Magnetism

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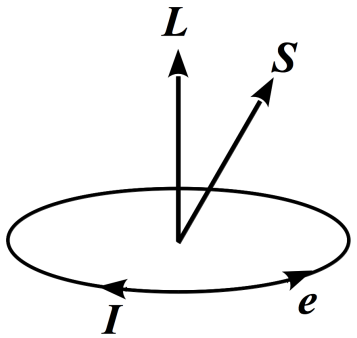
Outline

- Origin of magnetism:
  - Inside an atom
  - Between 2 atoms
  - Interaction with ligands
  - Interaction through ligands
  - Spin orientation
- Collinear magnetism in DFT
- Non-collinear magnetism in DFT
- Finite magnetic field
- Constrained magnetic moments

Origin of magnetism

(Semi) Classical picture: Bohr atom model (L) + electron spin S



Spin and Orbital contributions to the magnetization:

$$M = (2\langle S\rangle + \langle L\rangle)\,\mu_B \qquad\qquad \mu_B = \frac{\hbar e}{2mc}$$

In most cases $\langle S\rangle >> \langle L\rangle \longmapsto$ magnetism comes from the spins:

$$M \simeq 2\langle S\rangle \mu_B$$

Origin of magnetism: Inside an atom

2 electrons with the same l but different m_l (says, Φ_a and Φ_b orbitals):

$$H = H_1 + H_2 + H_{12} \qquad H_{12} = -\frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

and: $\langle\phi_a(r_i)|H_i|\phi_a(r_i)\rangle = E_1$, $\langle\phi_b(r_i)|H_i|\phi_b(r_i)\rangle = E_2$, $\langle\phi_i|\phi_j\rangle = \delta_{ij}$

Each electron can have spin up and down states $\longmapsto$ 4 spin-orbitals:

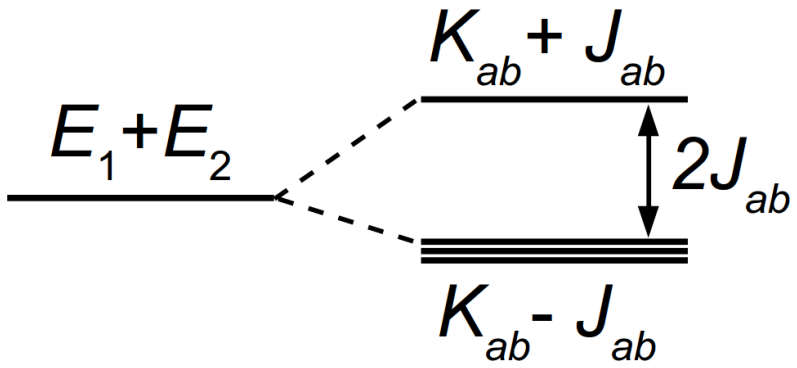
$$|\uparrow\uparrow\rangle \quad |\uparrow\downarrow\rangle \quad |\downarrow\uparrow\rangle \quad |\downarrow\downarrow\rangle$$

Such as we have:

$$H = E_1 + E_2 + \begin{pmatrix} K_{ab} - J_{ab} & 0 & 0 & 0 \\ 0 & K_{ab} & -J_{ab} & 0 \\ 0 & -J_{ab} & K_{ab} & 0 \\ 0 & 0 & 0 & K_{ab} - J_{ab} \end{pmatrix}$$

Origin of magnetism: Inside an atom

The diagonalization gives a triplet (FM) and a singlet (AFM) states:



where we have the Coulomb and Exchange integrals:

$$K_{ab} = \frac{e^2}{4\pi\varepsilon_0} \int d^3 r_1 \int d^3 r_2 \frac{|\phi_a(r_1)|^2 |\phi_b(r_2)|^2}{|r_{12}|} \quad (= U)$$

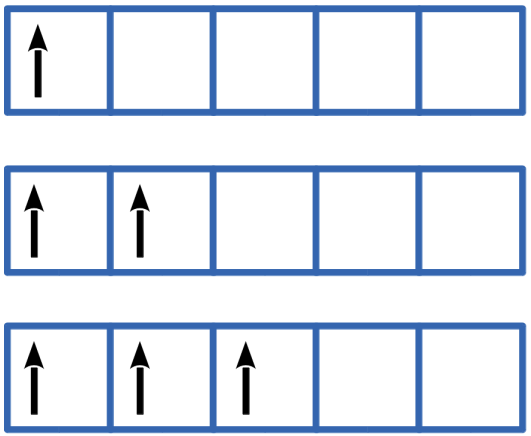
$$J_{ab} = \frac{e^2}{4\pi\varepsilon_0} \int d^3 r_1 \int d^3 r_2 \frac{\phi_a^*(r_1)\phi_b(r_1)\phi_b^*(r_2)\phi_a(r_2)}{|r_{12}|}$$

The Hamiltonian can be re-written in the Heisenberg form:

$$H = constant - 2J_{ab}\mathbf{S}_1 \cdot \mathbf{S}_2$$

Origin of magnetism: Inside an atom

To have $\langle S \rangle \neq 0$ one needs partially field orbitals ex: d^n orbitals

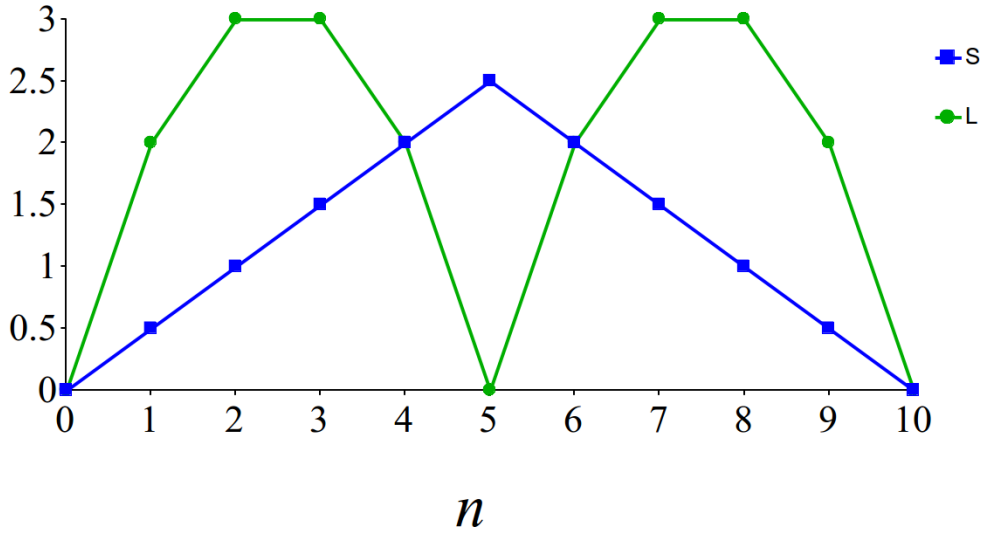


d^1

d^2

d^3

. . .



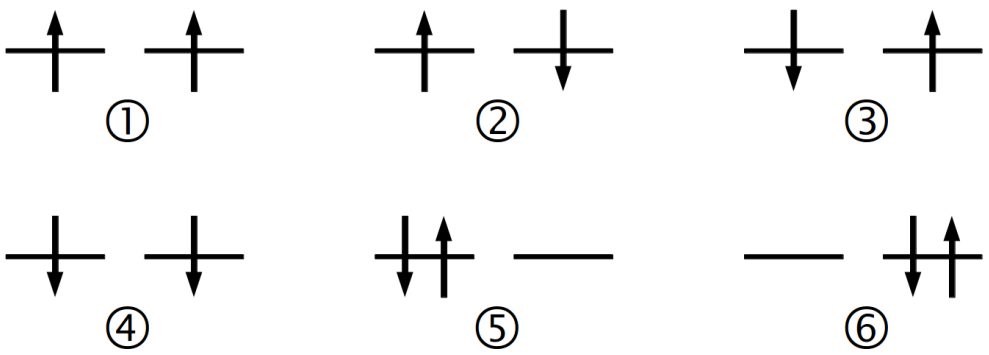
Hund's rules

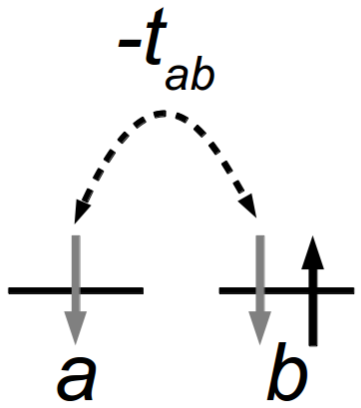
Most of the crystals are magnetic because they contain Transition-Metal and Rare Earth atoms (d and f electrons)

Origin of magnetism: Between two atoms

The FM state is lower in energy in an atom (Hund's rules).

