Basic Concepts in Magnetism

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Ireland.

1. Magnetostatics
2. Magnetism of multi-electron atoms
3. Crystal field
4. Magnetism of the free electron gas
5. Dilute magnetic oxides

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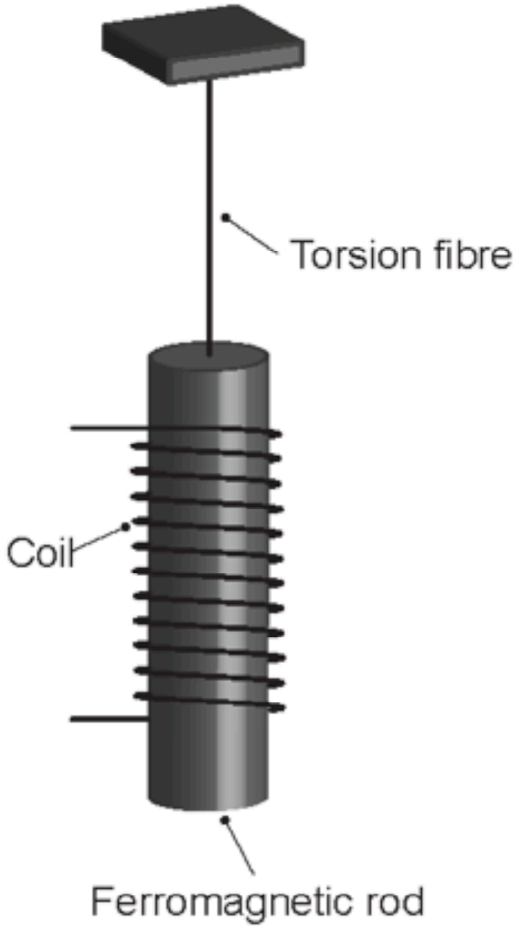
2. Magnetism of multi-electron atoms

2.1 Einstein-de Hass Experiment

Demonstrates the relation between magnetism and angular momentum.



A ferromagnetic rod is suspended on a torsion fibre.

The field in the solenoid is reversed, switching the direction of magnetization of the rod.

An angular impulse is delivered due to the reversal of the angular momentum of the electrons- conservation of angular momentum.

Three huge paradoxes; — Amperian surface currents

— Weiss molecular field

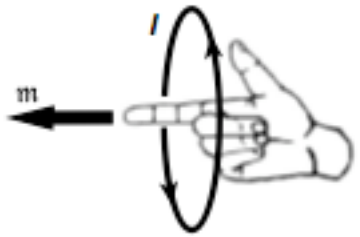
— Bohr - van Leeuwen theorem

The electron

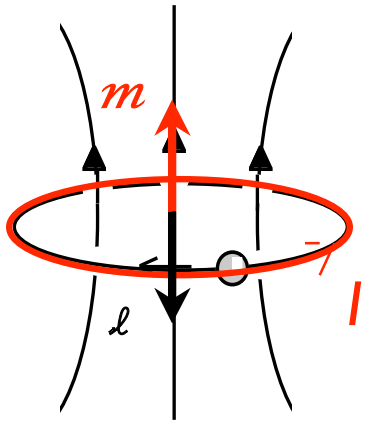
The magnetic properties of solids derive essentially from the magnetism of their electrons. (Nuclei also possess magnetic moments, but they are ≈ 1000 times smaller).

An electron is a point particle with:

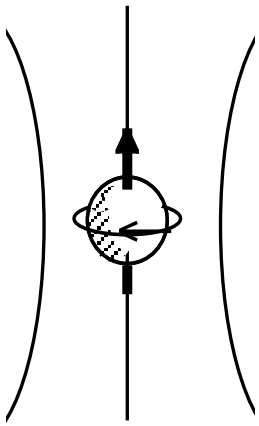
mass	$m_e = 9.109\ 10^{-31}$ kg
charge	$-e = -1.602\ 10^{-19}$ C
intrinsic angular momentum *(spin)*	$\hbar/2 = 0.527\ 10^{-34}$ J s



The corkscrew rule. When the tip of the right thumb traces the current, the index finger points along m.



Orbital moment



Spin

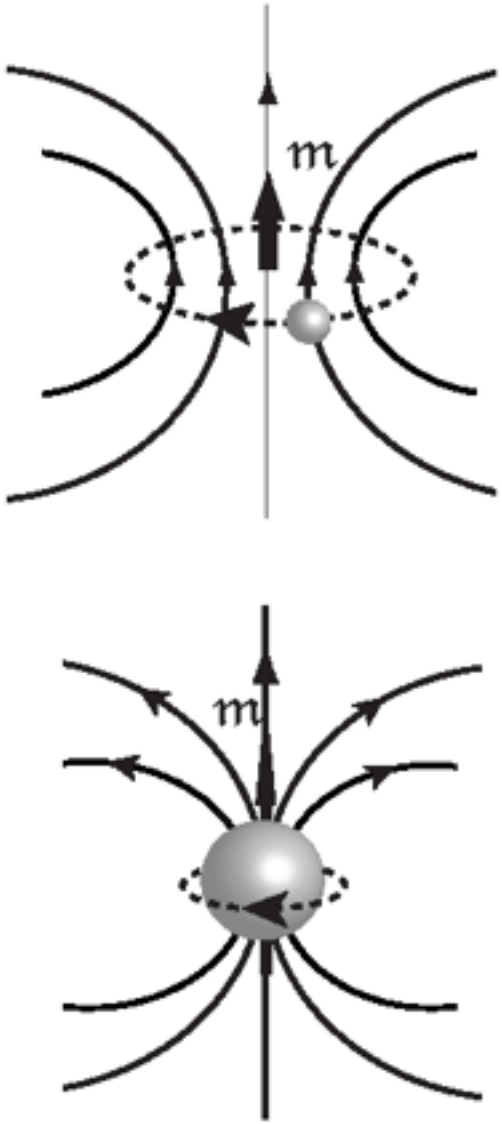
➢ *The same magnetic moment, the Bohr Magneton,* $\mu_B = 9.27\ 10^{-24}$ Am² *is associated with* $\hbar/2$ *of spin angular momentum or* $\hbar$ *of orbital angular momentum*

On an atomic scale, magnetism is always associated with *angular momentum*. Charge is negative, hence the angular momentum and magnetic moment are oppositely directed

2.2 Origin of Magnetism

At this point it seems that the whole of chemistry and much of physics is understood in principle. The problem is that the equations are much to difficult to solve….. *P. A. M. Dirac*

2.3 Orbital and Spin Moment



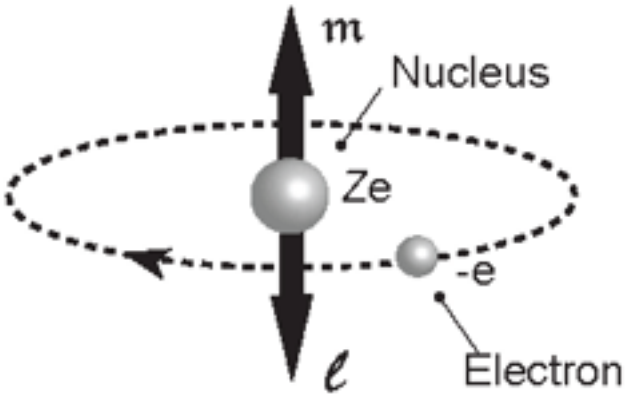
Magnetism in solids is due to the angular momentum of electrons on atoms.

