



# Magnetism and ABINIT

Bernard Amadon

CEA, DAM, DIF, and LMCE, Université Paris Saclay, Bruyères le Châtel, France

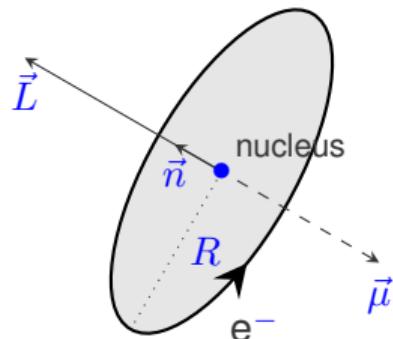
## A brief historical summary of magnetism research.

- Magnetite  $\text{Fe}_3\text{O}_4$  is the main magnetic ore.
- It was used 2000 years ago as a compass, or to magnetize an iron needle.
- Magnetic up to  $580^\circ\text{C}$ .



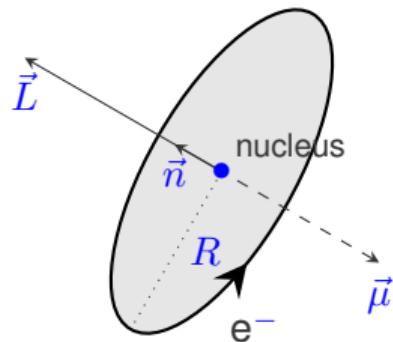
- 1820: Oersted: an electric loop deflects a magnetized needle.
- 1821: Faraday discovered induction (responsible for diamagnetism in solids).
- 1863: Maxwell's equations (link magnetic and electric fields).
- 1895: Lorentz wrote the expression for the magnetic force.

# Magnetic moment and electric current



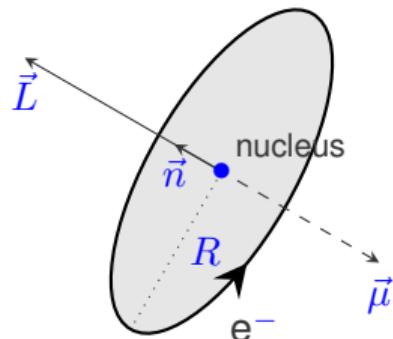
- The rotation of the electron creates an angular momentum  $\vec{L} = \vec{r} \times \vec{p}$  and an atomic magnetic moment  $\vec{\mu} = \frac{1}{2}e\vec{r} \times \vec{v}$ .

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- $\vec{\mu} = \gamma\vec{L}$  with  $\gamma$  the gyromagnetic factor equal to  $\frac{e}{2m}$ .

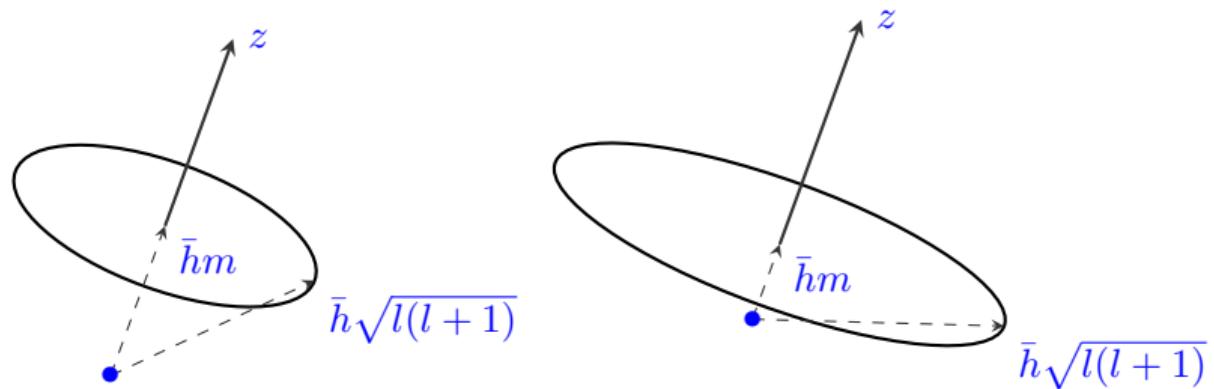
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- $\vec{L}$  is the orbital angular momentum.

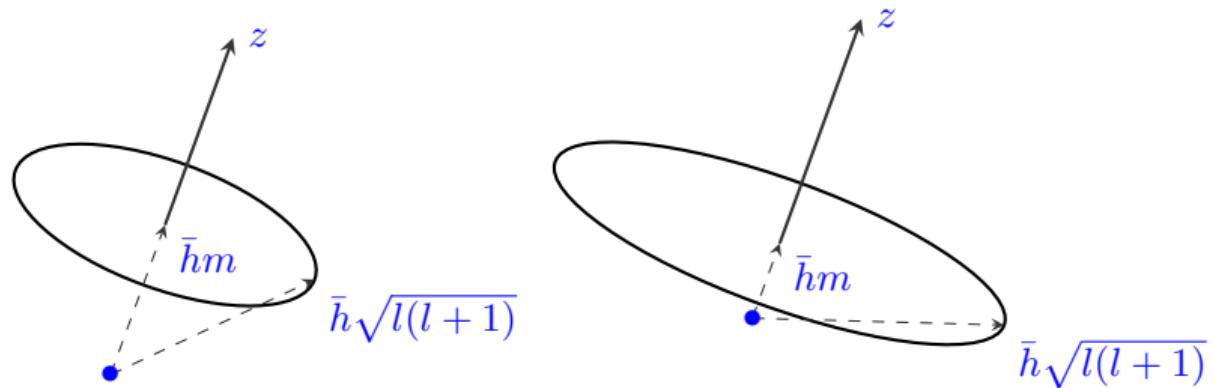
## Quantization of angular momentum in quantum mechanics

- Atomic physics: The measured angular momentum is quantized in quantum mechanics.
  - $l = 3$ : f orbitals (Pu).  $m = -3, -2, -1, 0, 1, 2, 3$



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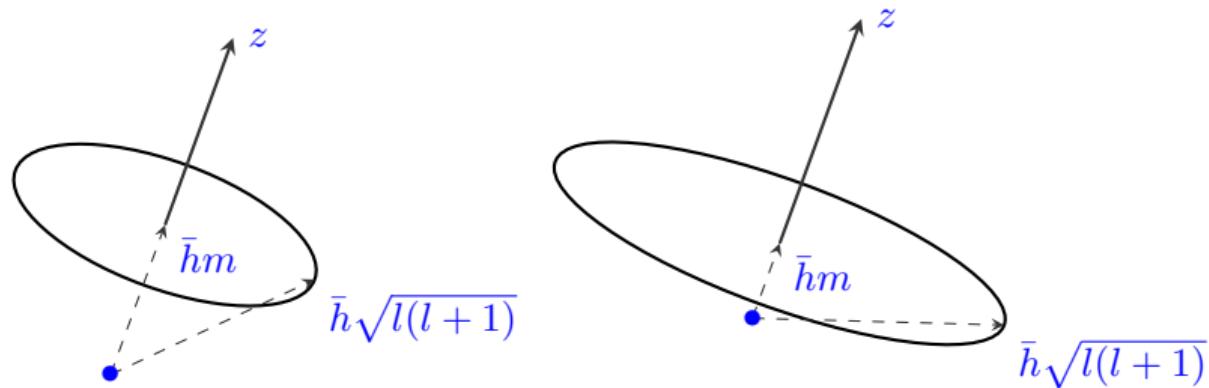
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- $\mu_z = \gamma L_z = \gamma \bar{h}m$
- $\mu_z = -\mu_B m$ .  $\mu_B = \frac{e\bar{h}}{2m}$  is the Bohr magneton.

# Spin magnetic moment

Spin was discovered by George Uhlenbeck and Samuel Goudsmit in 1925.

- Spin is linked to the electron, it is of relativistic origin and it is quantized.
- $s = 0.5$ ,  $ms = -0.5, 0.5$ . Two possible values for the projection of the spin angular momentum:
  - $s_z = +\frac{\hbar}{2}$
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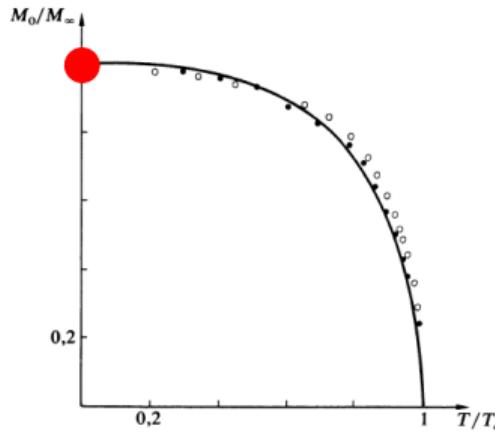
⇒ Electronic magnetism has two origins: spin and orbital moment.

⇒ What is the magnetic behavior of a set of atoms carrying these electrons?

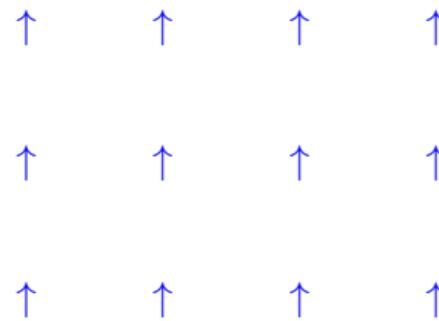
# Curie temperature

- Ferromagnetism

- At zero temperature: large magnetic moment  
(magnetic moments of iron aligned).

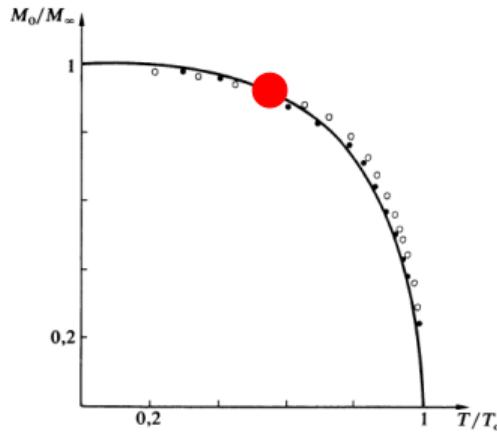


Ronds vides: fer  
Ronds pleins: cobalt et nickel



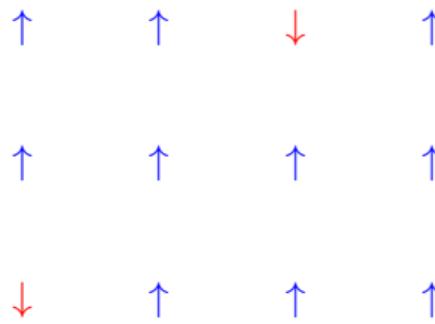
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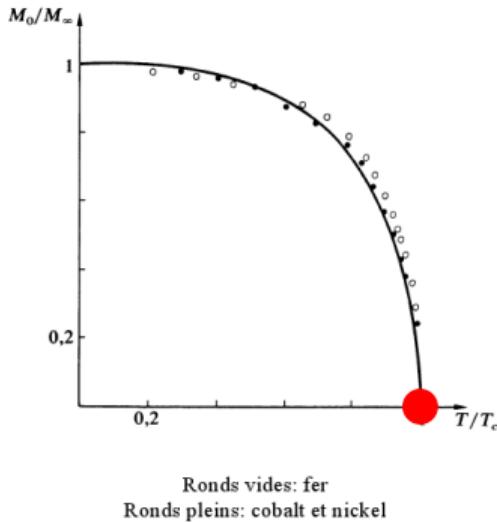
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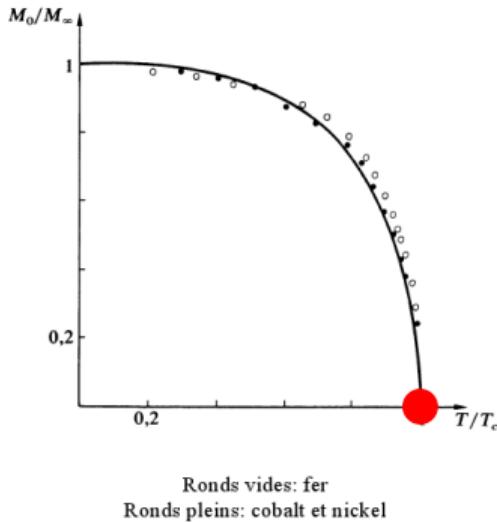


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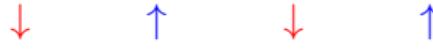


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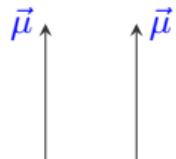


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# From the atomic magnetic moment to ferromagnetism

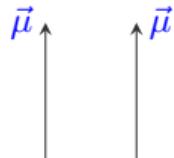
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- The dipole-dipole interaction of two magnetic moments  $\mu_B$  separated by 1Å is about 1K.

