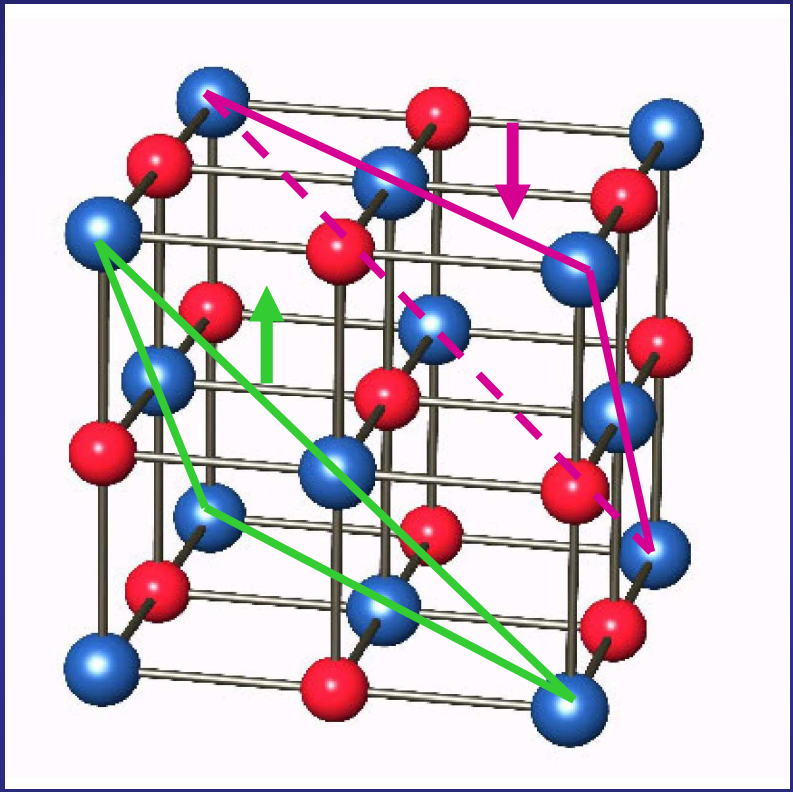
The LDA+U method: materials with strong electron correlations