Two contributions to the electron moment:

- *Orbital motion* about the nucleus
- *Spin*- the intrinsic (rest frame) angular momentum.

$$\boldsymbol{m} = -(\mu_B/\hbar)(\boldsymbol{l} + 2\boldsymbol{s})$$

2.3.1 Orbital moment



Circulating current is I; $I = -e/\tau = -ev/2\pi r$

The moment is * $m = IA$ $m = -evr/2$

Bohr: orbital angular momentum ***l*** is quantized in units of ħ; h is Planck's constant = 6.6226 10^{-34} J s; ħ = h/2π = 1.055 10^{-34} J s. $|\boldsymbol{l}| = n\hbar$

Orbital angular momentum: $\boldsymbol{l} = m_e \boldsymbol{r} \times \boldsymbol{v}$ Units: J s

Orbital quantum number l, $l_z = m_l\hbar$ $m_l = 0, \pm1, \pm2, \ldots, \pm l$ *so* $m_z = -m_l(e\hbar/2m_e)$

The Bohr model provides us with the natural unit of magnetic moment

Bohr magneton $\mu_B = (e\hbar/2m_e)$ $\mu_B = 9.274\ 10^{-24}$ A m^2 $m_z = m_l\mu_B$

In general $m = \gamma \boldsymbol{l}$ γ = *gyromagnetic ratio* Orbital motion $\gamma = -e/2m_e$

* Derivation can be generalized to noncircular orbits: $m = IA$ for any planar orbit.

g-factor

Ratio of magnitude of $\boldsymbol{m}$ in units of μ_B to magnitude of $\boldsymbol{l}$ in units of $\hbar$.

$$(\boldsymbol{m}/\mu_B) = g(\boldsymbol{l}/\hbar)$$

g = 1 for orbital motion

The Bohr model also provides us with a natural unit of length, the *Bohr radius*

$$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2 \qquad a_0 = 52.92 \text{ pm}$$

And a natural unit of energy, the *Rydberg* R_0

$$R_0 = (m/2\hbar^2)(e^2/4\pi\varepsilon_0)^2 \qquad R_0 = 13.606 \text{ eV}$$

2.3.2 Spin moment

Spin is a relativistic effect.

Spin angular momentum $\boldsymbol{s}$

Spin quantum number s s = 1/2 for electrons

Spin magnetic quantum number m_s $m_s = \pm 1/2$ for electrons

$s_z = m_s \hbar$ $m_s = \pm 1/2$ for electrons

$m_z = -(e/m_e) m_s \hbar = \pm \mu_B$ $\boldsymbol{m} = -(e/m_e)\boldsymbol{s}$

For spin moments of electrons we have:

$\gamma = -e/m_e$ $g \approx 2$

More accurately, after higher order corrections: $g = 2.0023$ $m_z = 1.00116 \mu_B$

An electron will usually have both orbital and spin angular momentum

$$\boldsymbol{m} = -(\mu_B/\hbar)(\boldsymbol{l} + 2\boldsymbol{s})$$

Quantum mechanics of spin

In quantum mechanics, physical observables are represented by operators - differential or matrix.

e.g. momentum $\boldsymbol{p} = -i\hbar\nabla$; energy $\mathbf{p}^2/2m_e = -\hbar^2\nabla^2$

n magnetic basis states ⇒ n x n Hermitian matrix

Spin operator (for s = 1/2)

$\boldsymbol{s} = \sigma\hbar/2$

Pauli spin matrices

$$\hat{\boldsymbol{\sigma}} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Electron: $s = 1/2 \Rightarrow m_s = \pm 1/2$ i.e spin up and spin down states

Represented by column vectors: $|\uparrow\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ $|\downarrow\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$

$\boldsymbol{s}\,|\uparrow\rangle = (\hbar/2)\,|\uparrow\rangle$; $\boldsymbol{s}|\downarrow\rangle = -(\hbar/2)|\downarrow\rangle$

$$\hat{\boldsymbol{s}}^2 = \hat{\boldsymbol{s}}_x^2 + \hat{\boldsymbol{s}}_y^2 + \hat{\boldsymbol{s}}_z^2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} 3\hbar^2/4$$

Eigenvalues of $\boldsymbol{s}^2$: $s(s+1)\hbar^2$

The fundamental property of angular momentum in QM is that the operators satisfy the commutation relations:

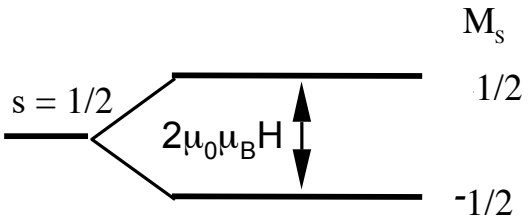
$$[\hat{\boldsymbol{s}}_x, \hat{\boldsymbol{s}}_y] = i\hbar\hat{\boldsymbol{s}}_z, \quad [\hat{\boldsymbol{s}}_y, \hat{\boldsymbol{s}}_z] = i\hbar\hat{\boldsymbol{s}}_x, \quad [\hat{\boldsymbol{s}}_z, \hat{\boldsymbol{s}}_x] = i\hbar\hat{\boldsymbol{s}}_y.$$

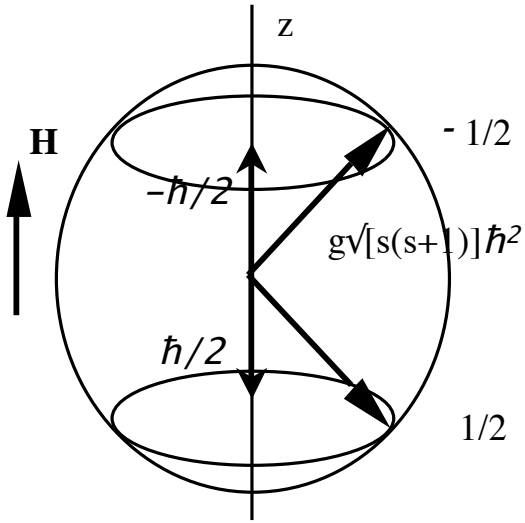
or $\quad \hat{\boldsymbol{s}} \times \hat{\boldsymbol{s}} = i\hbar\hat{\boldsymbol{s}}.$

Where [A,B] = AB - BA and [A,B] = 0 ⇒ A and B's eigenvalues can be measured simultaneously

$$[\boldsymbol{s}^2, s_z] = 0$$

Quantized spin angular momentum of the electron





The electrons have only two eigenstates, 'spin up'(↑, m_s = 1/2) and 'spin down' (↓, m_s = -1/2), which correspond to two possible orientations of the spin moment relative to the applied field.
Populations of the energy levels are given by Boltzmann statistics; ∝ exp{-E_i/k_BT}.
The thermodynamic average $\langle m \rangle$ is evaluated from these Boltzmann populations.

$$\langle m \rangle = \frac{[\mu_B \exp(x) - \mu_B \exp(-x)]}{[\exp(x) + \exp(-x)]} \qquad \text{where } x = \mu_0 \mu_B H / k_B T.$$

$$\boxed{\langle m \rangle = \mu_B \tanh(x)}$$

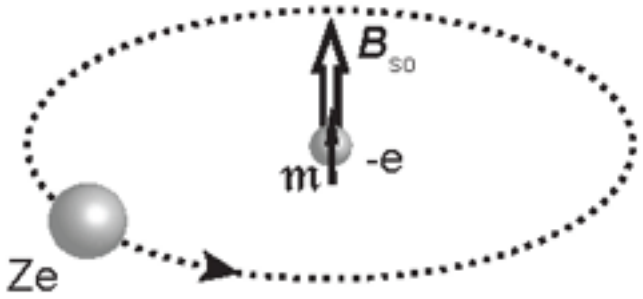
In small fields, tanh(x) ≈ x, hence the susceptibility $\chi = N\langle m \rangle / H$

$$\boxed{\chi = \mu_0 N \mu_B^2 / k_B T}$$

This is again the famous *Curie law* for the susceptibility, which varies as T^{-1}.

