

Magnetism and magnetic systems

P. Giannozzi

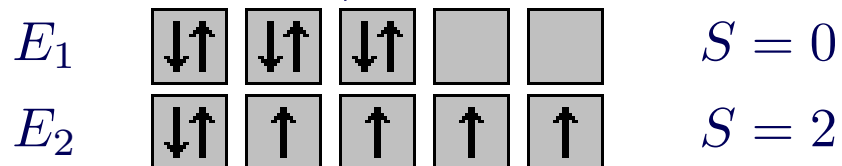
Università di Udine and CNR-IOM Democritos, Trieste, Italy

African School on Electronic Structure Methods, AIMS, 19-30 July 2010

Origin of magnetism: open-shell atoms

- Open-shell atoms: some electronic manifolds (typically d or f) are not complete.

- Example: Fe d^6 shell, 6 d electrons:



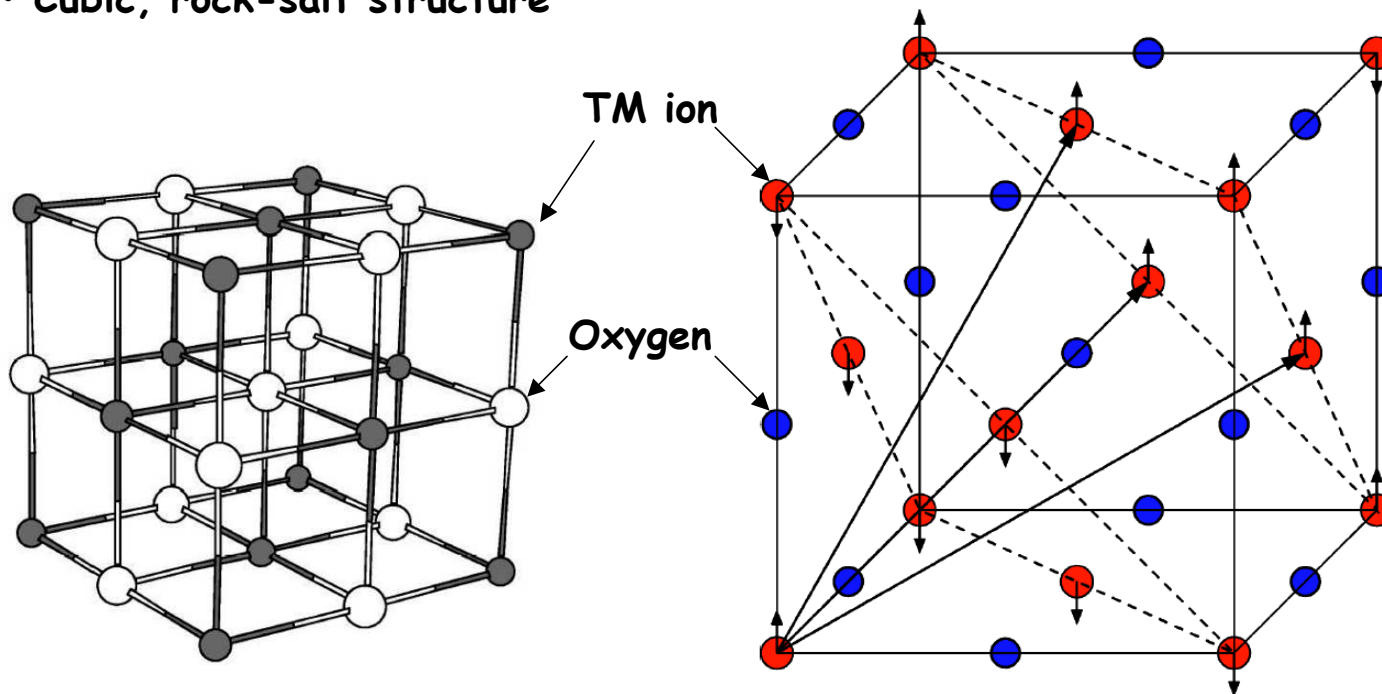
Hund's rule (from Coulomb repulsion and Pauli exclusion principle): $E_1 > E_2$

Spin alignment tends to be maximum and the atom has a magnetic moment.

