MAGNETISM ON THE SINGLE ATOM

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Main bibliographical sources:

[Coey] J. M. D. Coey, *"Magnetism and Magnetic Materials"*, Cambridge.

[TGS] E. du Trémolet de Lacheisserie, D. Gignoux & M. Schlenker, *"Magnetism. Fundamentals"*, Springer.

Magnetism at the atomic scale

(source: TGS)

The elements framed in **blue** are **non-magnetic** in the atomic state.

Those framed in **red** are **magnetic** in the solid state

Magnetism of pure elements in the atomic state

Free, isolated atoms can have a magnetic moment.

ORBITAL MAGNETIC MOMENT

Semi-classical single-electron model

$$\vec{m} = \frac{1}{2}\int_v \vec{r} \times \vec{j}(r)\ dV$$ magnetic moment created by a current density **j**

We consider an electron in orbital motion within an atom:

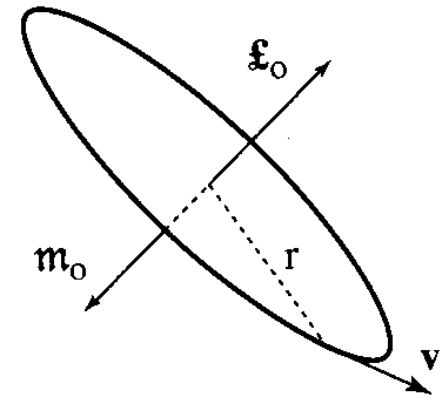$$\vec{j}(\vec{r}\,') = -e\vec{v}\ \underbrace{\delta(\vec{r}\,'-\vec{r})}$$

spatial charge distribution

Then:

$$\vec{m}_o = -\left(\frac{e}{2}\right)\ \vec{r}\times\vec{v} = -\left(\frac{e}{2m_e}\right)\vec{L}_o$$

(source: TGS)

Thus, the orbital magnetic moment of a charged particle is proportional to its angular momentum $\vec{L}_o = \vec{r}\times m_e\vec{v}$

Quantically, the electron states are limited.

HYDROGENIC ATOM

Let us consider a single electron in a **central Coulomb potential**:

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Z e^2}{4\pi\varepsilon_0 r}$$

In spherical coordinates:

$$\nabla^2 = \frac{1}{r^2 \sin\theta} \left[\sin\theta \, \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\partial}{\partial\theta} \left(\sin\theta \, \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin\theta} \, \frac{\partial^2}{\partial\phi^2} \right]$$

$$= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \, \frac{\partial}{\partial r} + \frac{1}{r^2} \underbrace{\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta \, \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \, \frac{\partial^2}{\partial\phi^2} \right)}_{\text{angular part: } -\hat{\boldsymbol{l}}^2/\hbar^2}$$

where $\hat{\boldsymbol{l}}$ is the orbital angular momentum operator.

We can solve Schrödinger's equation by separation of variables:

$$\Psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$$

Then:

$$\left[\frac{-\hbar^2}{2m_e} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{1}{\hbar^2 r^2} \hat{l}^2 \right) - \frac{Z e^2}{4\pi\varepsilon_0 r} \right] \Psi_i = \epsilon_i \Psi_i$$

- The **azimuthal part** of the solution is an eigenfunction of $\hat{l}_z = -i\hbar(\partial/\partial\phi)$:

$$\Phi(\phi) = \exp(i m_l \phi)$$

with eigenvalues $\quad m_l \hbar, \quad m_l = 0, \pm 1, \pm 2, ... \pm l$

- The **polar part** of the solution is a Legendre polynomial:

$$\Theta(\theta) = P_l^{m_l}(\theta)$$

and the **angular momentum quantum number** is $l = 0, 1, 2, ...$

The product of those 2 parts is a spherical harmonic:

$$Y_l^{m_l}(\theta, \phi) \propto P_l^{m_l}(\theta) \, e^{i m_l \phi}$$

- The **radial part** of the solution depends on two quantum numbers, n and l:

$$R(r) = V_n^{\,l} \left(\frac{Zr}{na_0} \right) \exp\left[-\frac{Zr}{na_0} \right]$$

$V_n^{\,l}$ are Laguerre polynomials, and $n = 1, 2, 3, \ldots$ is the **principal quantum number**: $n > l$

The Bohr radius $a_0 = \dfrac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 52.92$ pm.

The energy levels for one electron in a central Coulomb potential are:

$$\epsilon_n = -\frac{Z^2 m_e e^4}{8\varepsilon_0 h^2 n^2} = -\frac{Z^2 R_0}{n^2} \quad : \quad \text{the energies of levels depend only on } n!$$

$$R_0 = \frac{m_e e^4}{8\varepsilon_0^2 h^2} = 13.61 \text{ eV} : \text{ Rydberg}$$

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The square of the angular momentum $\hat{l}^2$ has eigenvalues $l(l+1)\hbar^2$.

Then:

▶ The orbital angular momentum has values $\sqrt{l(l+1)}\hbar$

▶ Its projection $\hat{l}_z$ along *Oz* has values $-l\hbar \leq m_l\hbar \leq +l\hbar$

$\hat{l}^2,\ \hat{l}_z$ can be measured simultaneously because their operators commute.

