Exchange Interaction

Eric Bousquet

ESM School, Liège, Belgium

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Outline

Origin of magnetism and exchange interactions:

- A bit of history
- Interaction inside an atom
- Interaction between 2 atoms
- Interaction through ligands

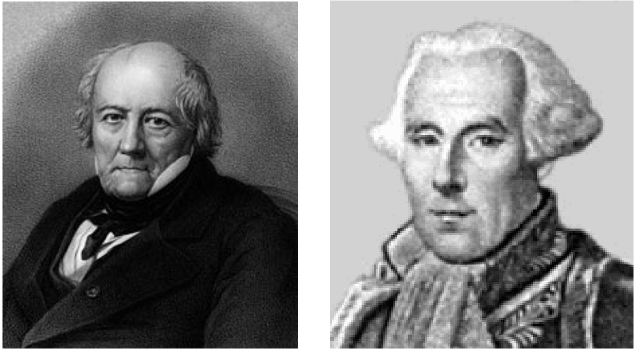
History of magnetism

1819: Hans Christian Oersted

First experimental evidence of the link between electric current and magnetic field.

History of magnetism

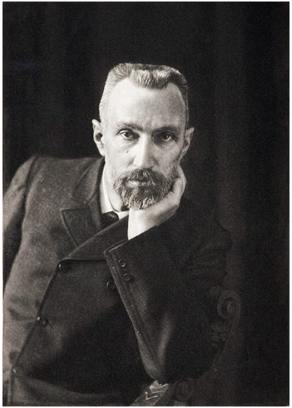
1820: Jean-Baptiste Biot and Felix Savart

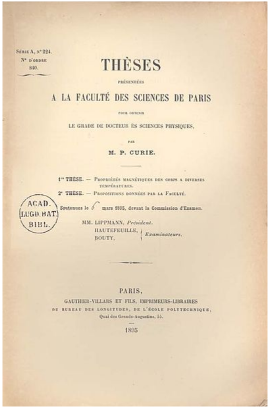


Mathematical expression of the magnetic field generated by an electric current flowing through a wire.

History of magnetism

1895: Pierre Curie





Série A, n° 224.
N° d'ordre
840.

THÈSES

PRÉSENTÉES

A LA FACULTÉ DES SCIENCES DE PARIS

POUR OBTENIR

LE GRADE DE DOCTEUR ÈS SCIENCES PHYSIQUES,

PAR

M. P. CURIE.

1re THÈSE. — Propriétés magnétiques des corps a diverses températures.
2e THÈSE. — Propositions données par la Faculté.

Soutenues le 6 mars 1895, devant la Commission d'Examen.

MM. LIPPMANN, *Président.*
HAUTEFEUILLE, } *Examinateurs.*
BOUTY, }

PARIS,
GAUTHIER-VILLARS ET FILS, IMPRIMEURS-LIBRAIRES
DU BUREAU DES LONGITUDES, DE L'ÉCOLE POLYTECHNIQUE,
Quai des Grands-Augustins, 55.

1895

Effect of temperature on paramagnetic susceptibilities (Curie's law).

History of magnetism

1907: Pierre-Ernest Weiss

First microscopic model to explain magnetism (molecular field).

History of magnetism: Curie-Weiss law

Some paramagnetic crystals do not follow the Curie law

Weiss postulated that the magnetic moments interact:

Weiss molecular field proportional to the magnetisation:

$$\mathbf{H}_W = \gamma \mathbf{M}$$

where γ is the molecular field constant and is such that the total field is given by $\mathbf{H}_{tot} = \mathbf{H} + \mathbf{H}_W$.

By using the relation $\chi = \mathbf{M}/\mathbf{H} = C/T$ we have:

$$\frac{\mathbf{M}}{\mathbf{H} + \gamma \mathbf{M}} = \frac{C}{T} \longmapsto \mathbf{M} = \frac{C\mathbf{H}}{T - \gamma C} \longmapsto \chi = \frac{C}{T - \theta},$$

$\mapsto$ Curie-Weiss law

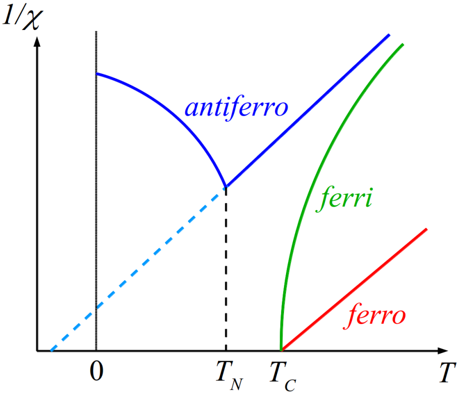
When the temperature is equal to the critical $T_C = \theta$, the susceptibility diverges, which corresponds to a transition toward an ordered phase: the ferromagnetic state!

History of magnetism

1930: Louis Néel

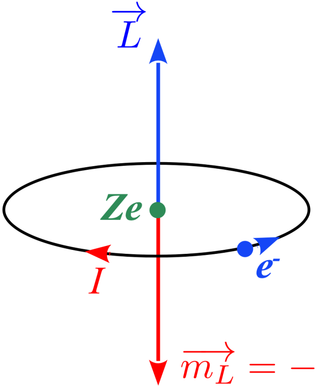
Extension of Weiss model to antiferromagnetism and ferrimagnetism.

History of magnetism



Origin of the Weiss molecular field?

Magnetic moments comes from electrons spinning around nuclei



$$\overrightarrow{m_L} = -\frac{e}{2}\overrightarrow{r} \times \overrightarrow{v}$$
$$= -\frac{e}{2m_e}\overrightarrow{L}$$

Origin of the Weiss molecular field?

Dipole-dipole interaction energy between the atom magnetic moments:

$$E_{dd} = \frac{\mu_0}{4\pi}\frac{\mathbf{m}_1\cdot\mathbf{m}_2 - 3(\mathbf{r}\cdot\mathbf{m}_1)(\mathbf{r}\cdot\mathbf{m}_2)}{r^3} \equiv \mu_0\mathbf{m}\cdot\mathbf{H}$$

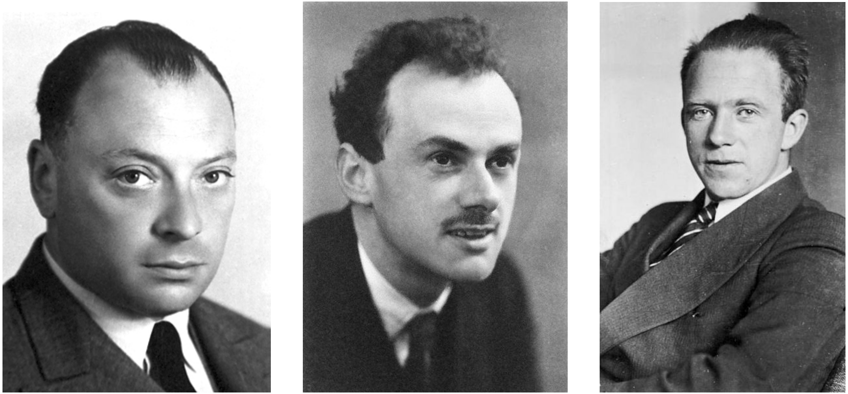
Order of magnitude: 10^{-25} J $\equiv$ 6.24 10^{-7} eV $\equiv$ 7 10^{-3} K

$\mapsto$ even at a temperature of 1K the thermal fluctuations are 2-3 order of magnitude larger than the dipole-dipole interaction!