In other terms $\chi = C/T$, where $C = \mu_0 N \mu_B^2 / k_B$ is a constant with dimensions of temperature; Assuming an electron density N of 6 10^{28} m^{-3} gives C ≈ 0.5 K.
The Curie law susceptibility at room temperature is of order 10^{-3}.

2.4 Spin-Orbit Coupling



Spin and angular momentum coupled to create total angular momentum ***j***.

$$\boldsymbol{m} = \gamma \boldsymbol{j}$$

From the electron's point of view, the nucleus revolves round it with speed $v \Rightarrow$ current loop

$$I = Zev/2\pi r$$

Which produces a magnetic field $\mu_0 I/2r$ at the centre

$$B_{so} = \mu_0 Zev/2\pi r^2$$

$$E = -\boldsymbol{m}.\boldsymbol{B} \qquad E_{so} = -\mu_B B_{so}$$

Since $r \approx a_0/Z$ and $m_e v r \approx \hbar$

$$E_{so} \approx -\mu_0 \mu_B^2 Z^4/4\pi a_0^3$$

2.5 Magnetism of the hydrogenic atom

Orbital angular momentum

The orbital angular momentum operators also satisfy the commutation rules:

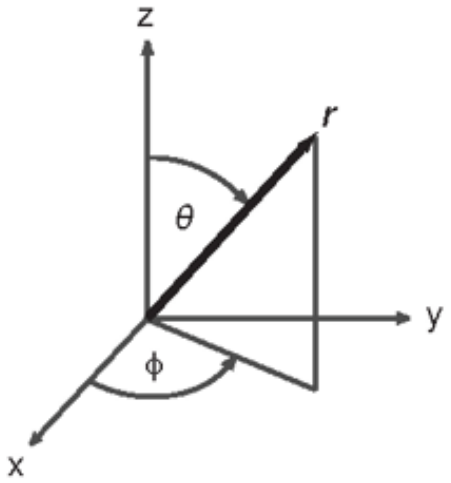
$\boldsymbol{l} \times \boldsymbol{l} = i\hbar \boldsymbol{l}$ and $[\boldsymbol{l}^2, l_z] = 0$

Spherical coordinates

$x = r \sin\theta \cos\phi$

$y = r \sin\theta \sin\phi$

$z = r \cos\theta$



$$\begin{aligned}
\hat{\boldsymbol{l}}_x &= i\hbar(\sin\phi\partial/\partial\theta + \cot\theta\cos\phi\partial/\partial\phi), \\
\hat{\boldsymbol{l}}_y &= i\hbar(-\cos\phi\partial/\partial\theta + \cot\theta\sin\phi\partial/\partial\phi), \\
\hat{\boldsymbol{l}}_z &= -i\hbar(\partial/\partial\phi).
\end{aligned}$$

$$\hat{\boldsymbol{l}}^2 = \hat{\boldsymbol{l}}_x^2 + \hat{\boldsymbol{l}}_y^2 + \hat{\boldsymbol{l}}_z^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

QM operators for orbital angular momentum

Eigenvalues of l^2:

$l(l+1)\hbar^2$

(l is the orbital angular momentum quantum number)

l=1 case

$m_l = 1, 0, -1$ *corresponds to the eigenvectors*

$$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

l_x,l_y and l_z operators can be represented by the matrices;:

$$\begin{bmatrix} 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 \end{bmatrix} \hbar, \begin{bmatrix} 0 & -i/\sqrt{2} & 0 \\ i/\sqrt{2} & 0 & -i/\sqrt{2} \\ 0 & i/\sqrt{2} & 0 \end{bmatrix} \hbar, \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \hbar$$

where

$$\tilde{l}^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} 2\hbar^2$$

Single electron wave functions

Schrodinger's equation: $\mathcal{H}\psi_i = \varepsilon_i\psi_i$ $\quad \mathcal{H} = -(\hbar^2/2m_e)\nabla_i^2 - Ze^2/4\pi\epsilon_0 r$

$$\left[-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{1}{\hbar^2 r^2}\vec{l}^2\right)-\frac{Ze^2}{4\pi\epsilon_0 r}\right]\psi_i = \varepsilon_i\psi_i. \qquad \varepsilon_n = \frac{-Zme^4}{8\epsilon_0^2 h^2 n^2} = \frac{-ZR_0}{n^2}$$

Satisfied by the wavefunctions: $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$

Where: $R(r) = V_n^\ell(Zr/na_0)\exp[-(Zr/na_0)]$ *(V_n^l are Laguerre polynomials V^0_1=1)*

And the combined angular parts are $Y_\ell^{m_\ell}(\theta,\phi) \propto P_\ell^{m_\ell}(\theta)e^{im_\iota\phi}.$ *(Legendre polynomials)*

Normalized spherical harmonics:

s	$Y_0^0 = \sqrt{1/4\pi}$		
p	$Y_1^0 = \sqrt{3/4\pi}\cos\theta$	$Y_1^{\pm1} = \pm\sqrt{3/8\pi}\sin\theta\exp(\pm i\phi)$	
d	$Y_2^0 = \sqrt{5/16\pi}(3\cos^2\theta - 1)$	$Y_2^{\pm1} = \pm\sqrt{15/8\pi}\sin\theta\cos\theta\exp(\pm i\phi)$	
f	$Y_3^0 = \sqrt{7/16\pi}(5\cos^3\theta - 3\cos\theta)$	$Y_3^{\pm1} = \pm\sqrt{21/64\pi}(5\cos^2\theta - 1)\sin\theta\exp(\pm i\phi)$	
s			
p			
d	$Y_2^{\pm2} = \sqrt{15/32\pi}\sin^2\theta\exp(\pm 2i\phi)$		
f	$Y_3^{\pm2} = \sqrt{105/32\pi}\sin^2\theta\cos\theta\exp(\pm 2i\phi)$	$Y_3^{\pm3} = \pm\sqrt{35/64\pi}\sin^3\theta\exp(\pm 3i\phi)$	