Since the orbital magnetic moment is proportional
to the angular momentum $\boldsymbol{L_o} = \hbar\boldsymbol{l}$:

$$\boldsymbol{m_o} = -\frac{e}{2m_e}\boldsymbol{L_o} = -\frac{\hbar e}{2m_e}\boldsymbol{l} = -\mu_B\boldsymbol{l}$$

The Bohr magneton, $\mu_B = 0.927\times 10^{-23}$ A m²,

is the smallest possible value of an electronic

magnetic moment.
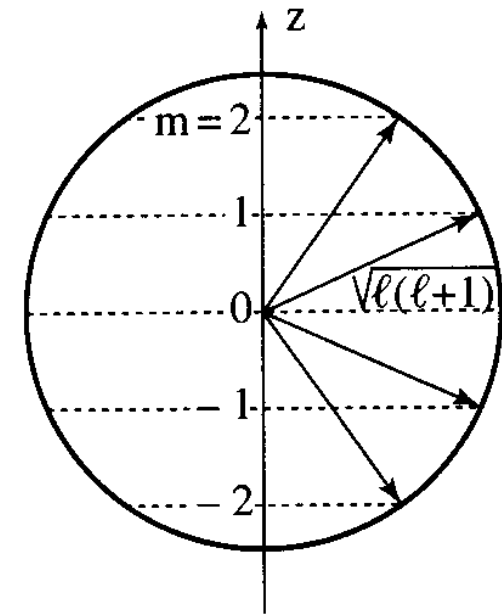
(source: TGS)

SPIN MAGNETIC MOMENT

☞ Intrinsic property of electrons (and other subatomic particles).

☞ Demonstrated experimentally by Stern & Gerlach (1922),

☞ Analogous (but inaccurate!) to a charged particle spinning around its axis.

☞ Electrons, and fermions, can only have two spin states: $\sigma = \pm 1/2$
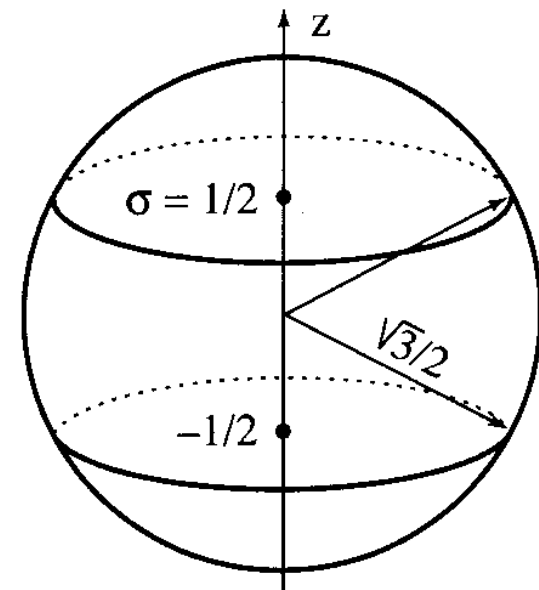
Analogously to the orbital magnetic momentum:

$$\boldsymbol{L_s} = \hbar s$$

$$\langle s^2 \rangle = s(s+1)$$

$$\langle s_z \rangle = \pm 1/2$$

$$\boldsymbol{m_s} = -2\mu_B \boldsymbol{s}$$

Then, $\langle (m_s)_z \rangle = \pm 1 \mu_B$

(source: TGS)

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The total magnetic moment is thus:

$$\boldsymbol{m_t} = \boldsymbol{m_o} + \boldsymbol{m_s}$$

Which needs not be collinear with the total angular momentum:

$$\boldsymbol{L_t} = \hbar(\boldsymbol{l} + \boldsymbol{s})$$

✓ Every particle has a magnetic moment, and an intrinsic angular momentum;

- Proton: $\boldsymbol{m_p} = g_p\left(\dfrac{\hbar e}{2m_p}\right)\hbar\boldsymbol{L}, \quad g_p = 2.793$

- Neutron: does not carry electric charge, but it has both an intrinsic angular momentum and a magnetic moment:

$$\boldsymbol{m_n} = g_n\left(\dfrac{\hbar e}{2m_n}\right)\hbar\boldsymbol{L}, \quad g_p = 1.913$$

✓ These magnetic moments are much smaller than that of the electron, due to the different masses.

$$H_0 = \sum_i \left[-\left(\frac{\hbar^2}{2m_e} \right) \nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right] + \underbrace{\sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}}_{\text{repulsion between electrons}}$$

This Hamiltonian is insoluble.

Approximation: average effective potential with spherical symmetry.

➜ The degeneracy of energy levels with equal *n* is lifted:

Energy depends on *l*: $E(2p_{+1}) \neq E(2p_0) \neq E(2p_{-1})$

Filling sequence of electronic levels!