The dipole-dipole energy is way too small to explain the robust magnetisation observed experimentally at temperature much larger than this interaction!

History of magnetism

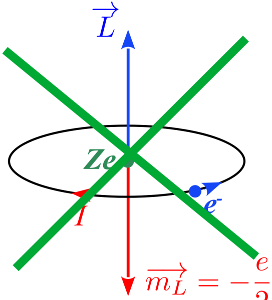
Pauli, Dirac, Heisenberg



Magnetism cannot be explained without quantum mechanics!

History of magnetism

Magnetism cannot be explained without quantum mechanics!



$$\overrightarrow{m_L} = -\frac{e}{2}\overrightarrow{r}\times\overrightarrow{v}$$
$$= -\frac{e}{2m_e}\overrightarrow{L}$$

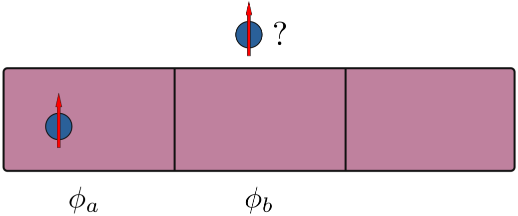
Magnetic moments comes mostly from electron spin!

Electrons should be treated through a wave function!

See lecture of H. Ronnow

Two electrons in the same orbital: Heitler-London

2 electrons in the same shell of the same atom?



electrons can be described by the spin orbitals $\phi(\mathbf{r})\chi(\mathbf{s})$ where ϕ is the one electron *p*-wave function and χ its spin part: $\chi = \alpha = |\uparrow\rangle$ or $\chi = \beta = |\downarrow\rangle$.

Two electrons in the same orbital: Heitler-London

$$H = H_1 + H_2 + H_{12}$$

with

$$H_1 = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} \equiv \text{ idem for } H_2 \ 1 \longleftrightarrow 2$$

$$H_{12} = \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

We assume:

$$\langle\phi_a(r_i)|H_i|\phi_a(r_i)\rangle = \varepsilon_a \qquad \langle\phi_b(r_i)|H_i|\phi_b(r_i)\rangle = \varepsilon_b$$

and with

$$\langle\phi_a(r_i)|\phi_b(r_i)\rangle = \int \phi_a^*(r_i)\phi_b(r_i)d^3r = 0 \ ; \ \langle\uparrow|\downarrow\rangle = 0,$$

$$\langle\phi_a(r_i)|\phi_a(r_i)\rangle = \langle\phi_b(r_i)|\phi_b(r_i)\rangle = 1 \ ; \ \langle\uparrow|\uparrow|\rangle = \langle\downarrow|\downarrow|\rangle = 1,$$

Heitler-London

In each orbital we can have one spin up and one spin down state, hence, giving 4 possible states in our system: (↑↑, ↑↓, ↓↑, ↓↓).

The corresponding wave functions are (Slater determinantal procedure to get the antisymmetric wave functions):

- (↑↑) state:

$$\psi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(r_1)\alpha_1 & \phi_a(r_2)\alpha_2 \\ \phi_b(r_1)\alpha_1 & \phi_b(r_2)\alpha_2 \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \alpha_1 \alpha_2 [\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)]$$

- (↓↓) state:

$$\psi_4 = \frac{1}{\sqrt{2}} \beta_1 \beta_2 [\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)]$$

Heitler-London

- $(\uparrow\downarrow)$ state:

$$\psi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(r_1)\alpha_1 & \phi_a(r_2)\alpha_2 \\ \phi_b(r_1)\beta_1 & \phi_b(r_2)\beta_2 \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} [\phi_a(r_1)\phi_b(r_2)\alpha_1\beta_2 - \phi_a(r_2)\phi_b(r_1)\alpha_2\beta_1]$$

- $(\downarrow\uparrow)$ state:

$$\psi_3 = \frac{1}{\sqrt{2}} [\phi_a(r_1)\phi_b(r_2)\beta_1\alpha_2 - \phi_a(r_2)\phi_b(r_1)\beta_2\alpha_1] .$$

Heitler-London

- (↑↑) state:

$$\psi_1 = \frac{1}{\sqrt{2}}\alpha_1\alpha_2\left[\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)\right]$$

- (↓↓) state:

$$\psi_4 = \frac{1}{\sqrt{2}}\beta_1\beta_2\left[\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)\right]$$

- (↑↓) state:

$$\psi_2 = \frac{1}{\sqrt{2}}\left[\phi_a(r_1)\phi_b(r_2)\alpha_1\beta_2 - \phi_a(r_2)\phi_b(r_1)\alpha_2\beta_1\right]$$

- (↓↑) state:

$$\psi_3 = \frac{1}{\sqrt{2}}\left[\phi_a(r_1)\phi_b(r_2)\beta_1\alpha_2 - \phi_a(r_2)\phi_b(r_1)\beta_2\alpha_1\right].$$

Heitler-London

Calculation of $\mathbf{E_1}(\uparrow\uparrow) = \langle\psi_1|H|\psi_1\rangle = \cdots$

Heitler-London

$$\mathbf{E_1}(\uparrow\uparrow) = \quad \langle \psi_1 | H | \psi_1 \rangle = \tfrac{1}{2} \times \alpha_1^* \alpha_2^* \alpha_1 \alpha_2$$

$$\begin{array}{rr}
\langle \phi_a(r_1) | H_1 | \phi_a(r_1) \rangle & (= \varepsilon_a) \\
+\langle \phi_a(r_2) | H_2 | \phi_a(r_2) \rangle & (= \varepsilon_a) \\
+\langle \phi_b(r_1) | H_1 | \phi_b(r_1) \rangle & (= \varepsilon_b) \\
+\langle \phi_b(r_2) | H_2 | \phi_b(r_2) \rangle & (= \varepsilon_b)
\end{array}$$

$$\begin{array}{rr}
+\langle \phi_a(r_1)\phi_b(r_2) | H_{12} | \phi_a(r_1)\phi_b(r_2) \rangle & (= K_{ab}) \\
+\langle \phi_a(r_2)\phi_b(r_1) | H_{12} | \phi_a(r_2)\phi_b(r_1) \rangle & (= K_{ba} = K_{ab})
\end{array}$$

$$\begin{array}{rr}
-\langle \phi_a(r_1)\phi_b(r_2) | H_{12} | \phi_b(r_1)\phi_a(r_2) \rangle & (= -J_{ab}) \\
-\langle \phi_a(r_2)\phi_b(r_1) | H_{12} | \phi_b(r_2)\phi_a(r_1) \rangle & (= -J_{ba} = -J_{ab})
\end{array}$$

$$= \quad \varepsilon_\mathbf{a} + \varepsilon_\mathbf{b} + \mathbf{K_{ab}} - \mathbf{J_{ab}}$$