Objectives

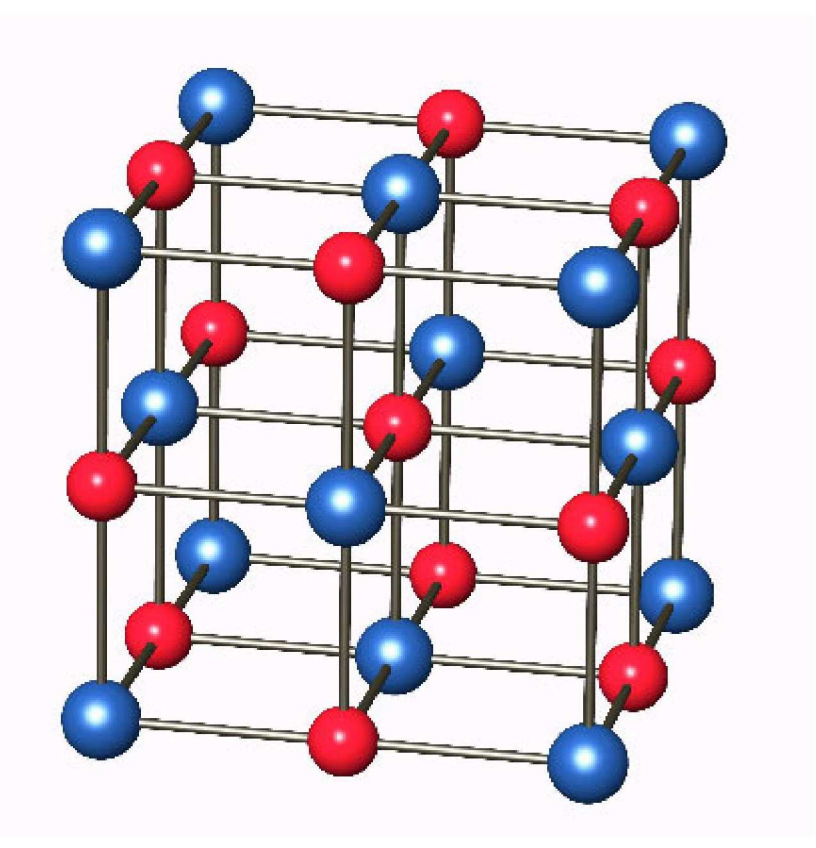
-Use of the LDA+U method within SIESTA

-Study the electronic structure of MnO

Transition metal oxides are prototypes of highly correlated materials

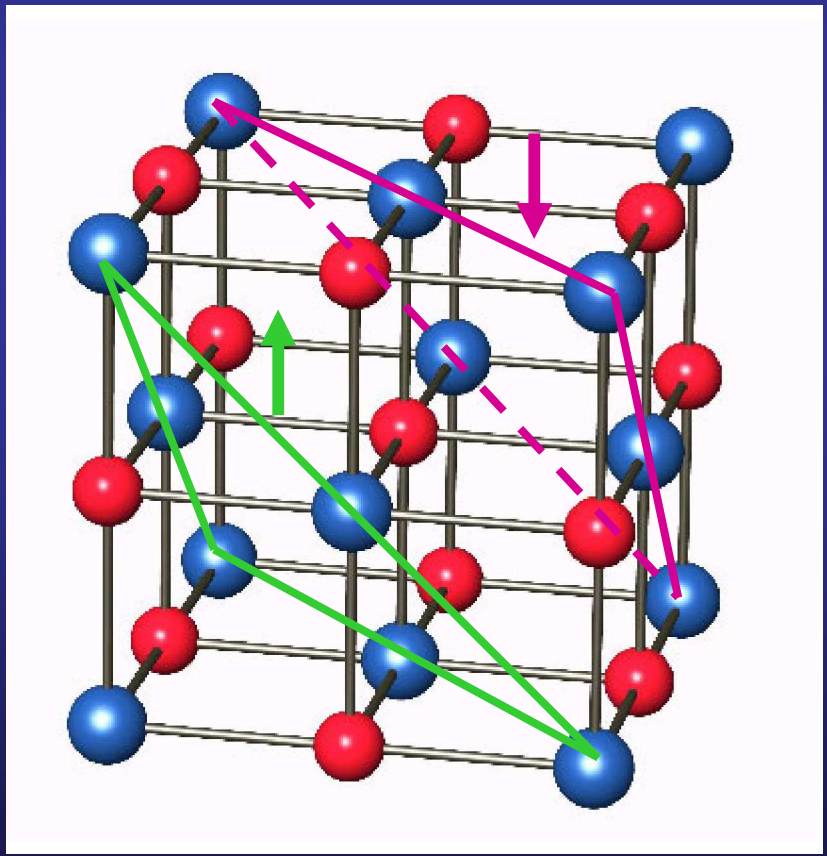
An example: MnO (NaCl structure)

The NaCl structure follows a FCC lattice with 2 atoms of basis, however….



MnO (NaCl structure)

The NaCl structure follows a FCC lattice with 2 atoms of basis, however…. the ground state of MnO corresponds to a ferromagnetic alignment of the Mn atoms within the (111) planes and the antiferromagnetic alignment of those planes



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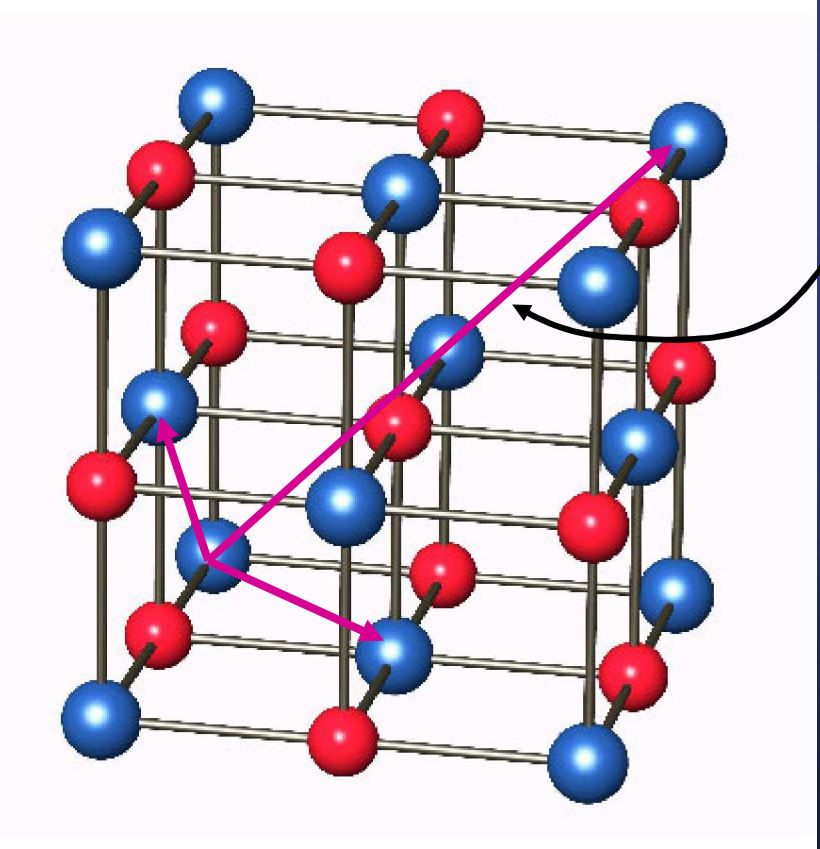