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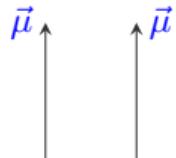
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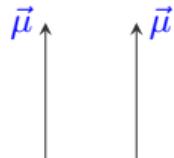
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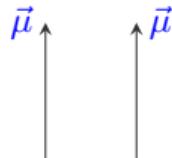
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Werner Heisenberg in 1929 showed that the interactions responsible for the Weiss field and thus magnetism in matter are of electrostatic and quantum origin (caused by the Coulomb interaction).

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- Let's write the different possible spin states:
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- In quantum mechanics, the wave function is antisymmetric:
  - $\frac{1}{\sqrt{2}}[|\phi_a\uparrow\rangle|\phi_b\uparrow\rangle - |\phi_b\uparrow\rangle|\phi_a\uparrow\rangle]$
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- $|\Psi_1\rangle = \frac{1}{\sqrt{2}} [|\phi_a\uparrow\rangle|\phi_b\uparrow\rangle - |\phi_b\uparrow\rangle|\phi_a\uparrow\rangle]$
- $|\Psi_2\rangle = \frac{1}{\sqrt{2}} [|\phi_a\uparrow\rangle|\phi_b\downarrow\rangle - |\phi_b\downarrow\rangle|\phi_a\uparrow\rangle]$
- $|\Psi_3\rangle = \frac{1}{\sqrt{2}} [|\phi_a\downarrow\rangle|\phi_b\uparrow\rangle - |\phi_b\uparrow\rangle|\phi_a\downarrow\rangle]$
- $|\Psi_4\rangle = \frac{1}{\sqrt{2}} [|\phi_a\downarrow\rangle|\phi_b\downarrow\rangle - |\phi_b\downarrow\rangle|\phi_a\downarrow\rangle]$

The Coulomb interaction Hamiltonian between two electrons is given by:

$$\hat{V} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

We compute the values of this operator in this basis:

$$\begin{pmatrix} \langle\Psi_1|\hat{V}|\Psi_1\rangle & \langle\Psi_1|\hat{V}|\Psi_2\rangle & \langle\Psi_1|\hat{V}|\Psi_3\rangle & \langle\Psi_1|\hat{V}|\Psi_4\rangle \\ \langle\Psi_2|\hat{V}|\Psi_1\rangle & \langle\Psi_2|\hat{V}|\Psi_2\rangle & \langle\Psi_2|\hat{V}|\Psi_3\rangle & \langle\Psi_2|\hat{V}|\Psi_4\rangle \\ \langle\Psi_3|\hat{V}|\Psi_1\rangle & \langle\Psi_3|\hat{V}|\Psi_2\rangle & \langle\Psi_3|\hat{V}|\Psi_3\rangle & \langle\Psi_3|\hat{V}|\Psi_4\rangle \\ \langle\Psi_4|\hat{V}|\Psi_1\rangle & \langle\Psi_4|\hat{V}|\Psi_2\rangle & \langle\Psi_4|\hat{V}|\Psi_3\rangle & \langle\Psi_4|\hat{V}|\Psi_4\rangle \end{pmatrix}$$

## Interaction between magnetic moments: exchange

The matrix element  $\langle \Psi_1 | \hat{V} | \Psi_1 \rangle$  is given by:

$$\langle \Psi_1 | \hat{V} | \Psi_1 \rangle = \frac{1}{\sqrt{2}} [\langle \phi_a \uparrow | \langle \phi_b \uparrow | - \langle \phi_b \uparrow | \langle \phi_a \uparrow ] \hat{V} | \frac{1}{\sqrt{2}} [|\phi_a \uparrow \rangle | \phi_b \uparrow \rangle - |\phi_b \uparrow \rangle | \phi_a \uparrow \rangle ] \rangle$$

Expanding this, we get:

$$\begin{aligned} \langle \Psi_1 | \hat{V} | \Psi_1 \rangle = & \frac{1}{2} \left[ \langle \phi_a \uparrow | \langle \phi_b \uparrow | \hat{V} | \phi_a \uparrow \rangle | \phi_b \uparrow \rangle - \langle \phi_a \uparrow | \langle \phi_b \uparrow | \hat{V} | \phi_b \uparrow \rangle | \phi_a \uparrow \rangle - \langle \phi_b \uparrow | \langle \phi_a \uparrow | \hat{V} | \phi_a \uparrow \rangle | \phi_b \uparrow \rangle + \right. \\ & \left. \langle \phi_b \uparrow | \langle \phi_a \uparrow | \hat{V} | \phi_b \uparrow \rangle | \phi_a \uparrow \rangle \right] \end{aligned}$$

Due to the symmetry of the Coulomb interaction operator  $\hat{V}$ , the first and fourth terms are identical, as are the second and third terms:

$$\langle \phi_a \uparrow | \langle \phi_b \uparrow | \hat{V} | \phi_a \uparrow \rangle | \phi_b \uparrow \rangle = \langle \phi_b \uparrow | \langle \phi_a \uparrow | \hat{V} | \phi_b \uparrow \rangle | \phi_a \uparrow \rangle$$

$$\langle \phi_a \uparrow | \langle \phi_b \uparrow | \hat{V} | \phi_b \uparrow \rangle | \phi_a \uparrow \rangle = \langle \phi_b \uparrow | \langle \phi_a \uparrow | \hat{V} | \phi_a \uparrow \rangle | \phi_b \uparrow \rangle$$

## Interaction between magnetic moments: exchange

Thus, the expression simplifies to:

$$\langle \Psi_1 | \hat{V} | \Psi_1 \rangle = \frac{1}{2} \left[ 2\langle \phi_a \uparrow | \langle \phi_b \uparrow | \hat{V} | \phi_a \uparrow \rangle | \phi_b \uparrow \rangle - 2\langle \phi_a \uparrow | \langle \phi_b \uparrow | \hat{V} | \phi_b \uparrow \rangle | \phi_a \uparrow \rangle \right] = K - J$$

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with

$$K = \langle \phi_a \phi_b | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_a \phi_b \rangle = \int d\mathbf{r} \int d\mathbf{r}' \frac{|\phi_a(\mathbf{r})|^2 |\phi_b(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}$$

and

$$J = \langle \phi_a \phi_b | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_b \phi_a \rangle = \int d\mathbf{r} \int d\mathbf{r}' \frac{\phi_a(\mathbf{r}') \phi_b(\mathbf{r}) \phi_a^*(\mathbf{r}) \phi_b^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

## Interaction between magnetic moments: exchange

Calculating all other elements:

$$\begin{pmatrix} K - J & 0 & 0 & 0 \\ 0 & K & -J & 0 \\ 0 & -J & K & 0 \\ 0 & 0 & 0 & K - J \end{pmatrix}$$

with

- $|\Psi_1\rangle = \frac{1}{\sqrt{2}} [|\phi_a\uparrow\rangle|\phi_b\uparrow\rangle - |\phi_b\uparrow\rangle|\phi_a\uparrow\rangle]$
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## Interaction between magnetic moments: exchange

The matrix element  $\langle \Psi_2 | \hat{V} | \Psi_3 \rangle$  is given by:

$$\langle \Psi_2 | \hat{V} | \Psi_3 \rangle = \left( \frac{1}{\sqrt{2}} [\langle \phi_a \uparrow | \langle \phi_b \downarrow | - \langle \phi_b \downarrow | \langle \phi_a \uparrow |] \right) \hat{V} \left( \frac{1}{\sqrt{2}} [|\phi_a \downarrow \rangle | \phi_b \uparrow \rangle - |\phi_b \uparrow \rangle | \phi_a \downarrow \rangle] \right)$$

Expanding this, we get:

$$\langle \Psi_2 | \hat{V} | \Psi_3 \rangle = \frac{1}{2} \left[ -\langle \phi_a \uparrow | \langle \phi_b \downarrow | \hat{V} | \phi_b \uparrow \rangle | \phi_a \downarrow \rangle - \langle \phi_b \downarrow | \langle \phi_a \uparrow | \hat{V} | \phi_a \downarrow \rangle | \phi_b \uparrow \rangle \right]$$

Due to the symmetry of the operator  $\hat{V}$ , the terms simplify as:

$$\langle \phi_a \uparrow | \langle \phi_b \downarrow | \hat{V} | \phi_b \uparrow \rangle | \phi_a \downarrow \rangle = \langle \phi_b \downarrow | \langle \phi_a \uparrow | \hat{V} | \phi_a \downarrow \rangle | \phi_b \uparrow \rangle$$

Thus, the expression becomes:

$$\langle \Psi_2 | \hat{V} | \Psi_3 \rangle = \frac{1}{2} \left[ 0 - 2 \langle \phi_a \uparrow | \langle \phi_b \downarrow | \hat{V} | \phi_b \uparrow \rangle | \phi_a \downarrow \rangle \right] = -J$$

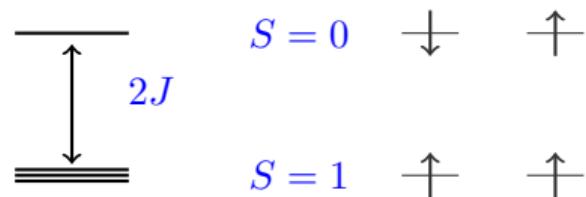
where  $J$  is the exchange integral defined by:

$$J = \int d\mathbf{r} \int d\mathbf{r}' \frac{\phi_a(\mathbf{r}') \phi_b(\mathbf{r}) \phi_a^*(\mathbf{r}) \phi_b^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

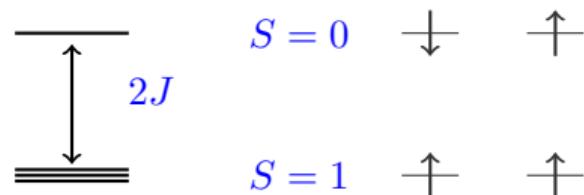
- The diagonalization of the Hamiltonian gives

$$\begin{aligned}
 |\Psi_4\rangle &= \frac{1}{\sqrt{2}}[\phi_a\phi_b - \phi_b\phi_a]|\downarrow\downarrow\rangle & S = 1 & m_S = -1 & K - J \\
 \frac{1}{2}(|\Psi_2\rangle + |\Psi_3\rangle) &= \frac{1}{\sqrt{2}}[\phi_a\phi_b - \phi_b\phi_a]\frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle] & S = 1 & m_S = 0 & K - J \\
 |\Psi_1\rangle &= \frac{1}{\sqrt{2}}[\phi_a\phi_b - \phi_b\phi_a]|\uparrow\uparrow\rangle & S = 1 & m_S = 1 & K - J \\
 \frac{1}{2}(|\Psi_2\rangle - |\Psi_3\rangle) &= \frac{1}{\sqrt{2}}[\phi_a\phi_b + \phi_b\phi_a]\frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle] & S = 0 & m_S = 0 & K + J
 \end{aligned}$$

## Application: Hund's rule in matter



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- On the same atom  $J > 0$ : Hund's rule.