Heitler-London

Calculation of $\mathbf{E_4}(\downarrow\downarrow) = \langle \psi_4 | H | \psi_4 \rangle = \cdots$

$$\mathbf{E_4}(\downarrow\downarrow) = \langle \psi_{\mathbf{4}} | \mathbf{H} | \psi_{\mathbf{4}} \rangle = \varepsilon_{\mathbf{a}} + \varepsilon_{\mathbf{b}} + \mathbf{K_{ab}} - \mathbf{J_{ab}} = \mathbf{E_1}$$

Heitler-London

Calculation of $\mathbf{E_2}(\uparrow\downarrow) =$ $\langle\psi_2|H|\psi_2\rangle = \frac{1}{2}\times$

$$2\varepsilon_a + 2\varepsilon_b$$

$$\begin{aligned}
&+\langle\phi_a(r_1)\phi_b(r_2)\alpha_1\beta_2|H_{12}|\phi_a(r_1)\phi_b(r_2)\alpha_1\beta_2\rangle \quad (= K_{ab})\\
&+\langle\phi_a(r_2)\phi_b(r_1)\alpha_2\beta_1|H_{12}|\phi_a(r_2)\phi_b(r_1)\alpha_2\beta_1\rangle \quad (= K_{ab})
\end{aligned}$$

$$\begin{aligned}
&-\langle\phi_a(r_2)\phi_b(r_1)\alpha_2\beta_1|H_{12}|\phi_a(r_1)\phi_b(r_2)\alpha_1\beta_2\rangle \quad (= 0)\\
&-\langle\phi_a(r_1)\phi_b(r_2)\alpha_1\beta_2|H_{12}|\phi_a(r_2)\phi_b(r_1)\alpha_2\beta_1\rangle \quad (= 0)
\end{aligned}$$

$$= \varepsilon_{\mathbf{a}} + \varepsilon_{\mathbf{b}} + \mathbf{K_{ab}}$$

Heitler-London

The same can be done for ψ_3:

$$\mathbf{E_3}(\downarrow\uparrow) = \mathbf{E_2} = \varepsilon_\mathbf{a} + \varepsilon_\mathbf{b} + \mathbf{K_{ab}}.$$

Only two off-diag terms are non-zero:

$$\langle \psi_2 | H_{12} | \psi_3 \rangle = \langle \psi_3 | H_{12} | \psi_2 \rangle = -J_{ab}$$

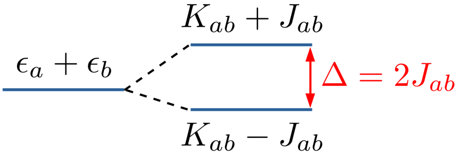
Heitler-London

Hence, the total matrix gives:

$$\varepsilon_a + \varepsilon_b + \begin{pmatrix} K_{ab} - J_{ab} & 0 & 0 & 0 \\ 0 & K_{ab} & -J_{ab} & 0 \\ 0 & -J_{ab} & K_{ab} & 0 \\ 0 & 0 & 0 & K_{ab} - J_{ab} \end{pmatrix}$$

Its diagonalization gives two states:

- triplet (degeneracy 3): $E_t = \varepsilon_a + \varepsilon_b + K_{ab} - J_{ab}$
- singlet (degeneracy 1): $E_s = \varepsilon_a + \varepsilon_b + K_{ab} + J_{ab}$



Heitler-London

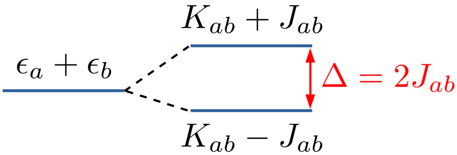
So-called *Coulomb* integral:

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

and Exchange integral:

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

where $K_{ab} \geq 0$ and $J_{ab} \geq 0$



Towards the Heisenberg Hamiltonian

On the spin basis $|S, S_z\rangle$:

$$|\psi_1\rangle = |1,1\rangle \qquad ; \qquad |\psi_4\rangle = |1,-1\rangle$$

$$\frac{1}{\sqrt{2}}(|\psi_2\rangle + |\psi_3\rangle) = |1,0\rangle \quad ; \quad \frac{1}{\sqrt{2}}(|\psi_2\rangle - |\psi_3\rangle) = |0,0\rangle$$

- triplet states (symmetric): $\{|1,1\rangle, |1,0\rangle; |1,-1\rangle\}$
- singlet state (antisymmetric): $\{|0,0\rangle\}$

we have $\mathbf{S}^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2 = S_1^2 + S_2^2 + 2\mathbf{S}_1\mathbf{S}_2$

- $= 2$ triplet
- $= 0$ singlet

Towards the Heisenberg Hamiltonian

Heisenberg trick:

- triplet: $(\mathbf{S_1}+\mathbf{S_2})^2-1=1$
- singlet: $(\mathbf{S_1}+\mathbf{S_2})^2-1=-1$

The total Hamiltonian can be rewritten as follows:

$$\begin{aligned} & \tfrac{E_s+E_t}{2}-\tfrac{E_s-E_t}{2}\left(2\mathbf{S}_1\mathbf{S}_2+\tfrac{1}{2}\right) \\ = \quad & \text{constant}-2J_{ab}\mathbf{S}_1\mathbf{S}_2 \end{aligned}$$

which looks like an “exchange” Hamiltonian $\longmapsto$ Heisenberg Hamiltonian!

Good even for more than 2 electrons:

$$H=-\sum_{ij}J_{ij}S_iS_j.$$

Remark: “no magnetic” (i.e. magnetostatic) interactions at play!

Summary

Electron interactions inside an atom can be reduced into a simple spin-spin Hamiltonian:

$$H = -\sum_{ij} J_{ij} S_i S_j.$$

The ground state of the electrons inside the same atom is ferromagnetic (1st Hund's rule, minimising the Coulomb energy together with Pauli's exclusion principle)

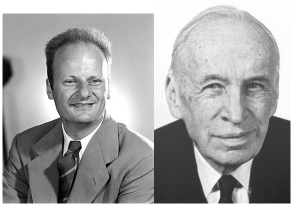
$\longmapsto$ It does not explain why there are antiferromagnets in nature!