- A local magnetic moment may persist in condensed-matter systems, giving rise to many different ordered configurations:
 - *Ferromagnetic* (FM): all magnetic moments are aligned, total magnetization is nonzero
 - *Antiferromagnetic* (AFM): two (or more) sublattices of atoms with opposite magnetic moments are present, total magnetization is zero
 - *Non-collinear* and other more complex arrangements

Example: transition metal oxides

- Cubic, rock-salt structure



- Antiferromagnetic (AF) ground state: neighbor (111) planes have opposite magnetization

Spin-polarized systems

So far we have “neglected” the spin of the electrons:

$$n(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\psi_i(\mathbf{r})|^2, \quad (N = \text{number of electrons}), \quad (1)$$

or, for metals:

$$n(\mathbf{r}) = 2 \sum_{i=1} f_i |\psi_i(\mathbf{r})|^2, \quad (\text{where } \sum_i f_i = N/2), \quad (2)$$

assuming implicitly that spin-up and spin-down Kohn-Sham orbitals and charge densities are the same:

$$\psi_i^\uparrow(\mathbf{r}) = \psi_i^\downarrow(\mathbf{r}), \quad n^\uparrow(\mathbf{r}) \equiv 2 \sum_{i=1}^{N/2} |\psi_i^\uparrow(\mathbf{r})|^2 = n^\downarrow(\mathbf{r}). \quad (3)$$

Advantage: we need just half of the orbitals (in insulators, $N/2$ instead of N).

Spin-polarized systems (2)

Let us choose a quantization axis for the spin (the same for all electrons) and assume different orbitals (at least N this time):

$$\{\psi_i^\uparrow(\mathbf{r})\}, \quad i = 1, \dots, N^\uparrow, \quad \{\psi_i^\downarrow(\mathbf{r})\}, \quad i = 1, \dots, N^\downarrow, \quad N^\uparrow + N^\downarrow = N. \quad (4)$$

The charge densities for spin-up and spin-down states are now

$$n^\uparrow(\mathbf{r}) = \sum_{i=1}^{N^\uparrow} |\psi_i^\uparrow(\mathbf{r})|^2, \quad n^\downarrow(\mathbf{r}) = \sum_{i=1}^{N^\downarrow} |\psi_i^\downarrow(\mathbf{r})|^2 \quad (5)$$

(extension to metals is straightforward: just add occupancy factors $f_i^\uparrow, f_i^\downarrow$) and we introduce the total charge and the magnetization:

$$n(\mathbf{r}) = n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r}), \quad m(\mathbf{r}) = n^\uparrow(\mathbf{r}) - n^\downarrow(\mathbf{r}) \quad (6)$$

The quantization axis is usually (but not necessarily) chosen as z axis.

DFT for spin-polarized systems

In principle, the exact exchange-correlation functional should be able to predict the magnetic ground states and the corresponding charge densities.

In practical approximated functionals, we have to explicitly account for the spin polarization, i.e. the total energy is a functional of the up and down charge densities:

$$E[n^\uparrow, n^\downarrow] = E_{kin} + E_{ext} + E_H + E_{xc}[n^\uparrow, n^\downarrow] \quad (7)$$

(note that $E_{ext} = E_{ext}[n^\uparrow + n^\downarrow] = E_{ext}[n]$ and the same holds for E_H). We need to calculate the functional derivatives to get the Hamiltonian. They will be different for spin-up and spin-down states:

$$\frac{\delta E}{\delta n^\uparrow} \neq \frac{\delta E}{\delta n^\downarrow} \quad (8)$$

It is usually convenient to write E_{xc} as $E_{xc}[n, m]$ and exploit:

$$\frac{\delta n(\mathbf{r})}{\delta n^\uparrow(\mathbf{r}')} = \frac{\delta n(\mathbf{r})}{\delta n^\downarrow(\mathbf{r}')} = \delta(\mathbf{r} - \mathbf{r}'), \quad \frac{\delta m(\mathbf{r})}{\delta n^\uparrow(\mathbf{r}')} = \delta(\mathbf{r} - \mathbf{r}'), \quad \frac{\delta m(\mathbf{r})}{\delta n^\downarrow(\mathbf{r}')} = -\delta(\mathbf{r} - \mathbf{r}') \quad (9)$$

(note the minus sign!).