Lattice vectors

Thus we need to have at least 4 atoms in the unit cell (2 Mn atoms and 2 O atoms)

LDA+U method

LDA (or GGA) is supplemented with a Hubbard-like term in order to have a better description of the effect of electron-electron interactions in a localized atomic shell of a particular atom in the solid, i.e. 3d shell of Mn in MnO

In particular this reduces the problem of Self-Interaction

$$E^{LDA+U} = E^{LDA} + U n_{\uparrow} n_{\downarrow} - \frac{U}{2} N(N-1)$$

with

$$n_{\sigma} = \langle \hat{n}_{\sigma} \rangle$$

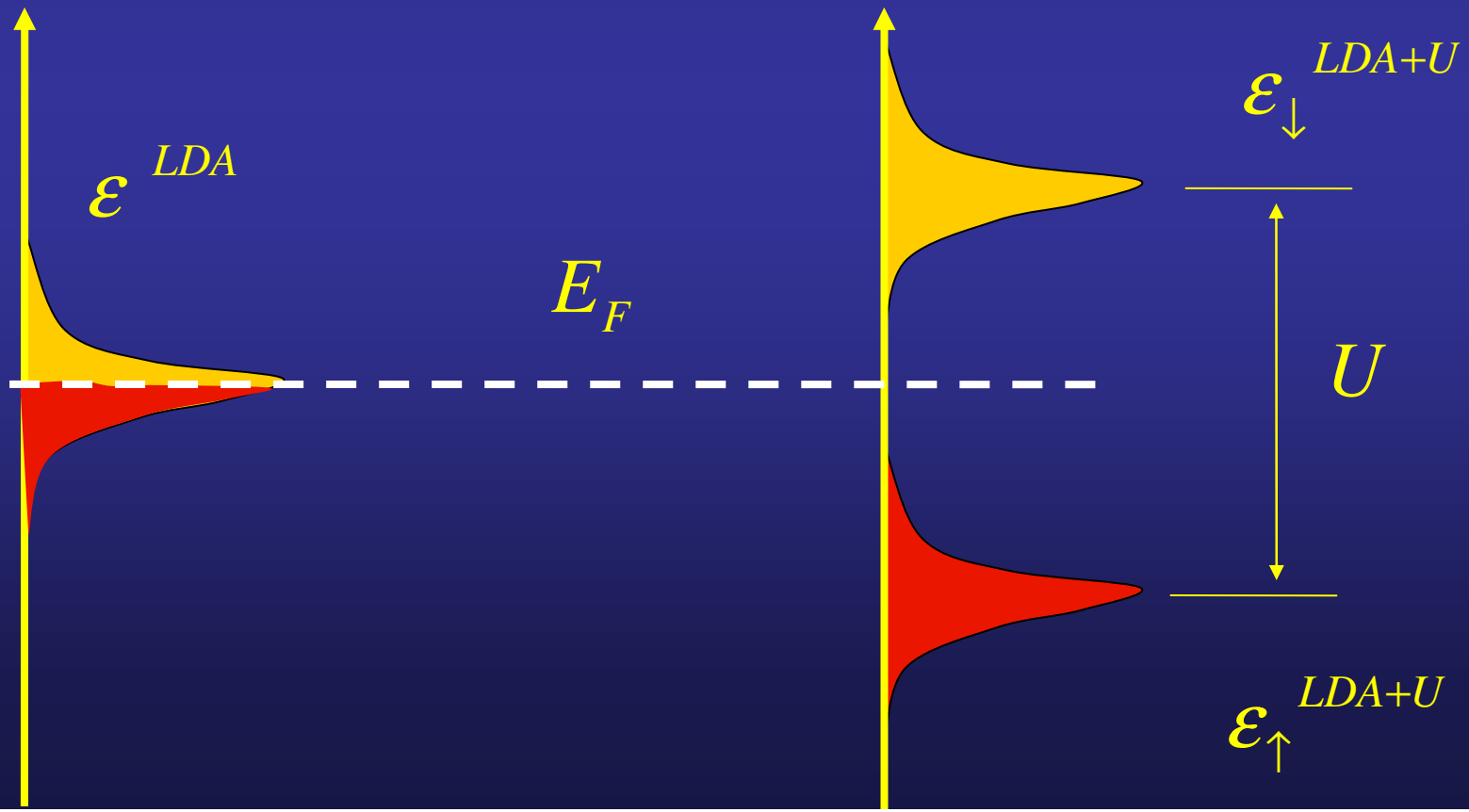
$$N = n_{\uparrow} + n_{\downarrow}$$

Double counting term (cancels the electron-electron interaction in the localized shell in LDA)