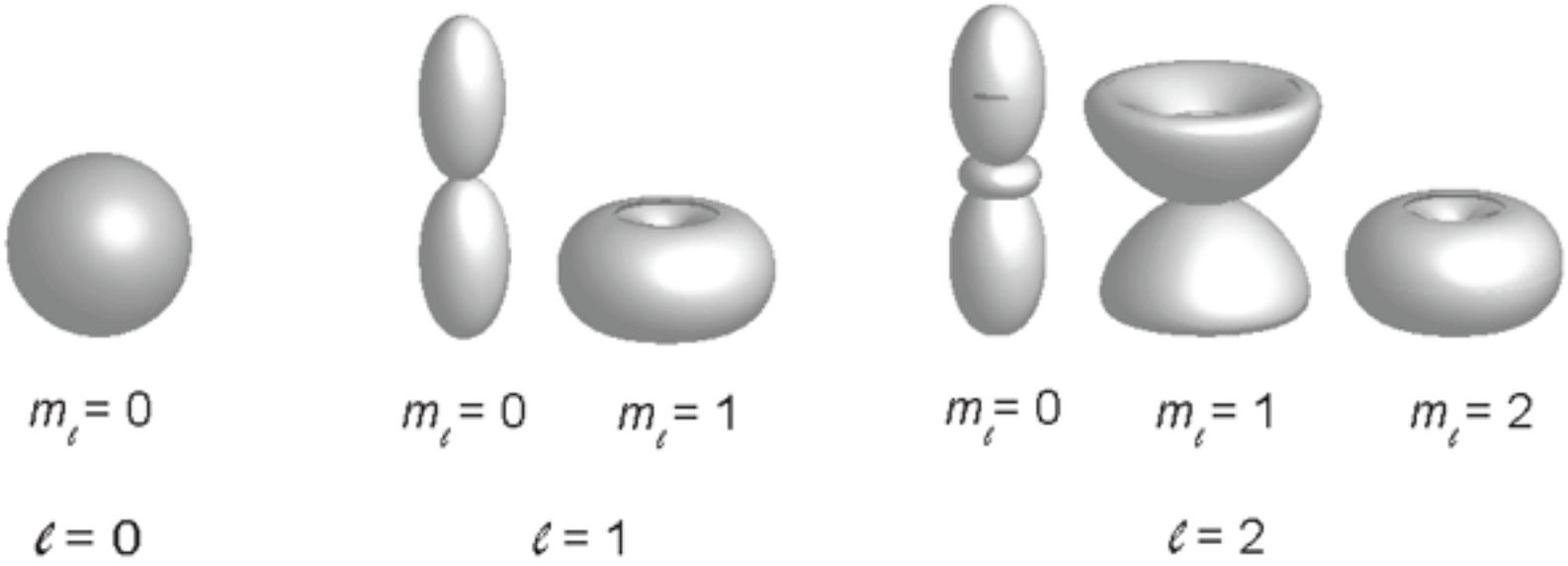
The three quantum number $n,l\ m_l$ denote an orbital.
Orbitals are denoted nx_{ml}, x = s,p,d,f... for l = 0,1,2,3,...
Each orbital can accommodate at most two electrons* (m_s=±1/2)

The hydrogenic orbitals: An orbital can accommodate 2(2*l*+1) electrons.

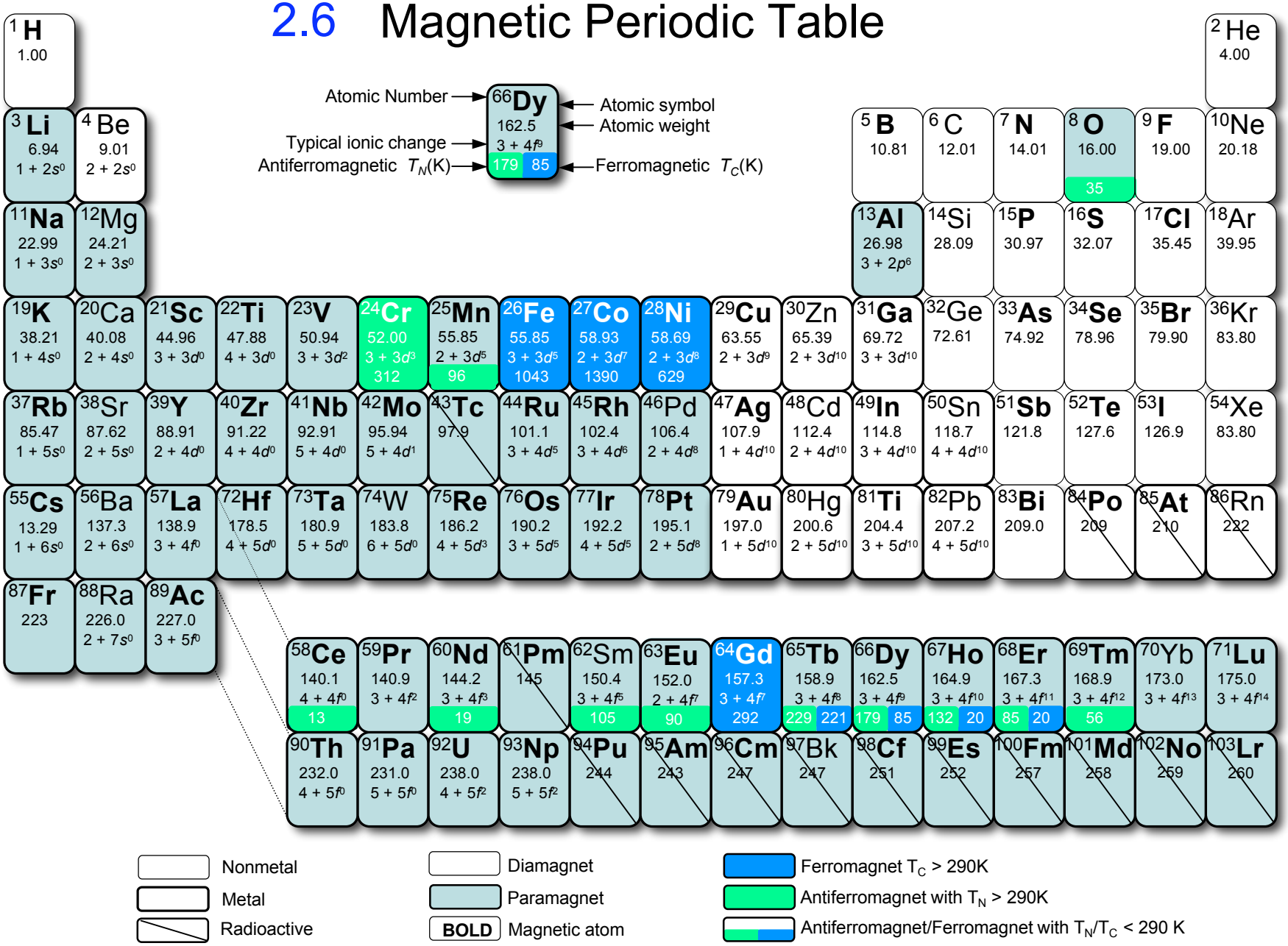
	n	l	m_l	m_s	No of states
1s	1	0	0	±1/2	2
2s	2	0	0	±1/2	2
2p	2	1	0,±1	±1/2	6
3s	3	0	0	±1/2	2
3p	3	1	0,±1	±1/2	6
3d	3	2	0,±1,±2	±1/2	10
4s	4	0	0	±1/2	2
4p	4	1	0,±1	±1/2	6
4d	4	2	0,±1,±2	±1/2	10
4f	4	3	0,±1,±2,±3	±1/2	14

