 n1 = 5
 n2 = 5    # number of unit cells used for extrapolating
 n3 = 5    # response matrices to larger supercells.
&end
```

This input is automatically generated and the executed by the script **ucalc_nio_r16.j**

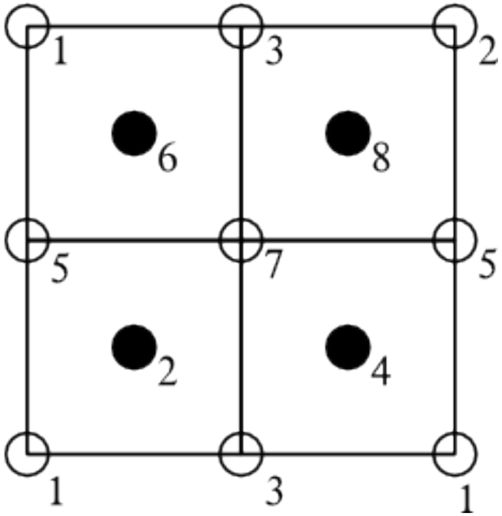
Calculation of U–NiO

- As we discussed earlier, the calculated values of U need to be converged with increasing super cell size.
- However, super cell calculations are **expensive**.
- One then extrapolates the obtained response to larger super cells; schematically:

starting



extrapolated



- The response between the equivalent pairs of neighbors is rescaled by multiplicity.
- Further pairs, response is equated to 0

We compute explicitly:

$$\chi_{11}, \chi_{12}, \chi_{21}, \chi_{22}$$

extrapolate