DFT for spin-polarized systems (2)

The Kohn-Sham equations become:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ext} + V_H + V_{xc} + B_{xc} \right] \psi_i^\uparrow = \epsilon_i^\uparrow \psi_i^\uparrow \quad (10)$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ext} + V_H + V_{xc} - B_{xc} \right] \psi_i^\downarrow = \epsilon_i^\downarrow \psi_i^\downarrow \quad (11)$$

(note the minus sign!) where

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n, m]}{\delta n(\mathbf{r})}, \quad B_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n, m]}{\delta m(\mathbf{r})} \quad (12)$$

Magnetism stems from the exchange-correlation functional: one spin is more energetically favorable than the other (as under a magnetic field).

This approach goes under the name of *Local Spin-Density Approximation*, or LSDA, even when the functional E_{xc} is based not on LDA but on GGA.

Spin-polarized functionals

Exchange: diagonal in spin, can be obtained from scaling arguments from the unpolarized case:

$$E_x^{LSDA}[n(\mathbf{r})] = \sum_{\sigma=\uparrow,\downarrow} \int F_x^{LSDA}[n^\sigma(\mathbf{r})] d\mathbf{r} = \sum_{\sigma=\uparrow,\downarrow} \int \frac{1}{2} F_x^{LDA}[2n^\sigma(\mathbf{r})] d\mathbf{r} \quad (13)$$

where

$$E_x^{LDA}[n(\mathbf{r})] = \int F_x^{LDA}[n(\mathbf{r})] d\mathbf{r}. \quad (14)$$

Correlation: from the interpolation of polarized and unpolarized functionals:

$$E_c^{LSDA}[n, m] = \int [\epsilon_c^U[n(\mathbf{r})] + f(\zeta(\mathbf{r})) (\epsilon_c^P(n(\mathbf{r})) - \epsilon_c^U(n(\mathbf{r})))] n(\mathbf{r}) d\mathbf{r} \quad (15)$$

where f is smooth interpolating function ($f(0) = 0, f(1) = 1$) of the polarization

$$\zeta(\mathbf{r}) = \frac{m(\mathbf{r})}{n(\mathbf{r})} = \frac{n^\uparrow(\mathbf{r}) - n^\downarrow(\mathbf{r})}{n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r})}. \quad (16)$$

Analogous equations hold for the spin-polarized GGA (σ -GGA).

Limitations and caveats

- Simple DFT approaches based on LDA or GGA will fail more often than not to give good results in magnetic systems. The presence of *strongly correlated electrons*, i.e. localized atomic-like states, seriously stresses the ability of LDA or GGA to describe magnetic systems.
- In molecules and finite systems. LSDA yields a well-defined value of S_z : in fact, $S_z = (N^\uparrow - N^\downarrow)\hbar/2$, but not of S^2 . This is known as *spin contamination* and implies that DFT states are superpositions of solutions with different values of S^2 . Usually a small effect, not a problem in crystals, but something to be aware of.
- There is (virtually) no *magnetic anisotropy*, i.e. dependence of the energy upon the quantization axis, in LSDA. More complex calculations that include the *spin-orbit interactions* are needed to obtain a sensible value of the magnetic anisotropy.
- In the spin-unpolarized case, self-consistency will always end up in the *global* minimum of the energy functional, e.g. in the ground state. In the spin-polarized case, if you can easily end up in a *local* minimum of the energy functional that is not the ground state.

Common misconceptions

- The “magnetic moment of an atom” μ_i in a molecule or solid is a useful but *ill-defined concept* (exactly as “the charge of a given atom”). You can project the magnetic moment onto atomic states and get an idea of which atoms are magnetized and which electron states contribute to the magnetization, but in general:
 - results will depend upon the specific choice of the atomic states, and
 - the sum of atomic magnetic moments μ_i will not sum up exactly to the total magnetization M_{tot} of the system.