*The Pauli exclusion principle: No two electrons can have the same four quan

Hydrogenic orbitals

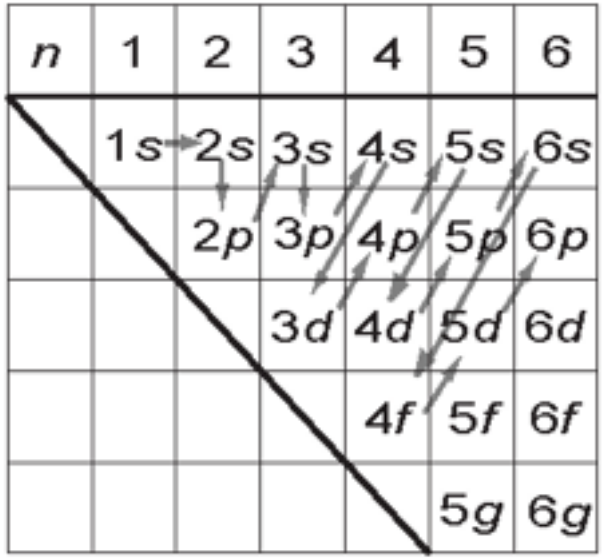


2.6 Magnetic Periodic Table



2.7 The Many Electron Atom

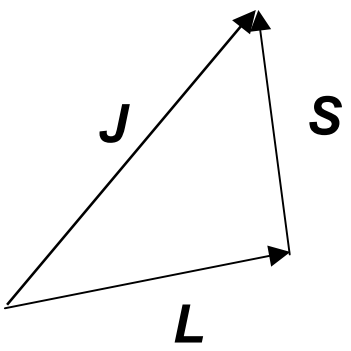
$$\mathcal{H}_0 = \sum_i [-(\hbar^2/2m_e)\nabla_i^2 - Ze^2/4\pi\epsilon_0 r_i] + \sum_{i<j} e^2/4\pi\epsilon_0 r_{ij}.$$



Hartree-Foch approximation

- No longer a simple Coulomb potential.
- *l* degeneracy is lifted.
- Solution: Suppose that each electron experiences the potential of a different spherically-symmetric potential.

Addition of angular momentum



First add the orbital and spin momenta l_i and s_i to form L and S. Then couple them to give the total J

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} \qquad |L\text{-}S| \leq J \leq |L\text{+}S|$$

Different *J*-states are termed *multiplets*.
Denoted by;

$$^{2S+1}X_J$$

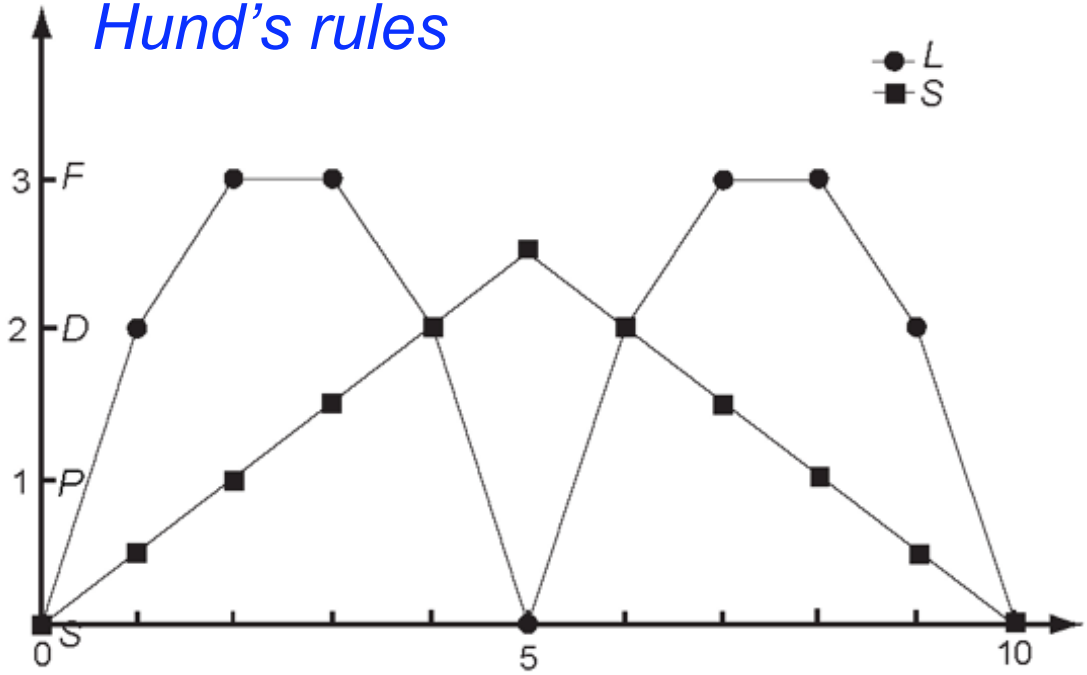
X = S,P,D,F,... for L = 0,1,2,3,...

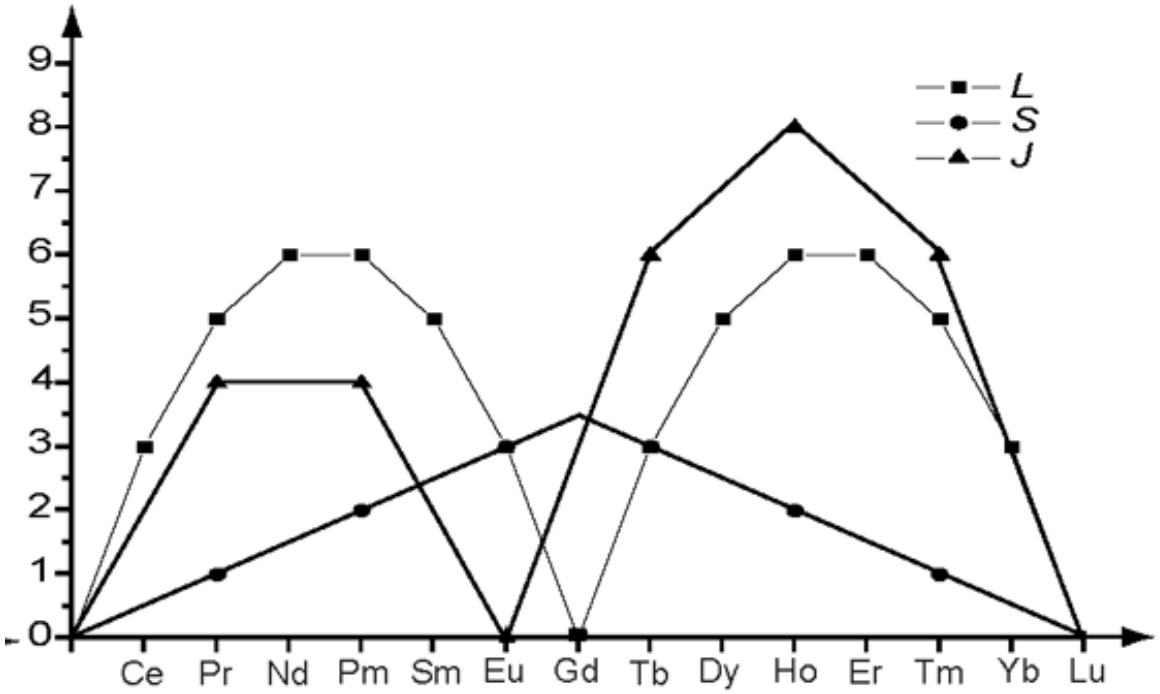
Hund's rules

For determining the ground-state of a multi-electron atom/ion.