But in H_2 molecule:





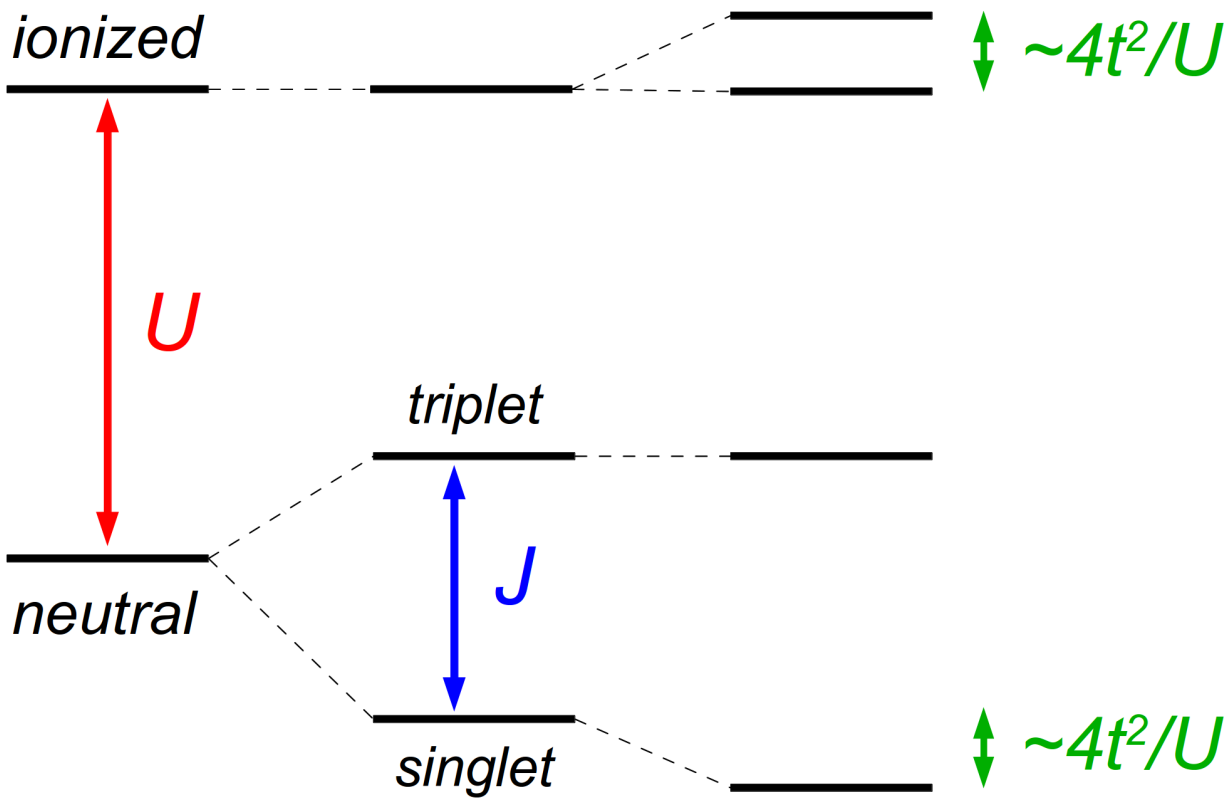
Similar Heisenberg Hamiltonian: $H = constant - 2J_{ab}\mathbf{S}_1 \cdot \mathbf{S}_2$

but with the 1s orbital overlap between the 2 atoms: $J < 0$

The singlet AFM state is lower in energy!

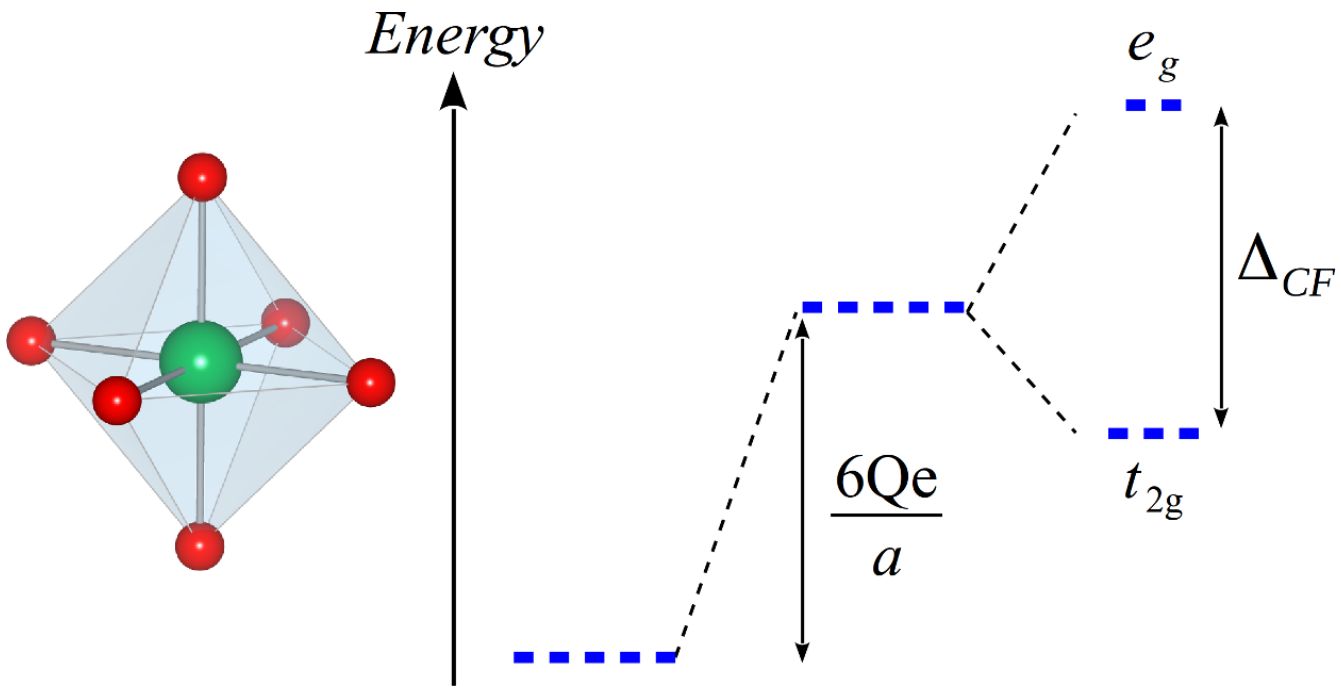
Origin of magnetism: Between two atoms

The hopping process reinforce the AFM state:



