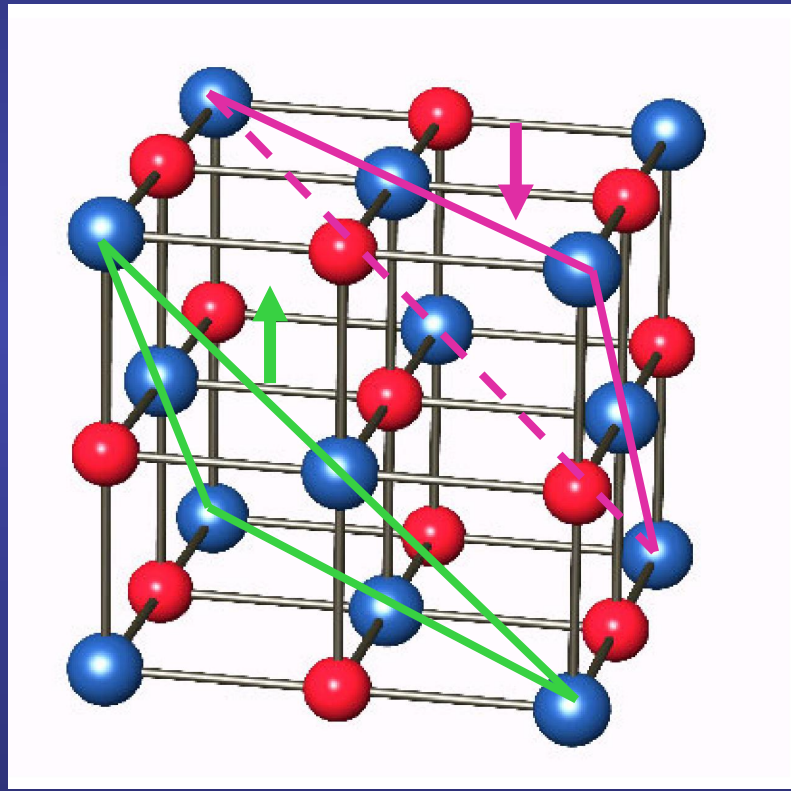
The LDA+U method: a primer and implementation within SIESTA

Daniel Sánchez-Portal

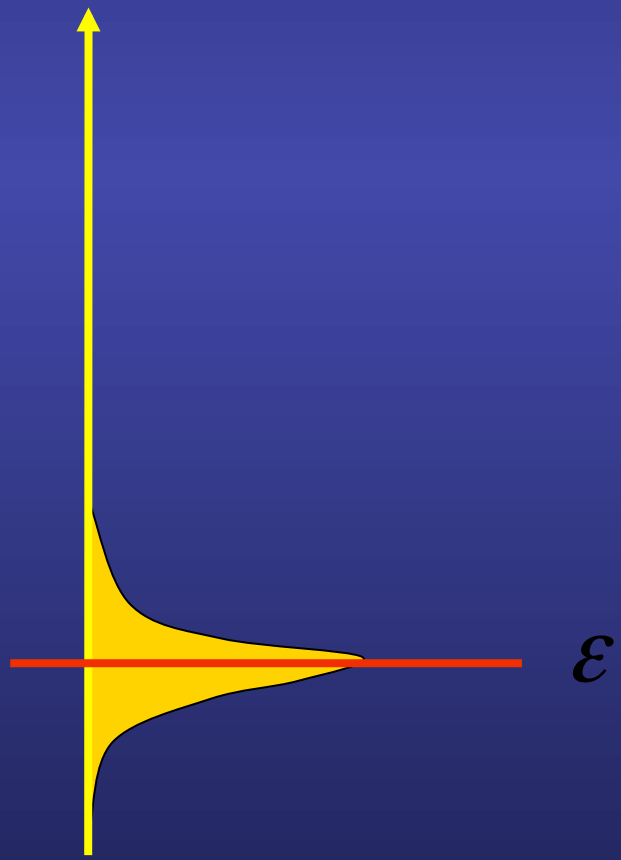


Thanks to Javier Junquera, Sampsa Riikonen and Eduardo Anglada

Source of the failure of LDA to describe Mott insulators

V. I. Anisimov, J. Zaanen and O. K. Andersen, Phys. Rev. B 44, 943 (1991)

Mean field character of the theory?



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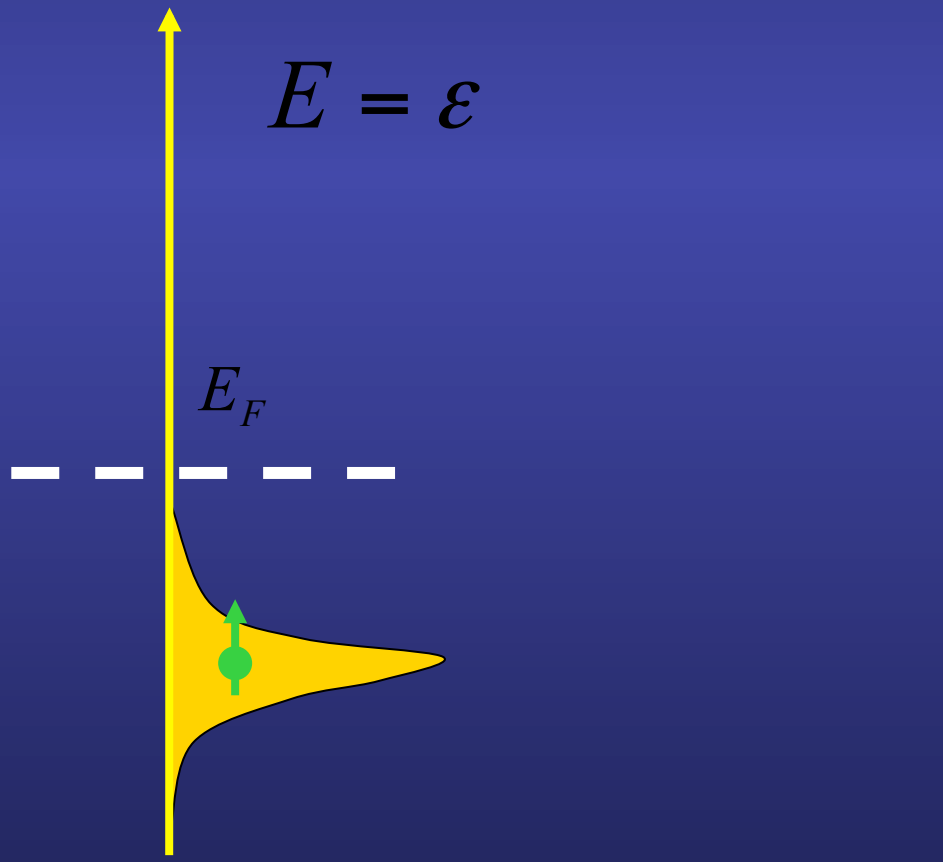

