

Magnetism and ABINIT

Bernard Amadon

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

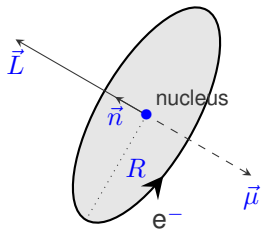
A brief historical summary of magnetism research.

- Magnetite Fe_3O_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°C .



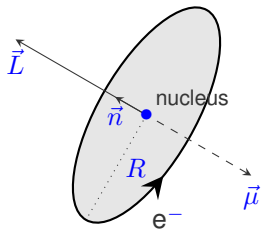
- 1820: Oersted: an electric loop deflects a magnetized needle.
- 1821: Faraday discovered induction (responsible for diamagnetism in solids).
- 1863: Maxwell's equations (link magnetic and electric fields).
- 1895: Lorentz wrote the expression for the magnetic force.

Magnetic moment and electric current



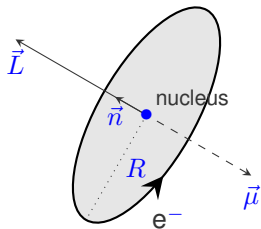
- The rotation of the electron creates an angular momentum $\vec{L} = \vec{r} \times \vec{p}$ and an atomic magnetic moment $\vec{\mu} = \frac{1}{2}e\vec{r} \times \vec{v}$.

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 $\vec{\mu} = \frac{1}{2}e\vec{r} \times \vec{v}$.
- $\vec{\mu} = \gamma\vec{L}$ with γ the gyromagnetic factor equal to $\frac{e}{2m}$.

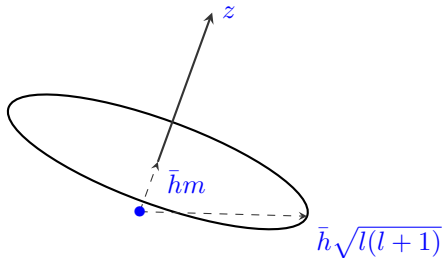
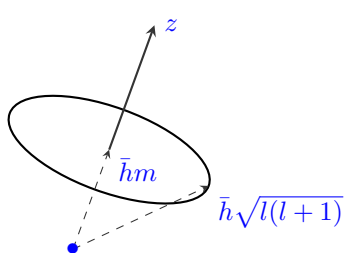
Magnetic moment and electric current



- The rotation of the electron creates an angular momentum $\vec{L} = \vec{r} \times \vec{p}$ and an atomic magnetic moment $\vec{\mu} = \frac{1}{2}e\vec{r} \times \vec{v}$.
- $\vec{\mu} = \gamma\vec{L}$ with γ the gyromagnetic factor equal to $\frac{e}{2m}$.
- \vec{L} is the orbital angular momentum.

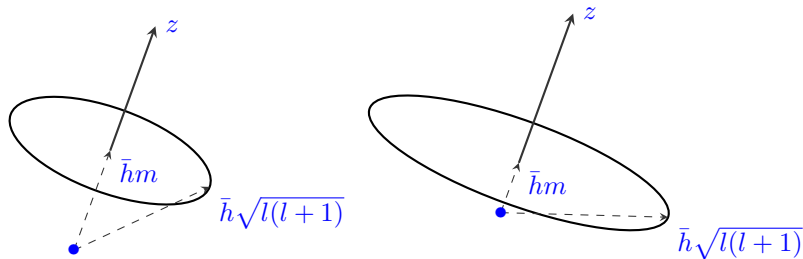
Quantization of angular momentum in quantum mechanics

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



Quantization of angular momentum in quantum mechanics

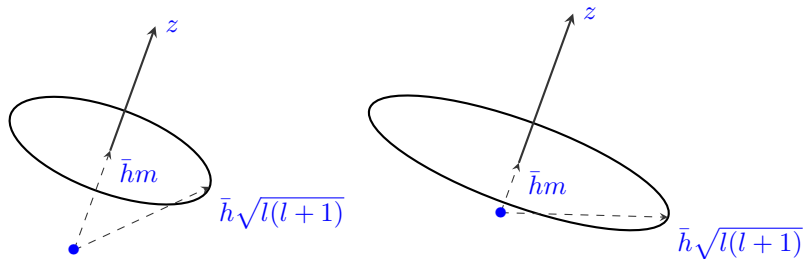
- Atomic physics: The measured angular momentum is quantized in quantum mechanics.
 - $l = 3$: f orbitals (Pu). $m = -3, -2, -1, 0, 1, 2, 3$



- $\mu_z = \gamma L_z = \gamma \bar{h}m$

Quantization of angular momentum in quantum mechanics

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



- $\mu_z = \gamma L_z = \gamma \hbar m$
- $\mu_z = -\mu_B m$. $\mu_B = \frac{e\hbar}{2m}$ 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.
- $s = 0.5$, $m_s = -0.5, 0.5$. Two possible values for the projection of the spin angular momentum:
 - $s_z = +\frac{\hbar}{2}$
 - $s_z = -\frac{\hbar}{2}$
- $\mu_z^s = -2\mu_B m_s$

⇒ **Electronic magnetism has two origins: spin and orbital moment.**

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.
- $s = 0.5$, $m_s = -0.5, 0.5$. Two possible values for the projection of the spin angular momentum:

- $s_z = +\frac{\hbar}{2}$

- $s_z = -\frac{\hbar}{2}$

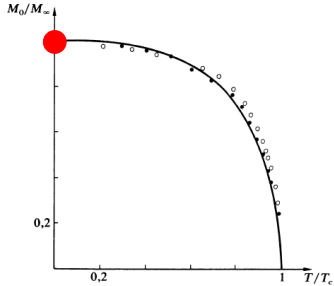
- $\mu_z^s = -2\mu_B m_s$

⇒ **Electronic magnetism has two origins: spin and orbital moment.**

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

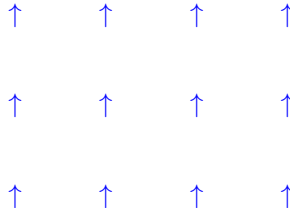
Curie temperature

- Ferromagnetism



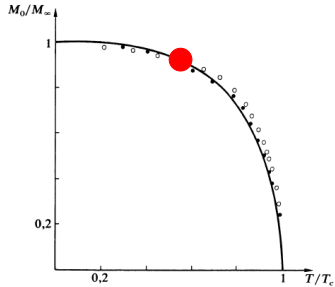
Ronds vides: fer
Ronds pleins: cobalt et nickel