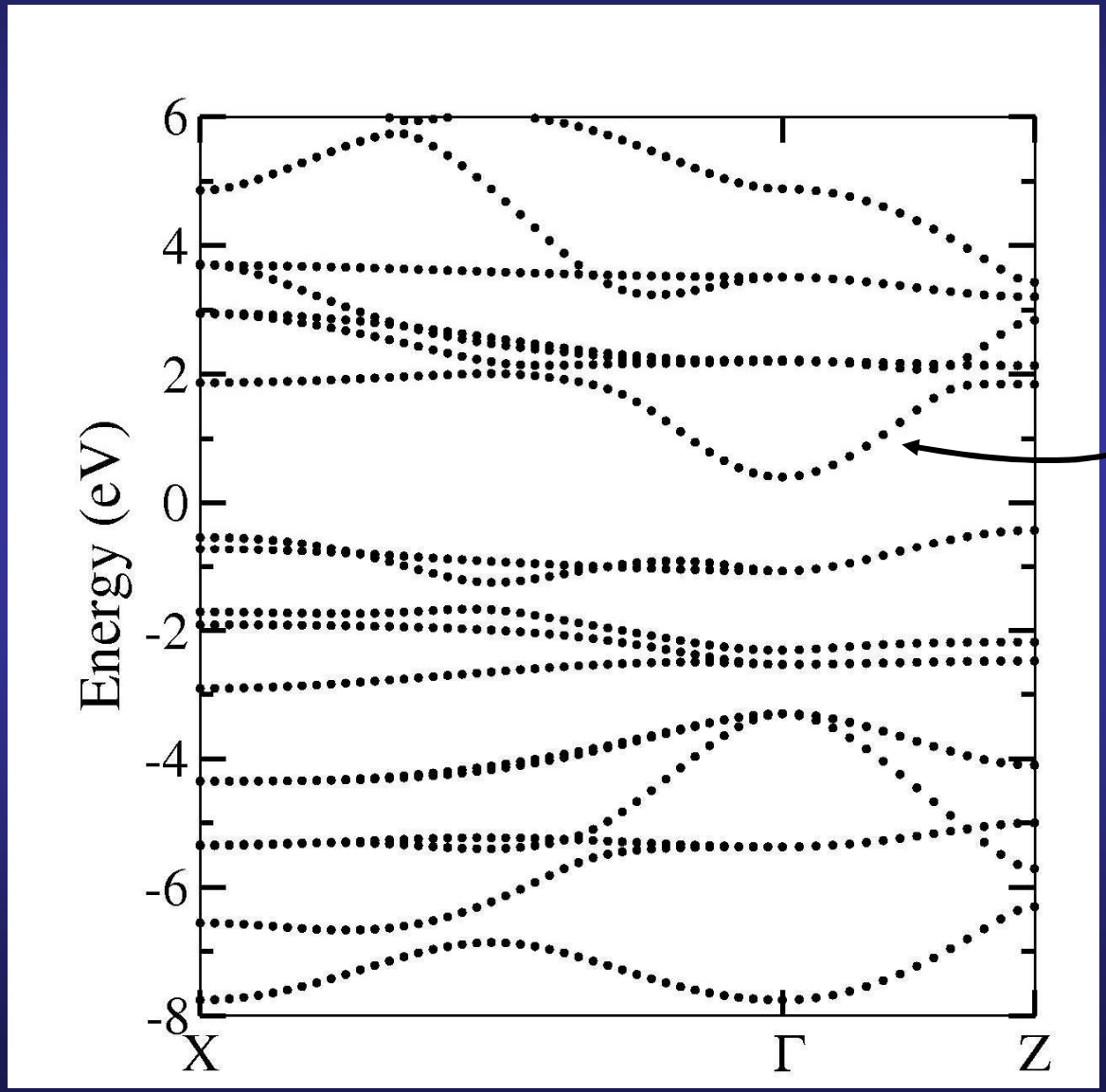
LDA+U method

$$\hat{H}_\sigma^{LDA+U} = \frac{\delta E^{LDA+U}}{\delta \langle \psi_\sigma |} = \hat{H}_\sigma^{LDA} + U\left(\frac{1}{2} - n_\sigma\right)\hat{n}_\sigma$$