Origin of magnetism: Interaction with ligands

Atom in a solid: Crystal Field Splitting

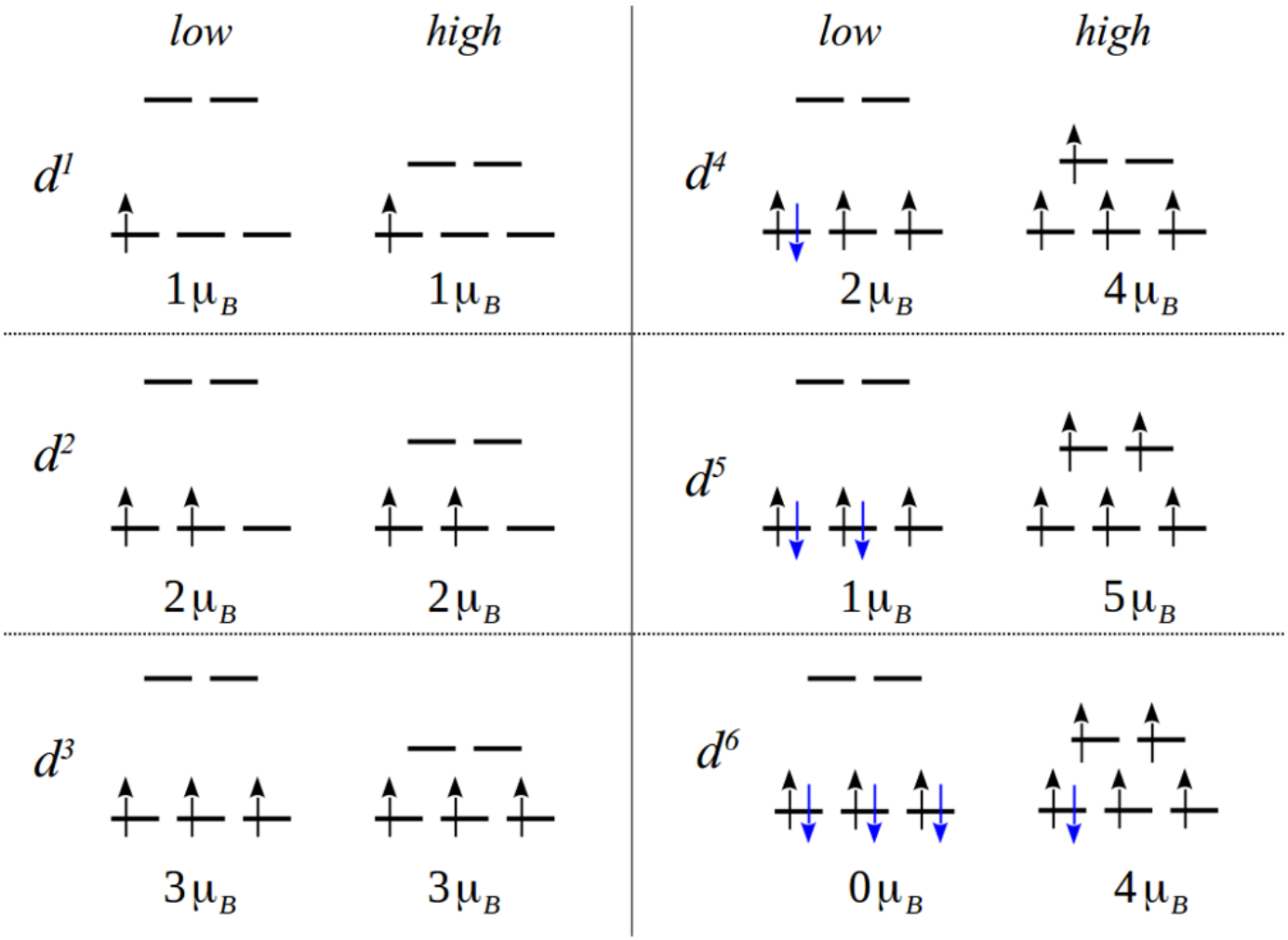


Atomic *d* (or *f*) orbitals splitted due to the surrounding atoms.

Hund's rules still apply.

Origin of magnetism: Interaction with ligands

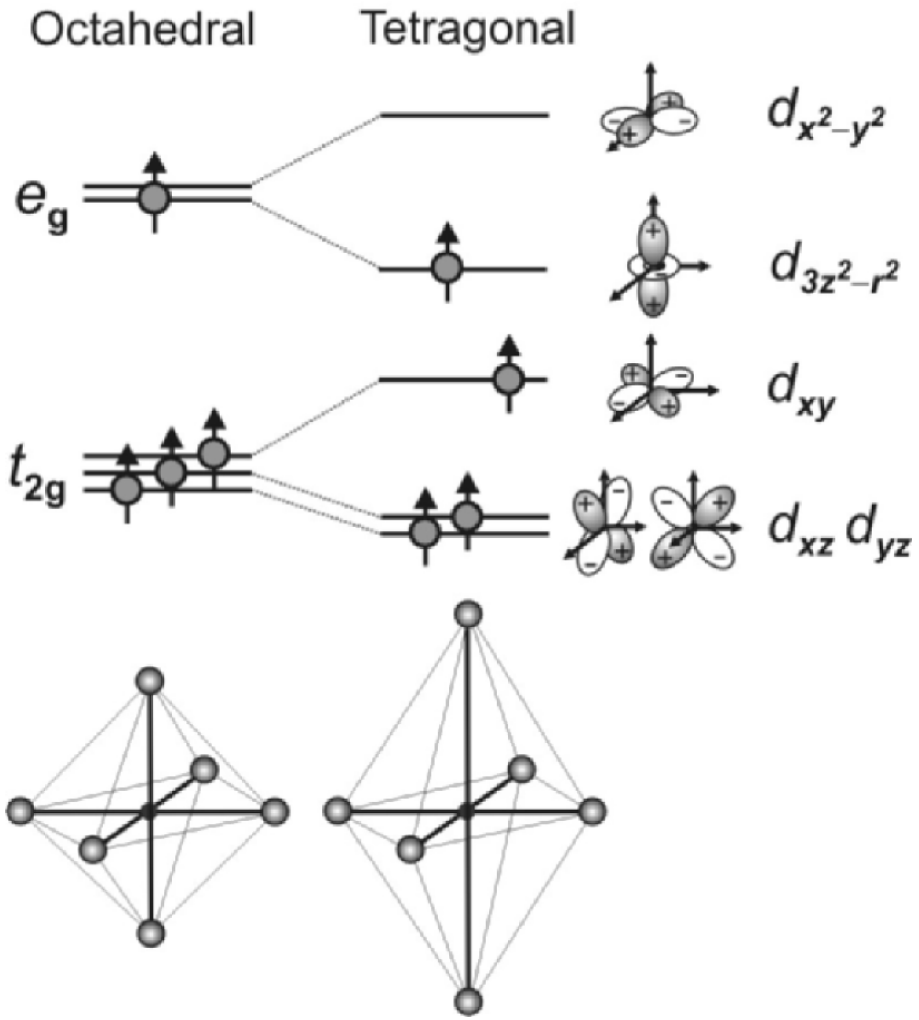
High-spin and low-spin configurations:



Depending on the size of Δ_{CF} relative to U.

Origin of magnetism: Interaction with ligands

Be aware of the Jahn-Teller effect:

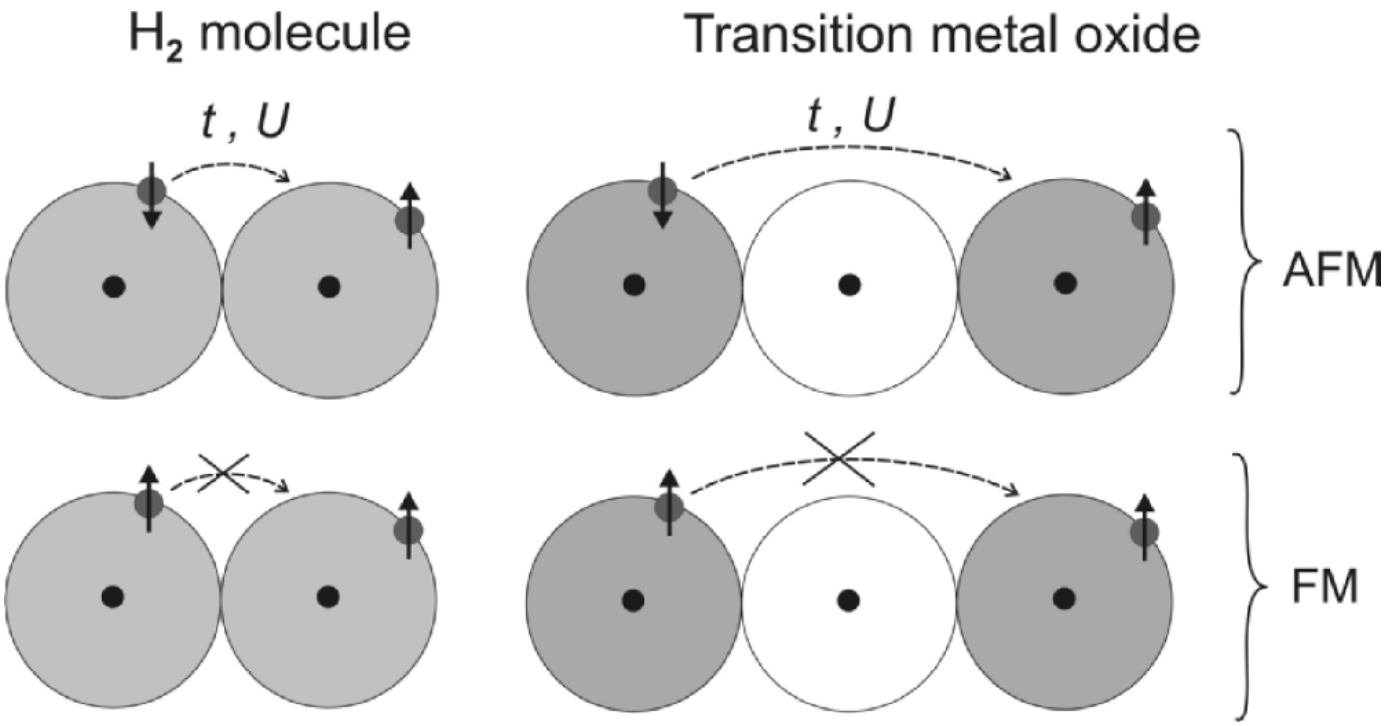


from Stöhr and Siegmann, Magnetism, Springer 2006

Very strong in Mn^{3+} (d^4), Cr^{2+} (d^4), Cu^{2+} (d^9)