1) Maximize S
2) Maximize *L* consistent with *S*.
3) Couple *L* and *S* to form *J.*
   - Less than half full shell $J = L\text{-}S$
   - Exactly half full shell $J = S$
   - More than half full shell $J = L\text{+}S$

Hund's rules


L
S
3
F
2
D
1
P
0
S
5
10


L
S
J
9
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4
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Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Examples of Hund's rules

Fe^{3+}	$3d^5$	↑↑↑↑↑| ooooo	
$S = 5/2$	$L = 0$	$J = 5/2$	$^6S_{5/2}$
Ni^{2+}	$3d^8$	↑↑↑↑↑|↓↓↓oo	
$S = 1$	$L = 3$	$J = 4$	$^3F_4$
Nd^{3+}	$4f^3$	↑↑↑oooo looooooo	
$S = 3/2$	$L = 6$	$J = 9/2$	$^4I_{9/2}$
Dy^{3+}	$4f^9$	↑↑↑↑↑↑↑|↓↓ooooo	
$S = 5/2$	$L = 5$	$J = 15/2$	$^6H_{15/2}$

2.8 Spin-Orbit Coupling

$\mathcal{H}_{so} = \Lambda \boldsymbol{L}.\boldsymbol{S}$

Λ is the spin-orbit coupling constant

$\Lambda > 0$ for the 1st half of the 3*d* or 4*f* series.
$\Lambda < 0$ for the 2nd half of the 3*d* or 4*f* series.

Single-electron atom case: $\mathcal{H}_{so} = \lambda \boldsymbol{l}.\boldsymbol{s}$

$$\Lambda = \pm (1/2)\lambda/2S$$

$$\boldsymbol{L}.\boldsymbol{S} = (1/2)(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2) = (\hbar^2/2)[J(J+1)-L(L+1)-S(S+1)]$$

2.9 Zeeman Interaction

$$\boldsymbol{m} = -(\mu_B/\hbar)(\boldsymbol{L}+2\boldsymbol{S})$$

The energy of a moment in a magnetic field is: $E = -\boldsymbol{m}.\boldsymbol{B}$

Hence:

$$\mathcal{H}_Z = (\mu_B/\hbar)(\boldsymbol{L}+2\boldsymbol{S}).\boldsymbol{B}$$

Lande g-factor

$g = -(\boldsymbol{m}.\boldsymbol{J}/\mu_B)/(\boldsymbol{J}^2/\hbar)$ Eigenvalues of $\boldsymbol{J}^2$ are: $J(J+1)\,\hbar^2$

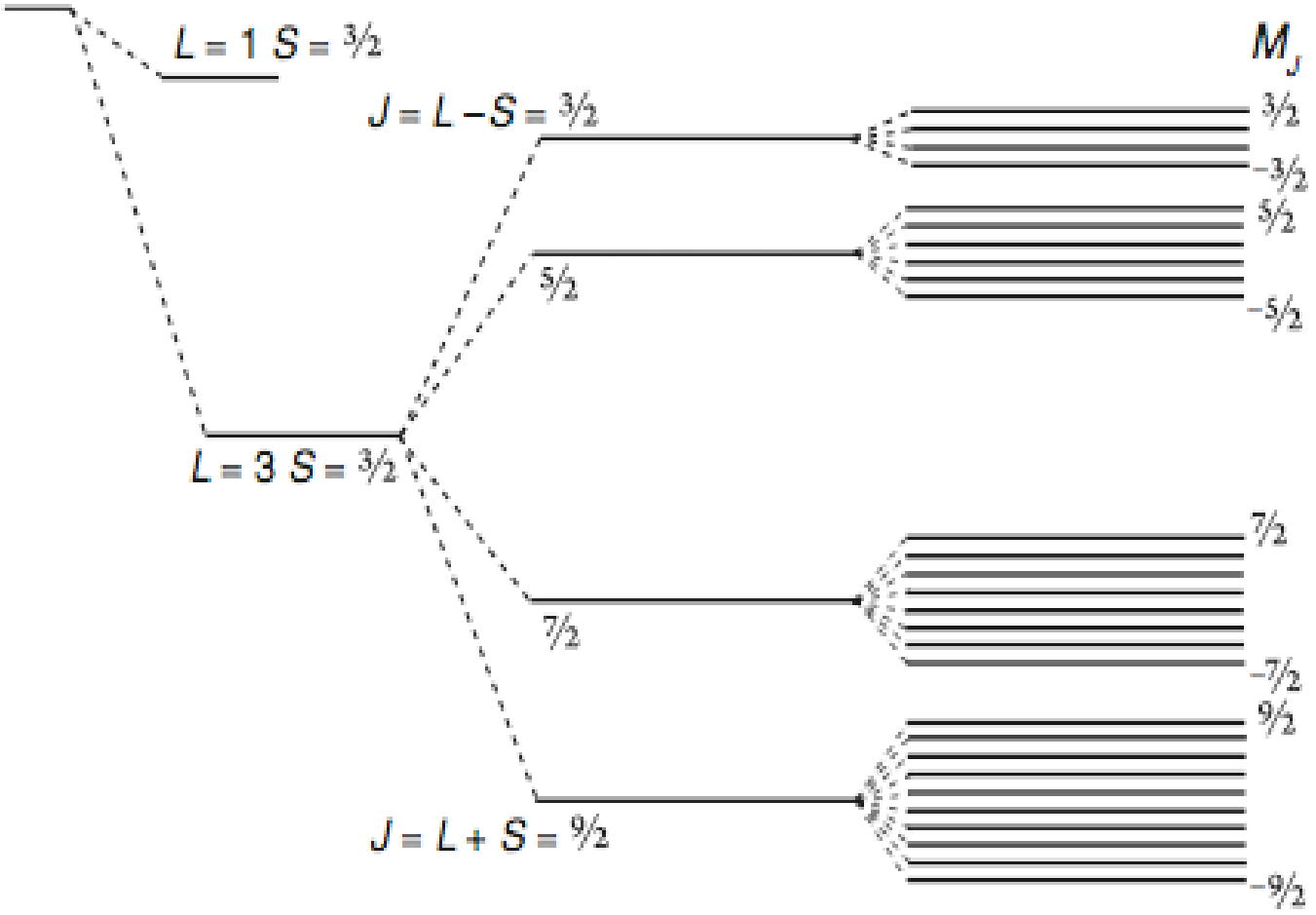
$$\begin{aligned}
\mathbf{m}.\boldsymbol{J} &= -(\mu_B/\hbar)[(\boldsymbol{L}+2\boldsymbol{S}).(\boldsymbol{L}+\boldsymbol{S})] \\
&= -(\mu_B/\hbar)[(\boldsymbol{L}^2+3\boldsymbol{L}.\boldsymbol{S}+2\boldsymbol{S}^2)] \text{ since } \boldsymbol{L} \text{ and } \boldsymbol{S} \text{ commute} \\
&= -(\mu_B/\hbar)[(\boldsymbol{L}^2+2\boldsymbol{S}^2+(3/2)(\boldsymbol{J}^2-\boldsymbol{L}^2-\boldsymbol{S}^2)] \\
&= -(\mu_B/\hbar)[(3/2)J(J+1)-(1/2)L(L+1)+(1/2)S(S+1)]
\end{aligned}$$