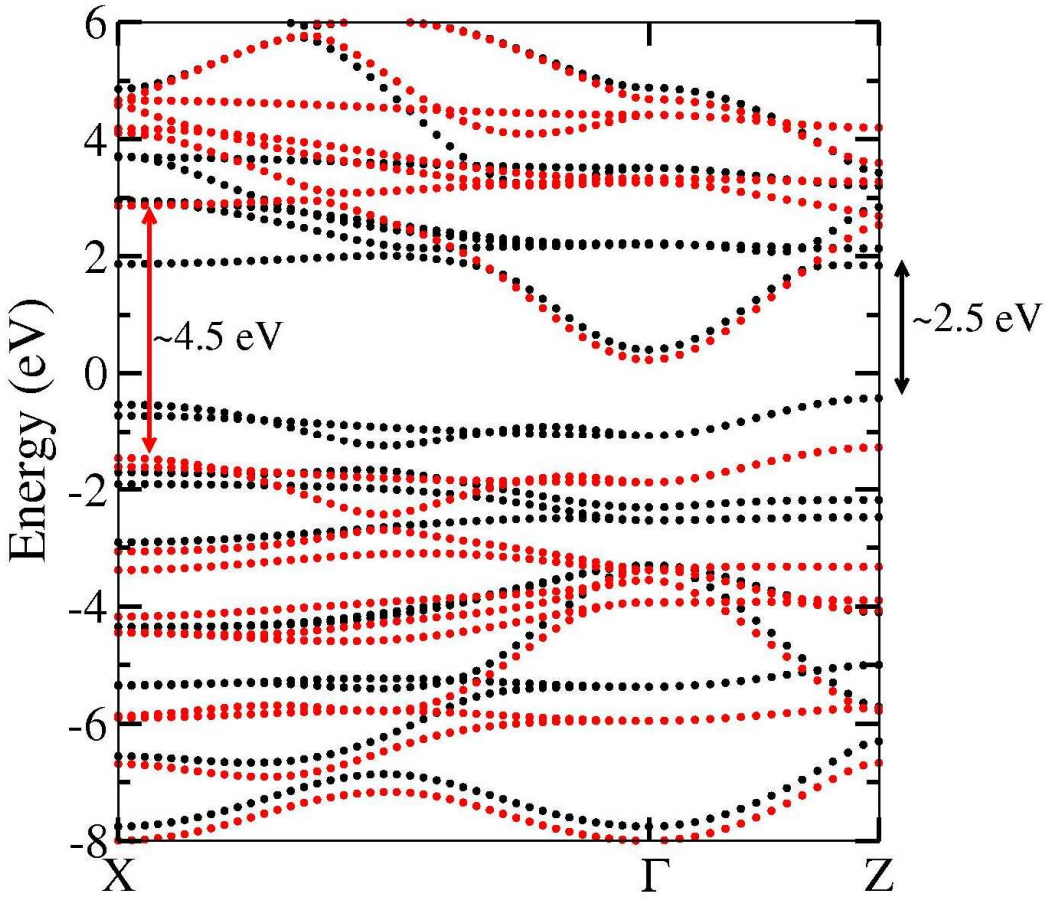
$$\varepsilon_\sigma^{LDA+U} = \frac{\delta E^{LDA+U}}{\delta n_\sigma} = \varepsilon_\sigma^{LDA} + U\left(\frac{1}{2} - n_\sigma\right)$$



GGA gap is too small for MnO



MnO bands can be corrected with the +U method




```
%block LDAU.proj
Mn   1              # number of shells of projectors
n=3   2             #  n, l
  3.000 0.000   # U(eV), J(eV)
  0.000 0.000    # rc, \omega (default values)
%endblock LDAU.proj
```

Notice that only the 3d Mn states are significantly shifted (~2 eV, of the order of U)

Mulliken population to obtain the local moment

```
siesta: Total spin polarization (Qup-Qdown) =     0.000000
```

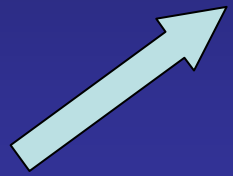
SIESTA output

WriteMullikenPop 1

```
mulliken: Atomic and Orbital Populations:

mulliken: Spin UP

Species: Mn
Atom   Qatom  Qorb
                 4s       4s       4Ppy     4Ppz     4Ppx     3dxy     3dyz     3dz2
                 3dxz     3dx2-y2  3dxy     3dyz     3dz2     3dxz     3dx2-y2
   1   5.554   0.006    0.241    0.143    0.143    0.143    0.989    0.989    0.958
               0.989    0.958   -0.015   -0.015    0.021   -0.015    0.021
   2   0.846  -0.078    0.264    0.119    0.119    0.119    0.038    0.038    0.111
               0.038    0.111   -0.007   -0.007   -0.007   -0.007   -0.007

Species: O
Atom   Qatom  Qorb
                 2s       2s       2py      2pz      2px      2py      2pz      2px
                 3Pdxy    3Pdyz    3Pdz2    3Pdxz    3Pdx2-y2
   3   3.300   0.872    0.015    0.862    0.862    0.862   -0.063   -0.063   -0.063
               0.004    0.004    0.002    0.004    0.002
   4   3.300   0.872    0.015    0.862    0.862    0.862   -0.063   -0.063   -0.063
               0.004    0.004    0.002    0.004    0.002

mulliken: Qtot =       13.000

mulliken: Spin DOWN

Species: Mn
Atom   Qatom  Qorb
                 4s       4s       4Ppy     4Ppz     4Ppx     3dxy     3dyz     3dz2
                 3dxz     3dx2-y2  3dxy     3dyz     3dz2     3dxz     3dx2-y2
   1   0.846  -0.078    0.264    0.119    0.119    0.119    0.038    0.038    0.111
               0.038    0.111   -0.007   -0.007   -0.007   -0.007   -0.007
   2   5.554   0.006    0.241    0.143    0.143    0.143    0.989    0.989    0.958
               0.989    0.958   -0.015   -0.015    0.021   -0.015    0.021

Species: O
Atom   Qatom  Qorb
                 2s       2s       2py      2pz      2px      2py      2pz      2px
                 3Pdxy    3Pdyz    3Pdz2    3Pdxz    3Pdx2-y2
   3   3.300   0.872    0.015    0.862    0.862    0.862   -0.063   -0.063   -0.063
               0.004    0.004    0.002    0.004    0.002
   4   3.300   0.872    0.015    0.862    0.862    0.862   -0.063   -0.063   -0.063
               0.004    0.004    0.002    0.004    0.002

mulliken: Qtot =       13.000
```