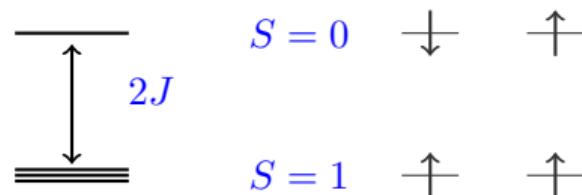
Manganese

$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
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Nickel

$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$
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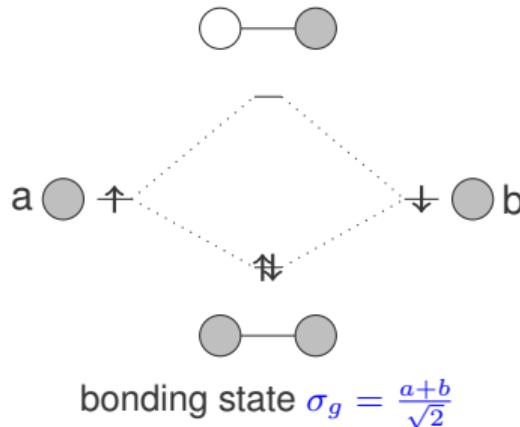
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Manganese	<table border="1" style="border-collapse: collapse; text-align: center;"><tr><td><math>\uparrow</math></td><td><math>\uparrow</math></td><td><math>\uparrow</math></td><td><math>\uparrow</math></td><td><math>\uparrow</math></td></tr></table>	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$		
Nickel	<table border="1" style="border-collapse: collapse; text-align: center;"><tr><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow</math></td><td><math>\uparrow</math></td></tr></table>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$		

- On different atoms, things are different because chemical bonding can appear, and favor the  $S=0$  state.

## Interaction between magnetic moments: chemical bond

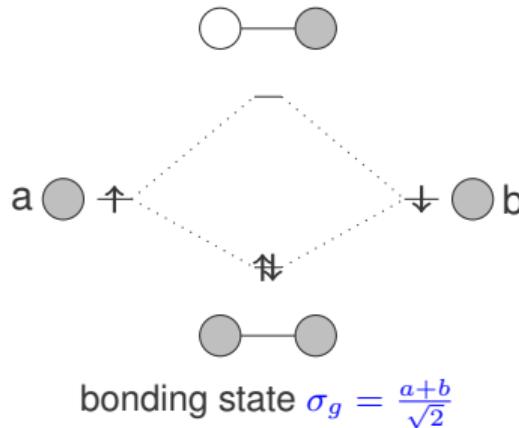
$$\text{antibonding state } \sigma_u = \frac{a-b}{\sqrt{2}}$$



- An electron can only jump to a neighboring site (forming a chemical bond) if the electron has opposite spin.
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- Electrons order antiferromagnetically.
- But the electrons are not each on their atom....this is not a real antiferromagnetic system.

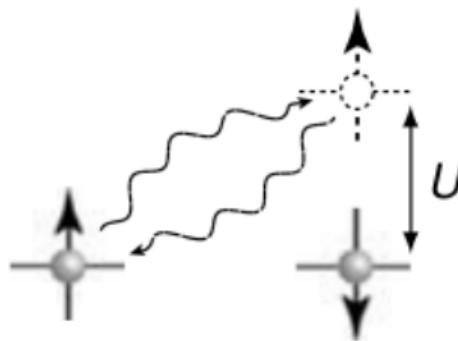
## "superexchange" (1)

- Ferromagnetic configuration
- Antiferromagnetic configuration (stabilized by interaction with an excited state)

(a)



(b)



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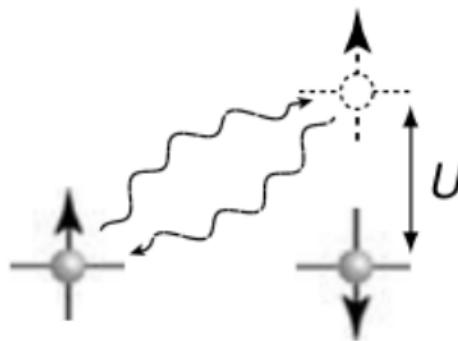
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(a)



- Antiferromagnetic configuration (stabilized by interaction with an excited state)
- ⇒ Localized electrons: antiferromagnetism.

(b)



## "superexchange" (1)

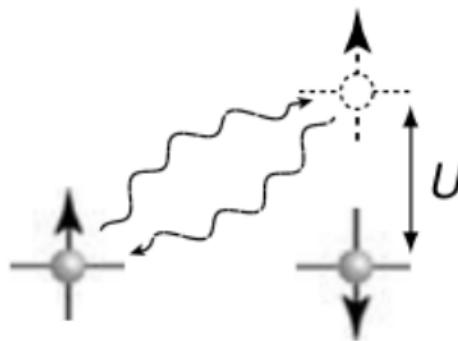
- Ferromagnetic configuration

(a)



- Antiferromagnetic configuration (stabilized by interaction with an excited state)

(b)



- $\Rightarrow$  Localized electrons: antiferromagnetism.
- $\Rightarrow$  This is not an exchange effect but an effect of hybridization and chemical bonding.

## "superexchange" (1)

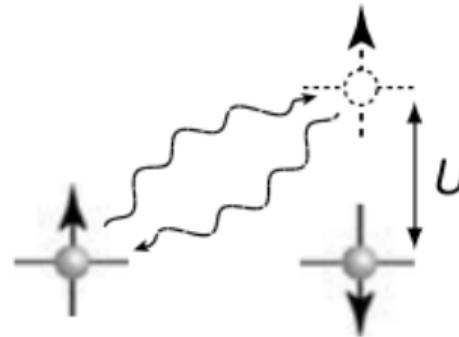
- Ferromagnetic configuration

(a)



- Antiferromagnetic configuration (stabilized by interaction with an excited state)

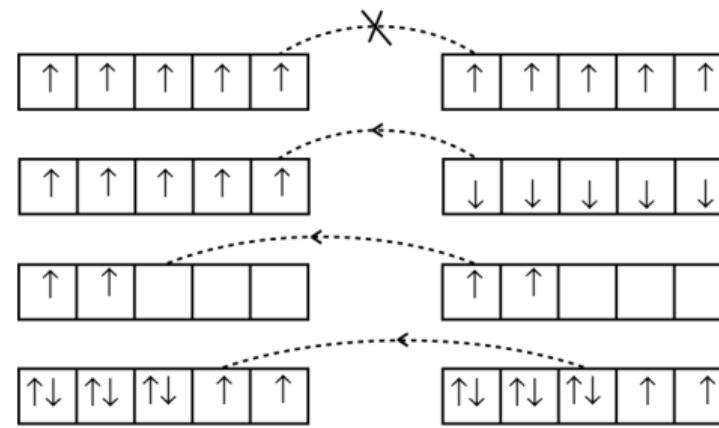
(b)



- $\Rightarrow$  Localized electrons: antiferromagnetism.
- $\Rightarrow$  This is not an exchange effect but an effect of hybridization and chemical bonding.
- $\Rightarrow$  Several electrons per atom?

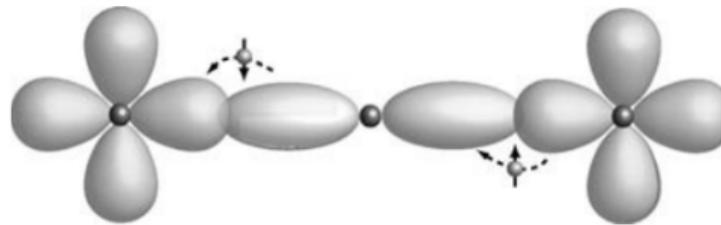
## If more orbitals (case of transition metals)

- 4 or 5 d electrons  
(Cr,Mn):  
antiferromagnetic.



- 7 or 8 d electrons  
(Co,Ni):  
ferromagnetic.

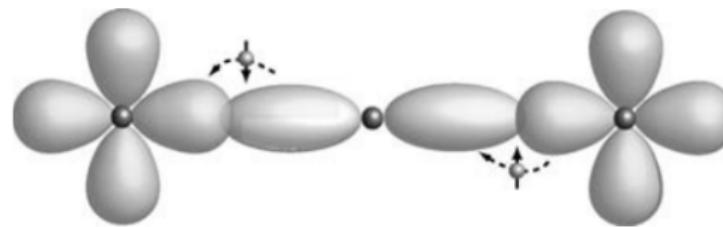
## "superexchange" (1): an explanation of antiferromagnetism.



- (a) Ferromagnetic configuration
- (b) Antiferromagnetic configuration

	3d(Mn)	2p(O)	3d(Mn)
(a)	↑	↑↓	↑
(b)	↓	↑↓	↑

## "superexchange" (1): an explanation of antiferromagnetism.



3d(Mn)

2p(O)

3d(Mn)

- (a) Ferromagnetic configuration
- (b) Antiferromagnetic configuration

(a)

↑

↑↓

↑

(b)

↓

↑↓

↑

How to take into account this into an ab-initio scheme ?

## The Hartree approximation

- Hartree (1927) proposed to write the many body wavefunction as the product of one particle wavefunctions.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \prod_i \phi_i(\mathbf{r}_i)$$

- The total energy  $\langle \Psi | H | \Psi \rangle$  can be written as

$$E_{\text{GS}}^{\text{Hartree}} = \underbrace{- \sum_i \int \phi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_i(\mathbf{r}) d\mathbf{r}}_{\text{Kinetic}} + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + \underbrace{\frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{\sum_{i \neq j} |\phi_i(\mathbf{r})|^2 |\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}}_{\text{electron electron interaction}}$$

## The Hartree Fock approximation

- As electrons are fermions, the Hartree many body wavefunction should be antisymmetrized (Slater determinant):

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \cdots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \cdots & \phi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

- If one uses this wavefunction to compute the ground state energy, one finds:

## The Hartree Fock approximation

$$E_{\text{GS}}^{\text{Hartree Fock}} = -\frac{1}{2} \sum_i \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r} + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{Hartree}}[n(\mathbf{r})]$$
$$\underbrace{-\frac{1}{2} \sum_{i \neq j, \sigma} \iint d\mathbf{r} d\mathbf{r}' \left( \frac{\phi_i^{*\sigma}(\mathbf{r}) \phi_j^\sigma(\mathbf{r}) \phi_j^\sigma(\mathbf{r}') \phi_i^{*\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right)}_{\text{Exchange term}}$$

The last term is the (Fock) exchange energy between 2 electrons of the **same spin**. It comes from the antisymmetry of the wavefunctions

## The Homogeneous electron gas: exchange

For a fully polarized homogeneous electron gas (all electrons have the same spin), the exchange energy per particle can be computed as:

$$\epsilon_x[n] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} n^{1/3}(\mathbf{r})$$

For a partially polarized system with spin densities  $n_{\uparrow}$  and  $n_{\downarrow}$ , the exchange energy per particle is :

$$\epsilon_x[n_{\uparrow}, n_{\downarrow}] = -\frac{3}{4} \left( \frac{6}{\pi} \right)^{1/3} \left( n_{\uparrow}^{1/3}(\mathbf{r}) + n_{\downarrow}^{1/3}(\mathbf{r}) \right)$$

# The correlation energy

We define  $n$  and  $\zeta$

$$n = (4\pi r_s^3/3)^{-1},$$

$$\zeta = (n_\uparrow - n_\downarrow)/n.$$

$\epsilon_c^U$  and  $\epsilon_c^P$  are the correlation energies for the unpolarized and polarized homogeneous electron gas known from QMC calculations.

$$\epsilon_c(r_s, \zeta) = \epsilon_c^U(r_s) + f(\zeta) [\epsilon_c^P(r_s) - \epsilon_c^U(r_s)],$$

where

$$f(\zeta) = \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2}{2^{4/3} - 2}.$$

# DFT with non polarized density

DFT:

$$E[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_{\text{Hartree}}[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r})$$

Kohn Sham:

$$\left[ -\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n(\mathbf{r})](\mathbf{r}) + v_{\text{xc}}[n(\mathbf{r})](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

# Introduction to Magnetism in DFT-LDA

## Magnetism in DFT

Magnetism is treated by introducing spin densities  $n_{\uparrow}(\mathbf{r})$  and  $n_{\downarrow}(\mathbf{r})$  for spin-up and spin-down electrons.