$\longmapsto$ What is happening between magnetic atoms inside crystals/molecles?

Theories of Bonding

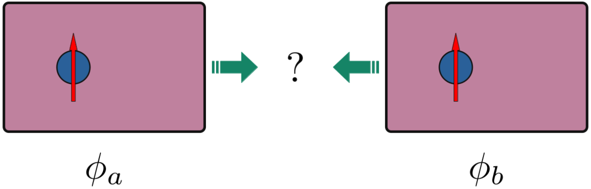
Three main models:

- The molecular orbital theory invented by Hund and Mulliken in 1928-1932.
- The valence bond theory (also called Heitler-London theory or Heitler-London-Slater-Pauling theory), generalised by Linus C. Pauling and John C. Slater in 1931.
- The crystal field theory, first proposed by J. Becquerel in 1929 and exact theory by H. Bethe in 1929, and with significant contributions from J. H. Van Vleck in the 1930s.



Heitler-London - Valence bond theory of H_2

Between two atoms: Hydrogen molecule and 1s orbitals



Heitler-London - Valence bond theory of H_2

Between two atoms: Hydrogen molecule and 1s orbitals

$$H(\mathbf{r}-\mathbf{R})\phi_{1s}(\mathbf{r}-\mathbf{R}) = \varepsilon_{1s}\phi_{1s}(\mathbf{r}-\mathbf{R})$$

with **R** the position of the proton and **r** the position of the electron. With two hydrogen atoms we have:

$$H_{tot} = H(\mathbf{r}_1-\mathbf{R}_a)+H(\mathbf{r}_2-\mathbf{R}_b)$$

$$-\frac{e^2}{|\mathbf{r}_1-\mathbf{R}_b|}-\frac{e^2}{|\mathbf{r}_2-\mathbf{R}_a|} \qquad \text{e-p interactions}$$

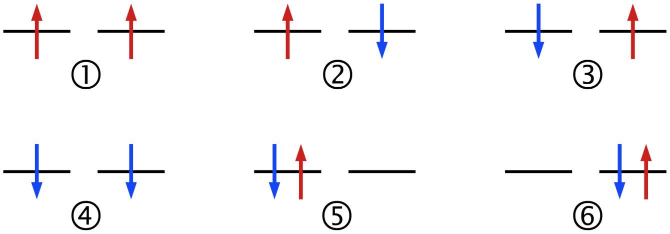
$$+\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|} \qquad \text{e-e interaction}$$

$$+\frac{e^2}{|\mathbf{R}_a-\mathbf{R}_b|} \qquad \text{p-p interaction}$$

Heitler-London - Valence bond theory of H_2

Between two atoms: Hydrogen molecule and 1s orbitals

6 possible states:



Notations: $\phi_{1s}(\mathbf{r}-\mathbf{R}_a)=\phi_a(\mathbf{r})$; $\phi_{2s}(\mathbf{r}-\mathbf{R}_b)=\phi_b(\mathbf{r})$ and the overlap between the two $1s$ orbitals:

$$\int \phi_a^*(\mathbf{r})\phi_b(\mathbf{r})d\mathbf{r}=O_{ab}\neq 0$$

Heitler-London - Valence bond theory of H_2

Wave functions for the four neutral configurations 1, 2, 3 and 4:

$$\psi_{\mathbf{1}}(\uparrow\uparrow, \mathbf{S_z} = \mathbf{1}) = \frac{1}{\sqrt{2(1 - O_{ab}^2)}} \begin{vmatrix} \phi_a(r_1)\alpha(s_1) & \phi_a(r_2)\alpha(s_2) \\ \phi_b(r_1)\alpha(s_1) & \phi_b(r_2)\alpha(s_2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2(1 - O_{ab}^2)}} \alpha_1 \alpha_2 \left[\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)\right]$$

Heitler-London - Valence bond theory of H_2

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$$= \frac{1}{\sqrt{2(1 - O_{ab}^2)}} \alpha_1 \alpha_2 [\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)]$$

$$\psi_{\mathbf{4}}(\downarrow\downarrow, \mathbf{S_z} = -\mathbf{1}) = \frac{1}{\sqrt{2(1 - O_{ab}^2)}} \beta_1 \beta_2 [\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)]$$

Heitler-London - Valence bond theory of H_2

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$$= \frac{1}{\sqrt{2(1-O_{ab}^2)}} \alpha_1\alpha_2 [\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)]$$

$$\psi_{\mathbf{4}}(\downarrow\downarrow, \mathbf{S_z} = -\mathbf{1}) = \frac{1}{\sqrt{2(1-O_{ab}^2)}} \beta_1\beta_2 [\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)]$$

$$\psi_{\mathbf{2}} = \frac{1}{\sqrt{2(1+O_{ab}^2)}} [\phi_a(r_1)\phi_b(r_2)\beta_1\alpha_2 - \phi_a(r_2)\phi_b(r_1)\alpha_1\beta_2]$$

$$\psi_{\mathbf{3}} = \frac{1}{\sqrt{2(1+O_{ab}^2)}} [\phi_a(r_1)\phi_b(r_2)\alpha_1\beta_2 - \phi_a(r_2)\phi_b(r_1)\beta_1\alpha_2]$$

Heitler-London - Valence bond theory of H_2

One can also obtain a triplet and a singlet state:

$$E_t = 2\varepsilon + \frac{C_{ab} - I_{ab}}{1 - O_{ab}^2}$$

$$E_s = 2\varepsilon + \frac{C_{ab} + I_{ab}}{1 + O_{ab}^2}$$

The splitting between *t* and *s* states is given by:

$$\Delta E_{st} = \varepsilon_t - \varepsilon_s = 2\frac{O_{ab}^2 C_{ab} - I_{ab}}{1 - O_{ab}^4}$$

Heitler-London - Valence bond theory of H_2

With “new” Coulomb C_{ab} and Exchange I_{ab} integrals:

$$C_{ab} = \quad e^2 \int dr_1 \int dr_2 \frac{|\phi_a(r_1)|^2 |\phi_b(r_2)|^2}{r_{12}}$$

$$- e^2 \int dr_1 \frac{|\phi_a(r_1)|^2}{|r_1 - R_b|} - e^2 \int dr_2 \frac{|\phi_b(r_2)|^2}{|r_2 - R_a|}.$$

$$I_{ab} = \quad e^2 \int dr_1 \int dr_2 \frac{\phi_a^*(r_1)\phi_b(r_1)\phi_b^*(r_2)\phi_a(r_2)}{r_{12}}$$

$$- e^2 O_{ab} \int dr_1 \frac{\phi_a^*(r_1)\phi_b(r_1)}{|r_1 - R_b|} - e^2 O_{ab} \int dr_2 \frac{\phi_b^*(r_2)\phi_a(r_2)}{|r_2 - R_a|}$$

Heitler-London - Valence bond theory of H_2

the Hamiltonian can be expressed as a Heisenberg spin exchange form:

$$H = constant + J_{12}\mathbf{S}_1\mathbf{S}_2$$

with $J_{12} = \Delta E_{st}$.