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



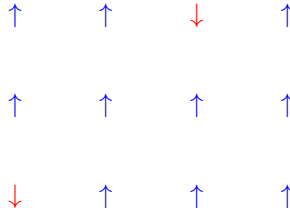
Curie temperature

- Ferromagnetism



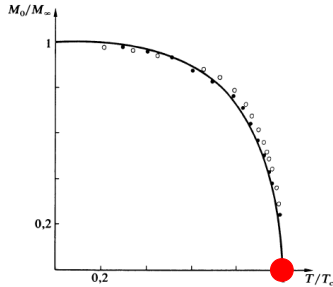
Ronds vides: fer
Ronds pleins: cobalt et nickel

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



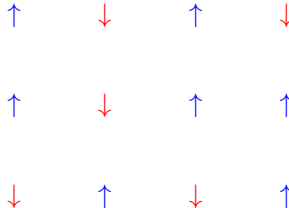
Curie temperature

- Ferromagnetism



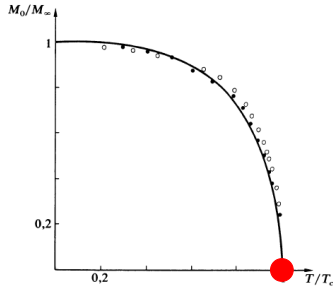
Ronds vides: fer
Ronds pleins: cobalt et nickel

- 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).



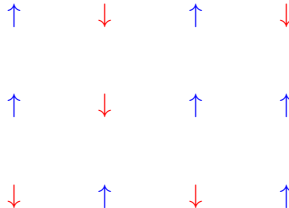
Curie temperature

- Ferromagnetism



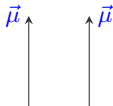
Ronds vides: fer
Ronds pleins: cobalt et nickel

- 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).



From the atomic magnetic moment to ferromagnetism

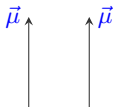
⇒ How do atomic magnetic moments order within solids?



- The dipole-dipole interaction of two magnetic moments μ_B separated by 1\AA is about 1K.

From the atomic magnetic moment to ferromagnetism

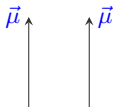
⇒ How do atomic magnetic moments order within solids?



- The dipole-dipole interaction of two magnetic moments μ_B separated by 1\AA is about 1K.
- However, the Curie temperature of magnetite is 860 K. There must be another origin for the magnetic order.

From the atomic magnetic moment to ferromagnetism

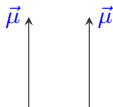
⇒ How do atomic magnetic moments order within solids?



- The dipole-dipole interaction of two magnetic moments μ_B separated by 1\AA is about 1K.
- However, the Curie temperature of magnetite is 860 K. There must be another origin for the magnetic order.
- ⇒ Magnetic moments couple through another mechanism without direct magnetic interaction!

From the atomic magnetic moment to ferromagnetism

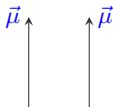
⇒ How do atomic magnetic moments order within solids?



- The dipole-dipole interaction of two magnetic moments μ_B separated by 1\AA is about 1K.
- However, the Curie temperature of magnetite is 860 K. There must be another origin for the magnetic order.
- ⇒ Magnetic moments couple through another mechanism without direct magnetic interaction!
- ⇒ Weiss, in 1907, postulated the presence of an internal field (*champ moléculaire*) in the material to explain this.

From the atomic magnetic moment to ferromagnetism

⇒ How do atomic magnetic moments order within solids?



- The dipole-dipole interaction of two magnetic moments μ_B separated by 1\AA is about 1K.
- However, the Curie temperature of magnetite is 860 K. There must be another origin for the magnetic order.
- ⇒ Magnetic moments couple through another mechanism without direct magnetic interaction!
- ⇒ Weiss, in 1907, postulated the presence of an internal field (*champ moléculaire*) in the material to explain this.

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).

Interaction between magnetic moments: exchange

- We consider two electrons, which are in the orbitals ϕ_a and ϕ_b .

Interaction between magnetic moments: exchange

- We consider two electrons, which are in the orbitals ϕ_a and ϕ_b .
- The wave function of the ensemble of the two electrons is $|\phi_a\rangle|\phi_b\rangle$.

Interaction between magnetic moments: exchange

- We consider two electrons, which are in the orbitals ϕ_a and ϕ_b .
- The wave function of the ensemble of the two electrons is $|\phi_a\rangle|\phi_b\rangle$.
- Let's write the different possible spin states:
 - $|\phi_a\uparrow\rangle|\phi_b\uparrow\rangle$
 - $|\phi_a\uparrow\rangle|\phi_b\downarrow\rangle$
 - $|\phi_a\downarrow\rangle|\phi_b\uparrow\rangle$
 - $|\phi_a\downarrow\rangle|\phi_b\downarrow\rangle$

Interaction between magnetic moments: exchange

- We consider two electrons, which are in the orbitals ϕ_a and ϕ_b .
- The wave function of the ensemble of the two electrons is $|\phi_a\rangle|\phi_b\rangle$.
- Let's write the different possible spin states:
 - $|\phi_a\uparrow\rangle|\phi_b\uparrow\rangle$
 - $|\phi_a\uparrow\rangle|\phi_b\downarrow\rangle$
 - $|\phi_a\downarrow\rangle|\phi_b\uparrow\rangle$
 - $|\phi_a\downarrow\rangle|\phi_b\downarrow\rangle$
- In quantum mechanics, the wave function is antisymmetric:
 - $\frac{1}{\sqrt{2}} [|\phi_a\uparrow\rangle|\phi_b\uparrow\rangle - |\phi_b\uparrow\rangle|\phi_a\uparrow\rangle]$
 - $\frac{1}{\sqrt{2}} [|\phi_a\uparrow\rangle|\phi_b\downarrow\rangle - |\phi_b\downarrow\rangle|\phi_a\uparrow\rangle]$
 - $\frac{1}{\sqrt{2}} [|\phi_a\downarrow\rangle|\phi_b\uparrow\rangle - |\phi_b\uparrow\rangle|\phi_a\downarrow\rangle]$
 - $\frac{1}{\sqrt{2}} [|\phi_a\downarrow\rangle|\phi_b\downarrow\rangle - |\phi_b\downarrow\rangle|\phi_a\downarrow\rangle]$