L-S coupling scheme: (important for most ions of interest in magnetism)

Individual spin and angular momenta add to give resultant quantum numbers:

$$S = \sum s_i, \quad M_S = \sum m_{si}, \quad L = \sum l_i, \quad M_L = \sum m_{li}$$

(Alternatively, when LS coupling is very strong, l_i and s_i first couple for each electron to yield j_i: ***j*** *–* ***j*** coupling scheme)

Set of empirical procedures to determine the ground state configuration of a multielectron atom:

1) First, maximize S

   (electrons minimize Coulomb repulsion by occupying different orbitals; intra-atomic exchange tends to keep spins parallel)

2) Then maximize L consistent with S

   (electrons orbit in the same sense if possible)

3) Finally combine L and S to obtain J:
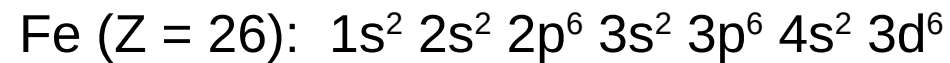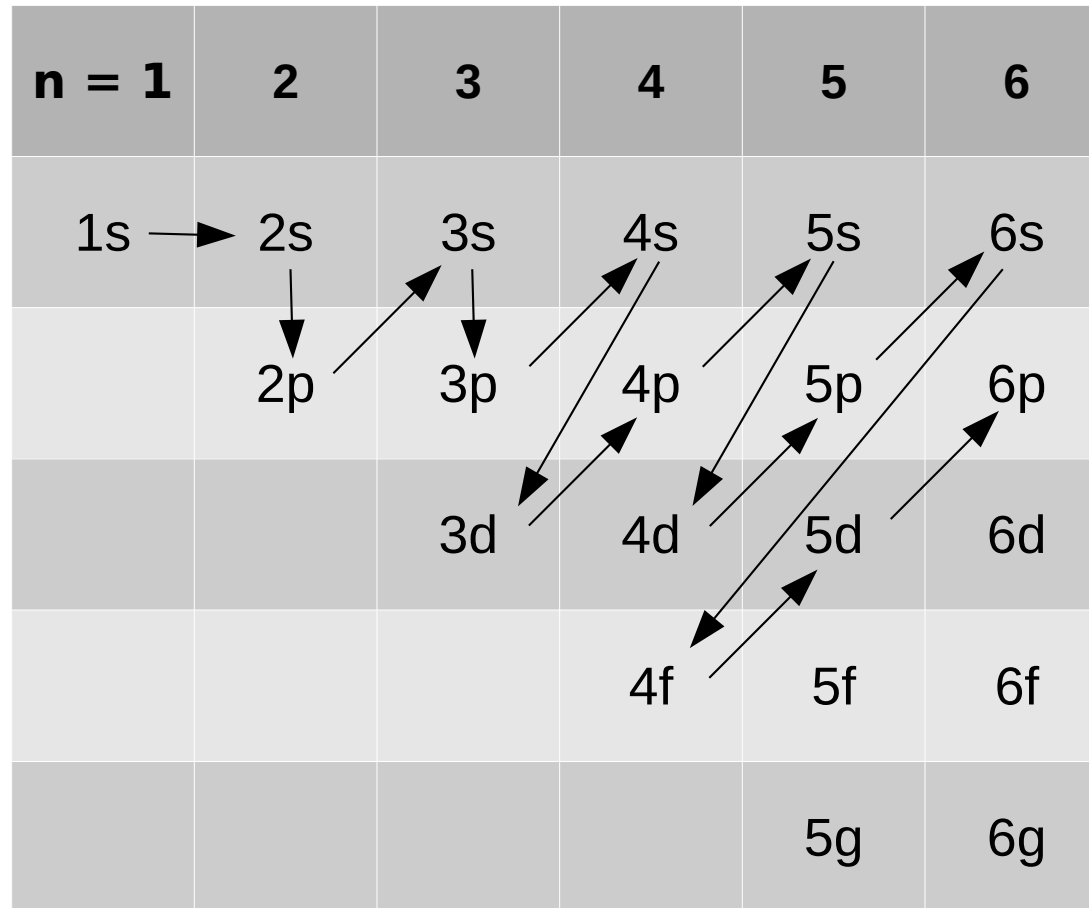
   i) J = L – S   if shell occupation < ½

   ii) J = L + S   if shell occupation > ½

   iii) If the shell occupation is = ½, then L = 0, J = S.

   (consequence of the sign of the spin-orbit coupling - SOC)

Graphically:

n = 1	2	3	4	5	6
1s → 2s		3s	4s	5s	6s
	2p	3p	4p	5p	6p
		3d	4d	5d	6d
			4f	5f	6f
				5g	6g

Fe (Z = 26): $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^6$

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TERMS

Split energy levels due to intra-atomic correlations.

Energy shifts dependent on L, S: ΔE ~ 10 eV.

Electronic configurations are represented by symbols: ^{2S+1}X

X accounts for the value of L: (0, 1, 2, 3, 4, 5, ...) ≡ (S, P, D, F, G, H, …)

Example: C ≡ $1s^2\ 2s^2\ 2p^2$ – there are 15 different ways to distribute 2 electrons among the 3 2p orbitals

	L	S	(M_L, M_S)
^1S	0	0	(0,0)
^3P	1	1	(1,1) (1,0) (1,-1) (0,1) (0,0) (0,-1) (-1,1) (-1,0) (-1,-1)
^1D	2	0	(2,0) (1,0) (0,0) (-1,0) (-2,0)

Applying Hund's rules gives S = 1, L = 1, J = L – S = 0, and thus the C atom is non-magnetic due to the SOC.