Well-defined quantities are the total M_{tot} and absolute M_{abs} magnetizations:

$$M_{tot} = -\mu_B \int m(\mathbf{r}) d\mathbf{r}, \quad M_{abs} = -\mu_B \int |m(\mathbf{r})| d\mathbf{r}. \quad (17)$$

For FM, $\sum_i \mu_i \sim M_{tot} \simeq M_{abs} \neq 0$; for AFM, $M_{tot} = 0$, $\sum |\mu_i| \sim M_{abs} \neq 0$.

- The FM and AFM ordering in the same system cannot be treated in the same way: the description of an AFM requires at least two sublattices with opposite magnetizations and may thus require a *supercell*, at least double the original cell.

Practical spin-polarized calculations

- *Fixed magnetization*: typically better suited for finite systems (e.g. molecules) but only for FM states.
 - Set the *total* magnetization to the desired (integer) value.
 - Perform several calculations at different magnetizations, choose the one with the smaller energy as ground state.
 - The system can be treated as an insulator, if so desired and appropriate.
- *Unconstrained magnetization*: typically better suited for crystals or for AFM states.
 - Set a *starting magnetization* to break the symmetry.
 - The calculation should find the lowest-energy spin state *compatible with the given crystal structure and not orthogonal to initial conditions* (e.g.: if you start with a FM alignment, you will hardly find an AFM final state even if it exists).
 - Perform several calculations at different starting magnetizations, choose the one with smaller energy as ground state.
 - The system must be in all cases treated as a metal, whether it is or not.

In principle, you should use pseudopotentials with the *nonlinear core correction*.

Density Of States: definitions

Density Of States (DOS):

$$g(E) = \sum_i \delta(E - \epsilon_i) \quad (18)$$

typically normalized so that $\int_{E \leq E_F} g(E) dE = N$, where N is the number of (valence) electrons in the unit cell. The DOS reflects the *electronic structure of a material*.

Spin-projected Density Of States (DOS):

$$g^{\uparrow\downarrow}(E) = \sum_i \delta(E - \epsilon_i^{\uparrow\downarrow}) \quad (19)$$

normalized so that

$$g(E) = g^{\uparrow}(E) + g^{\downarrow}(E), \quad \int_{E \leq E_F} g^{\uparrow\downarrow}(E) dE = N^{\uparrow\downarrow} \quad (20)$$

where $N^{\uparrow\downarrow}$ = number of (valence) electrons with up (\uparrow) or down (\downarrow) spin in the unit cell. Reminder: in a solid, the index i is replaced by a k-point + band index.

Projected Density Of States

The imbalance between up and down DOS indicates the presence of a total magnetization:

$$M_{tot} = -\mu_B \int m(\mathbf{r}) d\mathbf{r} = -\mu_B (N^\uparrow - N^\downarrow) \quad (21)$$

Given a set of atomic orbitals $\phi_{lm}^{(n)}$ for atom n (we assume only one valence state for a given l and m) the *projected DOS*, or PDOS, is calculated as

$$g_{lm}^{(n)}(E) = \sum_i |\langle \phi_{lm}^{(n)} | \psi_i \rangle|^2 \delta(E - \epsilon_i) \quad (22)$$

The PDOS tells you which atomic orbitals contribute to which region of energy.

Spin-projected PDOS are obviously defined as:

$$g_{lm}^{(n)\uparrow\downarrow}(E) = \sum_i |\langle \phi_{lm}^{(n)} | \psi_i^{\uparrow\downarrow} \rangle|^2 \delta(E - \epsilon_i^{\uparrow\downarrow}) \quad (23)$$

and give the same information as PDOS separately for states of up and down spin. One can sum over angular momentum components m to get

About the “charge on a given atom”

A simple way to have a rough estimate of “the charge on a given atom” is via the projection onto a given set of atomic orbitals, assumed to be orthonormal:

$$N^{(n)} = \sum_l N_l^{(n)}, \quad N_l^{(n)} = \sum_{m=-l}^{+l} \sum_i |\langle \phi_{lm}^{(n)} | \psi_i \rangle|^2. \quad (24)$$