Interaction between magnetic moments: exchange

- In quantum mechanics, the wave function is antisymmetric:

- $|\Psi_1\rangle = \frac{1}{\sqrt{2}} [|\phi_a\uparrow\rangle|\phi_b\uparrow\rangle - |\phi_b\uparrow\rangle|\phi_a\uparrow\rangle]$
- $|\Psi_2\rangle = \frac{1}{\sqrt{2}} [|\phi_a\uparrow\rangle|\phi_b\downarrow\rangle - |\phi_b\downarrow\rangle|\phi_a\uparrow\rangle]$
- $|\Psi_3\rangle = \frac{1}{\sqrt{2}} [|\phi_a\downarrow\rangle|\phi_b\uparrow\rangle - |\phi_b\uparrow\rangle|\phi_a\downarrow\rangle]$
- $|\Psi_4\rangle = \frac{1}{\sqrt{2}} [|\phi_a\downarrow\rangle|\phi_b\downarrow\rangle - |\phi_b\downarrow\rangle|\phi_a\downarrow\rangle]$

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:

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

Expanding this, we get:

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

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:

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

Interaction between magnetic moments: exchange

Thus, the expression simplifies to:

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

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

- $|\Psi_1\rangle = \frac{1}{\sqrt{2}} [|\phi_a\uparrow\rangle|\phi_b\uparrow\rangle - |\phi_b\uparrow\rangle|\phi_a\uparrow\rangle]$
- $|\Psi_2\rangle = \frac{1}{\sqrt{2}} [|\phi_a\uparrow\rangle|\phi_b\downarrow\rangle - |\phi_b\downarrow\rangle|\phi_a\uparrow\rangle]$
- $|\Psi_3\rangle = \frac{1}{\sqrt{2}} [|\phi_a\downarrow\rangle|\phi_b\uparrow\rangle - |\phi_b\uparrow\rangle|\phi_a\downarrow\rangle]$
- $|\Psi_4\rangle = \frac{1}{\sqrt{2}} [|\phi_a\downarrow\rangle|\phi_b\downarrow\rangle - |\phi_b\downarrow\rangle|\phi_a\downarrow\rangle]$

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:

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

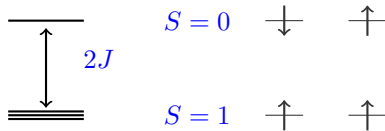
where J is the exchange integral defined by:

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

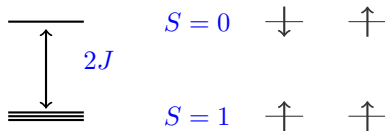
- The diagonalization of the Hamiltonian gives

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

Application: Hund's rule in matter

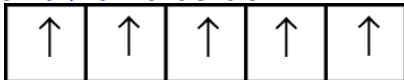


Application: Hund's rule in matter

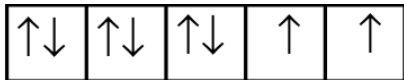


- On the same atom $J > 0$: Hund's rule.

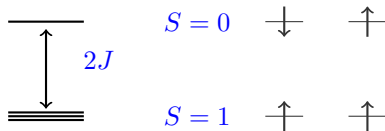
Manganese



Nickel

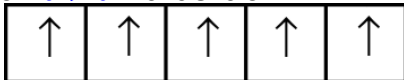


Application: Hund's rule in matter

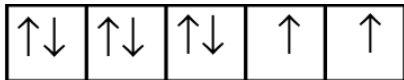


- On the same atom $J > 0$: Hund's rule.

Manganese

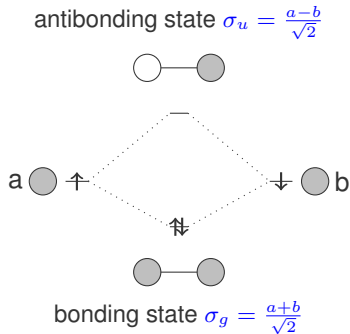


Nickel



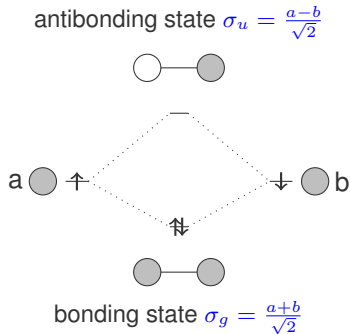
- On different atoms, things are different because chemical bonding can appear, and favor the $S=0$ state.

Interaction between magnetic moments: chemical bond



- An electron can only jump to a neighboring site (forming a chemical bond) if the electron has opposite spin.
- Electrons order antiferromagnetically.