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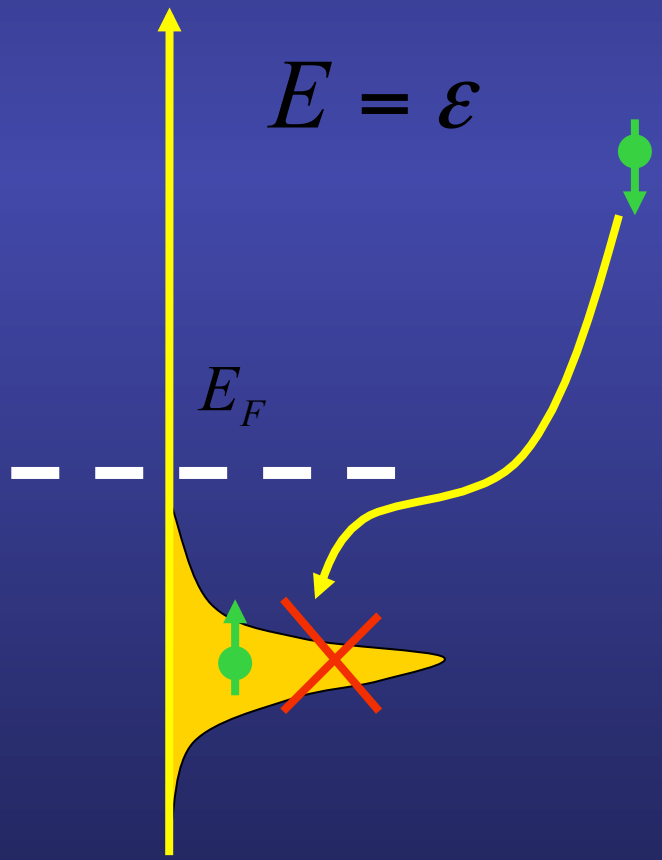

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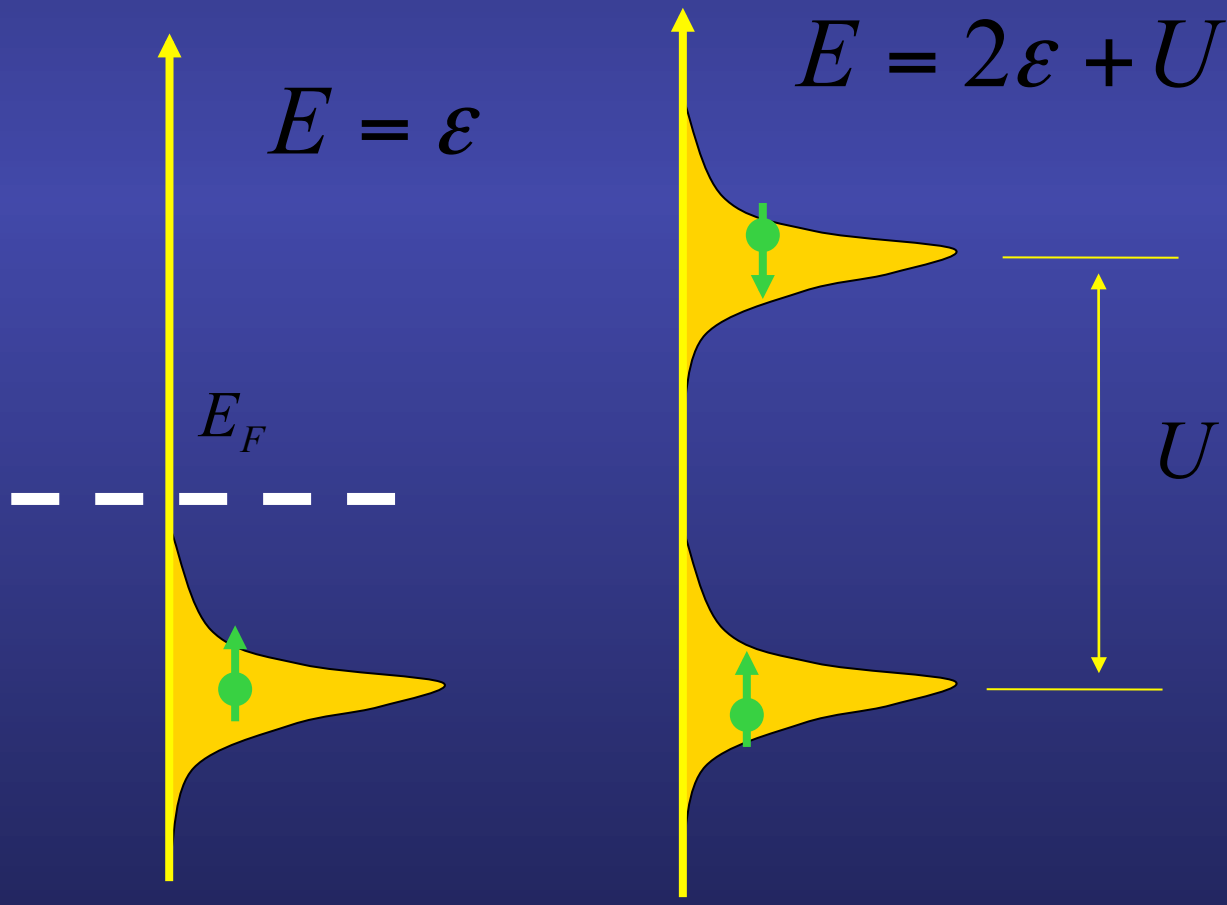