Do not take too seriously this formula: atomic states on different atoms are *not* orthonormal. Several recipes exist to account for non-orthonormality of the atomic orbitals, e.g., Mulliken, Löwdin. The spin-polarized extension is straightforward:

$$N^{(n)\uparrow\downarrow} = \sum_l N_l^{(n)\uparrow\downarrow}, \quad N_l^{(n)\uparrow\downarrow} = \sum_{m=-l}^{+l} \sum_i |\langle \phi_{lm}^{(n)} | \psi_i^{\uparrow\downarrow} \rangle|^2. \quad (25)$$

About “localized magnetic moments”

A simple way to get a rough measure of the “magnetic moment associated to an atom” is via “the charges on an atom”:

$$\mu^{(n)} \simeq -\mu_B(N^{\uparrow(n)} - N^{\downarrow(n)}) = -\mu_B \sum_l \left(N_l^{\uparrow(n)} - N_l^{\downarrow(n)} \right) \quad (26)$$

where μ_B is the Bohr magneton. This also gives an idea of which states contribute the most to the localized magnetic moment.

Who calculates what and where? Band structure

- Code `pw.x` performs a spin-polarized self-consistent calculation (scf)
- On input: specify `nspin=2`, `starting_magnetization()=...`, `occupations='smearing'`, `smearing=...`, `degauss=...`, as appropriate for a metallic system
- On output: the code prints
 - the spin-dependent band structure $\epsilon_i^{\uparrow\downarrow}$: locate the lines
End of self-consistent calculation
----- SPIN UP -----
followed by the list of ϵ_i^{\uparrow} , and
----- SPIN DOWN -----
followed by the list of ϵ_i^{\downarrow} , and by the Fermi energy:
the Fermi energy is 17.7560 ev
 - the various energy terms, followed by the total M_{tot} and absolute M_{abs} magnetizations:
total magnetization = 1.93 Bohr mag/cell
absolute magnetization = 2.02 Bohr mag/cell

Who calculates what and where? DOS

- Code `dos.x` calculates the DOS. Output data is written to a file whose name is specified in input variable `fildos`.

- Format of output file, unpolarized case: three columns containing

$$E_i, g(E_i), n(E_i)$$

where $n(E_i) = \int_{E \leq E_i} g(E) dE$.

- Format of output file spin-polarized case: four columns, containing

$$E_i, g^\uparrow(E_i), g^\downarrow(E_i), n(E_i)$$

Note that $n(E_F)$, where E_F is the Fermi energy as printed in the self-consistent step, is equal to N , number of electrons in the unit cell.

Complete documentation in file `Doc/INPUT_DOS.*` in the QE distribution.

Who calculates what and where? PDOS

- Code `projwfc.x` calculates Mulliken charges (printed at the end of the output file) and PDOS (written to files whose name is specified via input variable `filpdos`)

- Format of output file `filpdos.pdos_tot` for the spin-polarized case:

$$E_i, g^\uparrow(E_i), g^\downarrow(E_i), p^\uparrow(E_i), p^\downarrow(E_i)$$

where $p^{\uparrow\downarrow}(E_i) = \sum_{lm} \sum_n g_{lm}^{(n)\uparrow\downarrow}$ contain the sum of all PDOS's for all atoms and all states — close to but *not* exactly the same as $g^{\uparrow\downarrow}(E_i)$

- PDOS are written to file `filpdos.pdos_atm#n(x)_wfc#m(l)`, where:

n =atom number, x =atom symbol, m =atomic wavefunction number, $l = s, p, d, f$ (one file per atomic wavefunction found in the pseudopotential file)

- The format for the spin-polarized case is:

$$E_i, p_l^{(n)\uparrow}(E_i), p_l^{(n)\downarrow}(E_i), g_{l-l}^\uparrow(E_i), g_{l-l}^\downarrow(E_i), \dots, g_{ll}^{(n)\uparrow}(E_i), g_{ll}^\downarrow(E_i)$$

where $p_l^{(n)\uparrow\downarrow} = \sum_{m=-l}^{+l} g_{lm}^{(n)\uparrow\downarrow}$ is the sum of the PDOS over the manifold of $2l + 1$

components of angular momentum l