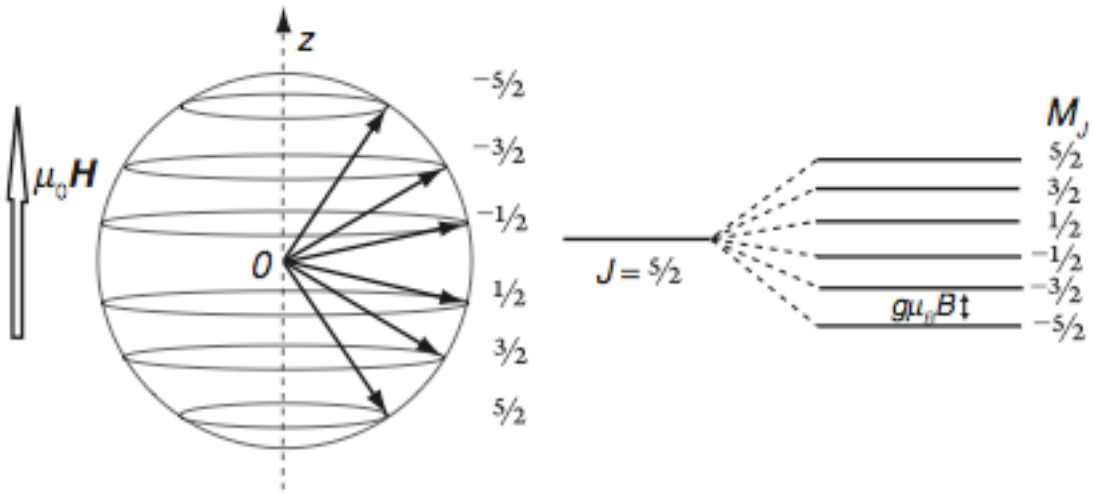
$$g = (3/2) + [S(S+1) - L(L+1)] / 2J(J+1)$$

$$\boldsymbol{m} = -g\mu_B\boldsymbol{J}/\hbar$$

Example: Co^{2+} free ion

The energy levels for a free ion with electronic configuration $3d^7$: Co^{2+}
$S = \frac{3}{2}, L = 3, J = \frac{9}{2}; g = \frac{5}{3}$.





Energy levels of an ion with J = 5/2 in an applied field

2.10 Curie Law Susceptibility

Curie law $\chi = C / T$

C is Curie's constant.
Units: Kelvin, K.
Typical values ~ 1K

The thermodynamic average of the moment:

$$\langle \mathfrak{m} \rangle = \frac{\sum_i \mathfrak{m}_i \exp(-\epsilon_i / k_B T)}{\sum_i \exp(-\epsilon_i / k_B T)}.$$

$\boldsymbol{B} = B\boldsymbol{z}$
$E = -\boldsymbol{m}.\boldsymbol{B}$ $\Rightarrow$

$$\langle \mathfrak{m}_z \rangle = \frac{\sum_{-J}^{J} -g\mu_B M_J (1 - \mu_0 g \mu_B M_J H / k_B T)}{\sum_{-J}^{J} (1 - \mu_0 g \mu_B M_J H / k_B T)}.$$

Using the identities:

$$\sum_{-J}^{J} 1 = 2J + 1; \qquad \sum_{-J}^{J} M_J = 0 \qquad \sum_{-J}^{J} M_J^2 = J(J+1)(2J+1)/3,$$

And the fact that $\chi = n \langle \boldsymbol{m} \rangle / H$

(*n* is the number density of atoms/ions)

We get that

$$C = \frac{\mu_0 n g^2 \mu_B^2 J(J+1)}{3 k_B}.$$

4f ions

Table 4.6. The 4 *f* ions. The paramagnetic moment m_{eff} and the saturation moment m_0 are in units of μ_B

$4f^n$		S	L	J	g	$m_0 = gJ$	$m_{eff} = g\sqrt{J(J+1)}$	m_{eff}^{exp}
1	Ce^{3+}	$\frac{1}{2}$	3	$\frac{5}{2}$	$\frac{6}{7}$	2.14	2.54	2.5
2	Pr^{3+}	1	5	4	$\frac{4}{5}$	3.20	3.58	3.5
3	Nd^{3+}	$\frac{3}{2}$	6	$\frac{9}{2}$	$\frac{8}{11}$	3.27	3.52	3.4
4	Pm^{3+}	2	6	4	$\frac{3}{5}$	2.40	2.68	
5	Sm^{3+}	$\frac{5}{2}$	5	$\frac{5}{2}$	$\frac{2}{7}$	0.71	0.85	1.7
6	Eu^{3+}	3	3	0	0	0	0	3.4
7	Gd^{3+}	$\frac{7}{2}$	0	$\frac{7}{2}$	2	7.0	7.94	8.9
8	Tb^{3+}	3	3	6	$\frac{3}{2}$	9.0	9.72	9.8
9	Dy^{3+}	$\frac{5}{2}$	5	$\frac{15}{2}$	$\frac{4}{3}$	10.0	10.65	10.6
10	Ho^{3+}	2	6	8	$\frac{5}{4}$	10.0	10.61	10.4
11	Er^{3+}	$\frac{3}{2}$	6	$\frac{15}{2}$	$\frac{6}{5}$	9.0	9.58	9.5
12	Tm^{3+}	1	5	6	$\frac{7}{6}$	7.0	7.56	7.6
13	Yb^{3+}	$\frac{1}{2}$	3	$\frac{7}{2}$	$\frac{8}{7}$	4.0	4.53	4.5

3d ions

Table 4.7. The 3*d* ions. m_{eff} is in units of μ_B

$3d^n$		S	L	J	g	$m_{eff} = g\sqrt{J(J+1)}$	$m_{eff} = g\sqrt{S(S+1)}$	m_{eff}^{exp}
1	Ti^{3+}, V^{4+}	$\frac{1}{2}$	2	$\frac{3}{2}$	$\frac{4}{5}$	1.55	1.73	1.7
2	Ti^{2+}, V^{3+}	1	3	2	$\frac{2}{3}$	1.63	2.83	2.8
3	V^{2+}, Cr^{3+}	$\frac{3}{2}$	3	$\frac{3}{2}$	$\frac{2}{5}$	0.78	3.87	3.8
4	Cr^{2+}, Mn^{3+}	2	2	0			4.90	4.9
5	Mn^{2+}, Fe^{3+}	$\frac{5}{2}$	0	$\frac{5}{2}$	2	5.92	5.92	5.9
6	Fe^{2+}, Co^{3+}	2	2	4	$\frac{3}{2}$	6.71	4.90	5.4
7	Co^{2+}, Ni^{3+}	$\frac{3}{2}$	3	$\frac{9}{2}$	$\frac{4}{3}$	6.63	3.87	4.8
8	Ni^{3+}	1	3	4	$\frac{5}{4}$	5.59	2.83	3.2
9	Cu^{2+}	$\frac{1}{2}$	2	$\frac{5}{2}$	$\frac{6}{5}$	3.55	1.73	1.9

b) Magnetization

To calculate the complete magnetization curve, set $y = g\mu_B\mu_0 H/k_B T$,

then

$\langle m \rangle = g\mu_B \partial/\partial y[\ln \Sigma_{-J}^{J} \exp\{M_J y\}]$ [d(ln z)/dy = (1/z) dz/dy]