Some important variables to control convergence

LDAU.FirstIteration	.true.
LDAU.ThresholdTol	1.0d-2
LDAU.PopTol	4.0d-4



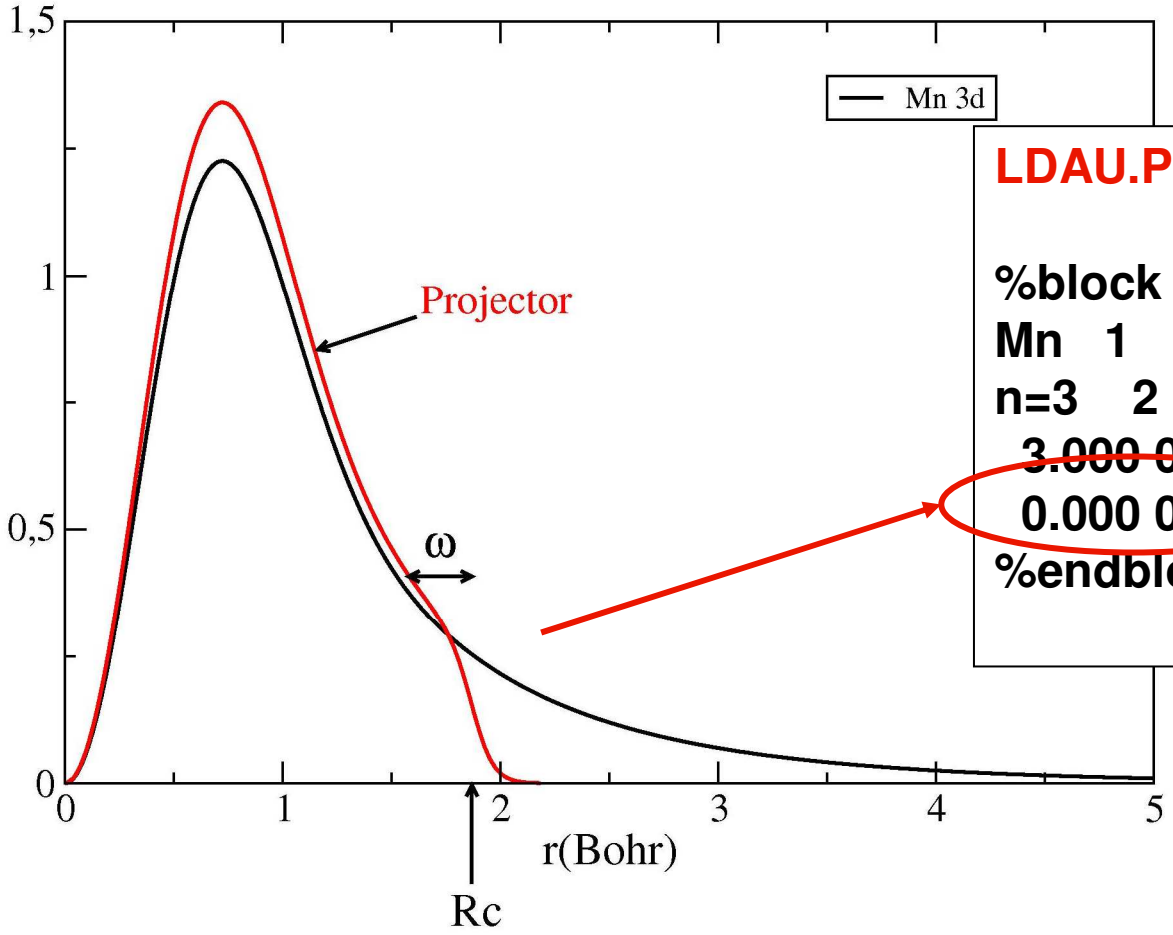
If .false. the Hubbard term is ignored in the first iterations