Origin of magnetism: Interaction through ligands

Atoms interacting through the ligands: Superexchange

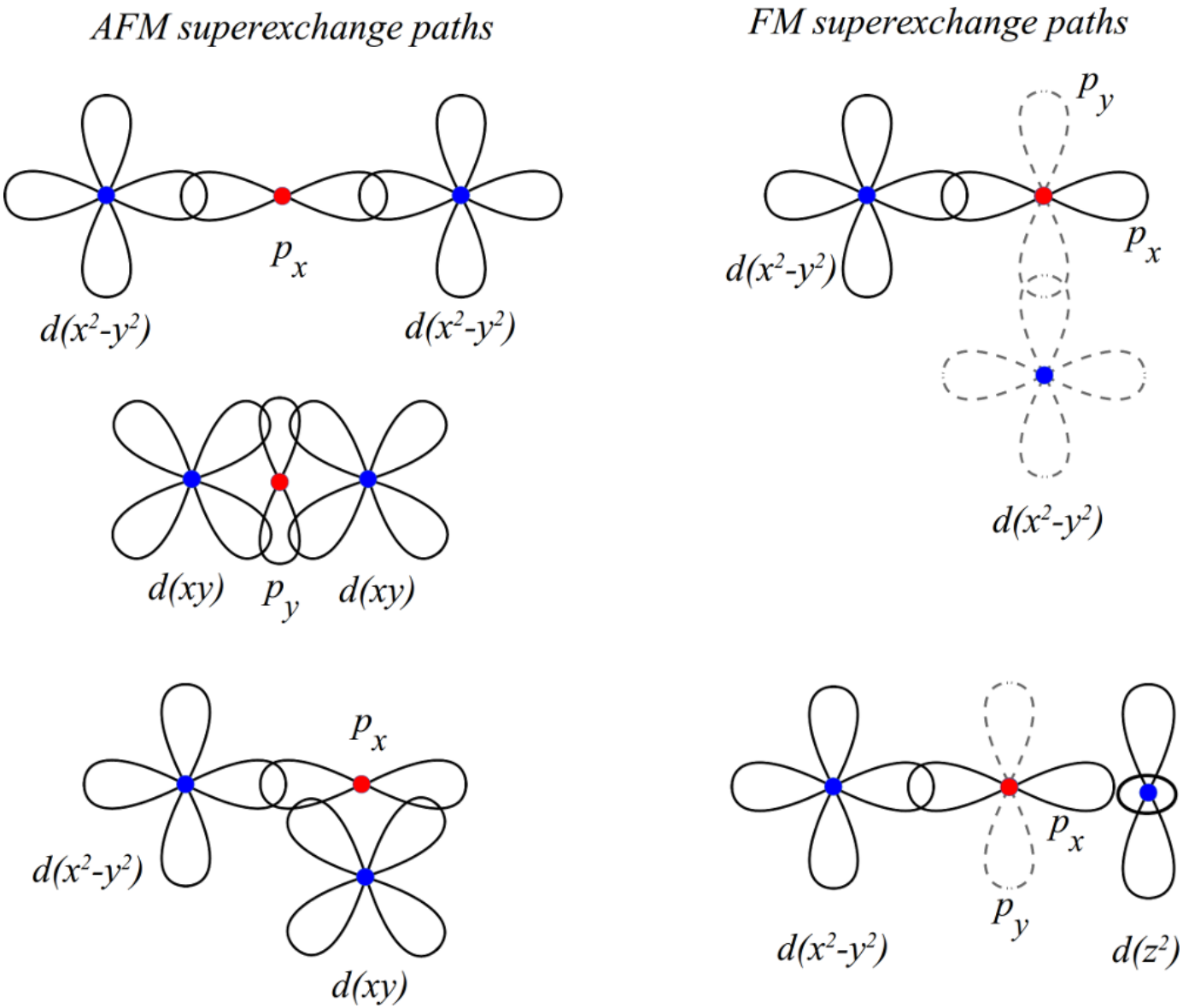


from Stöhr and Siegmann, Magnetism, Springer 2006

Heisenberg picture still holds (localised electrons, $t << $): $H = JS_1 S_2$

Origin of magnetism: Interaction through ligands

SE depends on the bonding: Goodenough-Kanamori rules



Origin of magnetism: Spin orientation

2nd order Heisenberg model for localised magnetic moments:

$$H = -2\left[J\mathbf{S}\cdot\mathbf{S}' + \mathbf{D}\cdot(\mathbf{S}\times\mathbf{S}') + \mathbf{S}\cdot\Phi\cdot\mathbf{S}'\right]$$

- $J \longmapsto$ Superexchange interaction (favors $S \parallel S'$)
- $\mathbf{D} \longmapsto$ Dzyaloshinsky-Moriya interaction (favors $S \perp S'$)
- $\Phi \longmapsto$ Single Ion Anisotropy (easy/hard spin orientation)

One wants to estimate J, D and Φ from DFT!

see for ex: PRB 84, p.224429 (2011), PRB 86, 094413 (2012)

Magnetism in DFT: Collinear case

DFT based on the charge density $\rho(r)$

To enlarge DFT to (collinear) magnetism, decomposition of the density:

$$\rho = \rho(\uparrow) + \rho(\downarrow)$$

The Hohenberg and Kohn theorem generalizes with an energy functional:

$$E = E[\rho(\uparrow), \rho(\downarrow)]$$

With 2 Kohn-Sham equations to be solved, one for each spin-channel σ:

$$(T + V_{Ri}(r) + V_H(r) + V_{xc,\sigma})\,\phi_{i\sigma}(r) = \varepsilon_{i\sigma}(r)$$

with

$$V_{xc,\sigma} = \frac{\delta E_{xc}[\rho(\uparrow), \rho(\downarrow)]}{\delta \rho_\sigma(r)}$$

Magnetism in DFT: Collinear case

Then minimizing the K-S equations we get the ground state with:

$$\rho = \rho(\uparrow) + \rho(\downarrow) \quad \text{and magnetization } m = \rho(\uparrow) - \rho(\downarrow)$$