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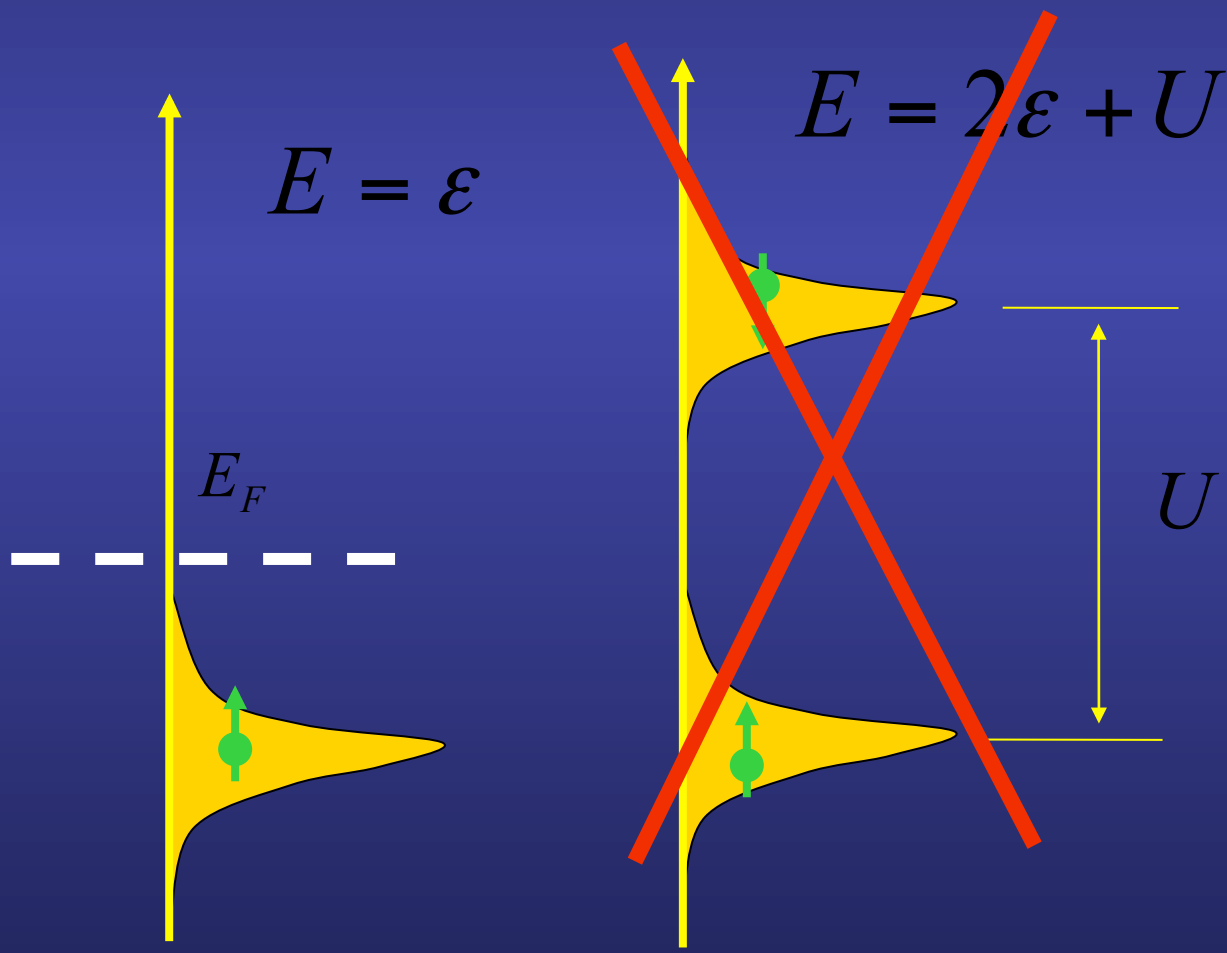

If U>>W few fluctuations of the occupation

Thus, the mean field character of LDA should not be a problem!!!!

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What if I have a poor description of exchange?

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What if I have a poor description of exchange?

Then, I will be mostly sensitive to the total population, but not to the spin or level distribution of the electrons…..

$$E(n_{\uparrow},0) = E(0,n_{\downarrow}) \approx E(n_{\uparrow}/2, n_{\downarrow}/2)$$

One source of the failure of LDA to describe materials with strong elecron-elecron interactions

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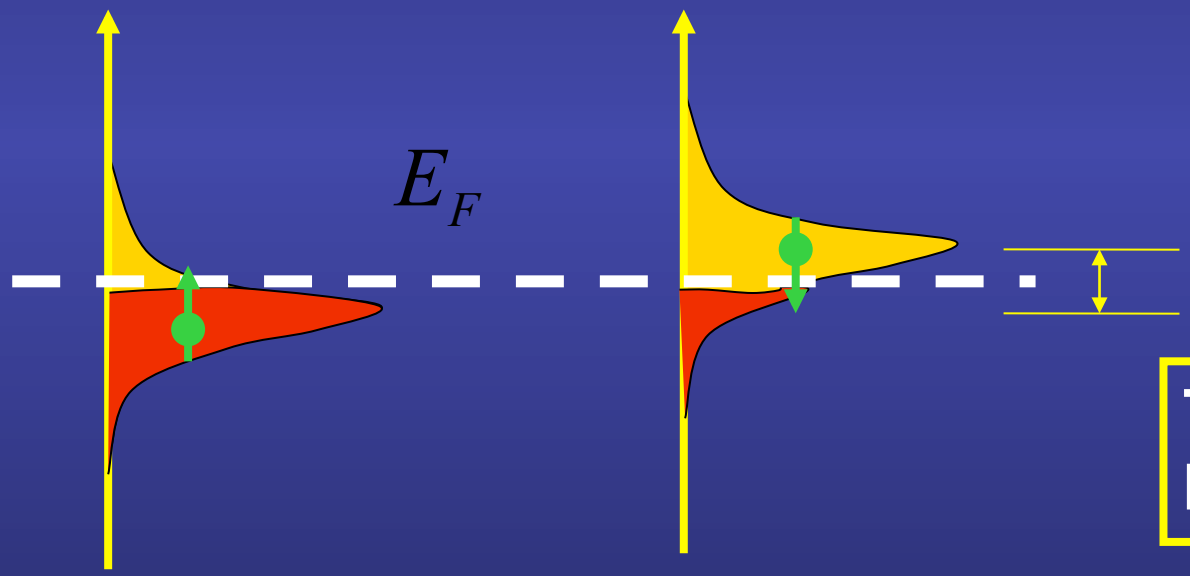

$J \leq W$

The Mott insulator may become a metal!!!!!

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Keyword: incomplete cancelation of self-interaction

- Typical pathology of LDA/GGA standard approaches when dealing with very localized states
- Due to the parametrization of Vxc from an homogeneous electron gas reference…
- …while the Hartree term is calculated for the real system

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$$E^{e-e} \approx \frac{U}{2} N(N-1) - \frac{J}{2}\left[N_{\uparrow}(N_{\uparrow}-1) + N_{\downarrow}(N_{\downarrow}-1)\right]$$

In LDA and similar functional, J is coming from the spin splitting of the free electron gas and, for a localized level, J<< U

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Question: which mean field?

Hartree-Fock has exact exchange although lacks correlations and is expensive for solids……

Idea: use Hartree-Fock for the localized shell and LDA for the rest of the electrons