Local populations that define that the Hamiltonian are only updated is converged within this value

Local populations have to be converged below this value in order for the calculations to be considered as converged

Populations calculated using localized projectors

$$n_i = \sum_{n \in occup.} \langle \Psi_n | \phi_i \rangle \langle \phi_i | \Psi_n \rangle$$



LDAU.ProjectorGenerationMethod 2

```
%block LDAU.proj
Mn   1            # number of shells of projectors
n=3   2           #  n, l
  3.000 0.000     # U(eV), J(eV)
  0.000 0.000     # rc, \omega (default values)
%endblock LDAU.proj
```

Rotationally invariant formulation

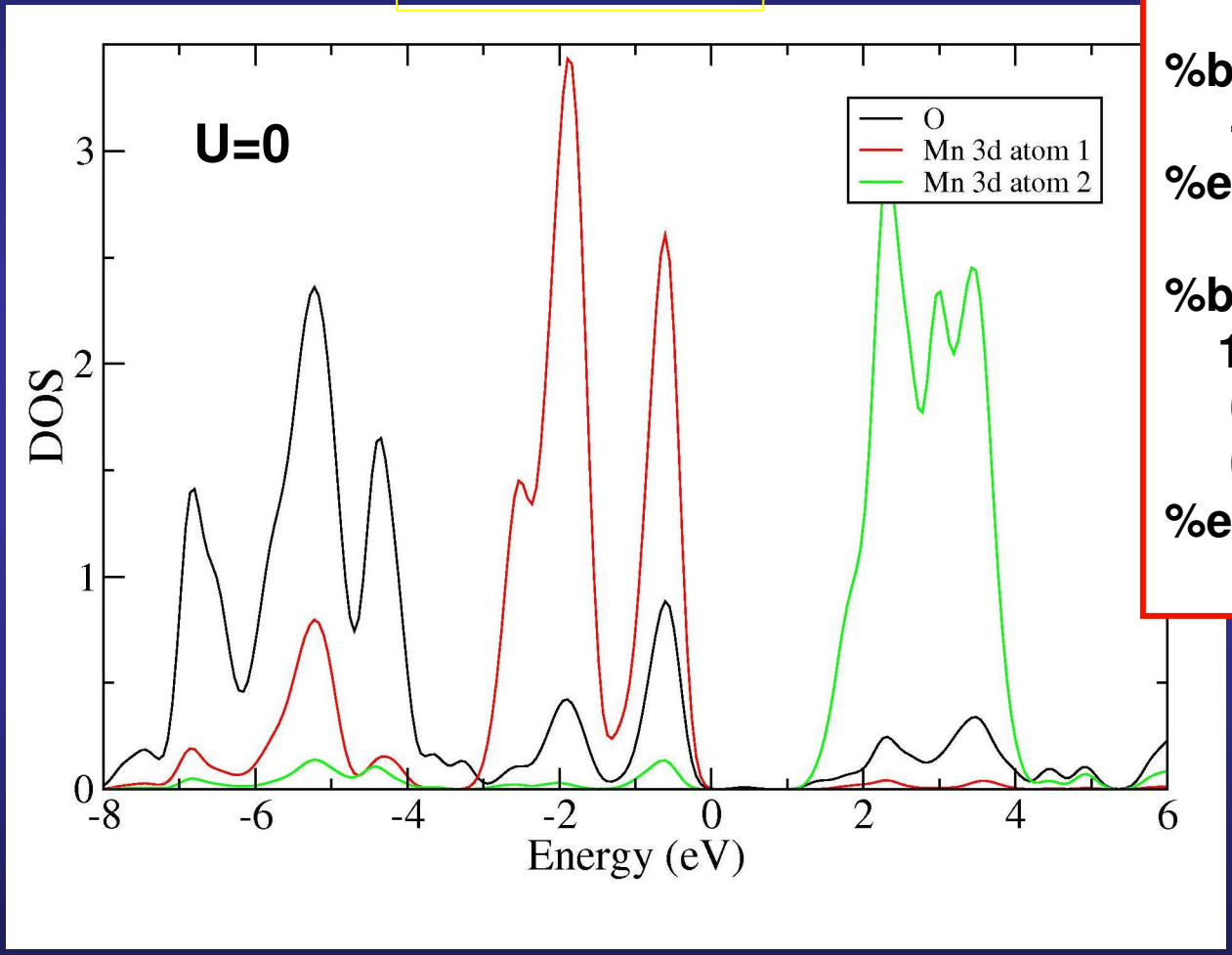
$$n_{mm'} = \sum_{n \in occup.} \langle \Psi_n | \phi_m \rangle \langle \phi_{m'} | \Psi_n \rangle$$

$$E^{LDA+U} = E^{LDA} + \frac{U^{eff}}{2} \mathrm{Tr}\left[\underset{\leftrightarrow}{n} - \underset{\leftrightarrow}{n}\underset{\leftrightarrow}{n}\right]$$