Other examples:

- Fe^{3+} ……….. 3d^5 ↑↑↑↑↑ **00000**

  S = 5/2,   L = 0,   J = S = 5/2, $^6S_{5/2}$

- Ni^{2+} ………… 3d^8 ↑↑↑↑↑ ↓↓↓**00**

  S = 1,   L = 3,   J = L+S = 4, $^3F_4$

- Nd^{3+} ……...... 4f^3 ↑↑↑**0000 0000000**

  S = 3/2,   L = 6,   J = L – S = 9/2, $^4I_{9/2}$

- Dy^{3+} ……….. 4f^9 ↑↑↑↑↑↑↑ ↓↓**00000**

  S = 5/2,   L = 5,   J = L + S = 15/2, $^6H_{15/2}$

WARNING: These rules work to derive the ground state (at T = 0) of **single atoms**. They are not applicable in general to solids, whose valence electrons form **bands**. This is particularly important for transition metals.

SPIN-ORBIT COUPLING

Interaction between individual orbital and spin angular momenta:

$$H_{ij}^{SO} = -\lambda_{ij} l_i s_j$$

It is negligible for i ≠ j, therefore: $\boldsymbol{H^{SO} = -\lambda L S}$

Weak interaction, proportional to Z (~10-2 eV for Fe, ~1 eV RE), but responsible for many phenomena in magnetism:

➢ Magnetocrystalline anisotropy

➢ Magnetostriction

➢ Anisotropic magnetoresistance, …

$$\boldsymbol{J = L + S} \quad \Rightarrow \quad \boldsymbol{J^2 = L^2 + S^2 + 2L \cdot S}$$

$$\boldsymbol{L \cdot S} = 1/2(\boldsymbol{J^2 - L^2 - S^2}) \quad \Rightarrow \quad \boldsymbol{H^{SO} = -\lambda L \cdot S} = -\frac{\lambda}{2}(\boldsymbol{J^2 - L^2 - S^2})$$

$$E_J = -\frac{\lambda}{2}[J(J+1) - L(L+1) - S(S+1)]$$

MULTIPLETS

Sets of different electronic energy levels after the degeneracy is lifted by SOC.

Characterized by **J** = **L** + **S**

There exist 2J + 1 states within a multiplet.

Degeneracy lifted by $E_J = -\dfrac{\lambda}{2}[J(J+1) - L(L+1) - S(S+1)]$

Term symbols: $^{2S+1}X_J$

$|L - S| < J < L + S$

Example: *(source: Coey)*

Co^{2+} $3d^7$

S = 3/2,   L = 3,   J = 9/2
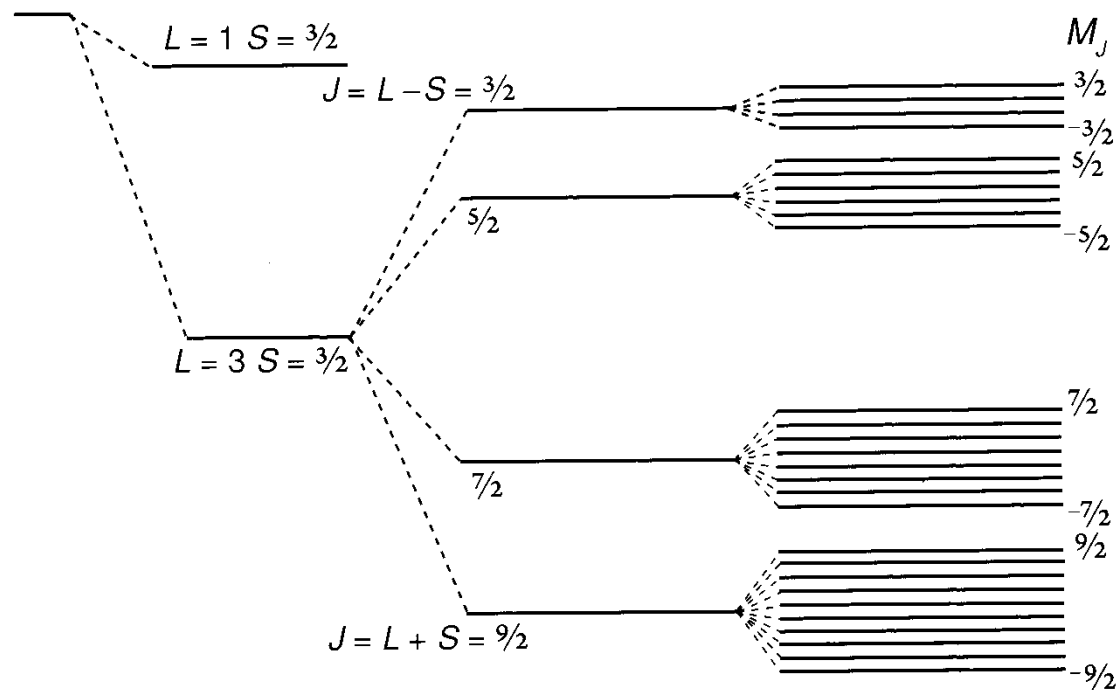
Summarizing:

$$m_o = -\mu_B L$$

$$m_s = -2\mu_B S$$

Within each multiplet, the total magnetic moment and the total angular moment are collinear:

$$m = -g_J \mu_B J$$

$$g_J = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

g_J is the Landé factor, characteristic of each multiplet.