The sign of J_{12} will thus drive the ground state to be *ferro* or *anti-ferro*

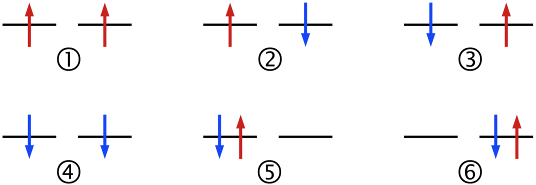
Regarding the sign of J_{12} we have different cases:

- $O_{ab} = 0$: $J_{12}(= -I_{ab}) < 0$ as seen before on a single atom
- For $O_{ab} \neq 0$: J_{12} changes sign when $O_{ab}^2 C_{ab} = I_{ab}$:
  - $J_{12} < 0$ for $O_{ab}^2 C_{ab} < I_{ab}$
  - $J_{12} >$ for $O_{ab}^2 C_{ab} > I_{ab}$.

This means that if the overlap integral O_{ab} is sufficiently large ($J_{12} > 0$), the exchange coupling is antiferro and the ground state energy is given by the singlet state.

Heitler-London - Valence bond theory of H_2

Taking into account the ionized states 5 and 6



Both electrons are on one of the two atoms:

$$|\psi_a\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(r_1)\alpha_1 & \phi_a(r_2)\alpha_2 \\ \phi_a(r_1)\beta_1 & \phi_a(r_2)\beta_2 \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} [\alpha_1\beta_2 - \beta_1\alpha_2]\phi_a(r_1)\phi_a(r_2)$$

$$|\psi_b\rangle = \frac{1}{\sqrt{2}} [\alpha_1\beta_2 - \beta_1\alpha_2]\phi_b(r_1)\phi_b(r_2)$$

Heitler-London - Valence bond theory of H_2

Putting two electrons on the same site will cost the Coulomb repulsion (on-site interaction):

$$U = \langle \psi_a | \frac{e^2}{r_{12}} | \psi_a \rangle = e^2 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{|\phi_a(\mathbf{r}_1)|^2 |\phi_a(\mathbf{r}_2)|^2}{r_{12}}$$

which is also called the Hubbard U term.

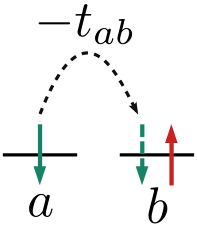
In this ionized configuration we have that $U > C_{ab} > I_{ab}$.

Heitler-London - Valence bond theory of H_2

Remaining term to take care of the connection between the empty and occupied atoms:

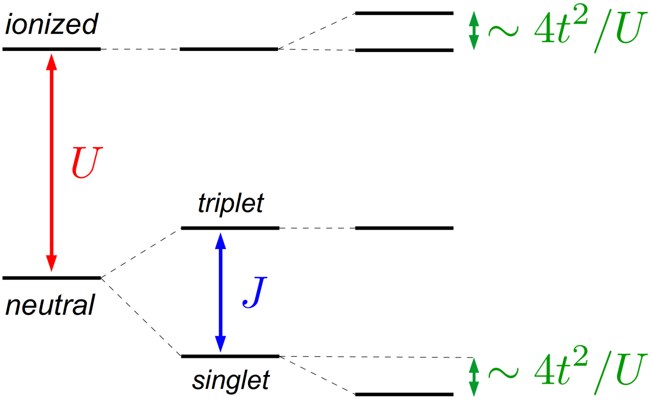
$$-t_{ab} = -e^2 \int d\mathbf{r} \frac{\phi_a^* \phi_b}{|\mathbf{r} - \mathbf{R}_b|}$$

which corresponds to the amplitude for the single-electron hopping between the two atoms (tight-binding hopping integral) or the probability for an electron to jump from an atom to the other one.



Heitler-London - Valence bond theory of H_2

Schematic view of energy level splitting of the Hydrogen molecule:



The AFM order (singlet) is the ground state!

Interaction through non magnetic atoms

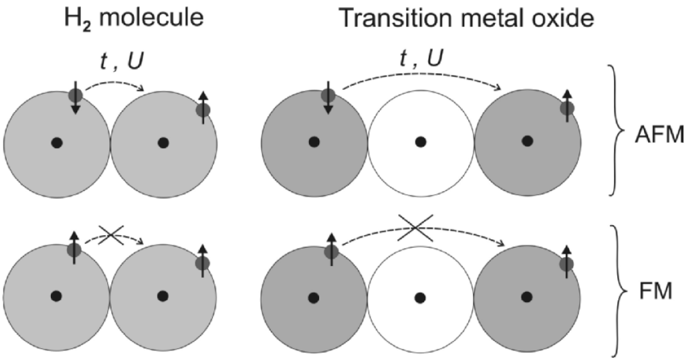
Electrons interacting through ligand atoms (O, F, N, etc)

Superexchange

Direct- versus SUPEREXCHANGE

Superexchange

Direct- versus super-exchange:



[J. Stöhr and H. C. Siegmann (Springer, 2006)]

Superexchange

Hubbard model between magnetic *d* orbitals and ligand *p* orbitals:

$$H = \sum_{\sigma} \left[\varepsilon_d \sum_i n_{i\sigma} + \varepsilon_p n_{p\sigma} - t_{pd} \sum_i \left(c^\dagger_{i\sigma} c_{p\sigma} + c^\dagger_{p\sigma} c_{i\sigma} \right) \right] + U_d \sum_i n_{i\uparrow} n_{i\downarrow}$$

(U_p is neglected),

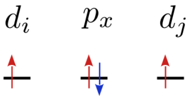
which gives the following effective superexchange coupling between the two magnetic cations:

$$J = \frac{4t_{pd}^4}{\left(U_d + \Delta_{pd}\right)^2} \left(\frac{1}{U_d} + \frac{1}{U_d + \Delta_{pd}} \right),$$

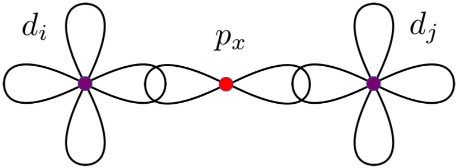
with $\Delta_{pd} = \varepsilon_d - \varepsilon_p$