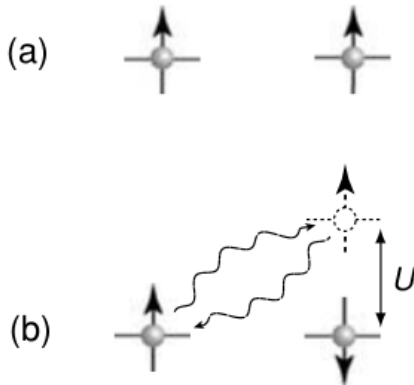
Interaction between magnetic moments: chemical bond



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

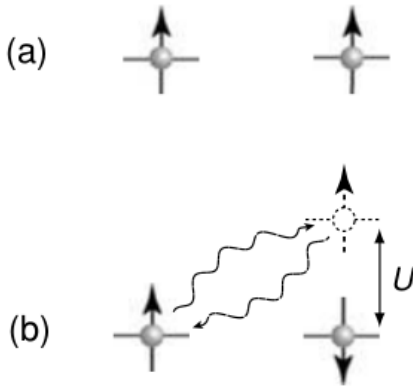
"superexchange" (1)

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



"superexchange" (1)

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

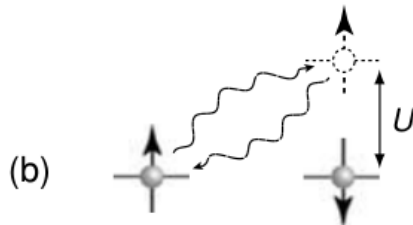


"superexchange" (1)

- Ferromagnetic configuration



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



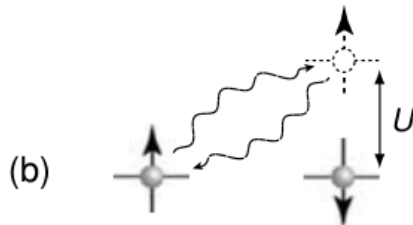
- \Rightarrow Localized electrons: antiferromagnetism.
- \Rightarrow This is not an exchange effect but an effect of hybridization and chemical bonding.

"superexchange" (1)

- Ferromagnetic configuration



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

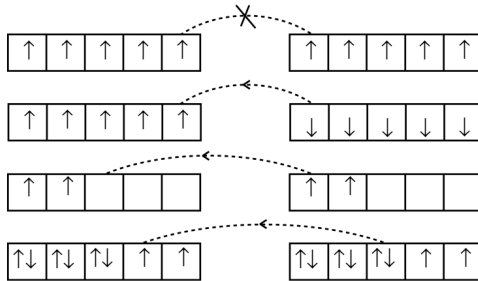


- \Rightarrow Localized electrons: antiferromagnetism.
- \Rightarrow This is not an exchange effect but an effect of hybridization and chemical bonding.
- \Rightarrow Several electrons per atom?

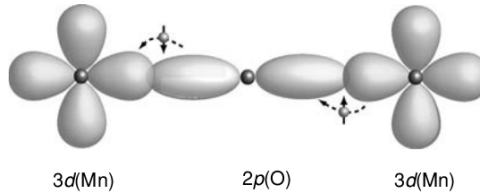
If more orbitals (case of transition metals)

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

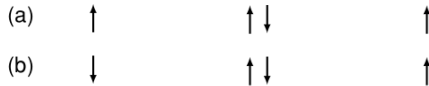
- 7 or 8 d electrons (Co, Ni):
ferromagnetic.



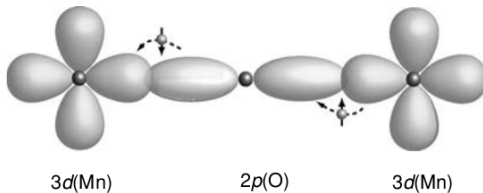
"superexchange" (1): an explanation of antiferromagnetism.



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



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



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



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

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

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 ζ

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

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

ϵ_c^U and ϵ_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 $V_{\text{KS}}^{\sigma}(\mathbf{r})$ 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:)

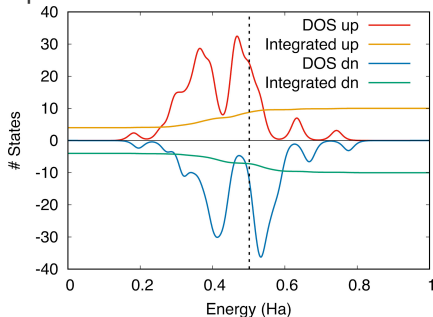
-3.04218	-1.69171	-1.69171	-1.68906	0.27331	0.40348	0.40348
----------	----------	----------	----------	---------	---------	---------

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 m

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, H₂O, Au.

Paramagnetism

Aligns with applied field. *Examples:* Al, O₂.

Ferromagnetism

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



Antiferromagnetism

Antiparallel alignment. *Examples:* MnO, Cr.



Ferrimagnetism

Antiparallel, unequal moments. *Examples:* Fe₃O₄.



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

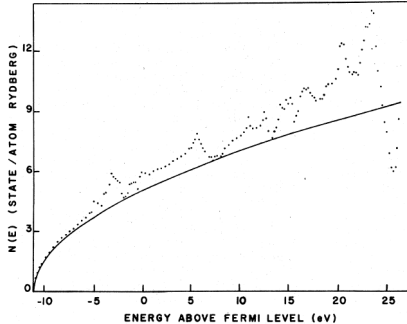
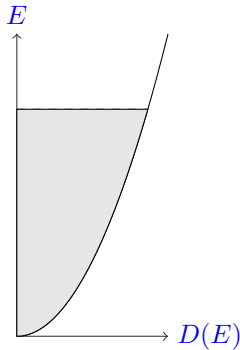
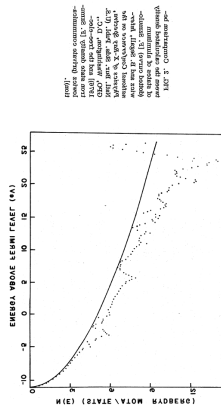


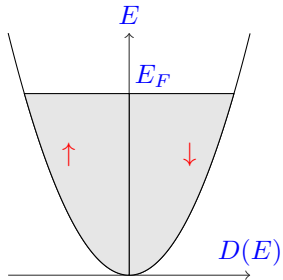
FIG. 2. Comparison between the calculated density of states of aluminum (dotted curve) [F. Szmulowicz and B. Segall, *International Conference on the Physics of X-Ray Spectra*, Natl. Bur. Stds. Publ. (U.S. GPO, Washington, D.C., 1976)] and the free-electron state density [F. Szmulowicz (private communication)].

- 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!