LDA+U implements this idea in a semiempirical way

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

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

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

with

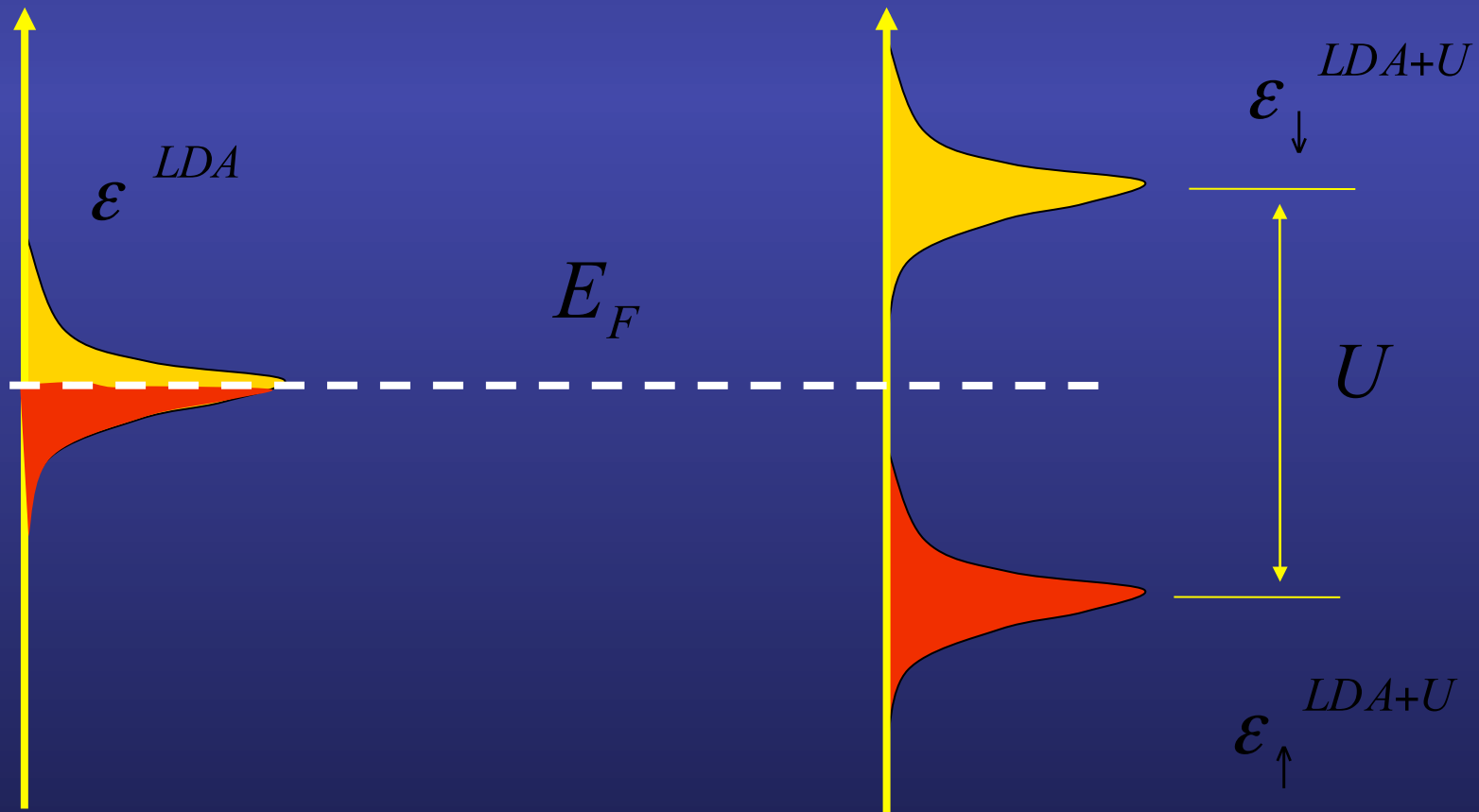
$$n_{\sigma} = \langle \hat{n}_{\sigma} \rangle$$

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

LDA+U method

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

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



Rotationally invariant formulation

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

$$E^U[\{n\}] = \tfrac{1}{2} \sum_{\{m\},\sigma} \{ \langle m, m'' | V_{ee} | m', m''' \rangle n^{\sigma}_{mm'} n^{-\sigma}_{m''m'''}$$
$$+ (\langle m, m'' | V_{ee} | m', m''' \rangle$$
$$- \langle m, m'' | V_{ee} | m''', m' \rangle) n^{\sigma}_{mm'} n^{\sigma}_{m''m'''} \},$$

V. I. Anisimov et al.

Formulation implemented in SIESTA

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

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

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

Interpretation of Dudarev et al. functional

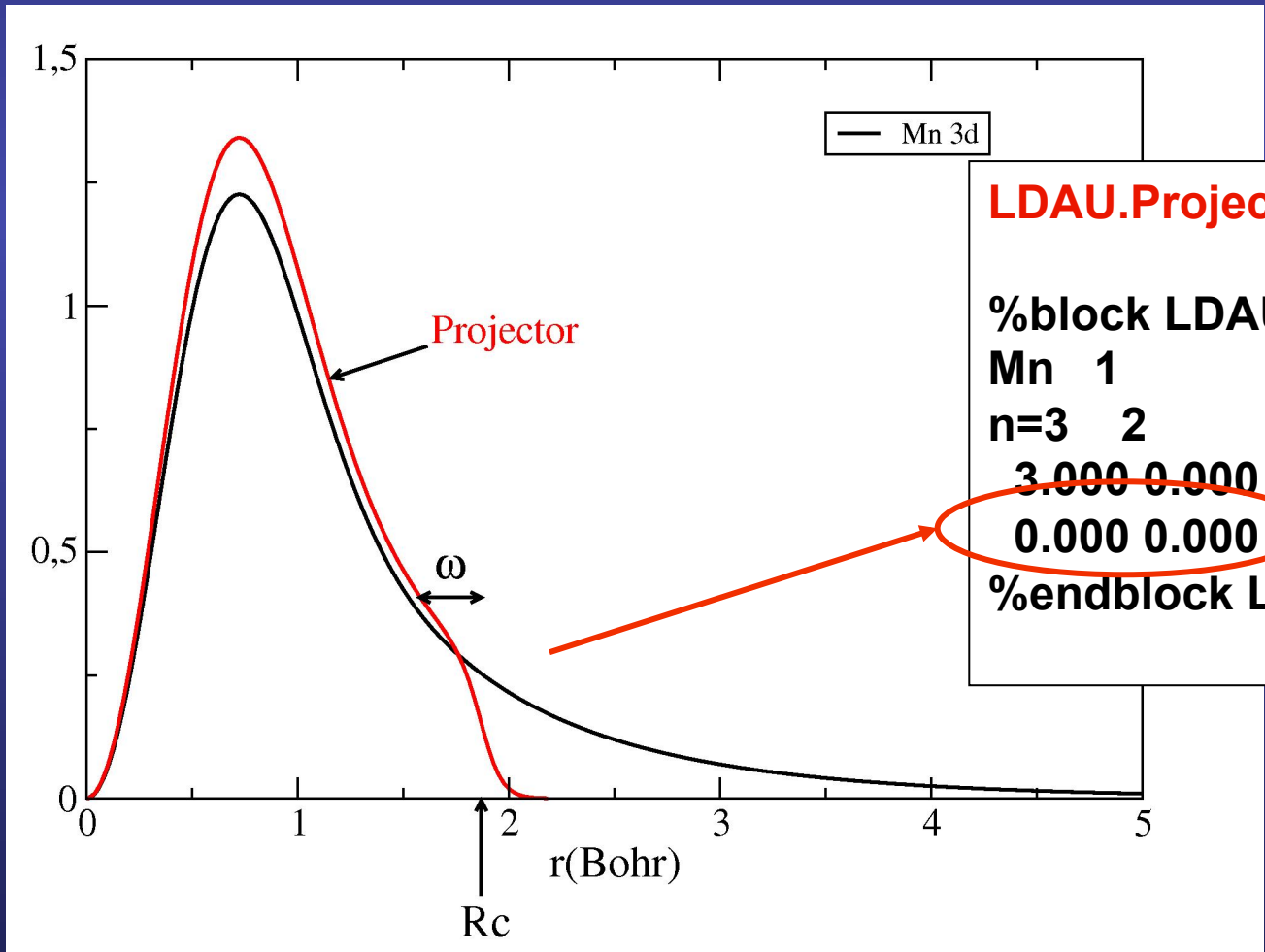
Minima in the energy for integer occupations (0 or 1)

$$E^{LDA+U} = E^{LDA} + \frac{U^{eff}}{2} \sum_{i} \lambda_i^{\sigma} (1 - \lambda_i^{\sigma})$$