Superexchange

180° bond case:

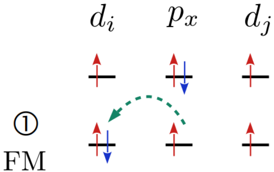


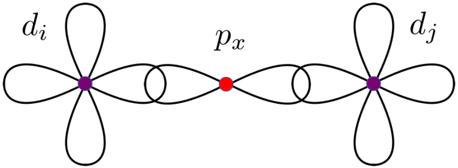
①
FM



Superexchange

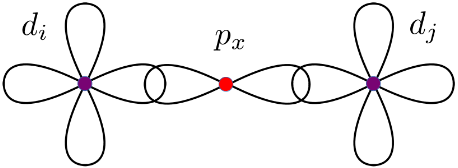
180° bond case:

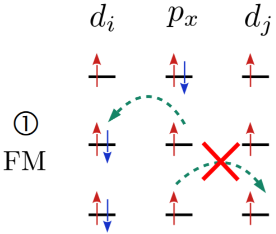




Superexchange

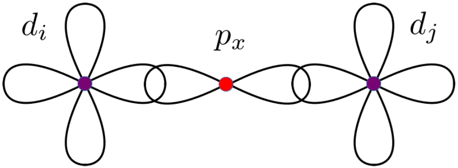
180° bond case:

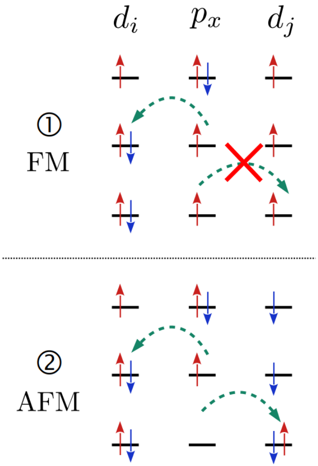




Superexchange

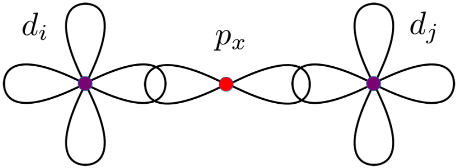
180° bond case:

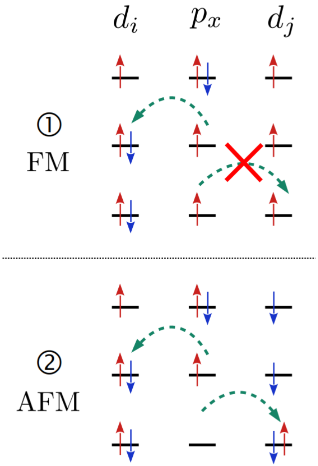




Superexchange

180° bond case:

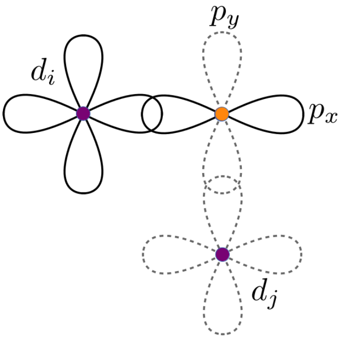


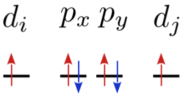


$E_2 < E_1$ The AFM case is the GS!

Superexchange

90° bond case:





①
FM

Superexchange

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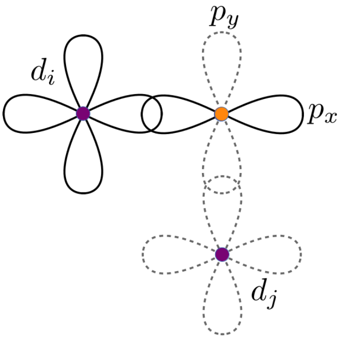
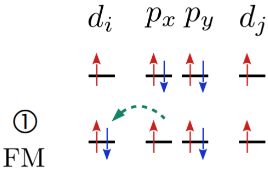
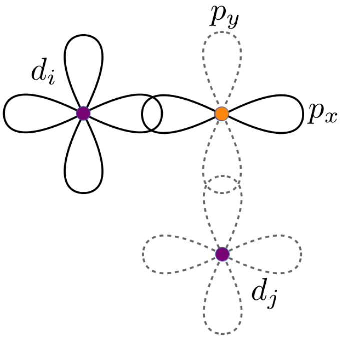
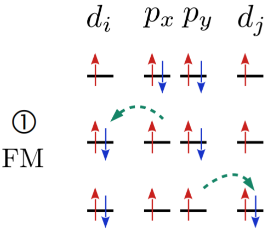




Superexchange

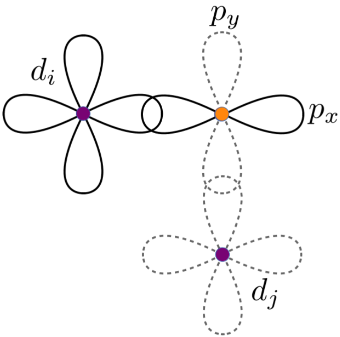
90° bond case:

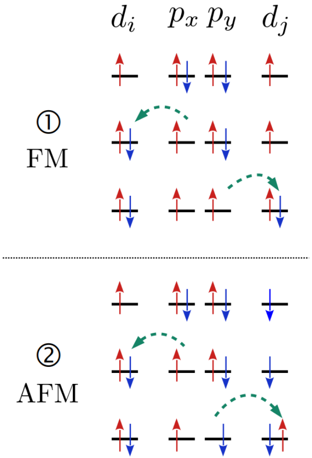




Superexchange

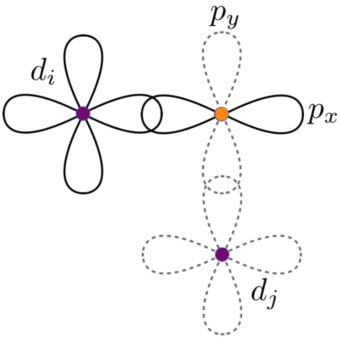
90° bond case:

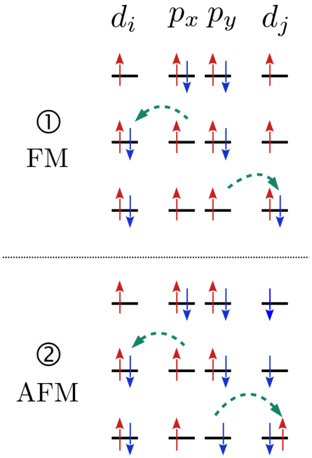




Superexchange

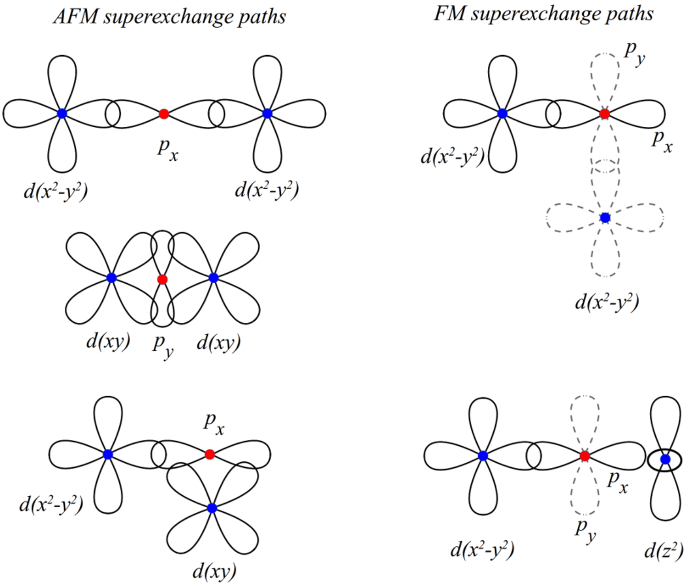
90° bond case:



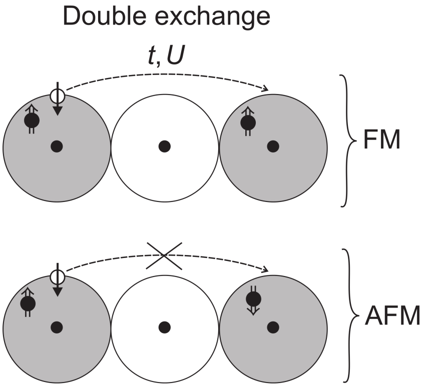


$E_2 > E_1$ The FM case is the GS!

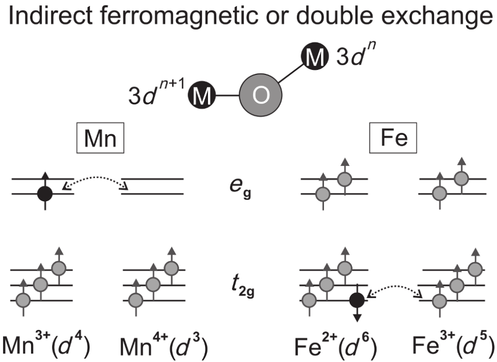
Superexchange: Goodenough-Kanamori rules



Double Exchange



Double Exchange



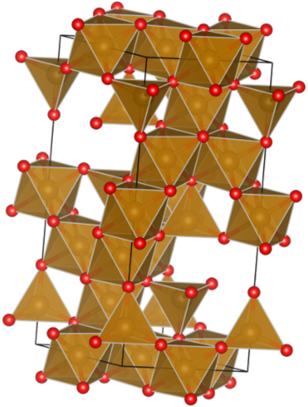
[J. Stöhr and H. C. Siegmann (Springer, 2006)]

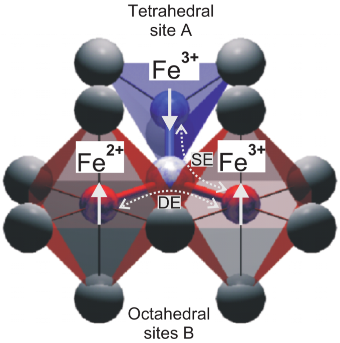
Application: Magnetite Fe_3O_4

Both octahedral and tetrahedral CF

Both Fe^{3+} ($5\mu_B$) and Fe^{2+} ($4\mu_B$) oxidization states

Both superexchange and double exchange mechanisms





Going beyond: Heisenberg model with spin directions

Taking into account spin directions (including spin-orbit coupling SOC):

$$H = -2\sum_{i,j} T_{ij}(\mathbf{r},\mathbf{r}')S_i(\mathbf{r})S_j(\mathbf{r}')$$

The tensor T can be decomposed into three parts as follows:

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

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- **D** is the antisymmetrical part of the T tensor ($T_{antisym} = \frac{1}{2}(T_{ij} - T_{ji})$), corresponds to the Dzyaloshinski-Moriya vector.

- The rest (Φ), *i.e.* the traceless part of T_{sym}, is a tensor of rank 2 and contains the energy interaction between the spin and the crystal field, i.e. the single ion anisotropy, as well as the symmetric anisotropic (pseudo dipole interaction) exchange.

Heisenberg Model

Isotropic exchange:

$$H = -2J\mathbf{S} \cdot \mathbf{S}'$$

- The isotropic exchange term J is the strongest one
- It is usually of the order of several meV in oxides
- Involves a dot product between the spins → tendency to align the spins parallel to each other
- SOC is not needed to account for this isotropic exchange interactions

Examples will be given in the TB2J tutorial (He Xu)

Heisenberg Model: DMI

Antisymmetric exchange or Dzyaloshinski-Moriya interaction (DMI):

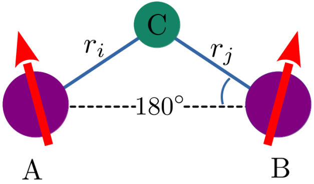
$\mathbf{D} \cdot (\mathbf{S} \times \mathbf{S}')$

- Exists through the SOC
- Usually one order of magnitude smaller than the isotropic exchange interaction J
- Minimizes the energy for 90° alignment of the spins
- In competition with the isotropic exchange interaction
- Accounts for most of the non-collinear magnetic ground state with spin canting (weak FM, weak AFM, . . .)

Heisenberg Model: DMI

The orientation of **D** is constrained by symmetry (Moriya)

- When a center of inversion is located at C: $\mathbf{D} = 0$
- When a mirror plane *m* perpendicular to AB passes through C: $\mathbf{D} \parallel m$
- When there is a mirror plane *m* including A and B: $\mathbf{D} \perp m$
- When a two-fold rotation axis C_2 perpendicular to AB passes through C: $\mathbf{D} \perp C_2$
- When there is an *n*-fold axis ($n \geq 2$) along AB: $\mathbf{D} \parallel$ AB



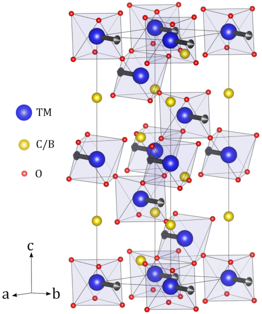
The orientation of **D** can be obtained as follows:

$$\mathbf{D}_{ij} \propto \mathbf{r}_i \times \mathbf{r}_j$$

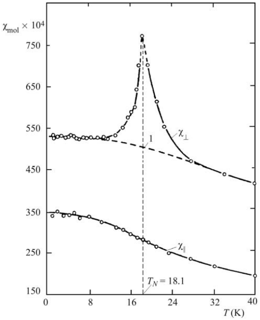
i.e. perpendicular to the triangle formed by the atoms A and B and the ligand