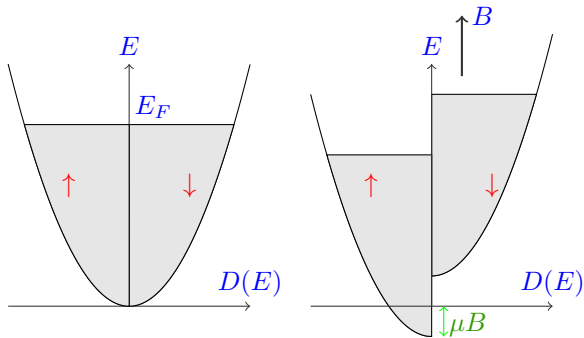
Non-interacting system (Aluminum)



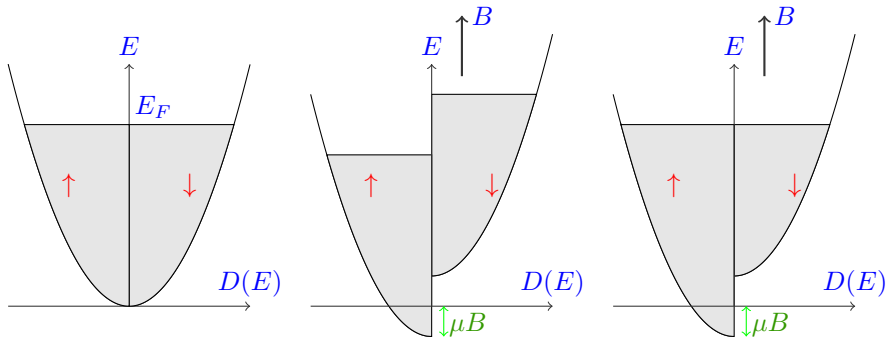
Non-interacting system (Aluminum)



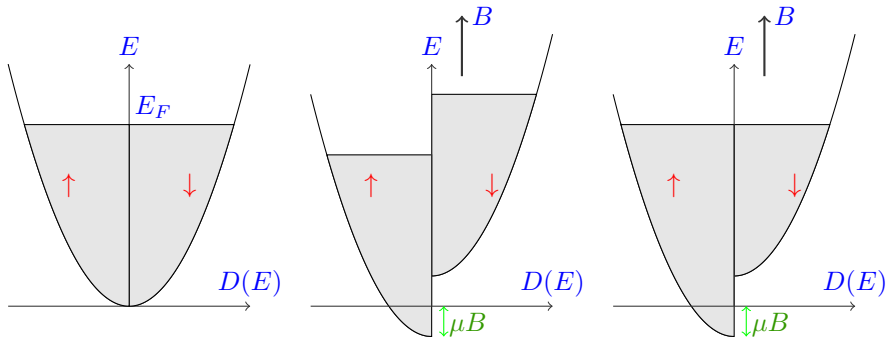
Non-interacting system (Aluminum)



Non-interacting system (Aluminum)

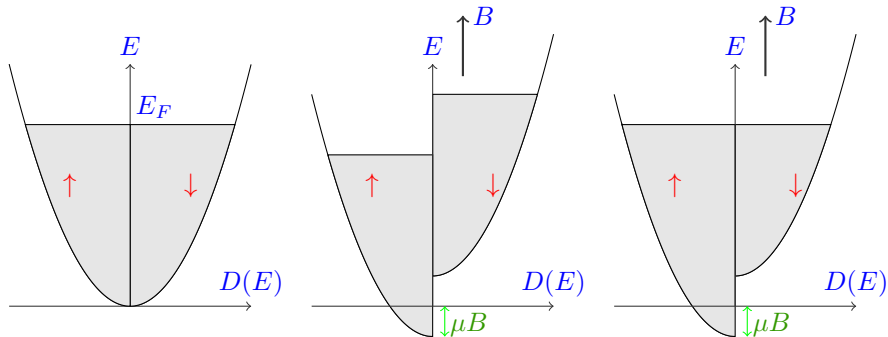


Non-interacting system (Aluminum)



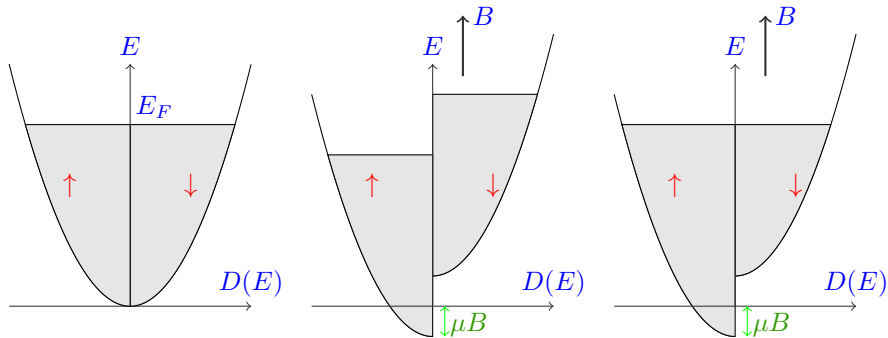
- Because of field B , \uparrow electrons are lowered in energy by $[\mu B]$.

Non-interacting system (Aluminum)



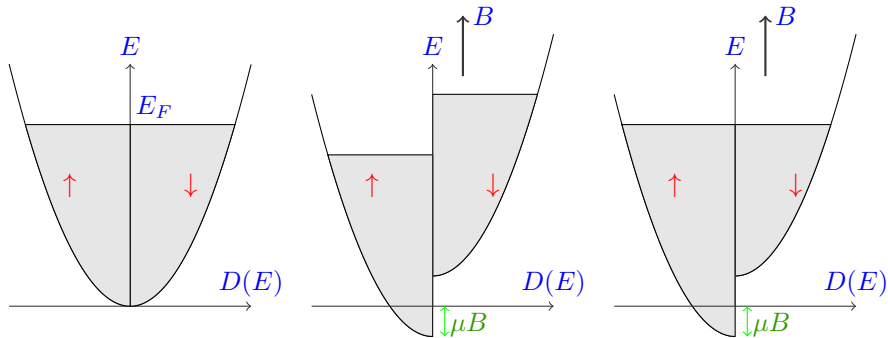
- Because of field B , \uparrow electrons are lowered in energy by $[\mu B]$.
- The number of \uparrow electrons in excess is $[\mu B]D(E_F)$, the excess magnetic moment is thus $M = \mu[\mu B]D(E_F)$.