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

Populations calculated using localized projectors

$$n_{ij} = \sum_{n \in occup.} \langle \Psi_n | \phi_i \rangle \langle \phi_j | \Psi_n \rangle$$



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
```

Ab initio calculation of U_{eff}

Cococcioni and de Gironcoli, Phys. Rev. B 71, 035105 (2005)
P. H. Dederichs et al., Phys. Rev.Lett. 53, 2512 (1984)
W. E. Pickett et al., Phys. Rev. B 58,1201 (1998)

Constrained local occupations
A lot of care needed

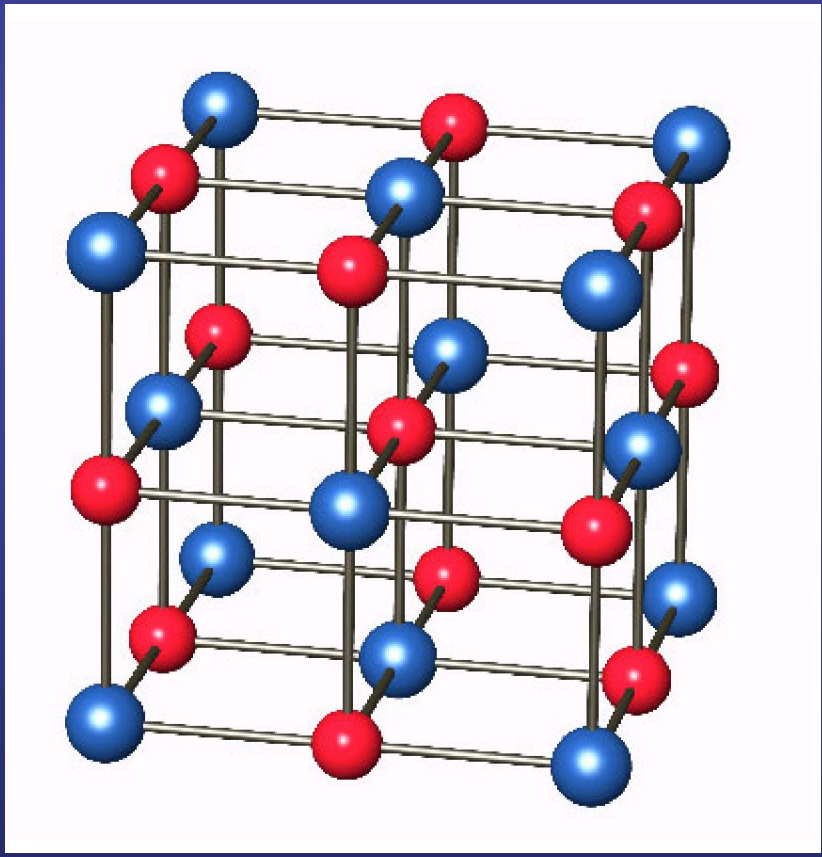
$$E^{LDA} \approx \frac{U^{eff}}{2} N(N-1)$$

$$\frac{\partial^2 E^{LDA}}{\partial N^2} \approx U^{eff}$$

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….