- $g_J = 1$,   if $S = 0$;
- $g_J = 2$,   if $L = 0$.

In general: $$m = -g\left(\frac{e}{2m_e}\right)L = \gamma L$$ γ: gyromagnetic factor

Magnetic ions (some): *(source: TGS)*

Ion 4f	$^{2S+1}L_J$	L	S	J	gJ	m_0 (μ_B)	m_{eff} (μ_B)
Ce^{3+} ($4f^1$)	$^2F_{5/2}$	3	1/2	5/2	6/7	2.14	2.54
Pr^{3+} ($4f^2$)	$^3H_4$	5	1	4	4/5	3.20	3.58
Nd^{3+} ($4f^3$)	$^4I_{9/2}$	6	3/2	9/2	8/11	3.27	3.62
Pm^{3+} ($4f^4$)	$^5I_4$	6	2	4	3/5	2.40	2.68
Sm^{3+} ($4f^5$)	$^6H_{5/2}$	5	5/2	5/2	2/7	0.71	0.85
Eu^{3+} ($4f^6$)	$^7F_0$	3	3	0	–	0	0
Gd^{3+} ($4f^7$)	$^8S_{7/2}$	0	7/2	7/2	2	7.00	7.94
Tb^{3+} ($4f^8$)	$^7F_6$	3	3	6	3/2	9.00	9.72
Dy^{3+} ($4f^9$)	$^6H_{15/2}$	5	5/2	15/2	4/3	10.00	10.65
Ho^{3+} ($4f^{10}$)	$^5I_8$	6	2	8	5/4	10.00	10.61
Er^{3+} ($4f^{11}$)	$^4I_{15/2}$	6	3/2	15/2	6/5	9.00	9.58
Tm^{3+} ($4f^{12}$)	$^3H_6$	5	1	6	7/6	7.00	7.56
Yb^{3+} ($4f^{13}$)	$^2F_{7/2}$	3	1/2	7/2	8/7	4.00	4.53

All non-magnetic free atoms in their ground state have J = 0!

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- Filled electronic shells are non-magnetic

- Only non-saturated shells have a magnetic moment

- The magnetic moment of free atoms or ions is given by:

$$\boldsymbol{m} = -g_J \mu_B \boldsymbol{J}$$

where $\hbar \boldsymbol{J}$ is the total angular momentum.

No other internal effects contribute to degeneracy lifting.

All other energy contributions must come from external sources

(interactions, applied fields)

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The Hamiltonian for an atom with a magnetic moment $\boldsymbol{m} = -g_J\mu_B\boldsymbol{J}$ under an applied magnetic field is

$$H_Z = g_J\mu_B\boldsymbol{J}\cdot\boldsymbol{B}$$

When the field is applied along Oz, $\boldsymbol{m}$ precesses rapidly about $\boldsymbol{J}$, so on average :

$$H_Z = g_J\mu_B J_Z B$$

$$\varepsilon_Z = g_J\mu_B M_J B$$

The Zeeman splitting between adjacent levels is

$$\Delta\varepsilon_Z = g_J\mu_B B \sim 1\text{ K for B = 1T.}$$
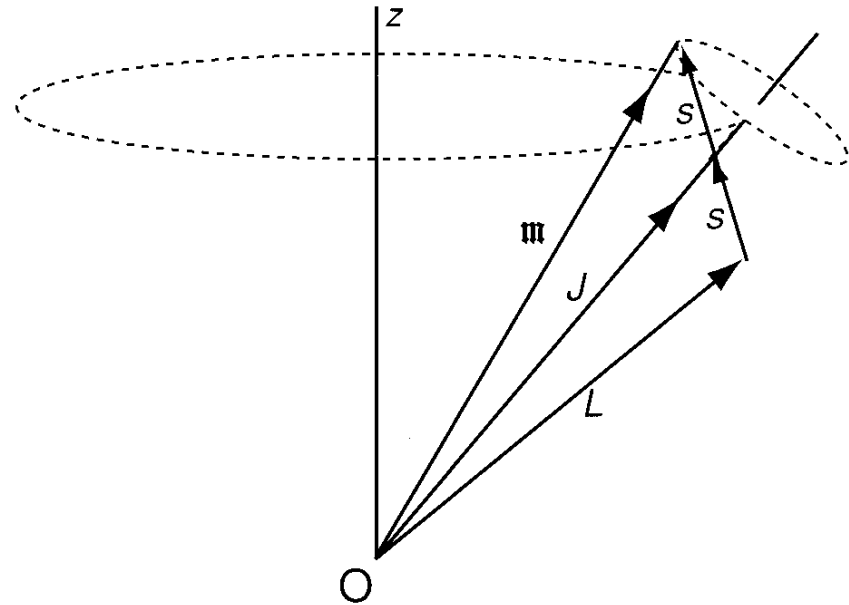
(source: TGS)

Diamagnetism: Response of non-magnetic atoms to applied magnetic fields

(no permanent magnetic moments)