Non-interacting system (Aluminum)



- Because of field B , \uparrow electrons are lowered in energy by $[\mu B]$.
- 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 $\mu^2 D(E_F)$)

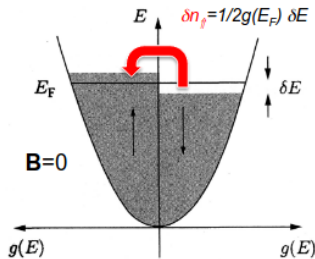
Non-interacting system (Aluminum)



- Because of field B , \uparrow electrons are lowered in energy by $[\mu B]$.
- 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 $B=0$?

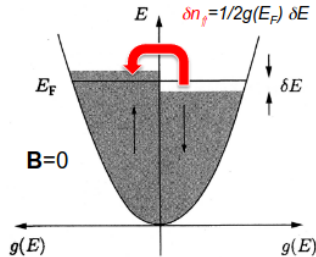


Let's take into account exchange, and compute the energy of the ferromagnetic state.

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

Completely delocalized electrons: Ferromagnetism

What happens if $B=0$?

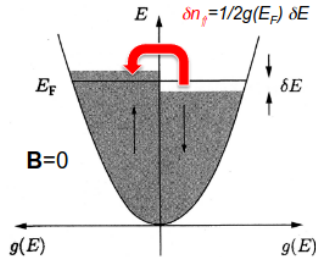


Let's take into account exchange, and compute the energy of the ferromagnetic state.

- Increase of number of \uparrow electrons δN in the energy δE , 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 $4(\delta N)^2 J$

Completely delocalized electrons: Ferromagnetism

What happens if $B=0$?

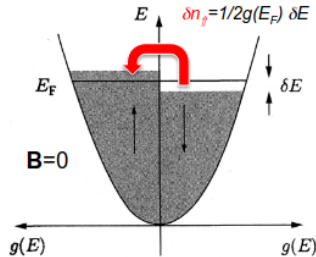


Let's take into account exchange, and compute the energy of the ferromagnetic state.

- Increase of number of \uparrow electrons δN in the energy δE , 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 $4(\delta N)^2 J$

Completely delocalized electrons: Ferromagnetism

What happens if $B=0$?

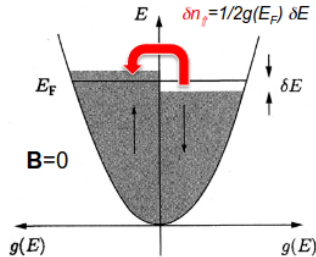


Let's take into account exchange, and compute the energy of the ferromagnetic state.

- Increase of number of \uparrow electrons δN in the energy δE , 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 $1/D(E_F) - 2J < 0$.

Completely delocalized electrons: Ferromagnetism

What happens if $B=0$?

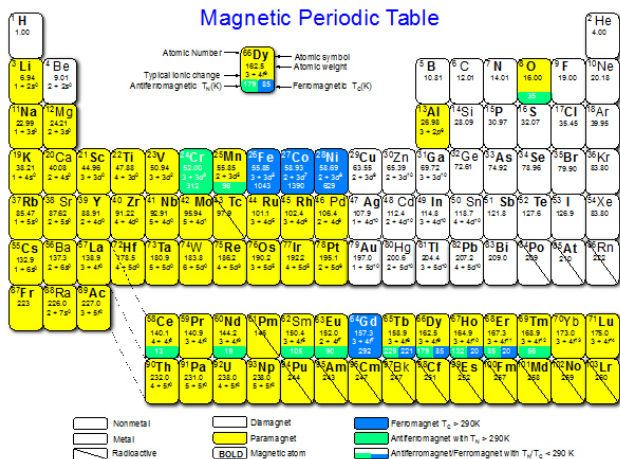


Let's take into account exchange, and compute the energy of the ferromagnetic state.

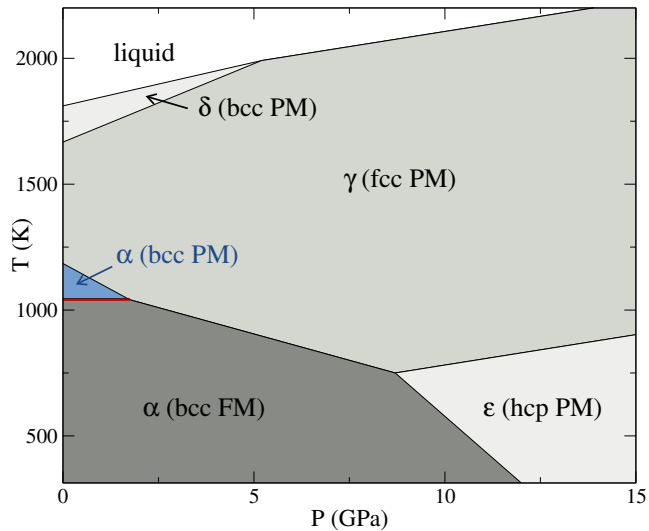
- Increase of number of \uparrow electrons δN in the energy δE , so an energy of $\delta N \delta E$ with $\delta N = \delta E D(E_F)/2$.
- Exchange energy is $J[N_{\uparrow}^2 + N_{\downarrow}^2]$. It increases by $4(\delta N)^2 J$
- Ferromagnetism is stable if $\delta 2N^2/D(E_F) - 4(\delta N)^2 J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