$$\chi^s_{12} = \chi^s_{32} = ... = \chi^s_{34} = ... = \chi^s_{78} = \frac{\chi_{12}}{4}$$

$$\chi^s_{15} = \chi^s_{13} = ... = \chi^s_{17} = ... = \chi^s_{37} = 0$$

This step is also performed by **resp_mat.f90**

Calculation of U-NiO

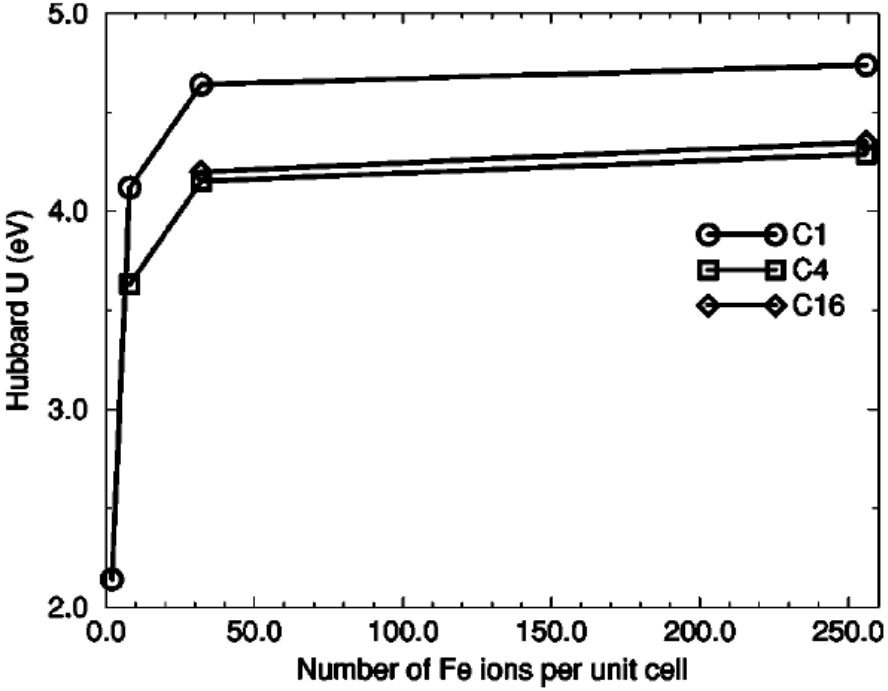
Check Ur16.out:

```
16 4.07869507114729 18.2067600029958
128 4.77585513557480 18.9533524768798
432 4.80515746873350 19.0032555863967
1024 4.80681945930046 19.0062407730070
2000 4.80692778243639 19.0064368341791
```

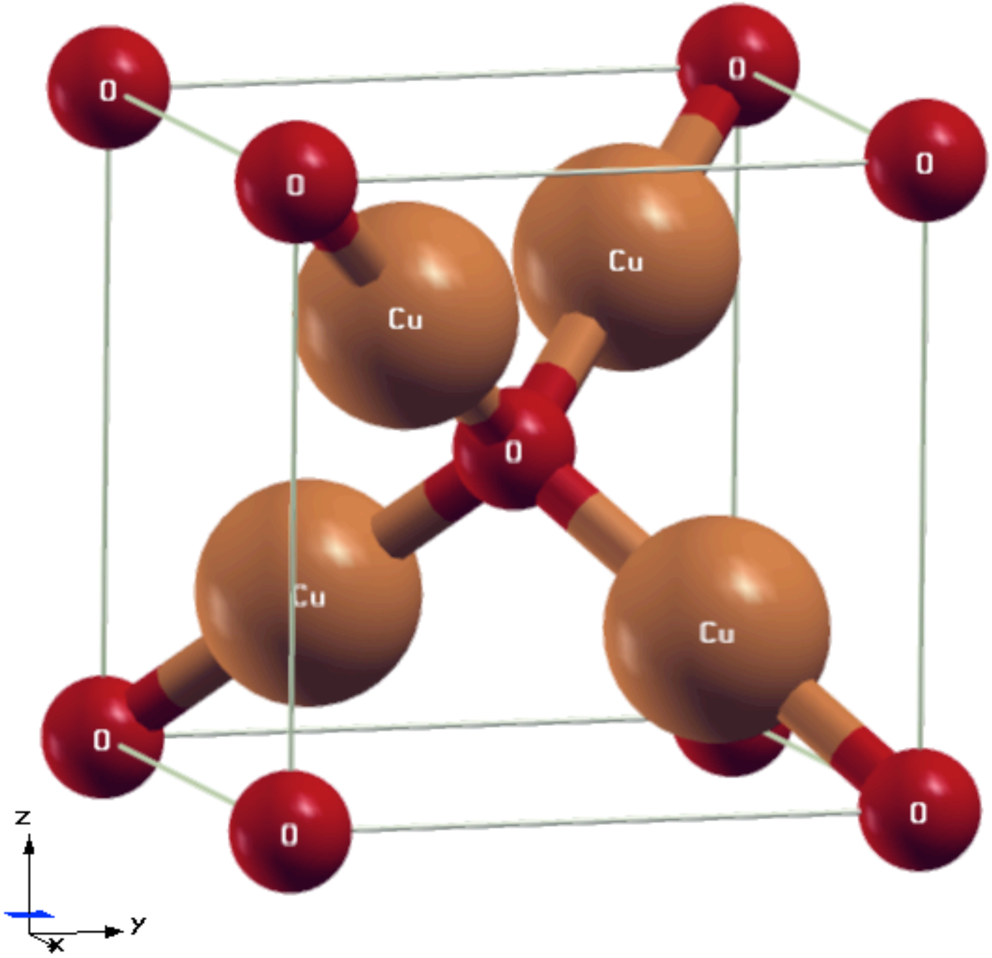
Number of atoms
In the super cell

Calculated U
on Ni-d

Calculated U
on O-p



Exercise: Cu_2O



- Cu_2O is a semiconductor.
- It is the parent material for many transparent conductive oxides (with p-type conductivity).