## Exchange-Correlation Energy

The exchange-correlation energy  $E_{xc}$  depends on the spin densities:

$$E_{xc}[n_{\uparrow}, n_{\downarrow}] = \int n(\mathbf{r}) \epsilon_{xc}(n_{\uparrow}, n_{\downarrow}) d\mathbf{r}$$

# Magnetism in DFT

$$n(\mathbf{r}) = n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r}) \quad n^\sigma(\mathbf{r}) = \sum_i |\phi_i^\sigma(\mathbf{r})|^2$$

- The total energy expression as a function of  $\phi(\mathbf{r})$  is

$$\begin{aligned} E_{v_{\text{ext}}} [n(\mathbf{r})] &= - \sum_{i\sigma=\uparrow\downarrow} \int \phi_i^\sigma(\mathbf{r}) \frac{\nabla^2}{2} \phi_i^\sigma(\mathbf{r}) d\mathbf{r} \\ &+ \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{Hartree}}[n(\mathbf{r})] + E_{\text{xc}}[n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})] \end{aligned}$$

- The effective Kohn Sham potential  $V_{\text{KS}}(\mathbf{r})$  is defined as

$$V_{\text{KS}}^\sigma(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})](\mathbf{r})$$

# Magnetism in DFT

- One obtains the one electron Kohn-Sham Equations

$$\left[ -\frac{\nabla^2}{2} + V_{\text{KS}}^{\sigma}(\mathbf{r}) \right] \phi_i^{\sigma}(\mathbf{r}) = \epsilon_i^{\sigma} \phi_i^{\sigma}(\mathbf{r})$$

Spin tutorial on Iron bcc FM:

Start the calculation with:

```
spinat 0 0 2
```

Eigenvalues for up and dn channel are different

(up channel:)

-3.09143	-1.74675	-1.74675	-1.74418	0.25777	0.36032	0.36032
----------	----------	----------	----------	---------	---------	---------

(dn channel:)

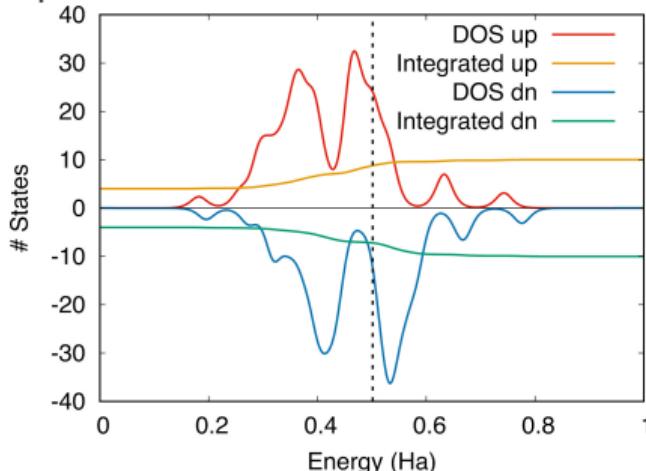
-3.04218	-1.69171	-1.69171	-1.68906	0.27331	0.40348	0.40348
----------	----------	----------	----------	---------	---------	---------

# Magnetism in DFT

- One obtains the one electron Kohn-Sham Equations

$$\left[ -\frac{\nabla^2}{2} + V_{\text{KS}}(\mathbf{r}) \right] \phi_i^\sigma(\mathbf{r}) = \epsilon_i^\sigma \phi_i^\sigma(\mathbf{r})$$

Spin tutorial on Iron bcc FM:



DOS is  $D_\sigma(E)$

Integrated DOS is  $\int_0^{E_F} D_\sigma(E) dE = N_\sigma$

# Magnetism in DFT

The magnetic density is thus  $m(\mathbf{r}) = n^{\uparrow}(\mathbf{r}) - n^{\downarrow}(\mathbf{r})$

It can be integrated fully to have the Total magnetization or only in atomic sphere.

Integrated electronic and magnetization densities in atomic spheres:

---

Radius=ratsph(iatom), smearing ratsm= 0.0000. Diff(up-dn)=approximate z local ma

Atom	Radius	up_density	dn_density	Total(up+dn)	Diff(up-dn)
1	2.00000	7.658786	6.158329	13.817115	1.500458

---

Sum: 7.658786 6.158329 13.817115 1.500458

Total magnetization (from the atomic spheres): 1.500458

Total magnetization (exact up - dn): 1.571040

---

# Types of Magnetism

## Diamagnetism

Opposes applied field. *Examples:* Cu, H<sub>2</sub>O, Au.

## Paramagnetism

Aligns with applied field. *Examples:* Al, O<sub>2</sub>.

## Ferromagnetism

Parallel alignment. Spontaneous magnetization. *Examples:* Fe, Co, Ni.



## Antiferromagnetism

Antiparallel alignment. *Examples:* MnO, Cr.



## Ferrimagnetism

Antiparallel, unequal moments. *Examples:* Fe<sub>3</sub>O<sub>4</sub>.



## Itinerant Ferromagnetism

Delocalized electrons. *Examples:* Fe, Ni.

## Paramagnetism and ferromagnetism in the homogeneous electron

- In metals without magnetic moments (Aluminum), a small Pauli paramagnetism independent of temperature is observed.

## Density of states of a metal

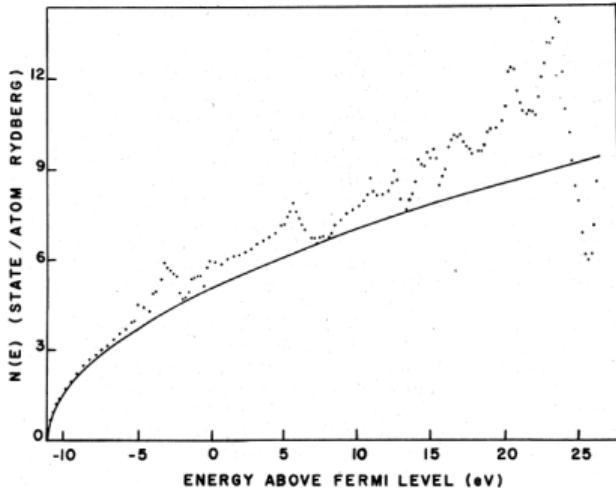
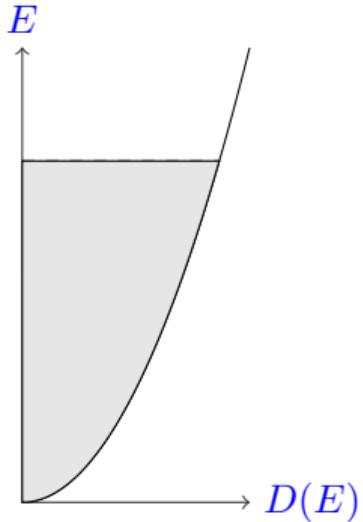
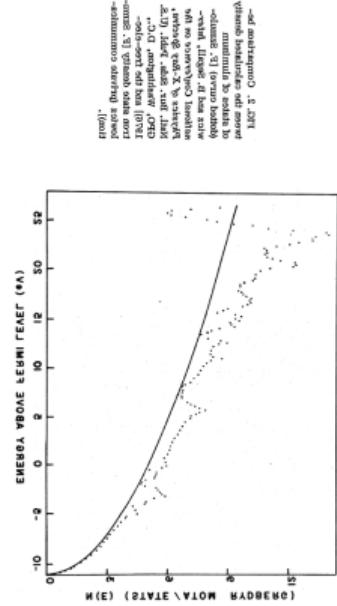


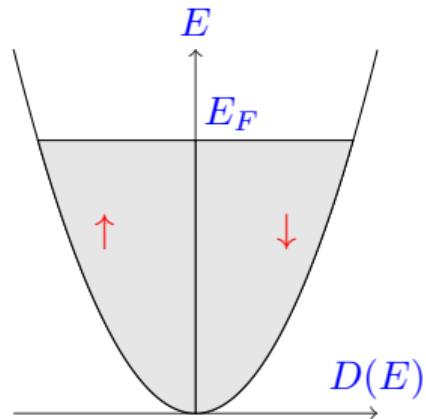
FIG. 2. Comparison between the calculated density of states of aluminum (dotted curve) [F. Szmulowicz and B. Segall, *International Conference on the Physics of X-Ray Spectra*, Natl. Bur. Stds. Publ. (U.S. GPO, Washington, D.C., 1976)] and the free-electron state density [F. Szmulowicz (private communication)].

- Ab-initio calculation of aluminum compared to the density of states of a non-interacting system
- The spectrum of aluminum is close to that of a non-interacting system!

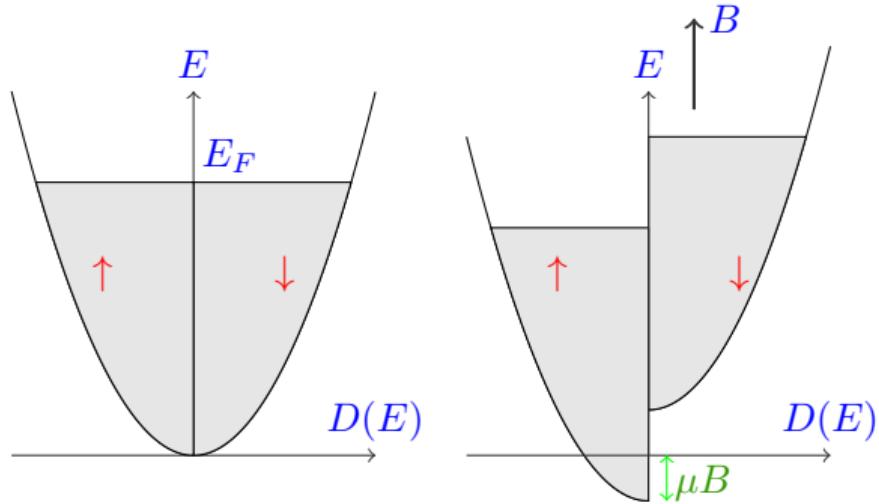
# Non-interacting system (Aluminum)