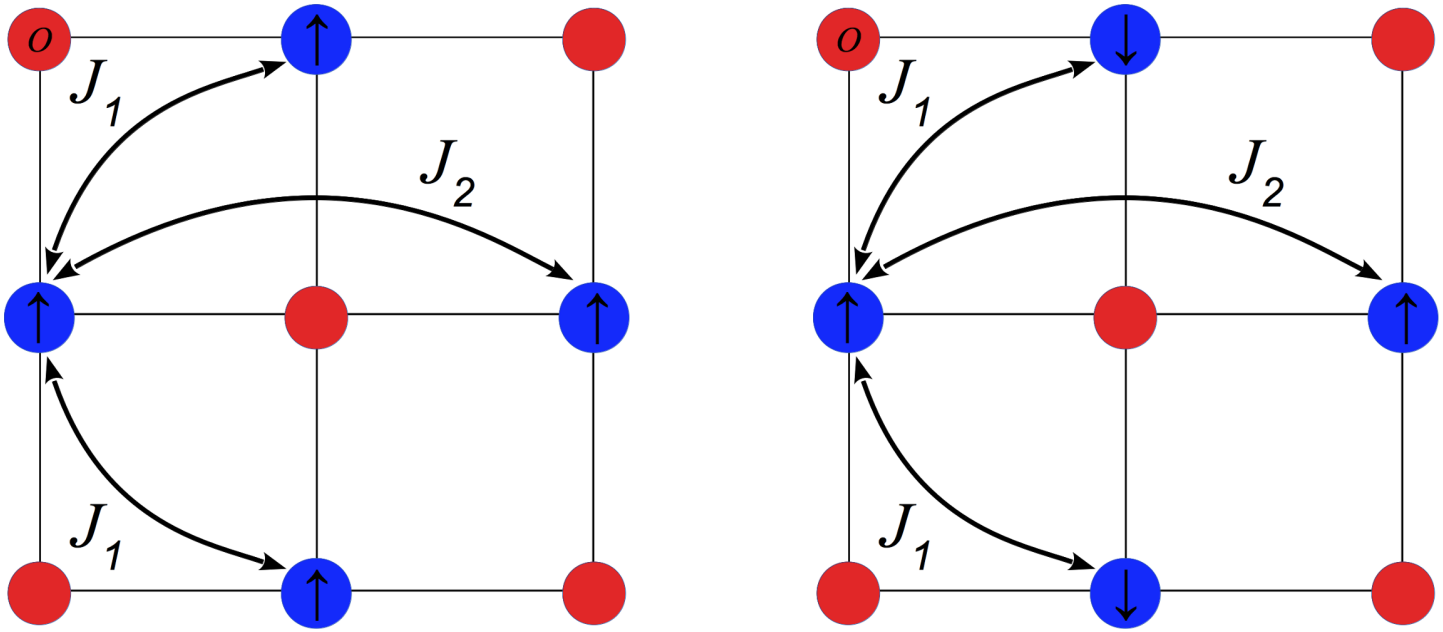
Supposing the magnetic moments are localised around the atoms (this is often the case for *d* and *f* electrons), one can compute magnetization on each atom (*prtdensph* input flag in ABINIT):

```
 Integrated total density in atomic spheres:
 -------------------------------------------
Atom  Sphere radius Integrated_up_density Integrated_dn_density Total(up+dn)  Diff(up-dn)
   1       1.71336             8.3387428             4.8812937   13.2200366    3.4574491
   2       1.71336             4.8812937             8.3387428   13.2200366   -3.4574491
   3       1.41192             2.8466448             2.8566529    5.7032978   -0.0100080
   4       1.41192             2.8466448             2.8566529    5.7032978   -0.0100080
   5       1.41192             2.8566529             2.8466448    5.7032978    0.0100080
   6       1.41192             2.8566529             2.8466448    5.7032978    0.0100080
Note: Diff(up-dn) can be considered as a rough approximation of a local magnetic moment.
```

(FeF_2 example)

Magnetism in DFT: Collinear case

Superexchange constants J can be estimated. Ex: Rock-Salt oxides



One needs to compute the energy for ferro and antiferro in order to extract J_1 and J_2 from:

$$E = E_0 + S\sum_i J_i S_i$$

see for ex: PRB 84, p.224429 (2011), PRB 86 86, 094413 (2012)

Magnetism in DFT: Non-collinear case

Wave functions are described by spinors:

$$\phi_i(r) = \begin{pmatrix} \phi_{i\uparrow} \\ \phi_{i\downarrow} \end{pmatrix}$$

Such as the density is a 2×2 matrix:

$$\rho = \begin{pmatrix} \rho^{\uparrow\uparrow} & \rho^{\uparrow\downarrow} \\ \rho^{\downarrow\uparrow} & \rho^{\downarrow\downarrow} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} n + m_z & m_x - i m_y \\ m_x + i m_y & n - m_z \end{pmatrix}$$

with n the electron density and m_i the magnetization density along the direction i

$$n(r) = \frac{1}{2} Tr\rho(r) = \sum_\alpha \rho^{\alpha\alpha}(r) \qquad \mathbf{m}(\mathbf{r}) = \sum_{\alpha\beta} \rho^{\alpha\beta}(\mathbf{r}) \cdot \sigma_{\alpha\beta}$$

with the Pauli matrices $\sigma_{\alpha\beta} = (\sigma_x, \sigma_y, \sigma_z)$:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Magnetism in DFT: Non-collinear case

Kohn-Sham equations with spinors:

$$\sum_{\beta} H^{\alpha\beta} |\phi_i^{\beta}\rangle = \varepsilon_i |\phi_i^{\alpha}\rangle$$

where the Hamiltonian is a 2×2 matrix:

$$H^{\alpha\beta} = T\delta_{\alpha\beta} + V(r)\delta_{\alpha\beta} + \int \frac{n(r')}{r - r'} dr' \delta_{\alpha\beta} + V_{xc}^{\alpha\beta}(r)$$

and:

$$V_{xc}^{\alpha\beta}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho^{\alpha\beta}(r)}$$

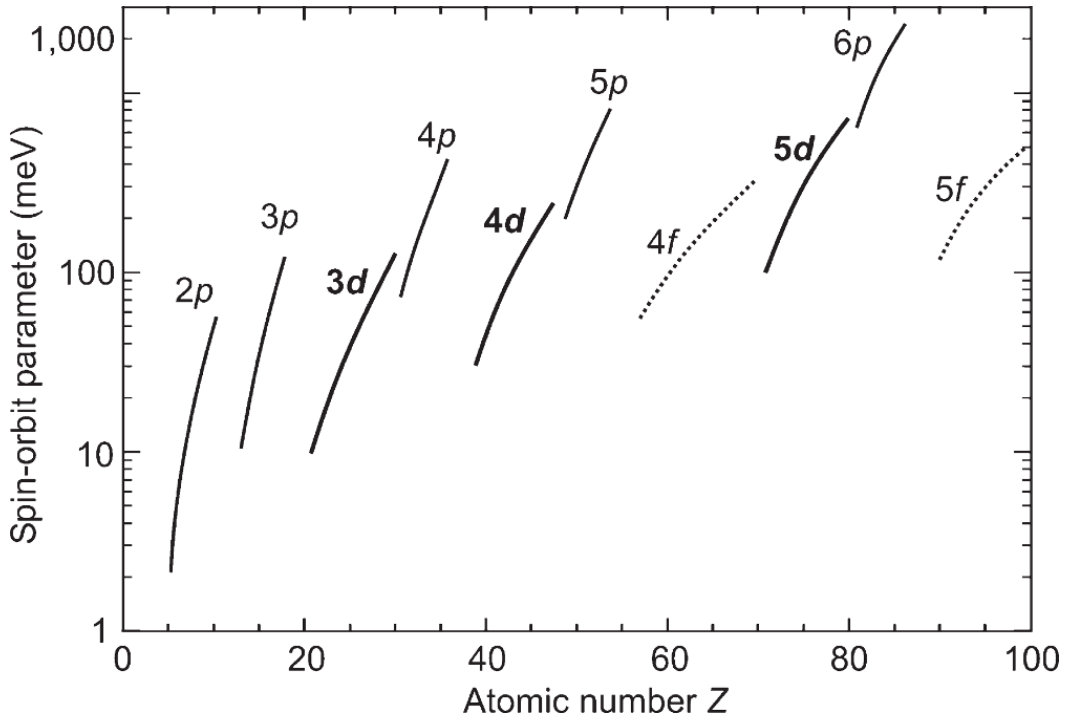
$\rho^{\alpha\beta}$ is diagonal when $m = m_z \longmapsto$ collinear case.

However one needs Spin-Orbit coupling in order to couple directions (space rotations) to the spins.

Magnetism in DFT: Non-collinear case

Spin-Orbit coupling:

$$H = H_{KS} + \lambda(r)\mathbf{L}\cdot\mathbf{S} = H_{KS} + \frac{\hbar^2}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{L}\cdot\mathbf{S}$$

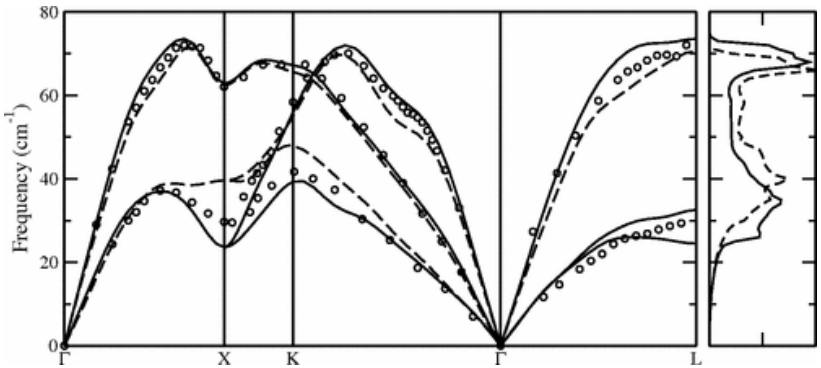


from Stöhr and Siegmann, Magnetism, Springer (2006)