- Non-magnetic
- $E_g \sim 2.2$ eV

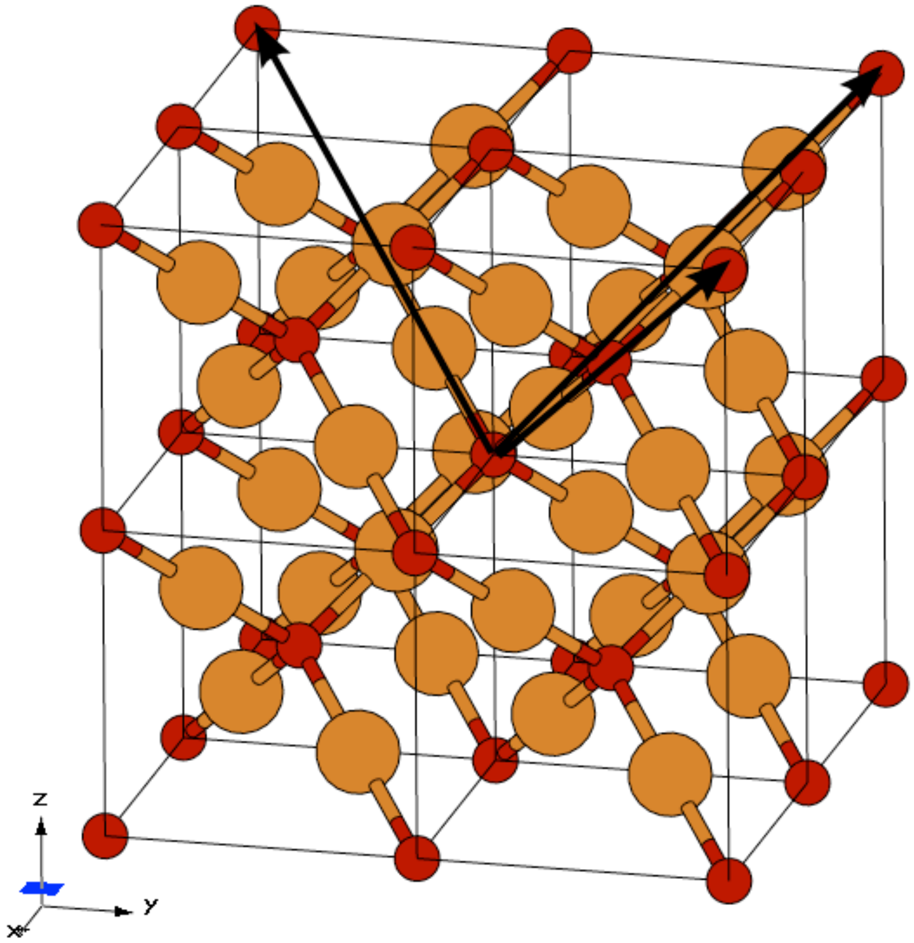
```
ibrav=1, celldm(1)=8.21
nspin = 1
```

```
ATOMIC_POSITIONS {crystal}
 Cu    0.25 0.25 0.25
 Cu    0.75 0.25 0.75
 Cu    0.75 0.75 0.25
 Cu    0.25 0.75 0.75
 O     0.00 0.00 0.00
 O     0.50 0.50 0.50
```

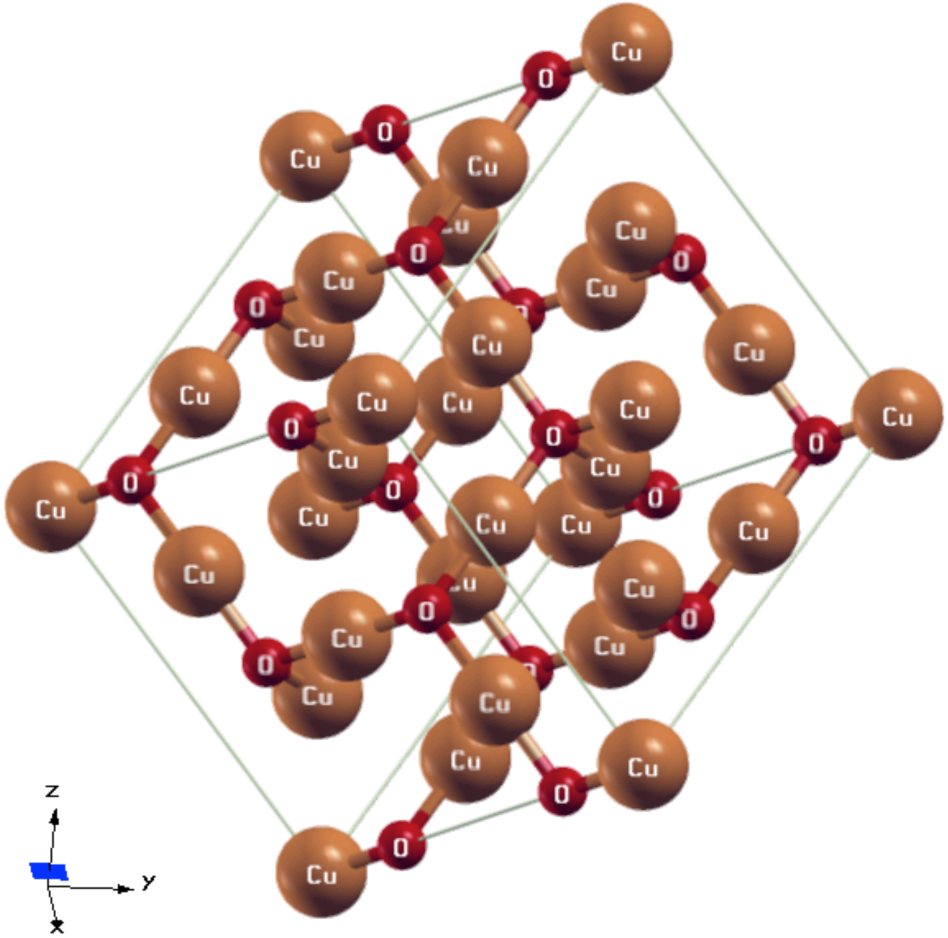
Exercise: Cu_2O

- Perform the GGA calculation and plot the DOS.