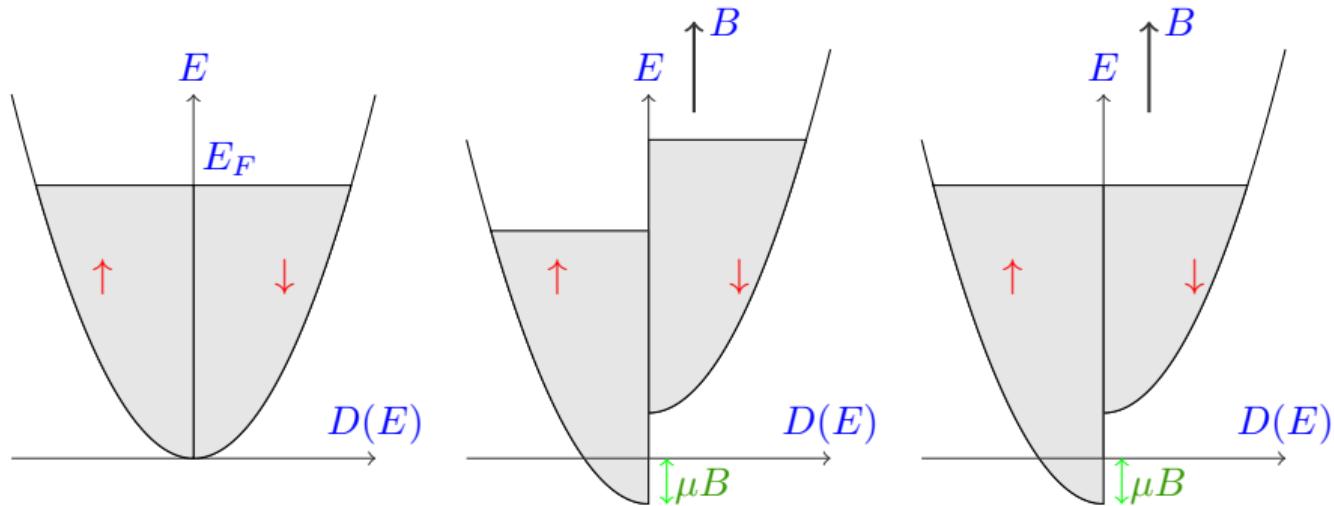
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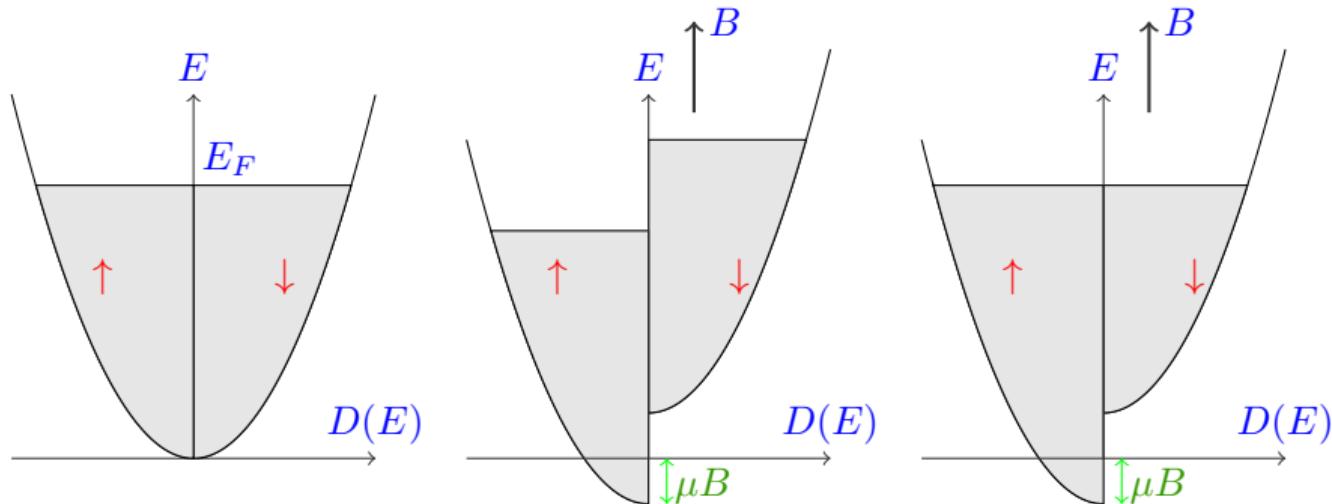
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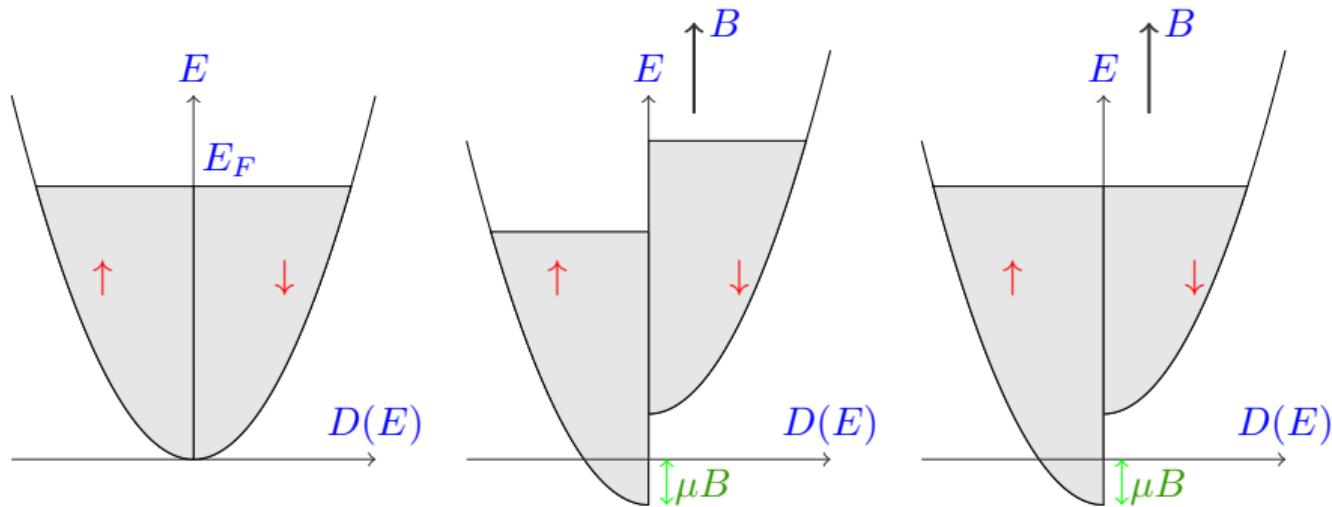


## Non-interacting system (Aluminum)



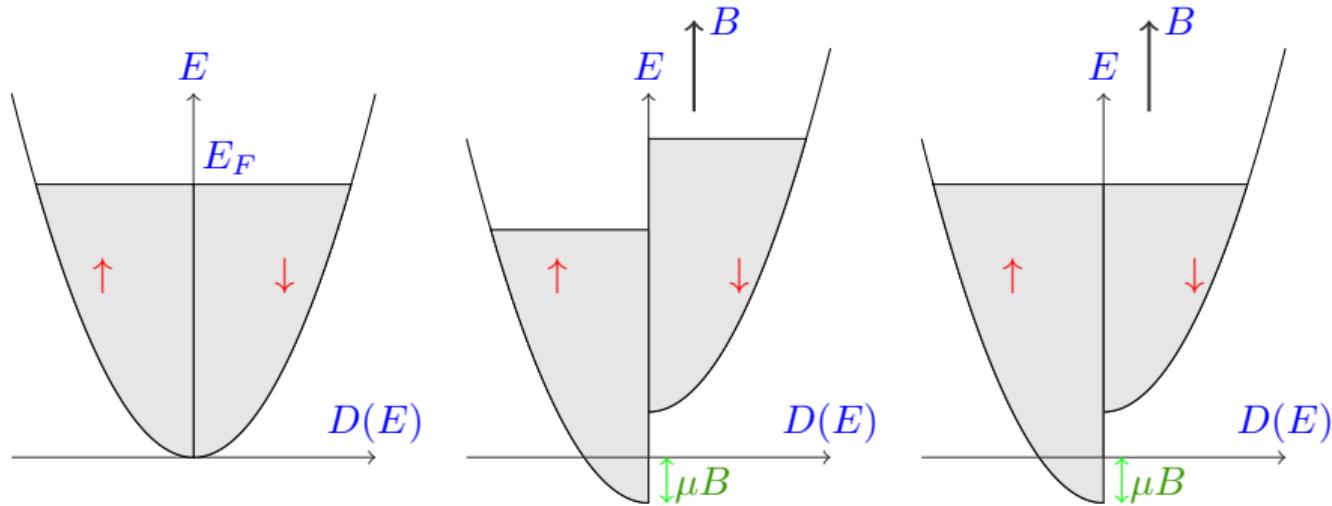
- Because of field  $B$ ,  $\uparrow$  electrons are lowered in energy by  $[\mu B]$ .

## Non-interacting system (Aluminum)



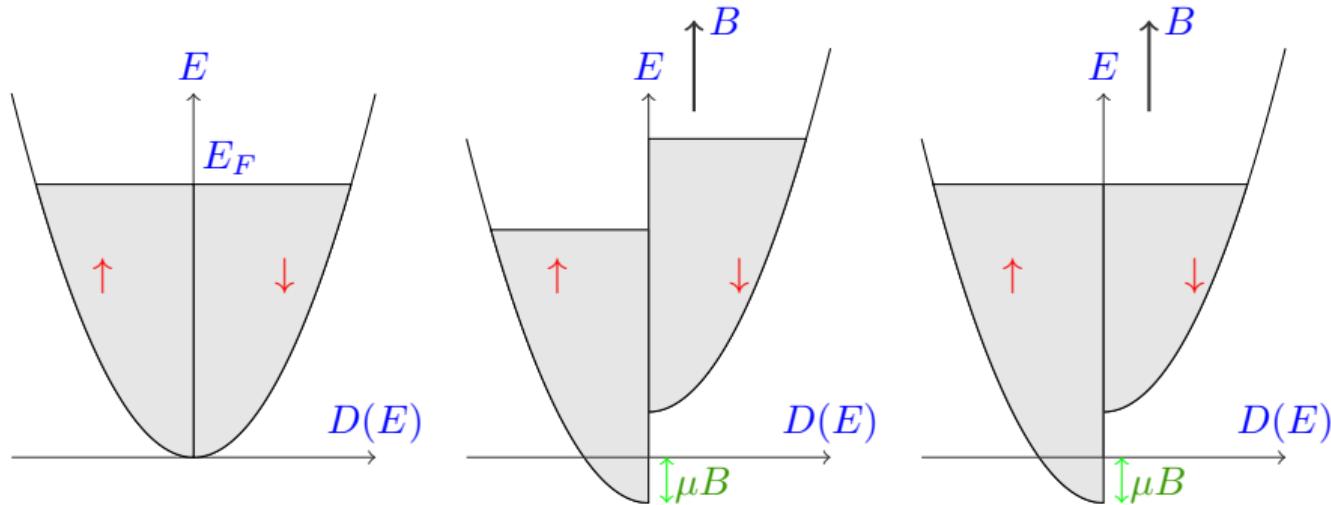
- Because of field  $B$ ,  $\uparrow$  electrons are lowered in energy by  $[\mu\mathbf{B}]$ .
- The number of  $\uparrow$  electrons in excess is  $[\mu\mathbf{B}]D(E_F)$ , the excess magnetic moment is thus  $M = \mu[\mu\mathbf{B}]D(E_F)$ .

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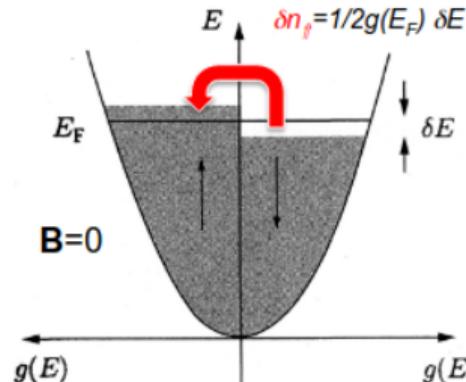
# Non-interacting system (Aluminum)



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- The number of  $\uparrow$  electrons in excess is  $[\mu B]D(E_F)$ , the excess magnetic moment is thus  $M = \mu[\mu B]D(E_F)$ .
- Pauli Paramagnetism** (susceptibility independent of temperature is  $\mu^2 D(E_F)$ )
- For simple metals (Na, Al): Pauli paramagnetism dominates.

## Completely delocalized electrons: Ferromagnetism

What happens if  $B=0$ ?

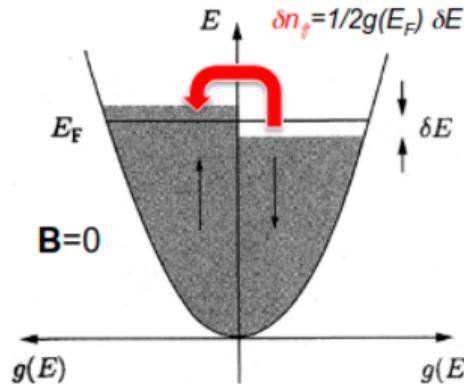


Let's take into account exchange, and compute the energy of the ferromagnetic state.