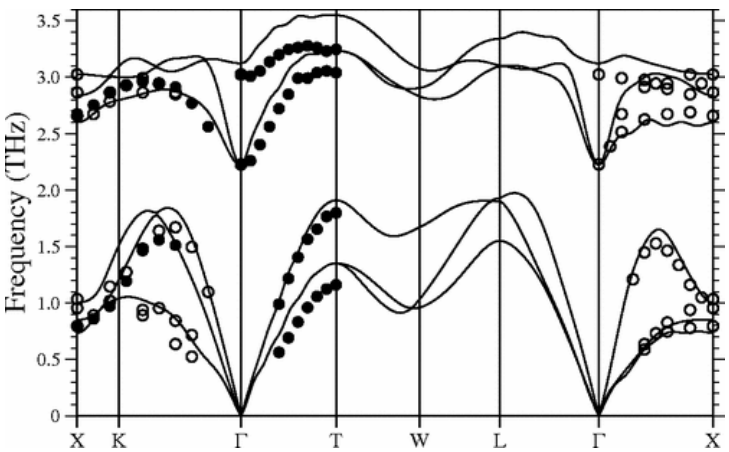
Magnetism in DFT: Non-collinear case

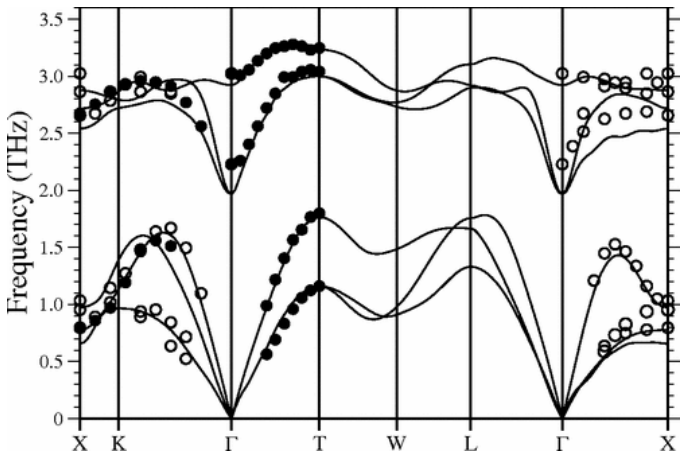
Spin-Orbit coupling important for heavy elements:

Phonons of Pb, Phys. Rev. B 78, 045119 (2008):



Phonons of Bi, Phys. Rev. B 76, 104302 (2007):





Magnetism in practice with Abinit

nsppol, *nspinor* and *nspden* input flags:

	nsppol	nspinor	nspden
Non-magnetic	1	1	1
Collinear FM	2	1	2
Collinear AFM	1	1	2
Non-Collinear	1	2	4

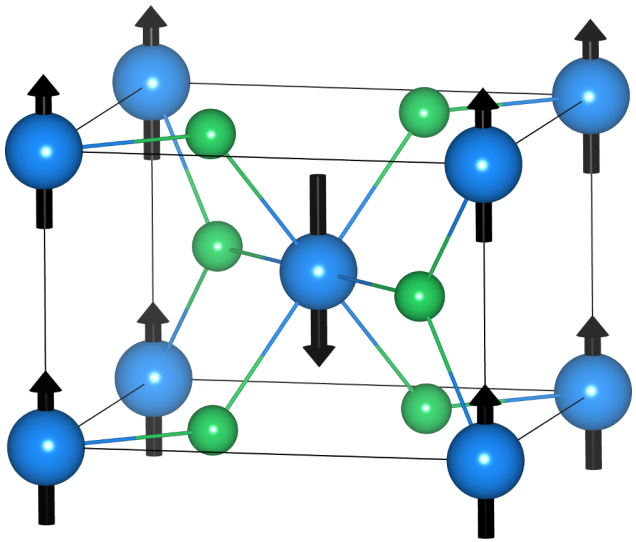
When the non-collinear flags are "on" the SOC coupling is switch on (controlled by *so_psp* or *pawspnorb* flags).

With SOC better not to use time-reversal symmetry (*kptopt* = 3 or 4).

Initialize *spinat* = (m_x, m_y, m_z) for each atom.

Ex: NiF_2

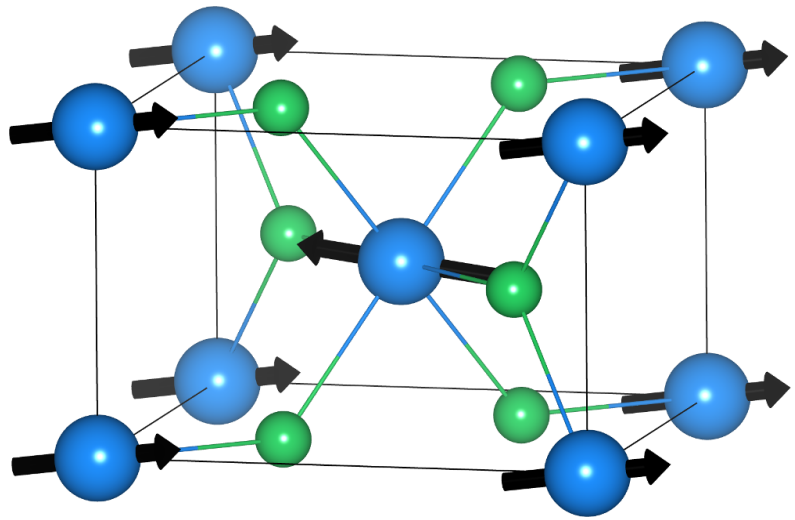
spinat = (0,0,m) $\longmapsto$ no canting



prtdensph

x_mag	y_mag	z_mag
-0.0000000	-0.0000000	1.4380590
0.0000000	-0.0000000	-1.4352794
0.0000000	0.0000000	-0.0517603
-0.0000000	-0.0000000	-0.0517603
-0.0000000	0.0000000	-0.0511159
0.0000000	-0.0000000	-0.0511159

spinat = (m,0,0) $\longmapsto$ canting along z



prtdensph

x_mag	y_mag	z_mag
1.7778831	-0.0574651	0.1310639
-1.7772407	0.0151209	0.1503122
-0.0301506	-0.0004283	0.0071212
-0.0301502	-0.0004282	0.0071204
0.0302100	-0.0016721	0.0068381
0.0301953	-0.0016709	0.0068350

Applied magnetic field

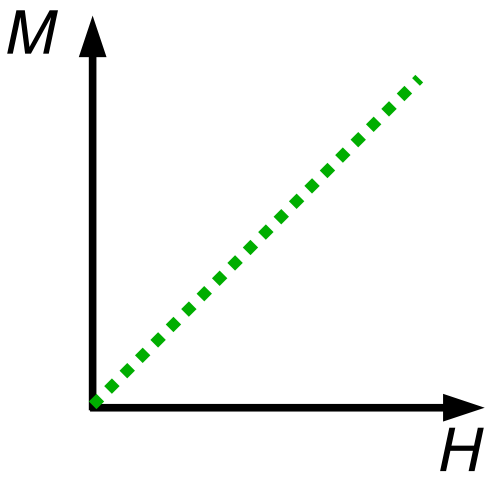
Applying a (Zeeman) magnetic field on the spins gives (*zeemanfield* flag):

$$V_H = -\mu_B \mu_0 \begin{pmatrix} H_z & H_x + iH_y \\ H_x - iH_y & -H_z \end{pmatrix}$$

Allows to access to:

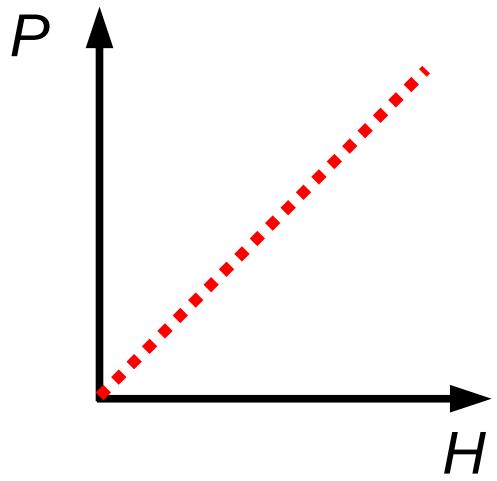
Linear magnetic susceptibility tensor

$$\mathbf{M} = \chi \mathbf{H}$$



Linear magnetoelectric tensor

$$\mathbf{P} = \alpha \mathbf{H}$$



As well as non-linear responses!