Dudarev *et al.*, Phys. Rev. B **57**, 1505 (1998)

Shift of the 3d Mn states (PDOS)

Majority Spin




```
%block ProjectedDensityOfStates
    -25.00  10.00  0.200  600 eV
%endblock ProjectedDensityOfStates

%block PDOS.kgrid_Monkhorst_Pack
   16   0   0  0.5
    0  16   0  0.5
    0   0  16  0.5
%endblock PDOS.kgrid_Monkhorst_Pack
```

Shift of the 3d Mn states (PDOS)

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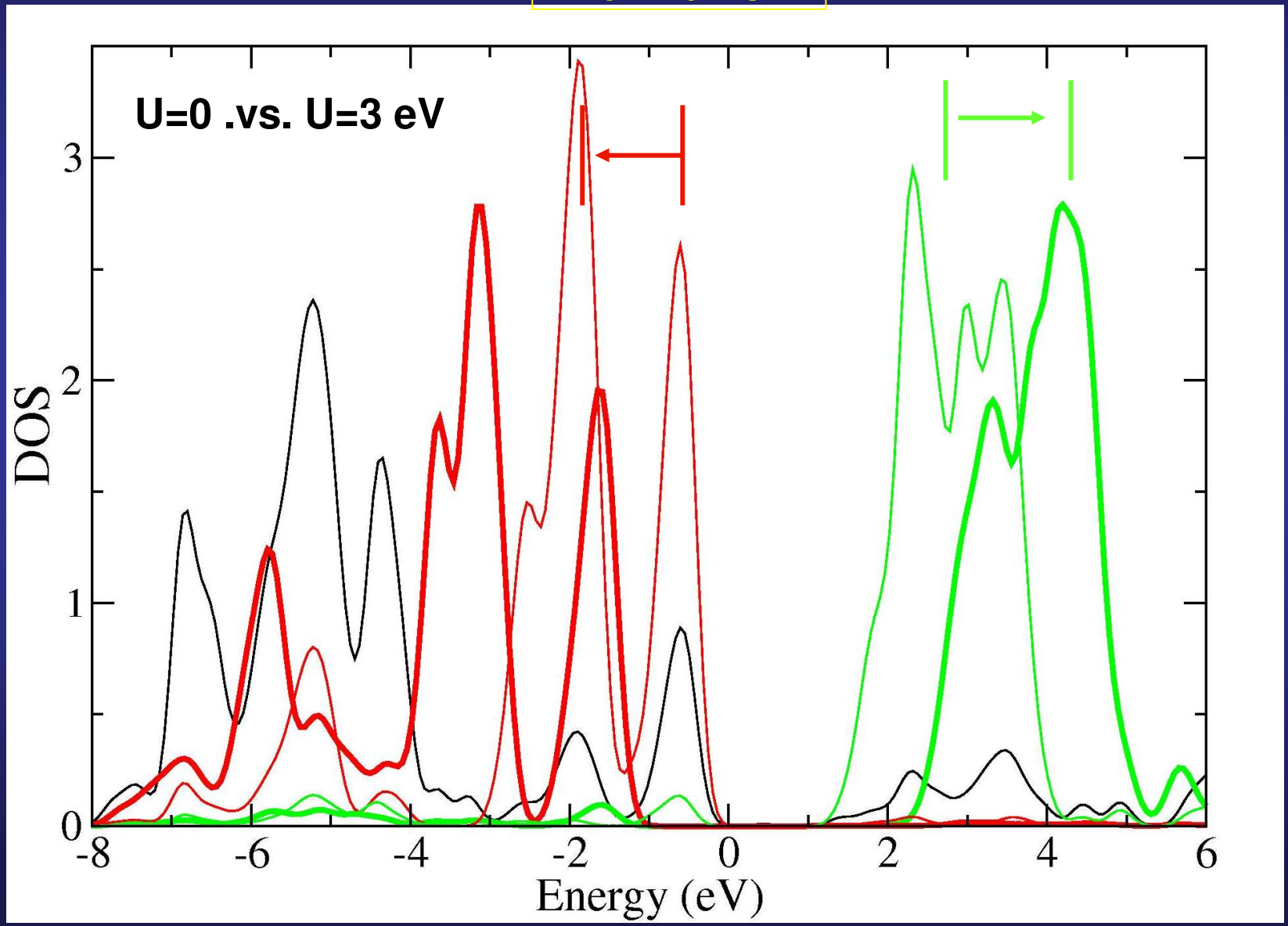

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