- What is the band gap?
- Compute U on Cu-d states using the linear response approach.
- Using the computed value of U, perform the GGA+U calculation.
- Investigate the changes in the DOS.
- How does the occupation matrices change? Which states increase their occupation?

Exercise: Cu_2O

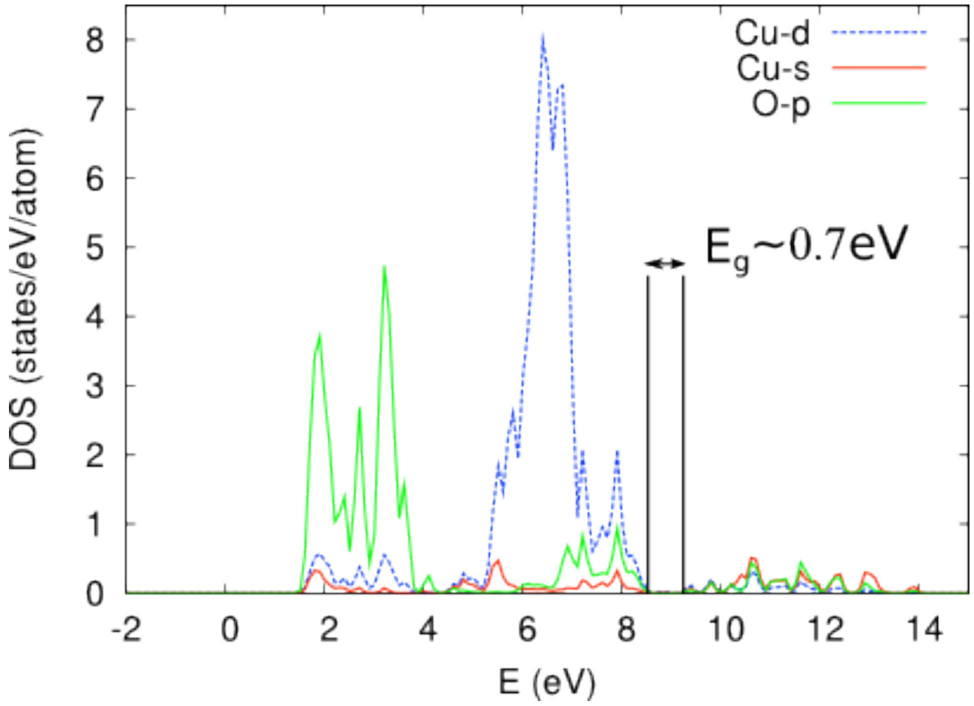


48 atoms super cell

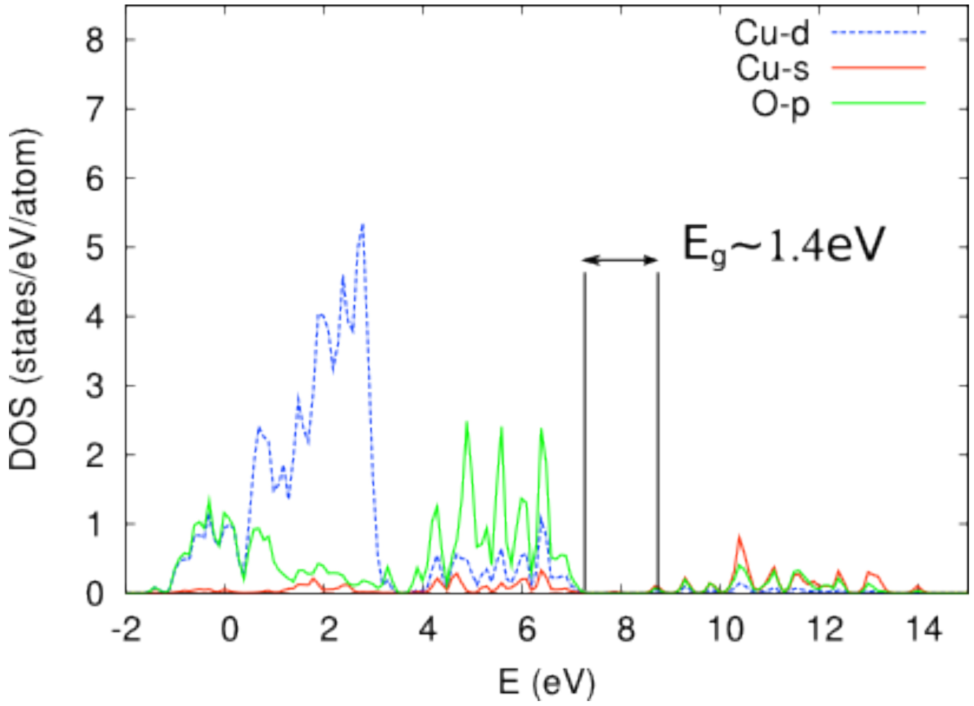