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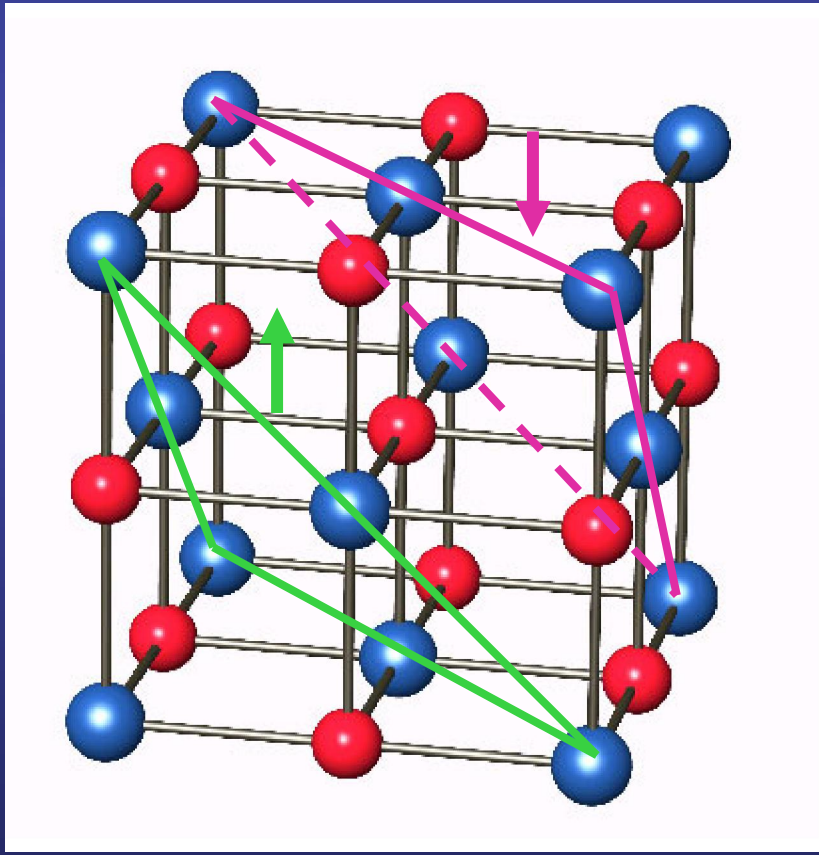
The NaCl structure follows a FCC lattice with 2 atoms of basis, however…. the ground state of MnO corresponds to a ferromagnetic alignment of the Mn atoms within the (111) planes and the antiferromagnetic alignment of those planes



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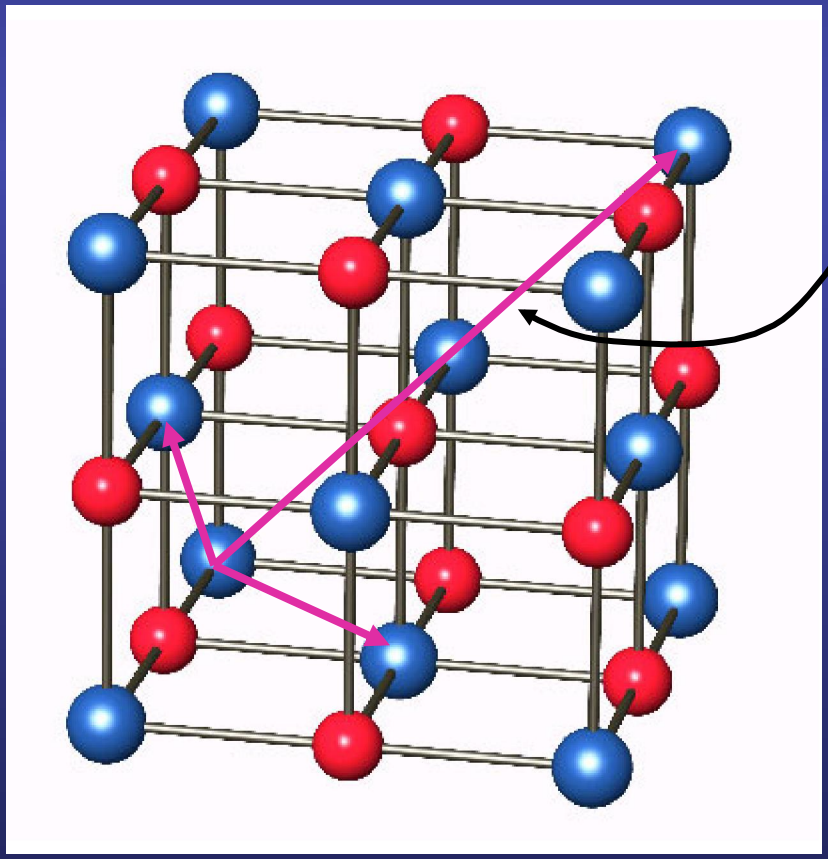
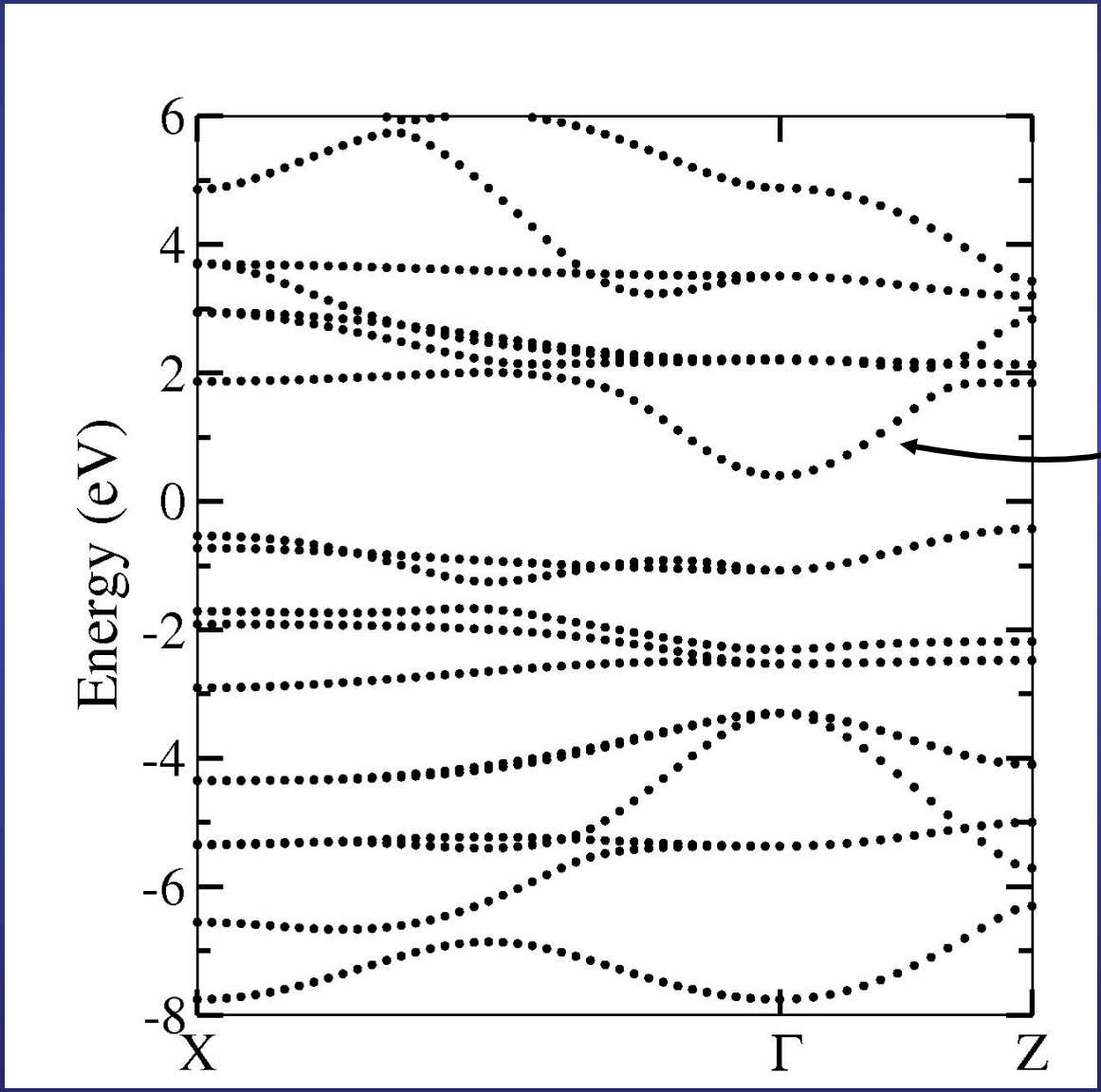


Lattice vectors

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

GGA gap is too small for MnO



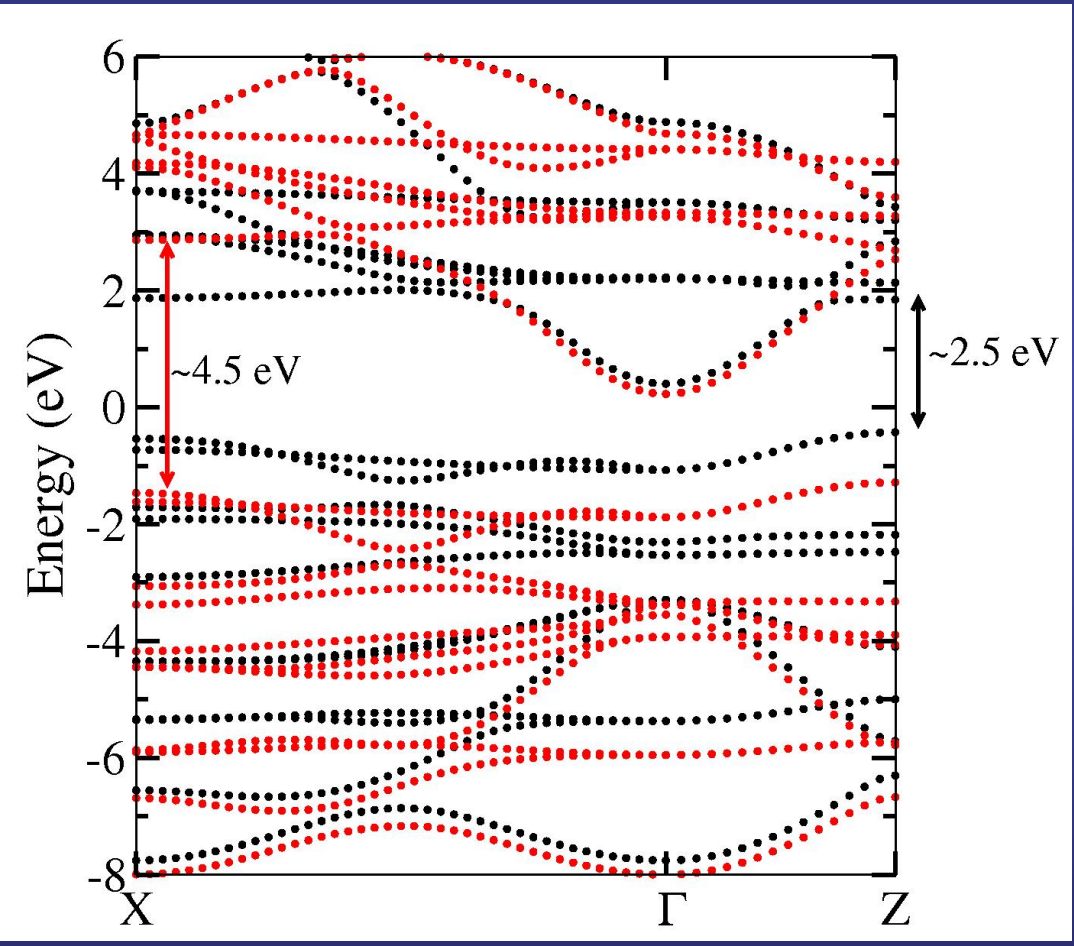
Mn 3d

Mn 4sp

Mn 3d

O 2p

MnO bands can be corrected with the +U method