- Increase of number of  $\uparrow$  electrons  $\delta N$  in the energy  $\delta E$ , so an energy of  $\delta N \delta E$  with  $\delta N = \delta E D(E_F)/2$ .

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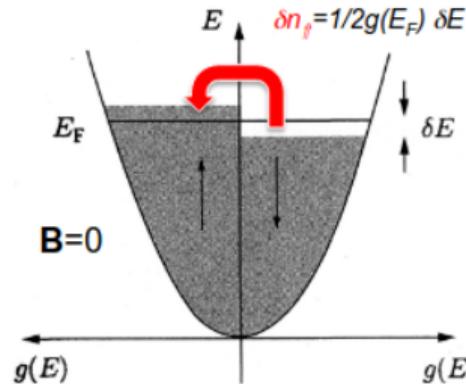


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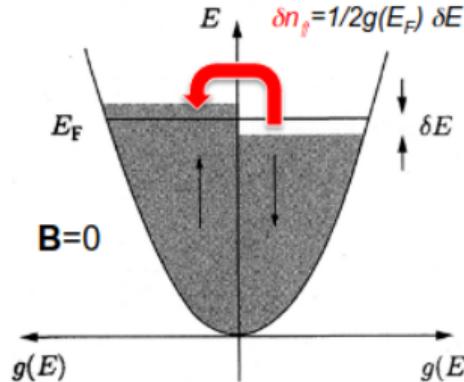


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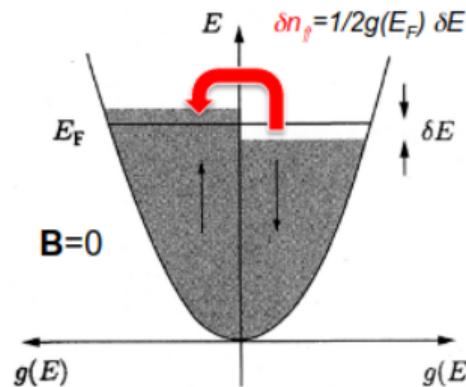


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- Ferromagnetism is stable if  $\delta 2N^2/D(E_F) - 4(\delta N)^2 J < 0$ , ie  $1/D(E_F) - 2J < 0$ .

## Completely delocalized electrons: Ferromagnetism

What happens if  $B=0$ ?

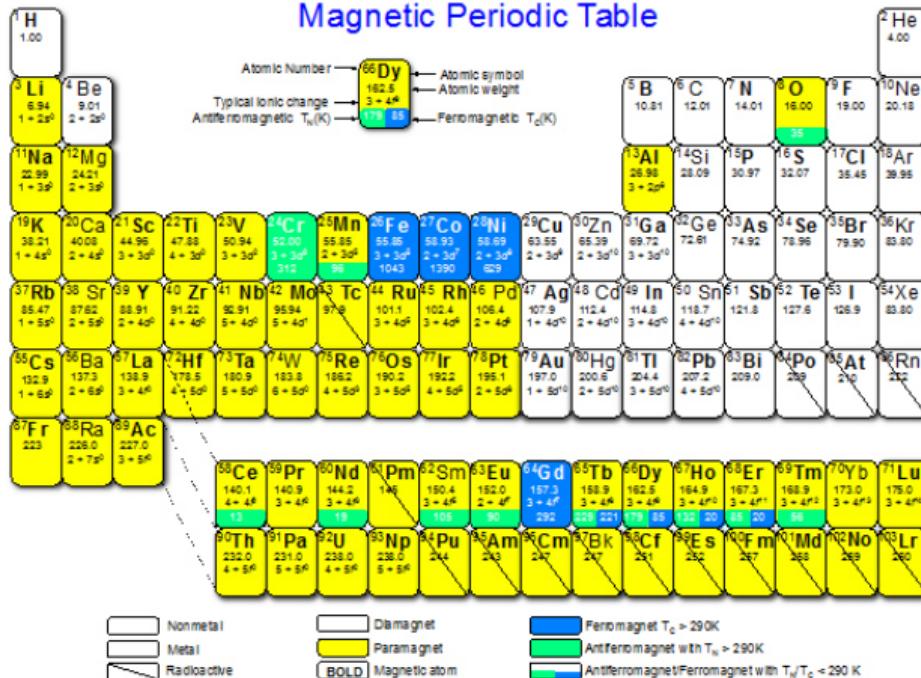


Let's take into account exchange, and compute the energy of the ferromagnetic state.

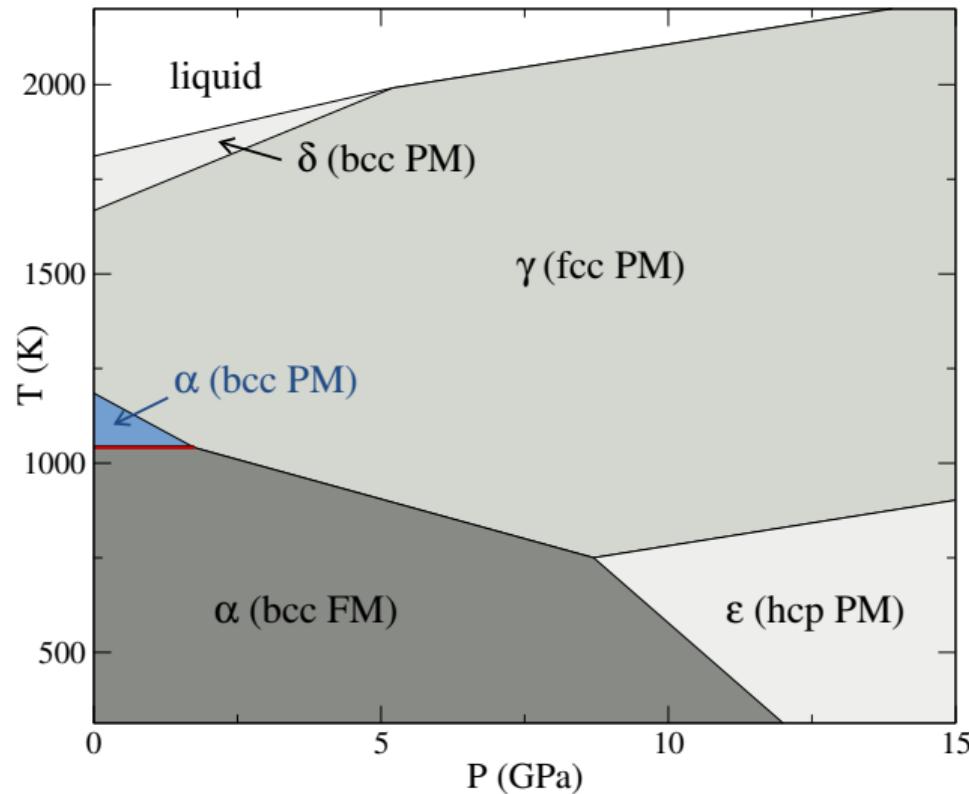
- Increase of number of  $\uparrow$  electrons  $\delta N$  in the energy  $\delta E$ , so an energy of  $\delta N \delta E$  with  $\delta N = \delta E D(E_F)/2$ .
- Exchange energy is  $J[N_{\uparrow}^2 + N_{\downarrow}^2]$ . It increases by  $4(\delta N)^2 J$
- Ferromagnetism is stable if  $\delta 2N^2/D(E_F) - 4(\delta N)^2 J < 0$ , ie  $1/D(E_F) - 2J < 0$ .

It is shown that if the density of states is very large, and the exchange is important, then ferromagnetism appears.

# Magnetism in the periodic table

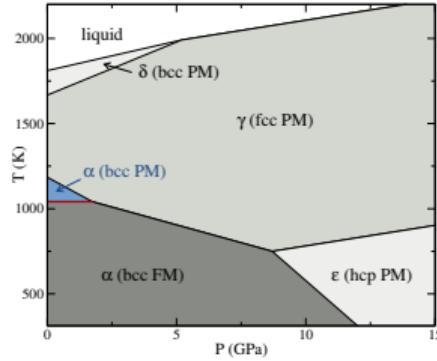
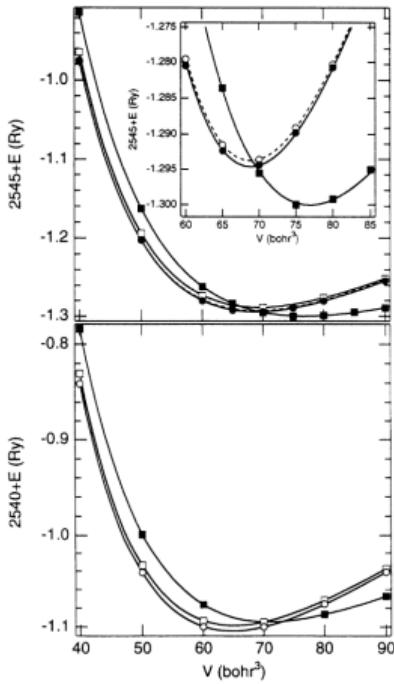


# Example of Iron

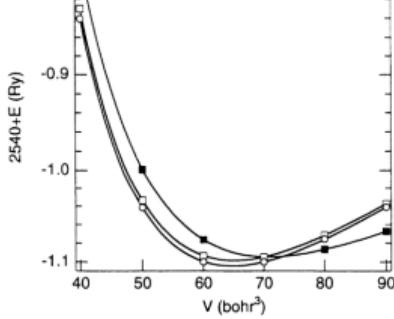


# Role of magnetism and functional in Iron

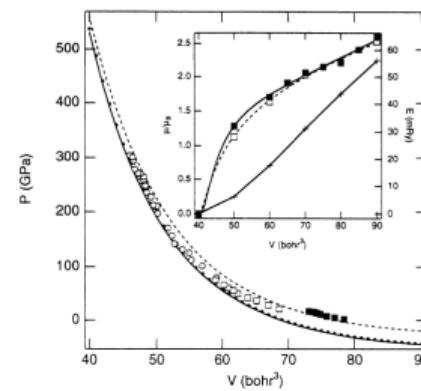
GGA



LDA



L. Stixrude, R. E. Cohen, and D. J. Singh,  
Phys. Rev. B 50, 6442  
(1994).

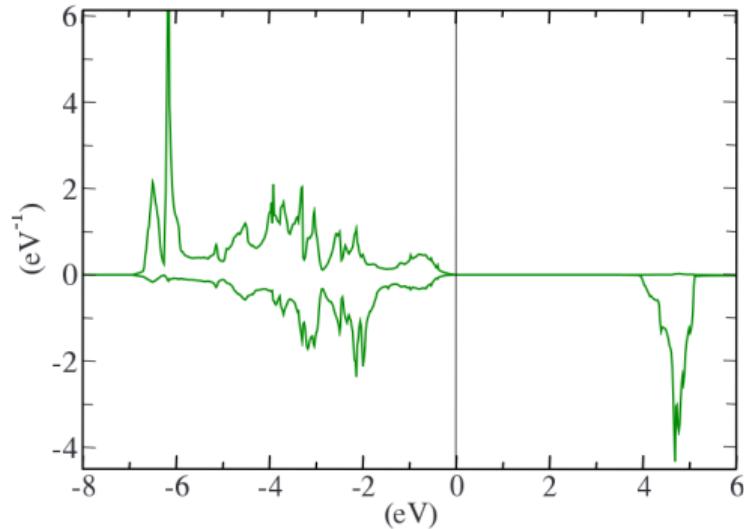


$E(V)$  and  $P(V)$  for bcc (solid squares), fcc (open squares) ideal hcp (open circles)