24 atoms super cell

Exercise: Cu_2O



GGA

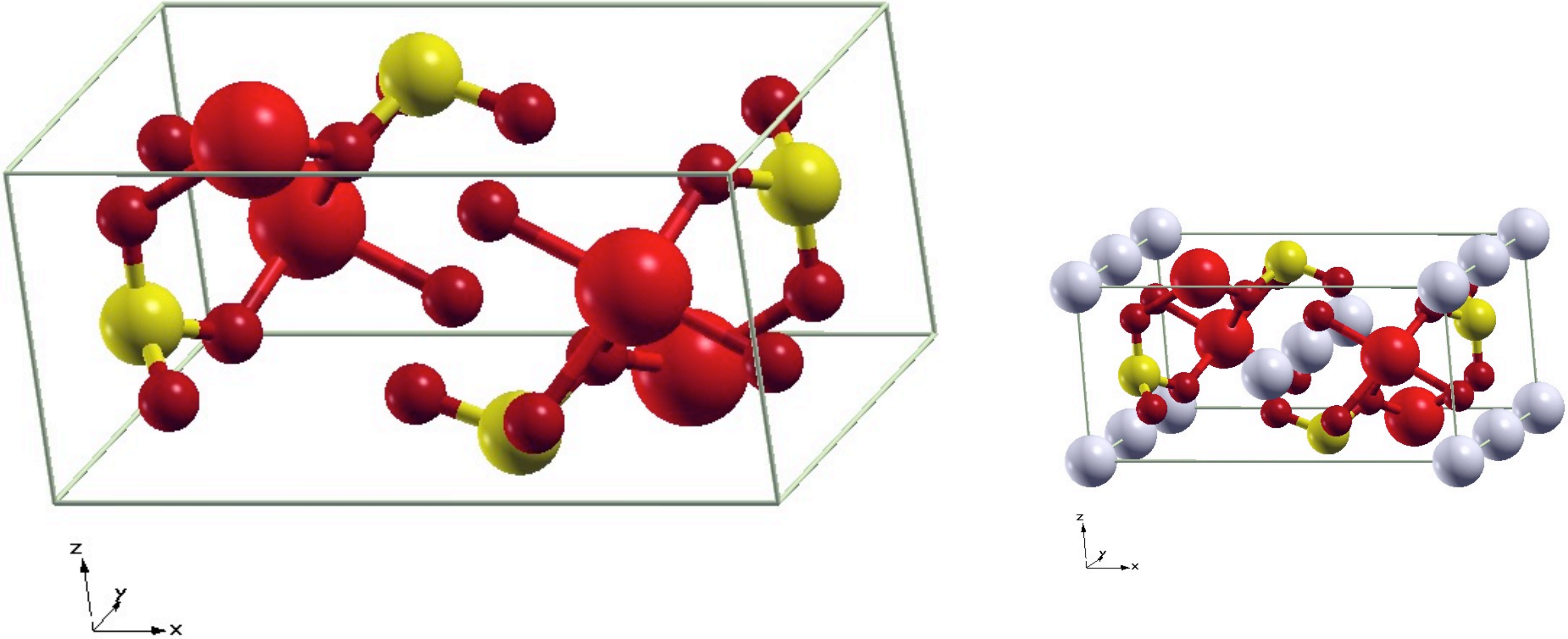


GGA+U

- Why the gap is still smaller than the experiment?
- Will it increase with U?
- What states do you find at the edge of valence and conduction bands?

Exercise: $FePO_4$

unit cell: 4 Fe, 4 P, 16 O (of 3 different “kinds”)



scf and perturbed runs have already been completed: just compute U