Linear magnetoelectric response

Free energy of a crystal under E and H fields:

$$-F(E,H) = \ldots + \frac{1}{2}\varepsilon_0\varepsilon_{ij}E_iE_j + \frac{1}{2}\mu_0\mu_{ij}H_iH_j + \alpha_{ij}E_iH_j + \ldots$$

Polarization:

$$P_j = -\frac{\partial F(E,H)}{\partial E_j} = \ldots + \varepsilon_0\varepsilon_{ij}E_i + \alpha_{ij}H_i + \ldots$$

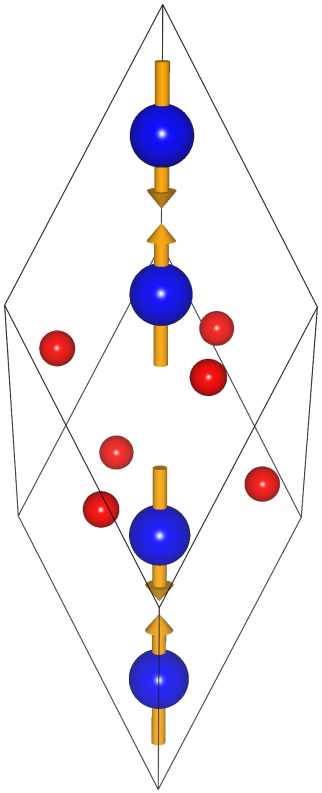
Magnetization:

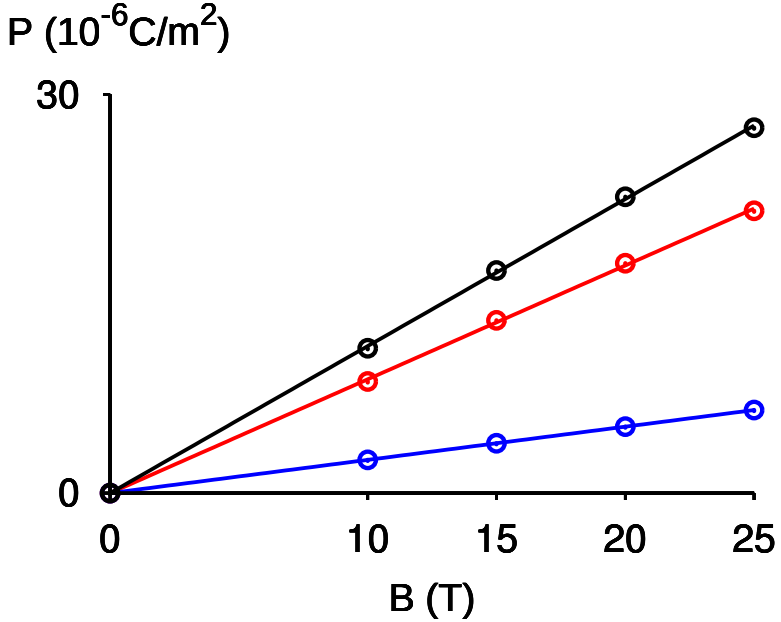
$$M_j = -\frac{\partial F(E,H)}{\partial H_j} = \ldots + \mu_0\mu_{ij}H_i + \alpha_{ij}E_j + \ldots$$

$$\alpha = \text{magnetoelectric tensor}$$

Ex: Linear ME in Cr_2O_3

- Collinear AFM oxide
- First experimental evidence of linear ME effect: *D. N. Astrov (1961)*





P_{tot} (Berry Phase)

P_{ion} ($\sum \frac{Z^* \delta_{ion}}{\Omega}$)

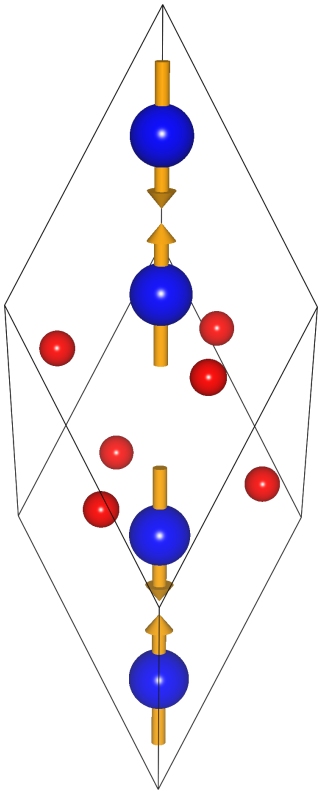
P_{elec} or clamped ion (Berry Phase)

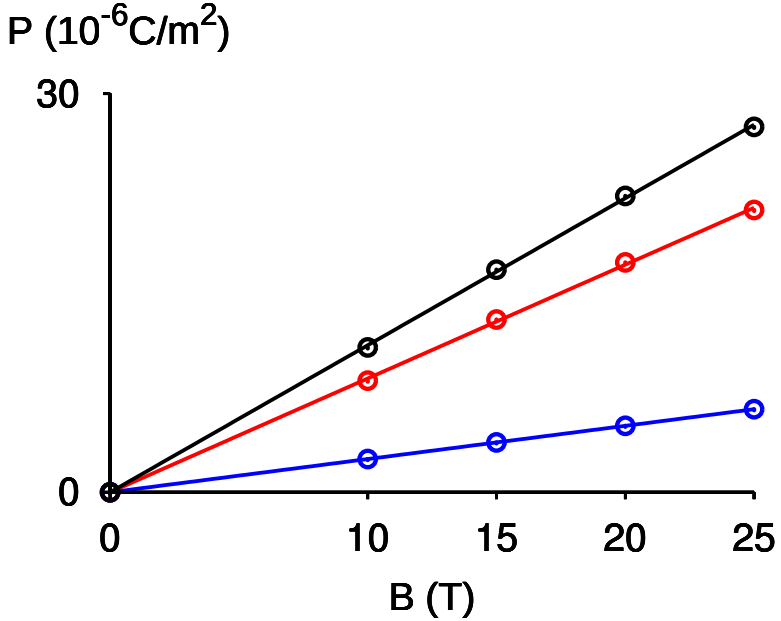
Precision on energy/potential is crucial for P_{elec} (toldfe $\sim 10^{-12}$ Ha)

Precision on forces is crucial for P_{ion} (toldmxf $\sim 10^{-7}$ Ha/Bohr)

Linear ME in Cr_2O_3

- Collinear AFM oxide
- First experimental evidence of linear ME effect: *D. N. Astrov (1961)*





ME coef:

$\alpha_{tot}^{spin} = 1.45$ ps.m^{-1}

($\alpha_{exp} = 1 - 4$ ps.m^{-1})

$\alpha_{ion}^{spin} = 1.1$ ps.m^{-1}

$\alpha_{elec}^{spin} = 0.34$ ps.m^{-1}

PRL 106, p.107202 (2011)

Constrained magnetic moment calculations (β *version*)

Constrain the direction of the magnetic moments (*magconon* flag =1) :

Lagrange multiplier: $$E = E_{KS} + \sum_i \lambda \left[\mathbf{m}_i - \mathbf{m}_i^0 (\mathbf{m}_i^0 \cdot \mathbf{m}_i) \right]^2$$