```
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n=3    2            #  n, l
  3.000 0.000    # U(eV), J(eV)
  0.000 0.000    # rc, \omega (default values)
%endblock LDAU.proj
```
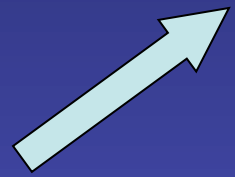
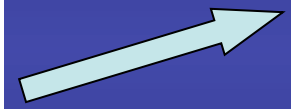

Notice that only the 3d Mn states are significantly shifted (~2 eV, of the order of U)

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

Mulliken population to obtain the local moment

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

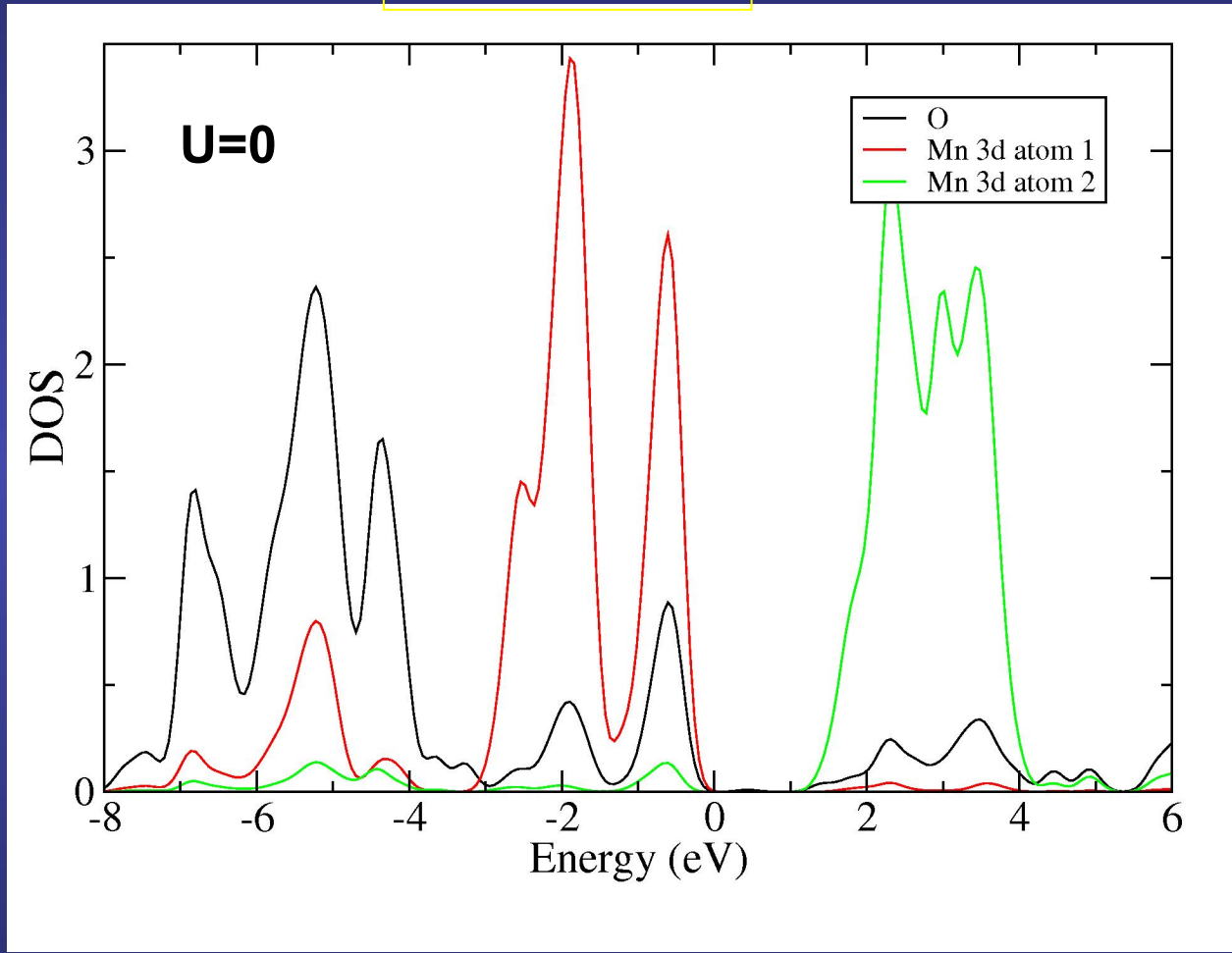
SIESTA output

WriteMullikenPop 1

```
mulliken: Atomic and Orbital Populations:

mulliken: Spin UP

Species: Mn
Atom  Qatom  Qorb
               4s       4s       3dxy     3dyz     3dz2     3dxz     3dx2-y2 3dxy
               3dyz     3dz2     3dxz     3dx2-y2 4Ppy     4Ppz     4Ppx
   1  5.513   0.053    0.211    0.991    0.991    0.958    0.991    0.956   -0.016
              -0.016    0.021   -0.016    0.021    0.123    0.123    0.123
   2  0.828  -0.040    0.244    0.041    0.041    0.116    0.040    0.116   -0.007
              -0.007   -0.007   -0.007   -0.007    0.103    0.103    0.103