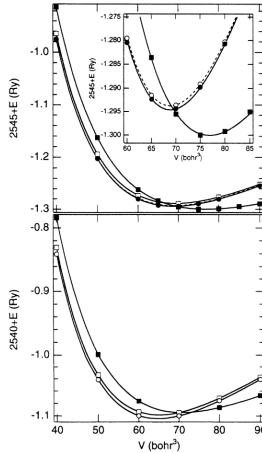


Example of Iron

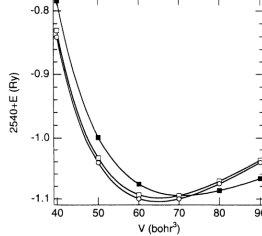


Role of magnetism and functional in Iron

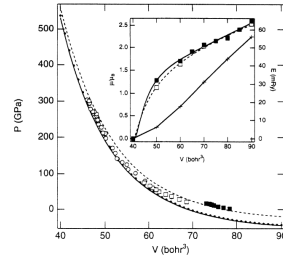
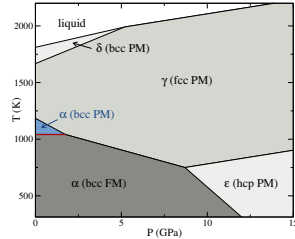
GGA



LDA



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

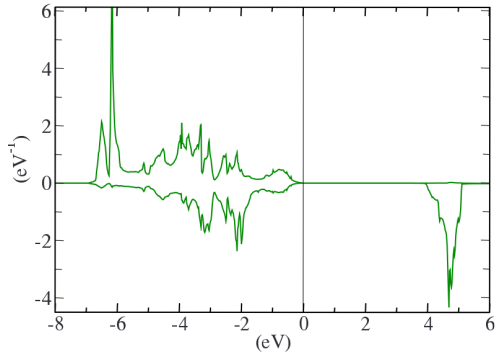


$E(V)$ and $P(V)$ for bcc (solid squares), fcc (open squares) ideal hcp (open circles)

Success of the theory to describe ordered magnetic moment

- Fe bcc, magnetic moment ($2.2 \mu_B$) well described in GGA.
- UO_2 , magnetic moment well described in DFT+U.
- \Rightarrow ordered phases well described in DFT/DFT+U

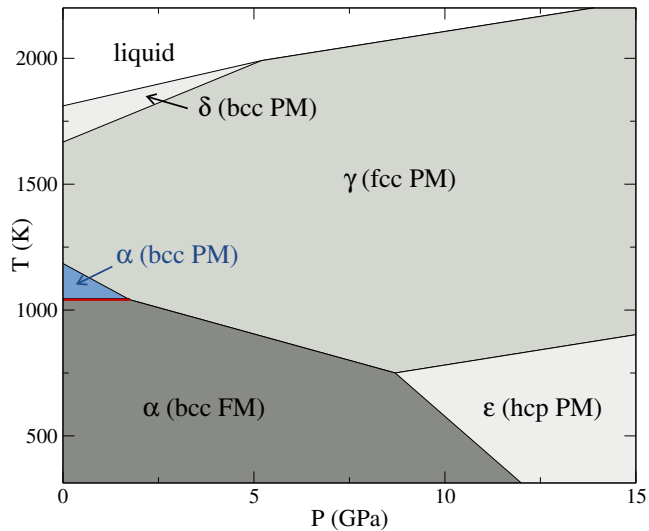
NiO: magnetic moment and density of states.



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

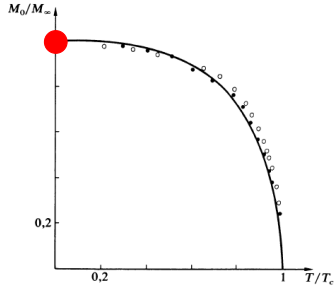
	Expt. ^a	PAW ^b LDA	LDA+U
μ_s	1.64–1.90	1.23	1.74
Gap (eV)	4.0–4.3	0.5	3.3

Example of Iron



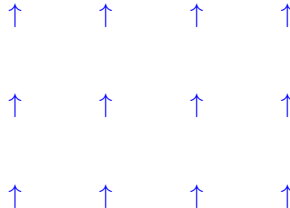
Curie temperature

- Ferromagnetism



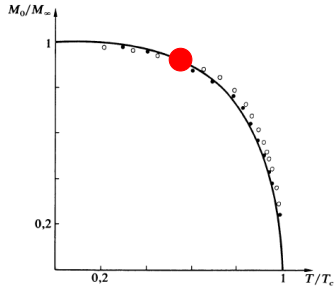
Ronds vides: fer
Ronds pleins: cobalt et nickel

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



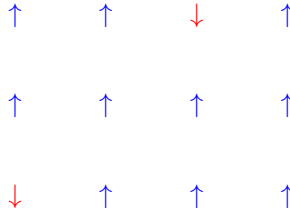
Curie temperature

- Ferromagnetism



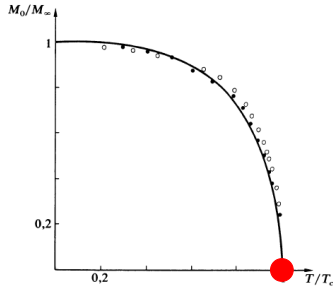
Ronds vides: fer
Ronds pleins: cobalt et nickel

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



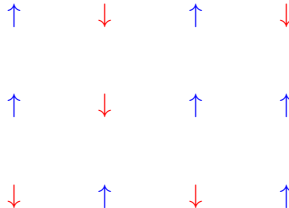
Curie temperature

- Ferromagnetism



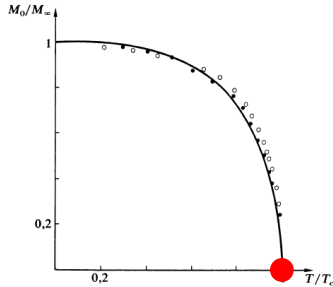
Ronds vides: fer
Ronds pleins: cobalt et nickel

- 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).