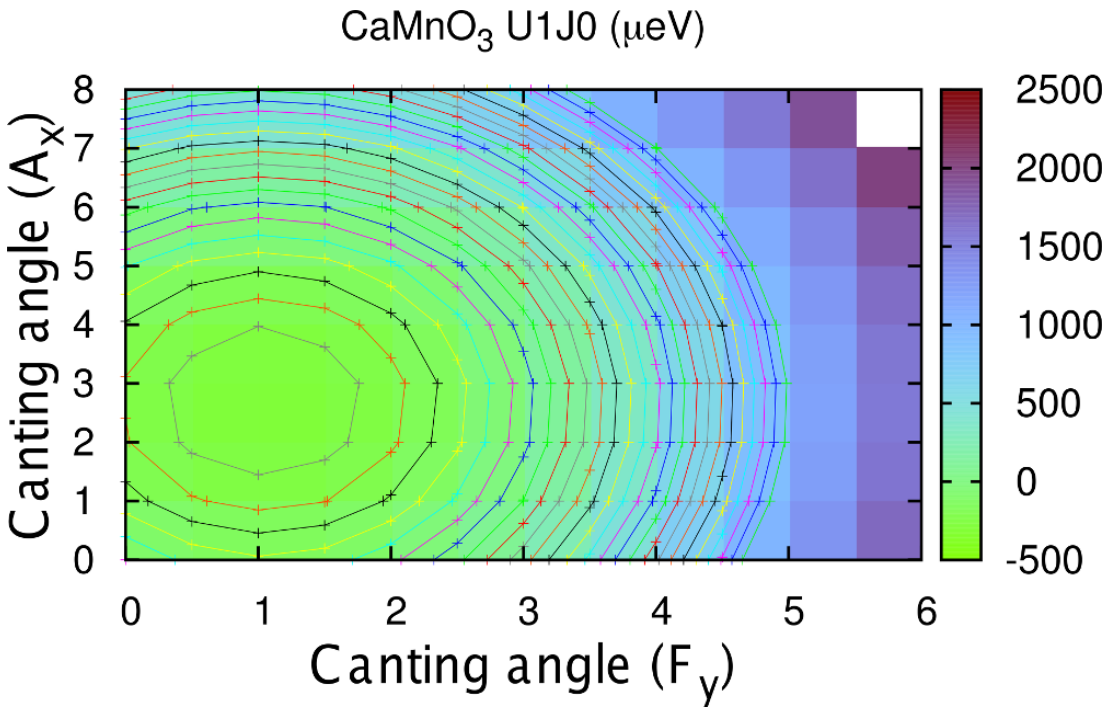
Constrain the direction and the amplitude of the magnetic moments (*magconon* flag =2) :

$$E = E_{KS} + \sum_i \lambda \left[\mathbf{m}_i - \mathbf{m}_i^0 \right]^2$$

with λ the strength of the Lagrange multiplier (*magcon_lambda* flag) and m_i^0 the desired magnetic moment on each atom i (given by *spinat*).

Constrained magnetic moment calculations (β *version*)

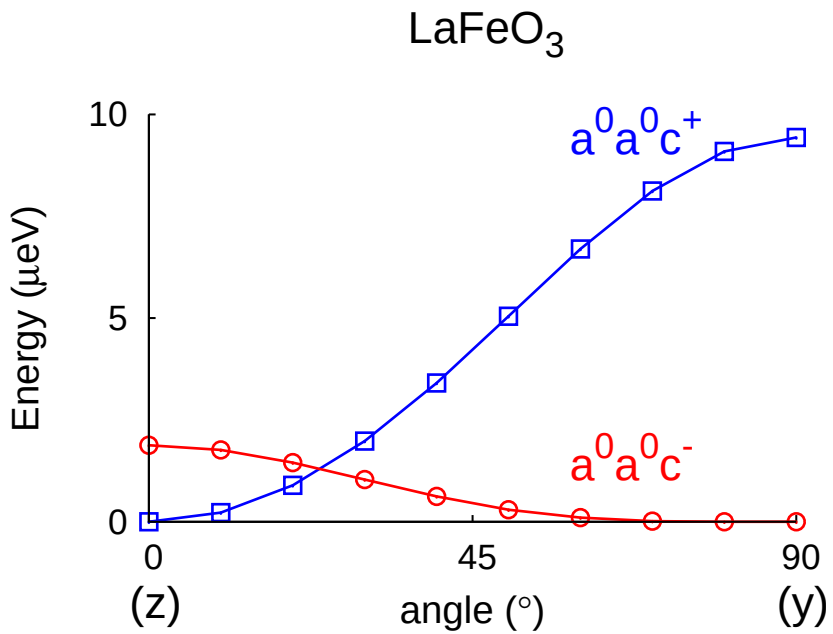
Useful to explore the spin energy landscape "by hand" (in case of multiple local minima of complex and flat energy landscapes):

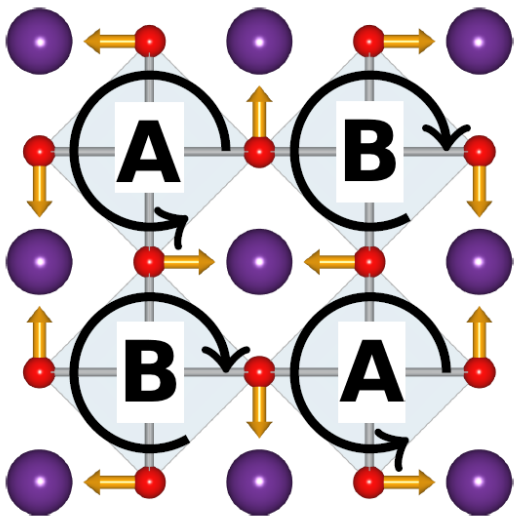


And also to compute the magnetocrystaline anisotropy energy.

Ex: Effect of distortions on SIA and MCA in $LaFeO_3$

Octahedra distortions ($a^0a^010^{+/-}$):

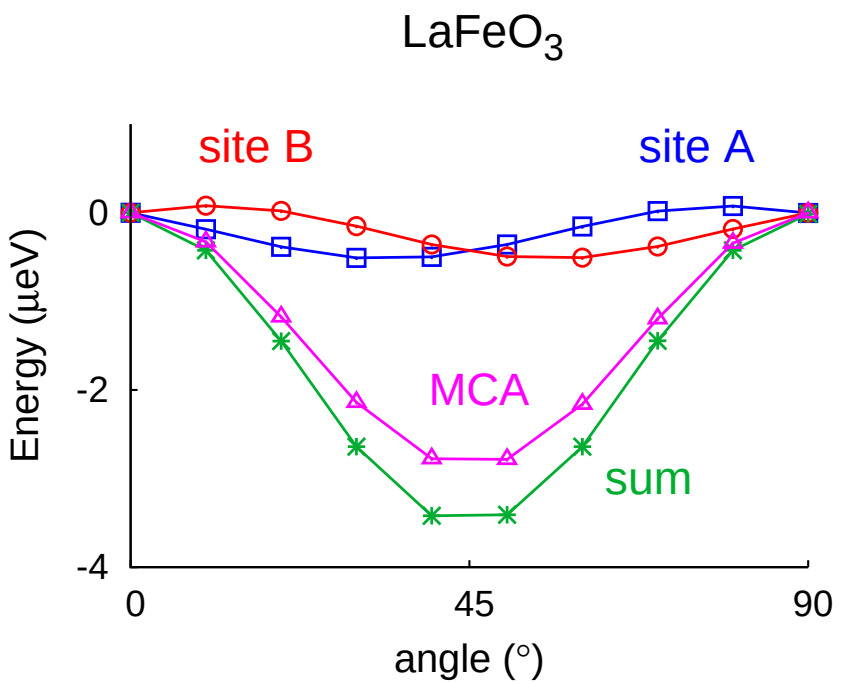


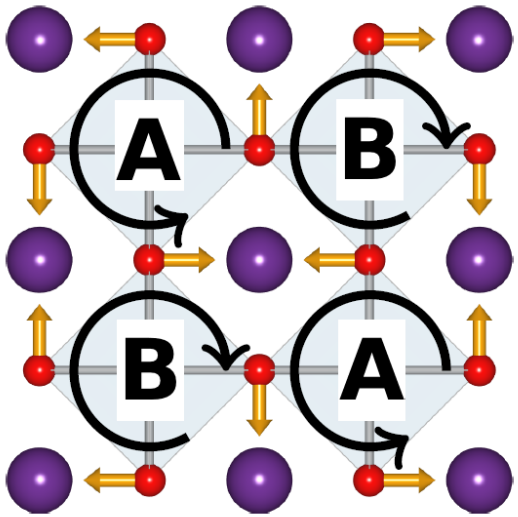


SIA in the *xy* plane with $a^0a^010^-$ and along *z* axis for $a^0a^010^+$

Effect of distortions on SIA and MCA in $LaFeO_3$

Octahedra distortions ($a^0a^010^-$): SIA local easy axis follows octahedra





"Global" easy-axis = [110]

PRB 86, p.094413 (2012)

Conclusions

DFT + spins:

- Collinear magnetism: easy to handle
- Non-Collinear magnetism: often less easy
- Often DFT+U or Hybrid functionals are better for magnetic systems
- Allows to compute:
  - (Super) Exchange interaction between spins (J).
  - Spin canting / Dzyaloshinsky-Moriya interaction (D)
  - Magnetic anisotropy
  - Response under Zeeman field (magnetic and magnetoelectric susceptibilities)

Future/on-going works:

- Orbital magnetism: J. Zwanziger and X. Gonze Phys. Rev. B 84, 064445 (2011)
- Constrained moments, spin dispersion
- DFPT with Zeeman field
- ...