Let us consider the **classical model** of an electron in a circular orbit:
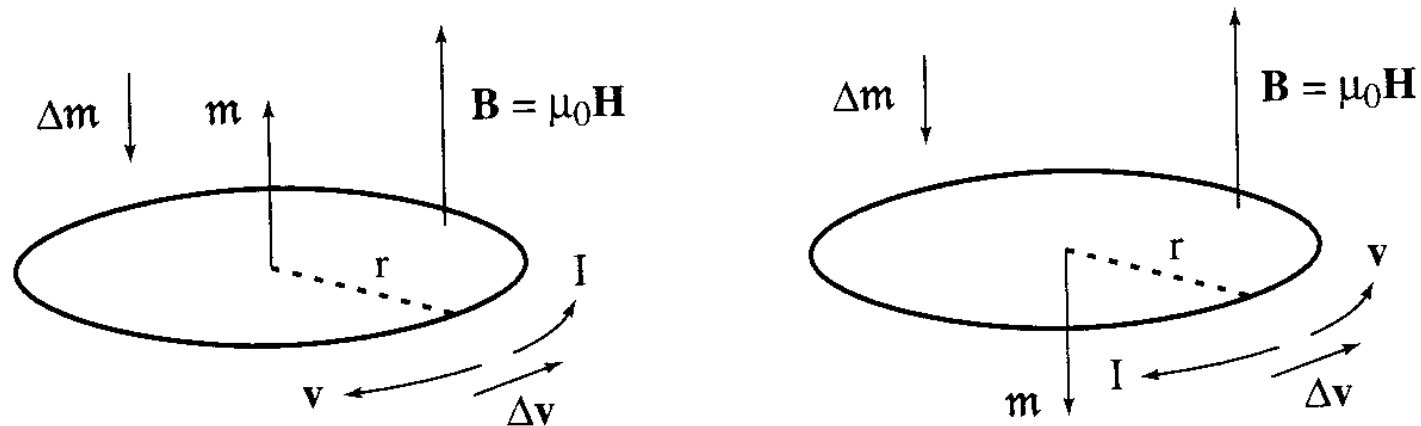
(source: TGS)

A magnetic field applied perpendicular to the current loop induces a variation of the orbital magnetic moment opposite to the field (Lenz's rule), irrespective of the sense of the electron movement.

As we have seen:

$$m_O = -erv/2$$

The induced electromotive force due to Lenz's rule is:

$$U = -\frac{d\Phi}{dt} = -\pi r^2 \frac{dB}{dt} = 2\pi r E$$

$$E = -\frac{r}{2}\frac{dB}{dt}$$

$$F = -eE = \frac{er}{2}\frac{dB}{dt} \quad \Rightarrow \quad \frac{dv}{dt} = \frac{er}{2m_e}\frac{dB}{dt}$$

$$\Delta v = \frac{er}{2m_e}\int_0^B dB = \frac{er}{2m_e}B$$

And the change in the magnetic moment is:

$$\Delta m_O = -\left(\frac{e^2 r^2}{4m_e}\right)B$$

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If the electron orbit is not perpendicular to the field, assuming a spherical orbital of radius

$$\sqrt{\langle R^2 \rangle} = \sqrt{\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle}$$

For the planar loop we have

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle = 2/3 \langle R^2 \rangle$$

And then:

$$\Delta m_O = -\left(\frac{e^2 r^2}{6 m_e} \right) B$$

For an atom with Z electrons:

$$\Delta m = -\left(\frac{e^2 B}{6 m_e} \right) \sum_n \langle r_n^2 \rangle$$

And the diamagnetic susceptibility is

$$\chi = \frac{\partial M}{\partial H} = -\frac{\mu_0 N e^2 Z R^2}{6 m_e}$$

▶ The susceptibilities of diamagnetic materials are $\sim 10^{-6}$ and weakly temperature dependent;

▶ Non-magnetic atoms implies $J = 0$: filled shells in the atomic state or by bonding to other atoms

- Noble gases (He, Ne, Ar)
- Molecular gases (H_2, N_2, …)
- Ionic solids (NaCl)
- Covalent compounds (organic molecules, etc)

▶ Diamagnetism exists also in atoms with permanent magnetic moments, but it is negligible compared to the other contributions

Behavior of materials with **non-interacting** permanent magnetic moments.

The **classical theory** of paramagnetism was developed in 1905 by P. Langevin.

Let us consider a set of magnetic moments **m** under an applied field **H**.