## Success of the theory to describe ordered magnetic moment

- Fe bcc, magnetic moment (2.2  $\mu_B$ ) well described in GGA.
- $\text{UO}_2$ , magnetic moment well described in DFT+U.
- $\Rightarrow$  ordered phases well described in DFT/DFT+U

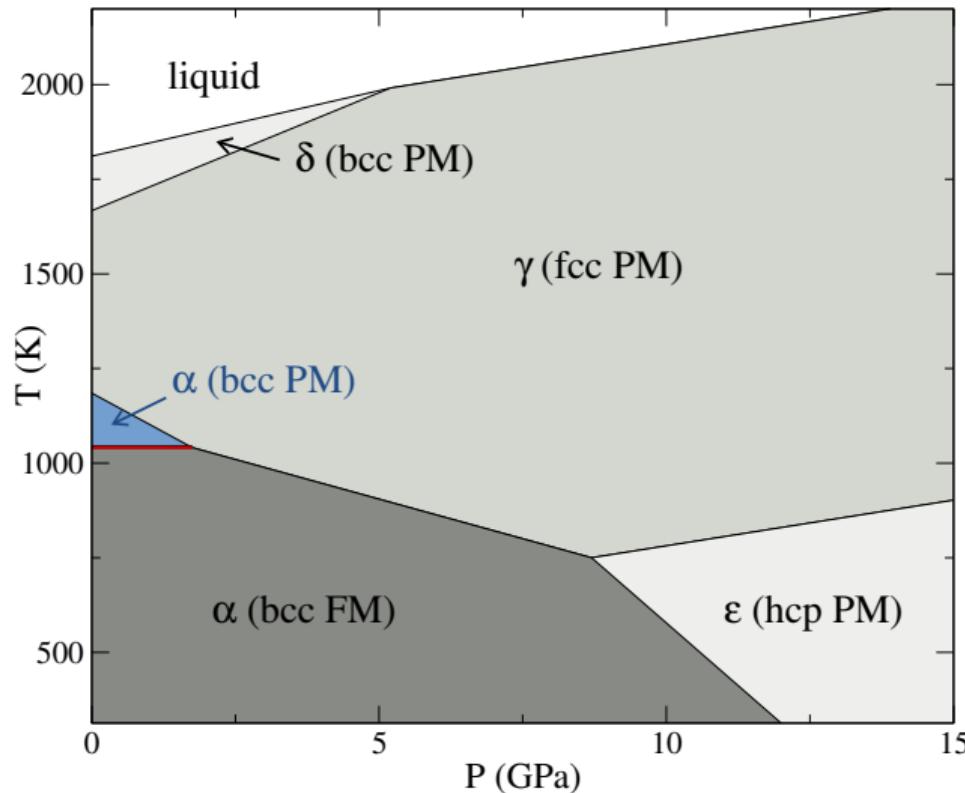
# NiO: magnetic moment and density of states.



2. (Color online) Projected  $d$ -density of states of NiO

	Expt. <sup>a</sup>	PAW <sup>b</sup>	
$\mu_s$	1.64–1.90	LDA	LDA+U
Gap (eV)	4.0–4.3	0.5	3.3

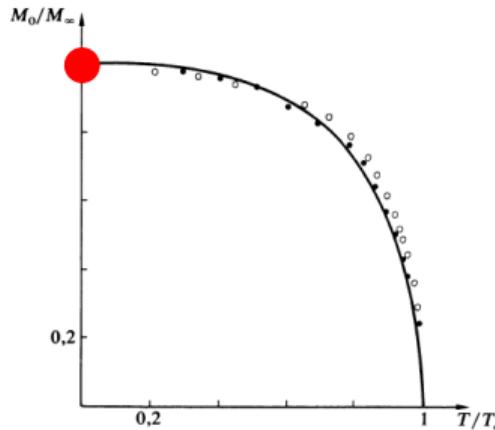
# Example of Iron



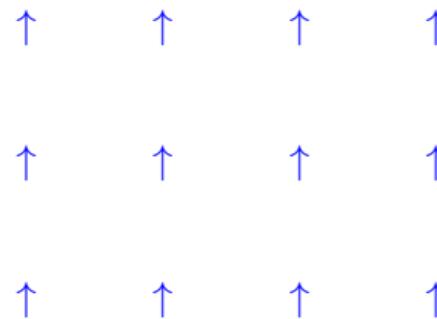
# Curie temperature

- Ferromagnetism

- At zero temperature: large magnetic moment  
(magnetic moments of iron aligned).

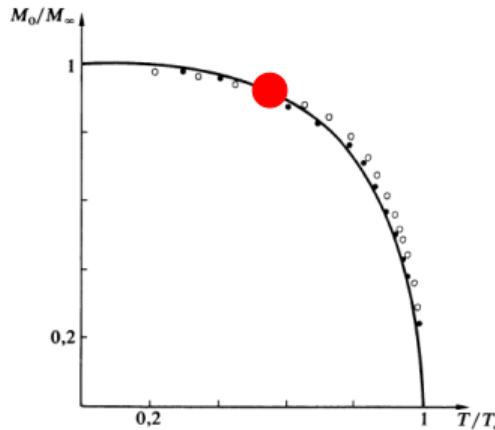


Ronds vides: fer  
Ronds pleins: cobalt et nickel



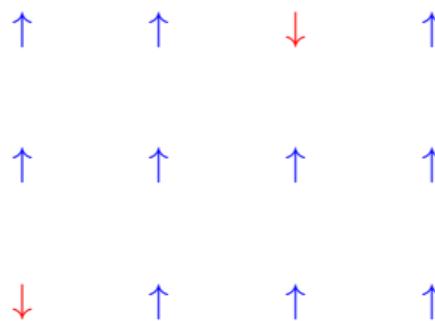
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- Ferromagnetism



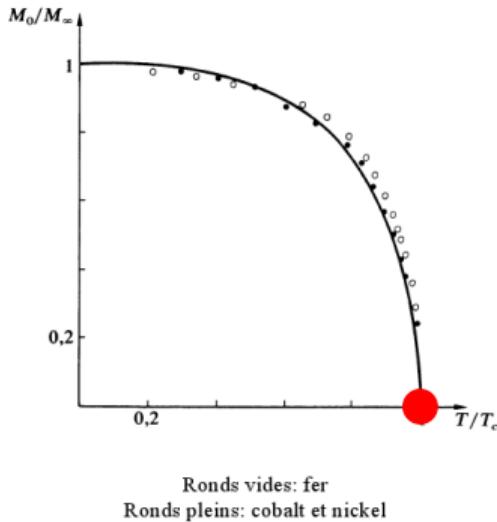
Ronds vides: fer  
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- At zero temperature: large magnetic moment (magnetic moments of iron aligned).
- Temperature increases, magnetic moment decreases (thermal agitation).



# Curie temperature

- Ferromagnetism

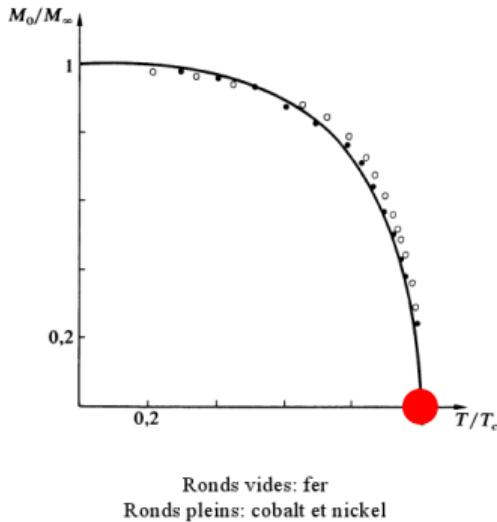


- At zero temperature: large magnetic moment (magnetic moments of iron aligned).
- Temperature increases, magnetic moment decreases (thermal agitation).
- Curie temperature: disappearance of the magnetic moment (disordered moments).



# Curie temperature

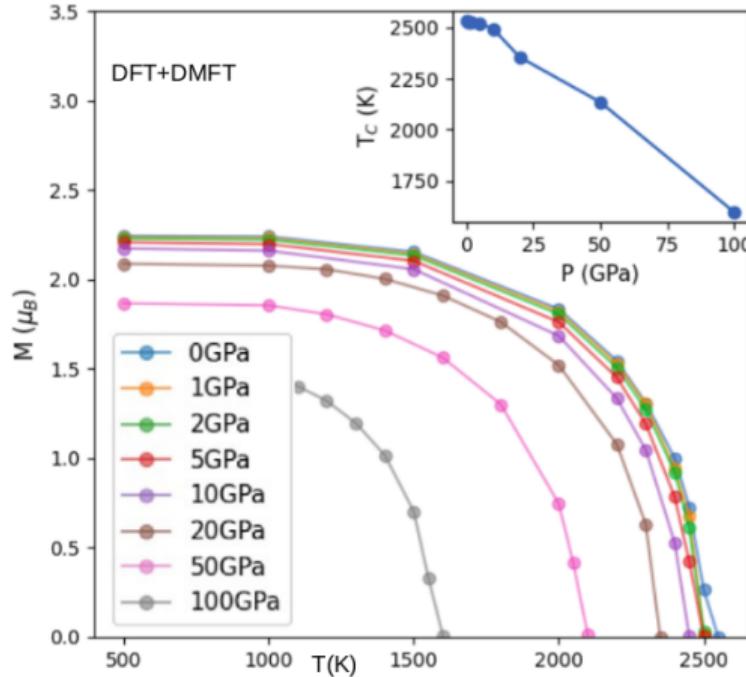
- Ferromagnetism



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- Temperature increases, magnetic moment decreases (thermal agitation).
- Curie temperature: disappearance of the magnetic moment (disordered moments).



# Curie temperature with DFT+DMFT in Abinit

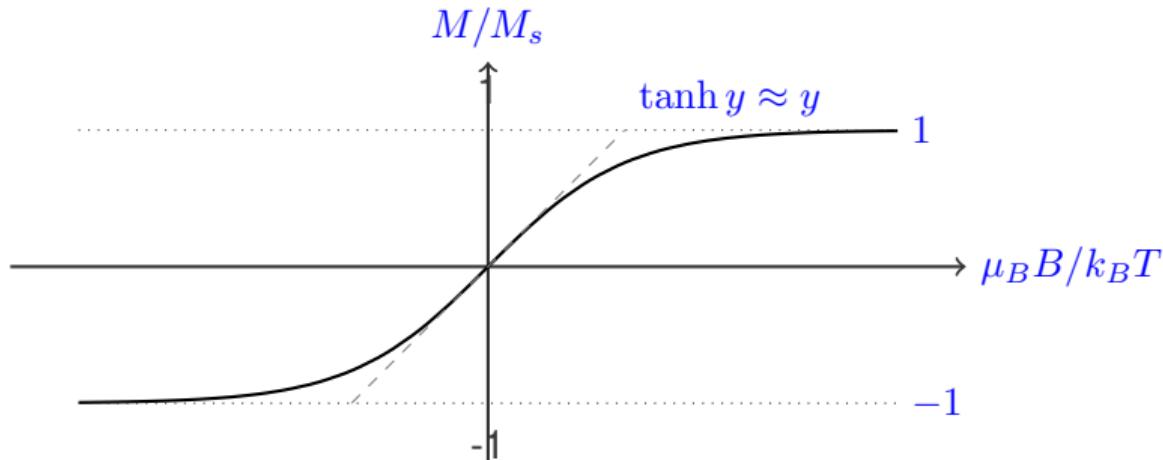


# Curie paramagnetism

For a system of spins in a magnetic field. There is a competition between magnetic order and temperature. The average moment is, for a system where the magnetic moments are either  $-\mu_B$  or  $\mu_B$  (assuming  $g = 2$ ) with corresponding energies  $\mu_B B$  or  $-\mu_B B$ .