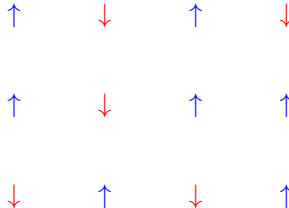
Curie temperature

- Ferromagnetism

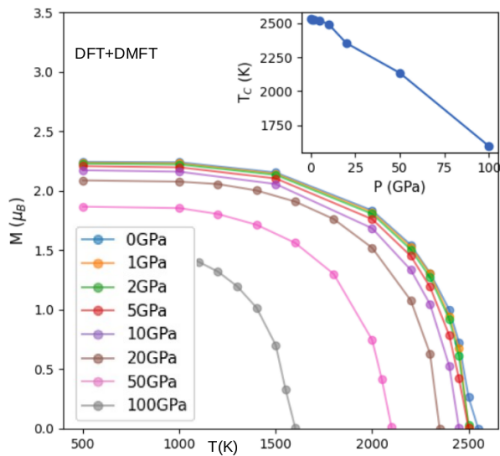


Ronds vides: fer
Ronds pleins: cobalt et nickel

- 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 with DFT+DMFT in Abinit

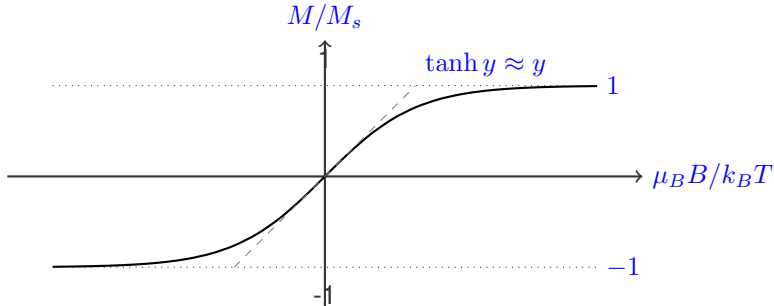


Curie paramagnetism

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 μ_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	Ψ	$n(\mathbf{r})$
collinear FM	2	1	2	$\Psi_{\uparrow}, \Psi_{\downarrow}$	$n_{\uparrow}(\mathbf{r}) \ n_{\downarrow}(\mathbf{r})$
collinear AFM	1	1	2	Ψ_{\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

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

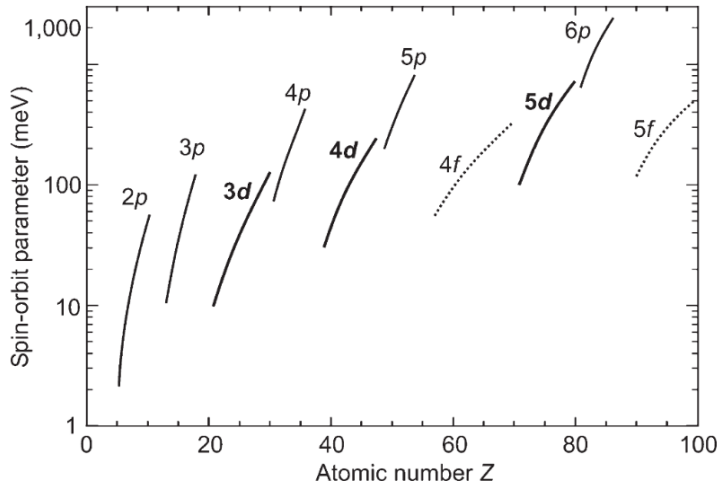
Spin is not a good quantum number

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

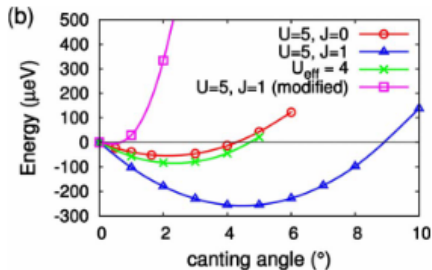
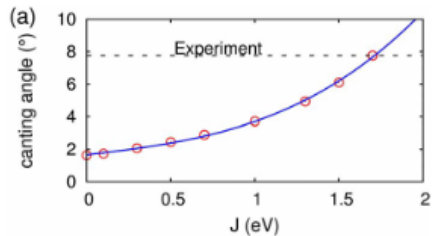
$$\vec{m}(\mathbf{r}) = \sum_{\alpha,\beta} n^{\alpha,\beta}(\mathbf{r}) \cdot \vec{\sigma}^{\alpha,\beta}$$

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

Spin orbit coupling strength

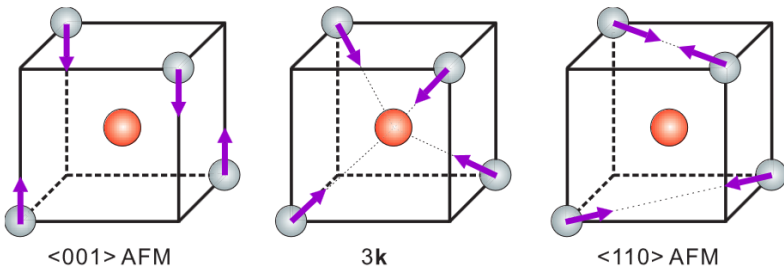


Canting in LiNiPO₄ (cathode material)



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

Non collinear magnetism in UO_2



Dudarev et al PHYSICAL REVIEW MATERIALS 3, 083802 (2019)

Conclusion

Magnetism

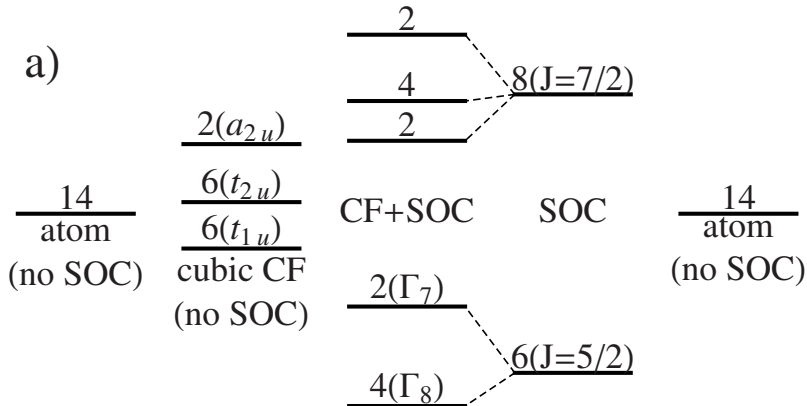
- Ordered magnetism can only exist in the presence of **interactions between electrons**.
- Magnetism informs us about the **localization of electrons**.

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 UO_2

a)



Canting in UO_2