The Zeeman energy is:

$$\varepsilon_z(\theta) = -\mu_0 m H \cos\theta$$

The probability of **m** forming an angle θ with **H** is:

$$P(\theta) = C \underbrace{2\pi\sin\theta}_{} \exp\left(\frac{\mu_0 H m \cos\theta}{k_B T}\right)$$

fraction of solid angle
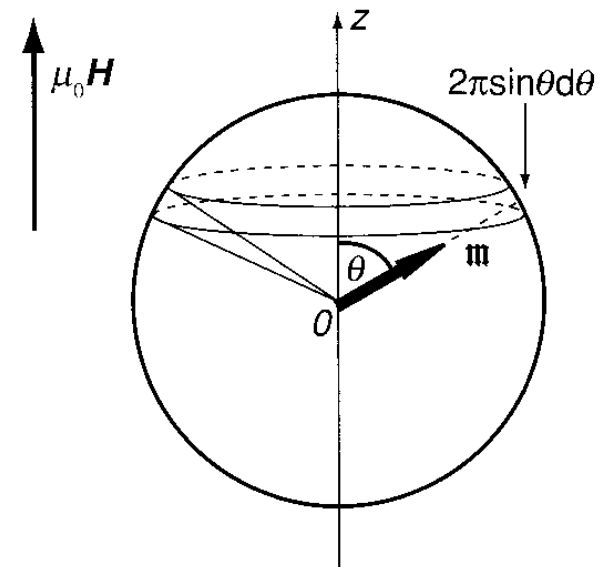
(source: Coey)

The expected value of the magnetic moment along the field direction is then:

$$\langle m_z \rangle = \frac{\int_0^\pi m \cos\theta \ P(\theta) d\theta}{\int_0^\pi P(\theta) d\theta} = m \left[\tanh^{-1}\left(\frac{\mu_0 m H}{k_B T}\right) - \left(\frac{\mu_0 m H}{k_B T}\right)^{-1} \right]$$

Langevin function
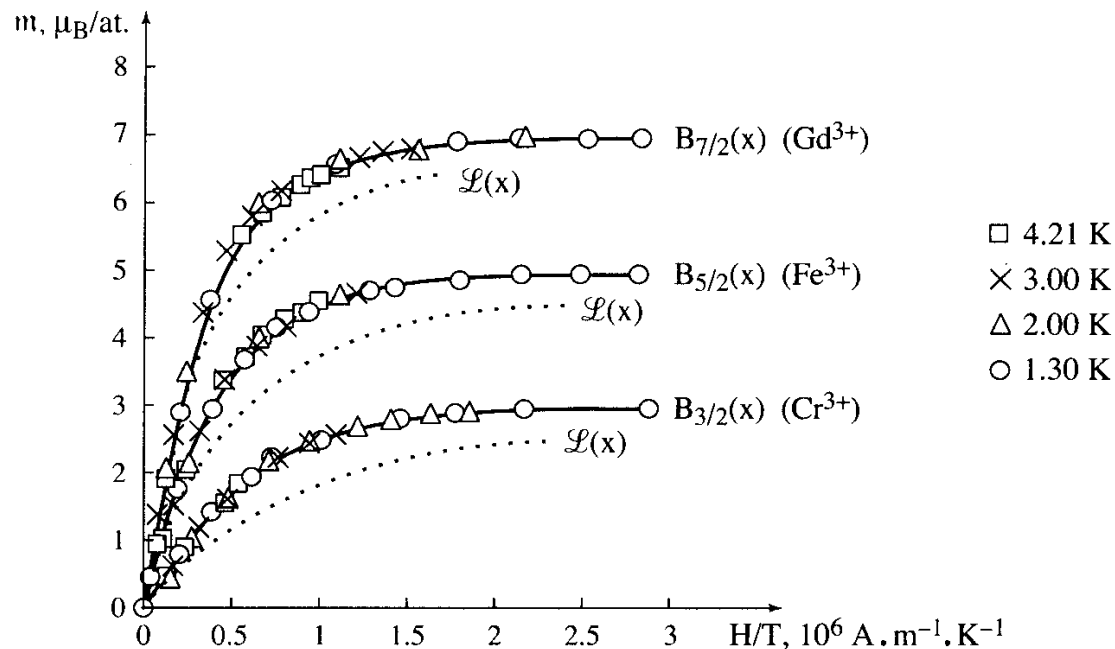
(source: TGS)

At low H or high T:

$$\frac{\mu_0 m H}{k_B T} \ll 1 \quad \Rightarrow \quad \langle m_z \rangle \approx \frac{\mu_0 m^2 H}{3 k_B T}$$

and the susceptibility is:

$$\chi = \frac{N \langle m_z \rangle}{H} = \frac{\mu_0 N m^2}{3 K_B T} = \frac{C}{T}$$

which is the Curie law, with $C = \dfrac{\mu_0 N m^2}{3 k_B}$ being Curie's constant.

Paramagnetic susceptibility is ~$10^{-5} - 10^{-4}$, much larger than the diamagnetic contribution (but much smaller than the ferromagnetic one!)

Quantically, we know that the electron magnetic moments are quantized:

$$m_z = -g_J \mu_B M_J, \quad -J \leq M_J \leq +J$$

Then, the energy is: $E = \mu_0 g_J \mu_B M_J H$

And applying Boltzmann statistics:

$$M = \frac{N}{Z} \sum_{-J}^{+J} -g_J \mu_B M_J \exp\left(-\frac{x M_J}{J}\right), \text{ with } x = \mu_0 g_J \mu_B J H / k_B T$$

Z is the partition function:

$$Z = \sum_{-J}^{+J} \exp\left(-\frac{x M_J}{J}\right) = e^x[1 + e^{x/J} + (e^{x/J})^2 + ... + (e^{x/J})^{2J}] = \frac{\sinh\left(\frac{2J+1}{2J}x\right)}{\sinh\left(\frac{x}{2J}\right)}$$

Then the magnetization is:

$$M = M_0 B_J(x)$$

M_0 is the maximum ("saturation") magnetization:

$$M_0 = N g_J \mu_B J = N m_0$$

and $B_J(x)$ is the **Brillouin function**:

$$B_J(x) = \left(\frac{2J+1}{2J}\right)\tanh^{-1}\left(\frac{2J+1}{2J}x\right) - \left(\frac{1}{2J}\right)\tanh^{-1}\left(\frac{1}{2J}x\right)$$

$B_J(x)$ reduces to the Langevin function in the limit $J \to \infty$.