Thus

$$\langle g\mu_B m_J \rangle = \frac{-\mu_B e^{\mu_B B/k_B T} + \mu_B e^{-\mu_B B/k_B T}}{e^{\mu_B B/k_B T} + e^{-\mu_B B/k_B T}} = \mu_B \tanh\left(\frac{\mu_B B}{k_B T}\right)$$



# Input variables

case	nsppol	nspinor	nspden	KS function	density
non-magnetic	1	1	1	$\Psi$	$n(\mathbf{r})$
collinear FM	2	1	2	$\Psi_{\uparrow}, \Psi_{\downarrow}$	$n_{\uparrow}(\mathbf{r}) n_{\downarrow}(\mathbf{r})$
collinear AFM	1	1	2	$\Psi_{\uparrow}$	$n_{\uparrow}(\mathbf{r}) n_{\downarrow}(\mathbf{r})$
non-collinear	1	2	4	$\Psi_{\uparrow} \uparrow\rangle + \Psi_{\downarrow} \downarrow\rangle$	$n_{\alpha,\beta}(\mathbf{r})$

In ABINIT, the variables are defined as follows:

- nsppol: Number of spin-polarized wavefunctions (1 for non-spin-polarized, 2 for collinear spin-polarized calculations).
- nspinor: Number of spinor components of a single wave functions (1 without spin-orbit coupling, 2 with spin-orbit coupling).
- nspden: Number of density components (1 for non-magnetic, 2 for collinear magnetic, and 4 for non-collinear magnetic calculations with spin-orbit coupling).

# Magnetism in DFT: non collinear case

- Spin-Orbit Coupling: Relativistic effect that originates from the Dirac Equation.
- Looks like a coupling between spin and orbital momentum

$$\frac{\hbar}{(2mc)^2} \underline{\sigma} \cdot (\nabla V(\mathbf{r}) \times \mathbf{p}) = \frac{\hbar}{(2mc)^2} \frac{1}{r} \frac{\partial V(r)}{\partial r} \underline{\sigma} \cdot (\mathbf{r} \times \mathbf{p}) = \xi \underline{\sigma} \cdot \mathbf{L},$$

with the Pauli matrices defined as

$$\underline{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \underline{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \underline{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

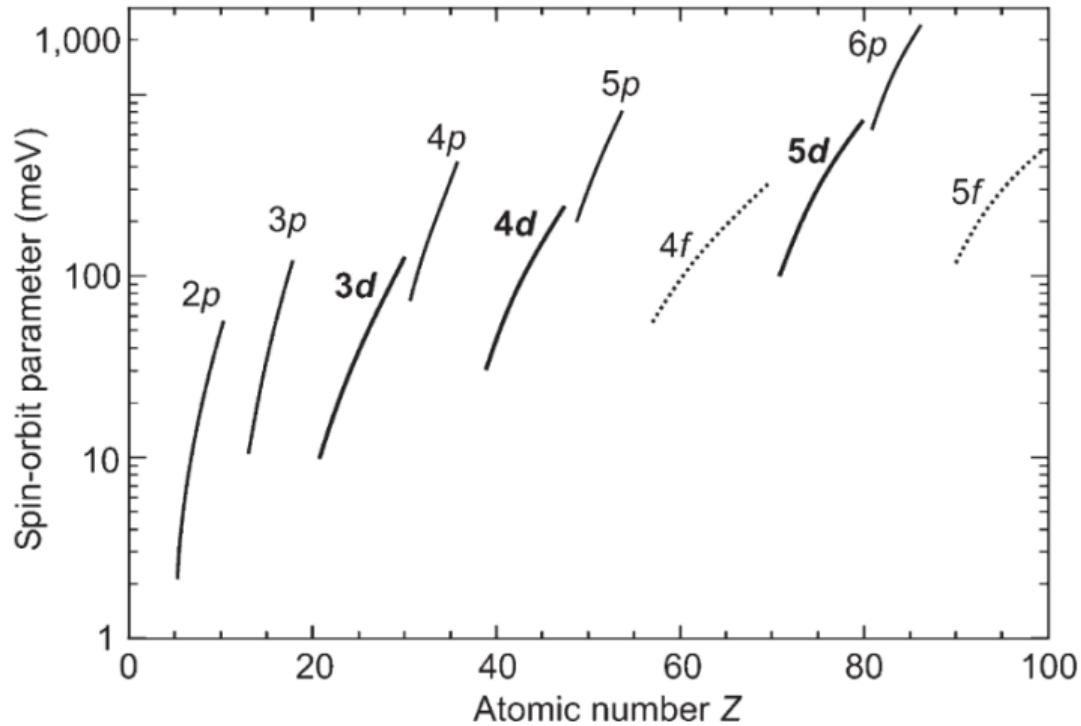
Spin is not a good quantum number

$$n(\mathbf{r}) = \begin{pmatrix} n^{\uparrow\uparrow}(\mathbf{r}) & n^{\uparrow\downarrow}(\mathbf{r}) \\ n^{\downarrow\uparrow}(\mathbf{r}) & n^{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix}$$

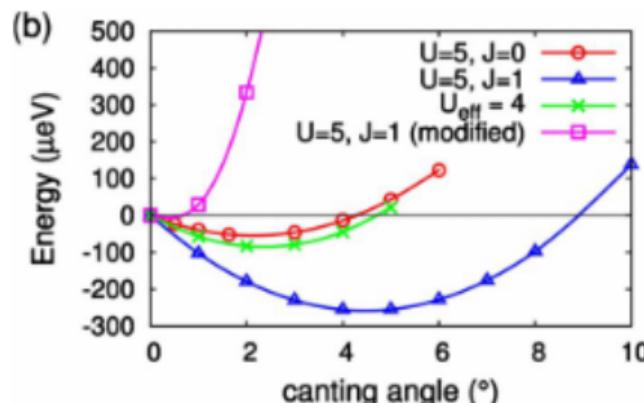
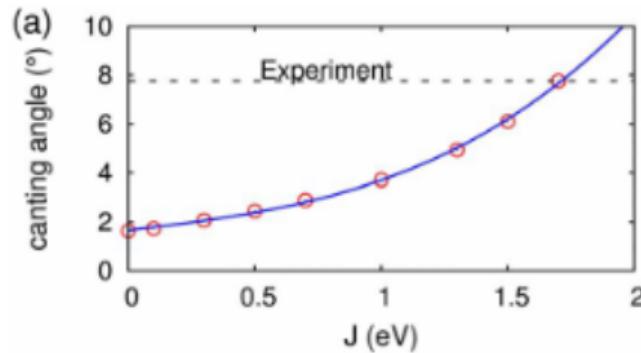
$$\vec{m}(r) = \sum_{\alpha, \beta} n^{\alpha, \beta}(\mathbf{r}) \cdot \vec{\sigma}^{\alpha, \beta}$$

$$\mathbf{B}_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n, \mathbf{m}]}{\delta \mathbf{m}(\mathbf{r})}$$

# Spin orbit coupling strength

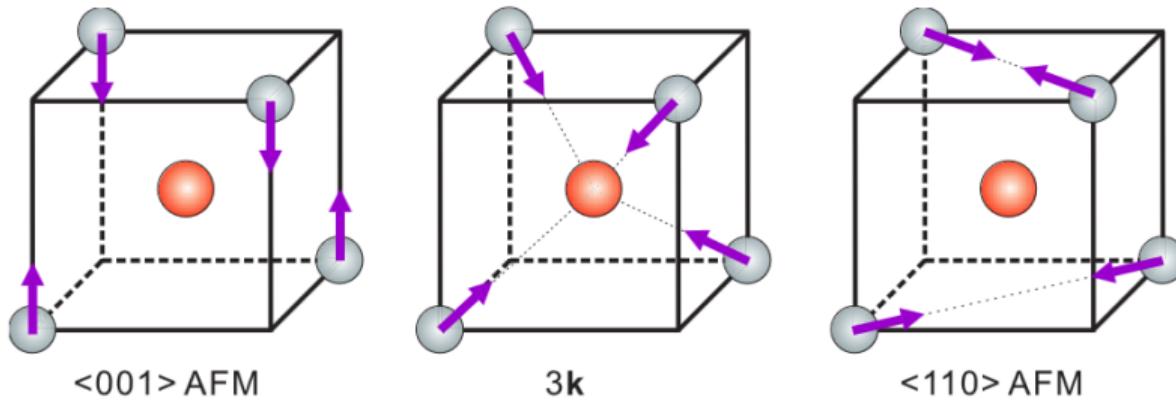


# Canting in LiNiPO<sub>4</sub> (cathode material)



$$V_{i,j} = \begin{pmatrix} V_{i,j}^{\uparrow\uparrow} & V_{i,j}^{\uparrow\downarrow} \\ V_{i,j}^{\downarrow\uparrow} & V_{i,j}^{\downarrow\downarrow} \end{pmatrix},$$

# Non collinear magnetism in $\text{UO}_2$



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# Conclusion

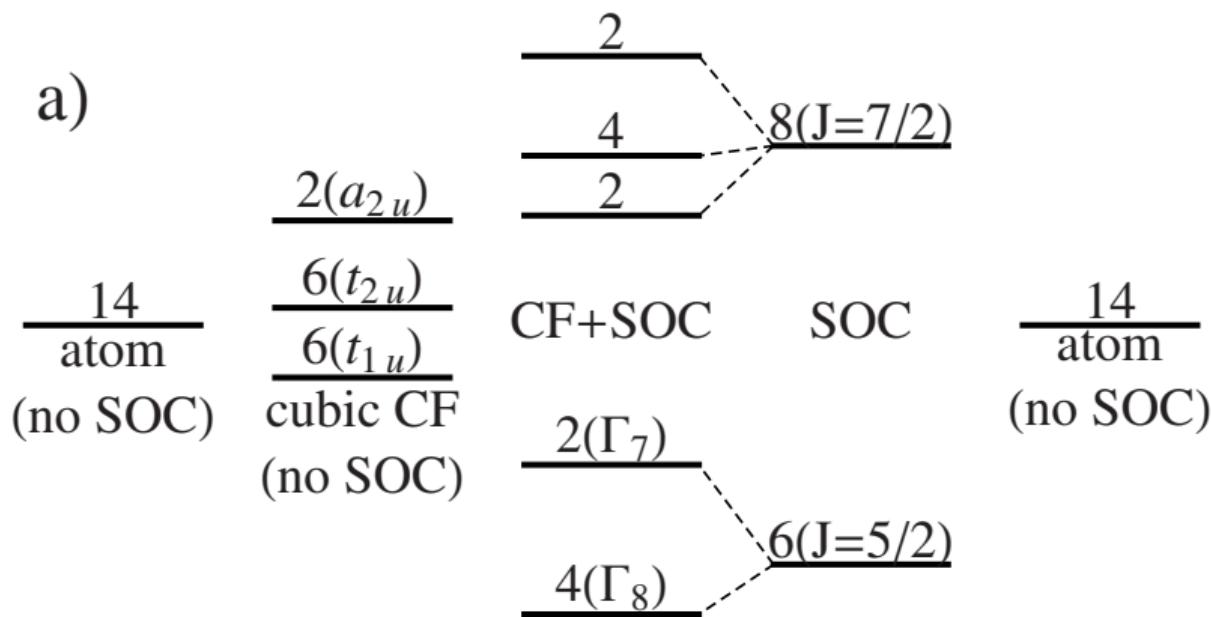
## Magnetism

- Ordered magnetism can only exist in the presence of **interactions between electrons**.
- Magnetism informs us about the **localization of electrons**.

## Magnetism in ABINIT: functionalities

- Collinear and non collinear magnetism
- Magnetic space groups
- Linear Response to a magnetic field (DFPT)
- Spin (zeemanfield) and orbital (orbmag) response to a magnetic field (eg. in NMR)
- Constrained DFT at fixed magnetic moment (magconon)
- DFT+U, Hybrid functionals can be important for magnetic systems
- DFT+DMFT for Curie paramagnetism

# Non collinear magnetism in $\text{UO}_2$



# Canting in $\text{UO}_2$