Species: O
Atom  Qatom  Qorb
               2s       2s       2py      2pz      2px      2py      2pz      2px
               2Pdxy    2Pdyz    2Pdz2    2Pdxz    2Pdx2-y2
   3  3.329   0.880    0.009    0.887    0.889    0.889   -0.080   -0.080   -0.080
              0.004    0.004    0.002    0.004    0.002
   4  3.329   0.880    0.009    0.887    0.889    0.889   -0.080   -0.080   -0.080
              0.004    0.004    0.002    0.004    0.002

mulliken: Qtot =       13.000

mulliken: Spin DOWN

Species: Mn
Atom  Qatom  Qorb
               4s       4s       3dxy     3dyz     3dz2     3dxz     3dx2-y2 3dxy
               3dyz     3dz2     3dxz     3dx2-y2 4Ppy     4Ppz     4Ppx
   1  0.828  -0.040    0.244    0.041    0.041    0.116    0.040    0.116   -0.007
              -0.007   -0.007   -0.007   -0.007    0.103    0.103    0.103
   2  5.513   0.053    0.211    0.991    0.991    0.958    0.991    0.956   -0.016
              -0.016    0.021   -0.016    0.021    0.123    0.123    0.123

Species: O
Atom  Qatom  Qorb
               2s       2s       2py      2pz      2px      2py      2pz      2px
               2Pdxy    2Pdyz    2Pdz2    2Pdxz    2Pdx2-y2
   3  3.329   0.880    0.009    0.887    0.889    0.889   -0.080   -0.080   -0.080
              0.004    0.004    0.002    0.004    0.002
   4  3.329   0.880    0.009    0.887    0.889    0.889   -0.080   -0.080   -0.080
              0.004    0.004    0.002    0.004    0.002

mulliken: Qtot =       13.000
```

Shift of the 3d Mn states (PDOS)

Majority Spin



Notice that here the zero of energy is taken at the top of the valence band, which is not done automatically neither by SIESTA nor by mprop utility

How to get the PDOS with *mprop* utility:

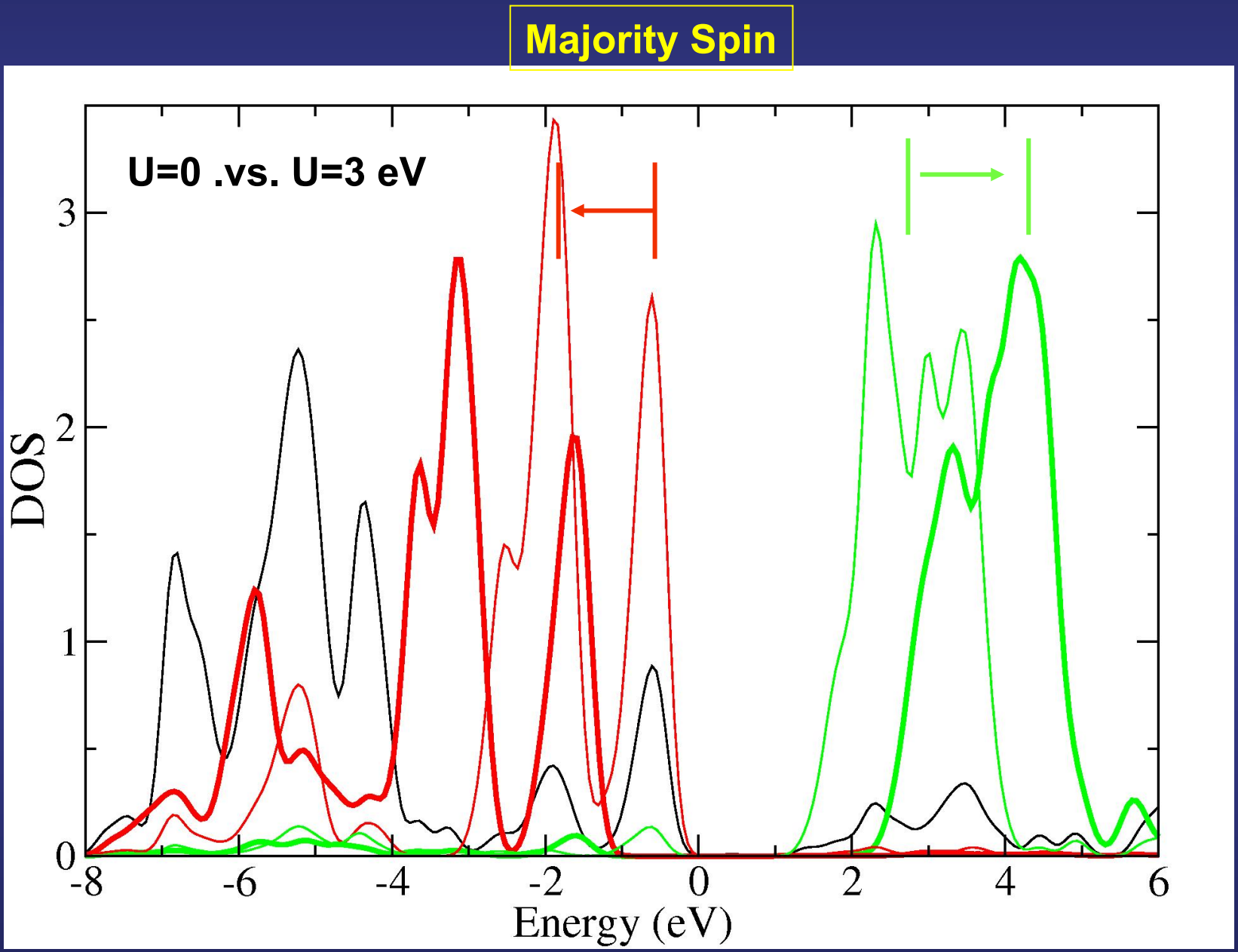
In *MnO.fdf* file set:
COOP.Write .true.

Run *mprop* utility:
#mprop -n 2000 -s 0.2 -w -12.00 -W 3.000 pdos

***pdos.mpr* file reads:**

MnO ==> SystemLabel, which defines the names of the files to be used
DOS ==> Keyword for mprop analysis tool
PDOS_3dMn1 ==> Label to construct the name of the output file
1_3d ==> PDOS on 3d orbitals first Mn atom
PDOS_3dMn2
2_3d ==> PDOS on 3d orbitals second Mn atom
PDOS_O
O ==> PDOS on all orbitals both O atoms
PDOS_Mn1
1 ==> PDOS on all orbitals first Mn atom
PDOS_Mn2
2 ==> PDOS on all orbitals second Mn atom

Shift of the 3d Mn states (PDOS)



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