In the small x limit:

$$B_J(x) \approx \left(\frac{J+1}{3J}\right)x - \frac{[(J+1)^2+J^2](J+1)}{90J^2}x^2 + ...$$

and the leading term reproduces Curie's law with an effective moment

$$m_{eff} = g_J \mu_B \sqrt{(J+1)J}$$

Comparison of the Langevin and Brillouin functions:

(source: Coey)
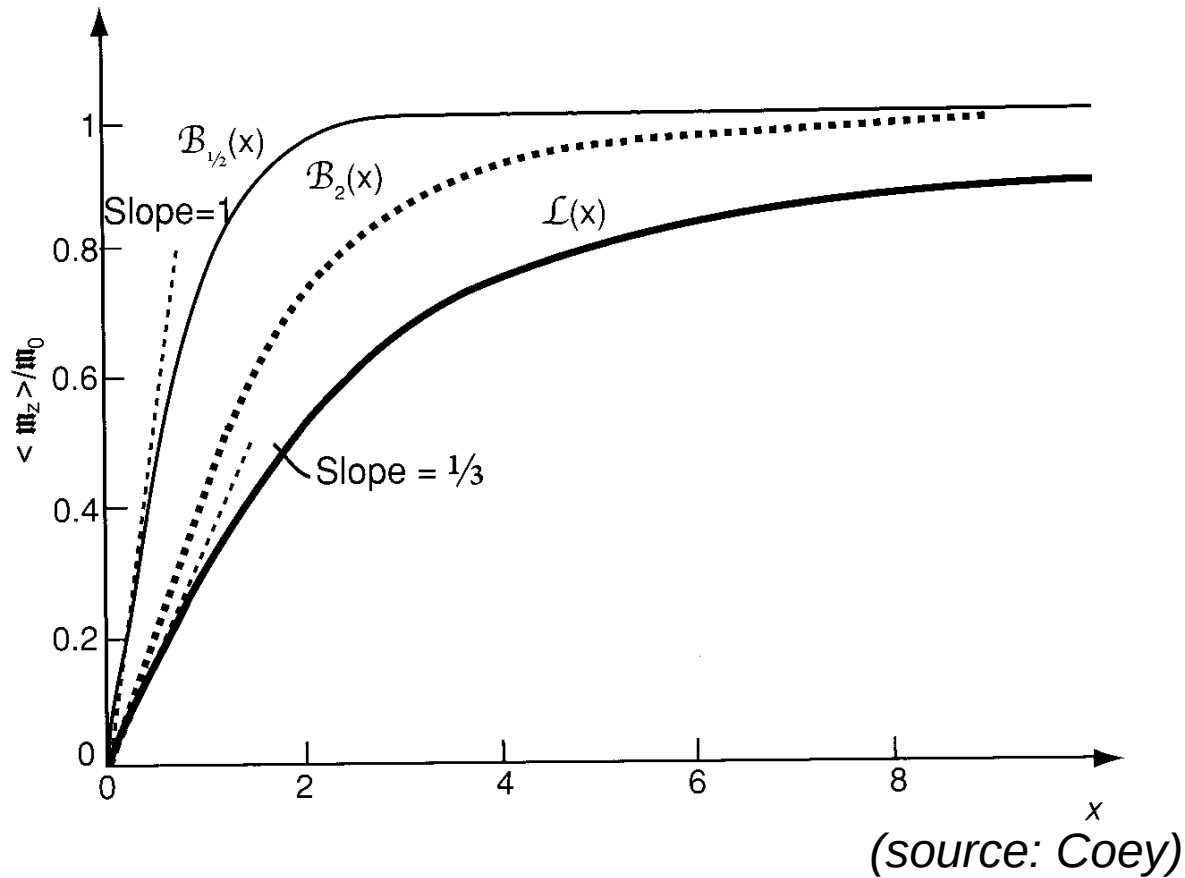
This theory works well for dilute magnetic materials (3*d*, 4*f*).

All possible electron configurations for the C atom

Table 4.3. Example of the six-electron carbon atom; $1s^2 2s^2 2p^2$

$1s$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
$2s$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
$2p_{-1}$	↑↓	↑	↑	↓	↓	↑	↑		↓	↓		↓		↑	
$2p_0$		↑	↓	↑	↓			↑↓			↓		↑		↑
$2p_1$						↑	↓		↑	↓	↓	↑	↑	↑	↑↓
M_L	2	1	1	1	1	0	0	0	0	0	−1	−1	−1	−1	−2
M_S	0	−1	0	0	+1	−1	0	0	0	+1	+1	0	0	−1	0

(source: Coey)

(source: TGS)

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