Heisenberg Model: DMI

Classical weak-FM: αFe$_2$O$_3$, NiF$_2$, ACO$_3$ (A=Mn, Fe, Co, Ni)



PRB 98, 104424 (2018)



JETP 39, 27 (1960)

CoCO$_3$ familly: intra-layer FM and inter-layer AFM superexchange

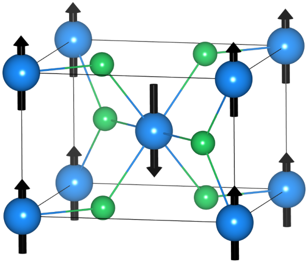
Easy-axis along *x* and w-FM canting along y

Typical “kink” in the AFM magnetic susceptibility

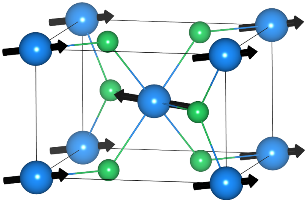
Heisenberg Model: DMI

AF_2 (rutile): wFM in A=Ni, Co but not for A=Fe, Mn

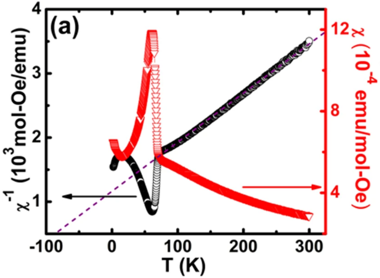
The only difference is in the easy-axis direction!



FeF_2, MnF_2



NiF_2, CoF_2

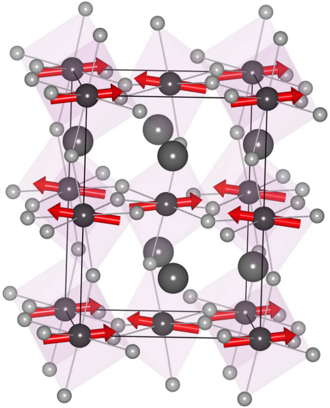


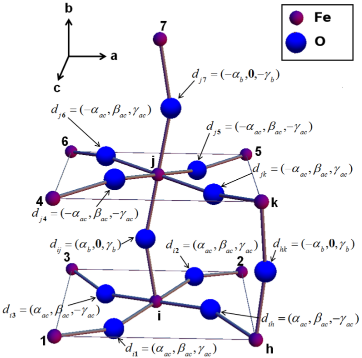
Sci. Rep. 9, 3200 (2019)

For extended examples see “Consequences of the Dzyaloshinskii-Moriya interaction”, Surf. Sci. Reports 78, 100605 (2023)

Heisenberg Model: DMI

Good source of weak-FM and weak-AFM in *Pnma*/*Pbnm* perovskites:





PRB 86, 094413 (2012)

See lecture on Multiferroics

Heisenberg Model

Single ion anisotropy (SIA):

Free energy expansion w.r.t. atom magnetic moment orientation:

$$F_a(\theta,\phi) = K_1 \sin^2\theta + K_1' \sin^2\theta \cos 2\phi + K_2 \sin^4\theta + K_2' \sin^4\theta \cos 4\phi$$

$\theta =$ polar angle [0,π]

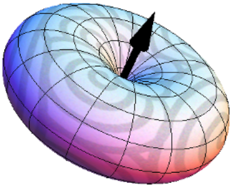
$\phi =$ is the azimuthal angle [0, 2π]

Depending on the sign of K_1 we have two situations:

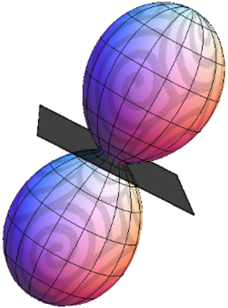
- $K_1 > 0$: easy axis SIA
- $K_1 < 0$: easy plane SIA

Heisenberg Model

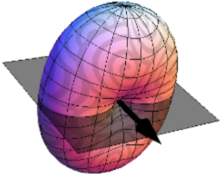
Single ion anisotropy (SIA)



$K_1 > 0$



$K_1 < 0$



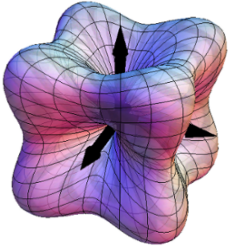
$K_1 < 0$ and $K_1' \neq 0$

Model not valid for cubic cases, needs higher order:

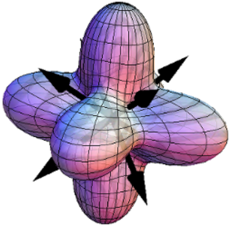
Heisenberg Model

Single ion anisotropy (SIA) - the cubic case

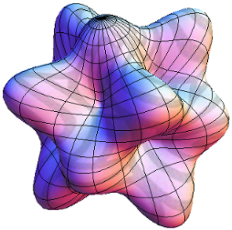
$$F_a(s_i) = K_2(s_x^2 s_y^2 + s_y^2 s_z^2 + s_x^2 s_z^2) + K_3(s_x^2 s_y^2 s_z^2)$$



$K_2 > 0$



$K_2 < 0$



$K_2 > 0$ and $K_3 \neq 0$

Heisenberg Model

SIA: SOC origin, common order of magnitude 1 to 100 μeV.

Compound	MCA (K_1 in μeV)
Fe (bcc)	1.4
Co (fcc)	1.6
Ni (fcc)	2.7
MnBi	89
α-Fe_2O_3	120
MnF_2	15

See lecture on Multiferroics for more examples in perovskites

Diverse misleading discussions

- Heisenberg model valid for localised magnetic moments (insulators), see itinerant magnetism models (metals) otherwise
- The magnetic moment direction in crystals (SIA, MCA) is given by the SOC
- The isotropic J favours parallel spin alignment vs DMI favours perpendicular alignment
- The isotropic superexchange is in most cases much larger than the SOC origin terms (DMI, anisotropic J, SIA)
- Bond directional effects (Kitaev, honeycomb lattices, 2D)
- Shape anisotropy: needs to put back the dipole-dipole magnetostatic interaction
- Orbital magnetization for unquenched $\mathbf{L}$
- Crystal-field theory, molecular orbitals theory

Conclusion

- Magnetic interactions can be understood only through quantum mecahnics
- Exchange interactions come from Coulomb interaction treated in QM, i.e. with spins and Pauli exclusion principles
- Reduction to Heisenberg model good for localized magnetic moments
- SOC necessary to explain anisotropies
- For some first-principles practice, numbers, etc: See tutorial of He Xu

Book list

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