The sum over the energy levels must be evaluated; it can be written as

$\exp(Jy)\{1 + r + r^2 + ...r^{2J}\}$ where $r = \exp\{-y\}$

The sum of a geometric progression $(1 + r + r^2 + ... + r^n) = (r^{n+1} - 1)/(r - 1)$

$\therefore \Sigma_{-J}^{J} \exp\{M_J y\} = (\exp\{-(2J+1)y\} - 1)\exp\{Jy\}/(\exp\{-y\}-1)$

multiply top and bottom by exp{y/2}

$= [\sinh(2J+1)y/2]/[\sinh y/2]$

$\langle m \rangle = g\mu_B(\partial/\partial y)\ln\{[\sinh(2J+1)y/2]/[\sinh y/2]\}$

$= g\mu_B/2\{(2J+1)\coth(2J+1)y/2 - \coth y/2\}$

setting x = Jy, we obtain

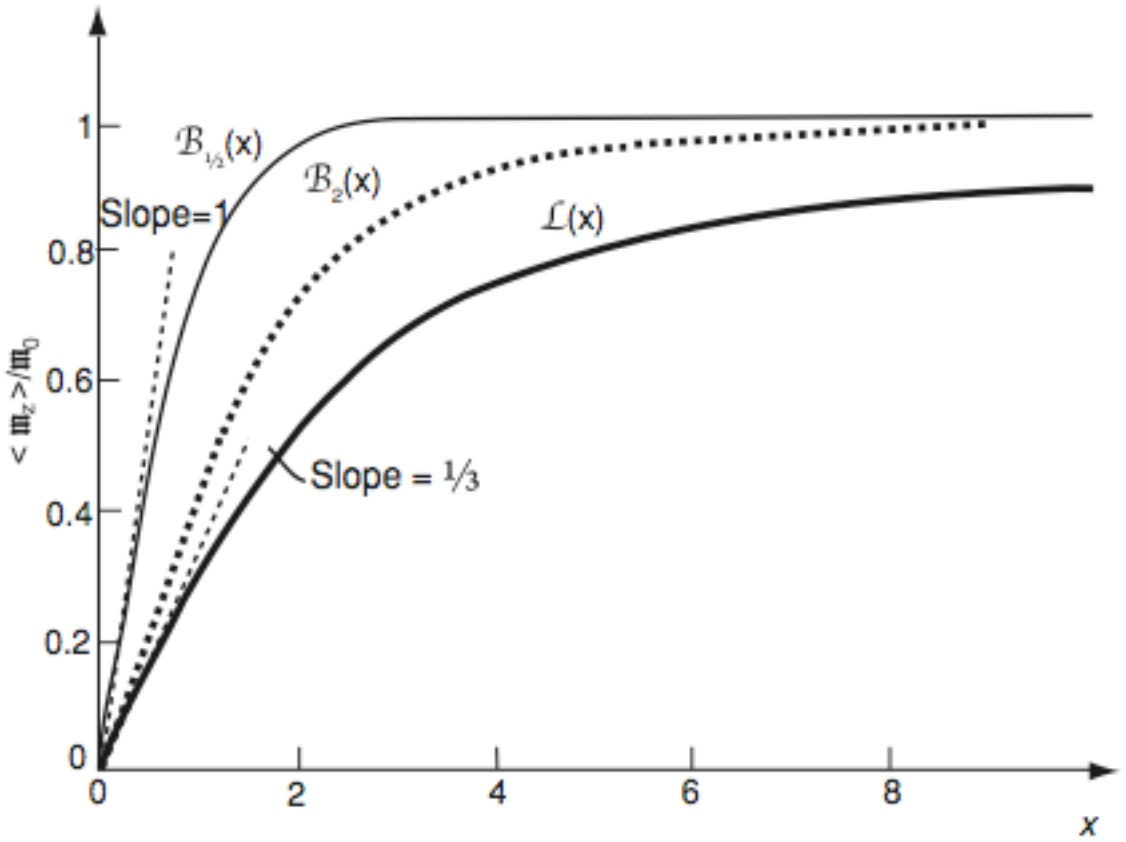
$$\langle m \rangle = m\,\mathcal{B}_J(x)$$

where the Brillouin function

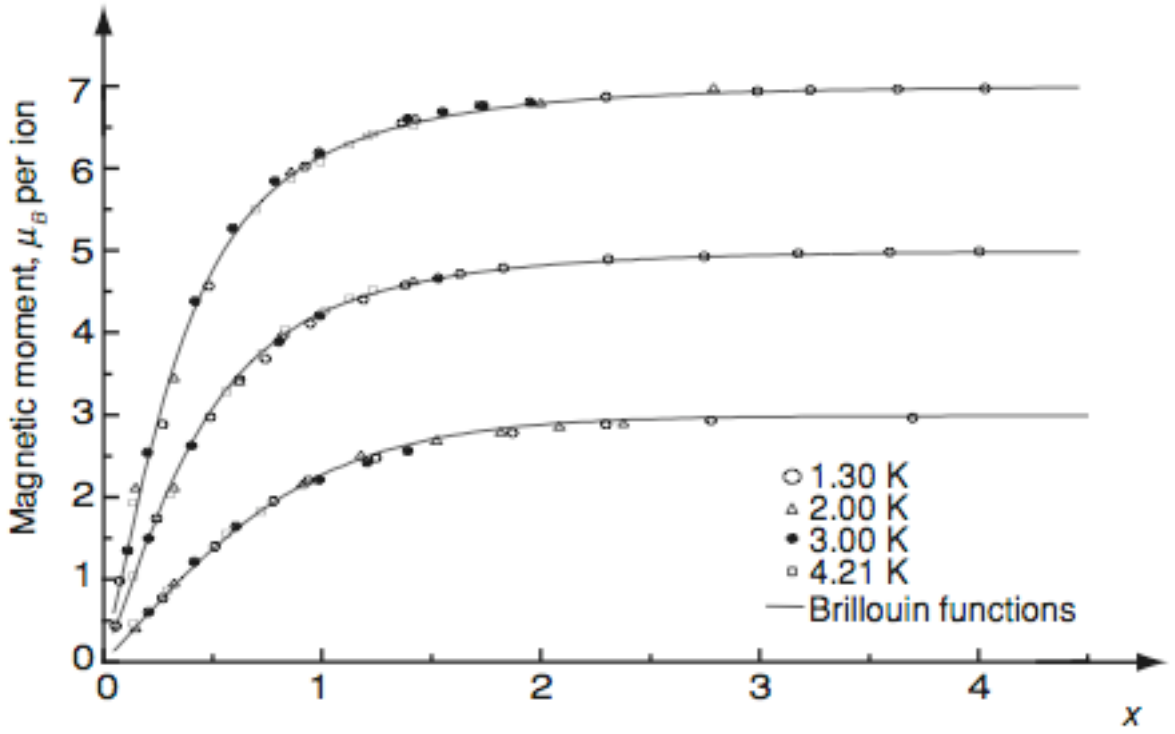
$\mathcal{B}_J(x)=\{(2J+1)/2J\}\coth(2J+1)x/2J-(1/2J)\coth(x/2J)$.

This reduces to $\langle m \rangle = \mu_B \tanh(x)$

in the limit J = 1/2, g = 2.



Comparison of the Brillouin functions for s = 1/2, S = 2 and the Langevin function (S = ∞)



Reduced magnetization curves of three paramagnetic salts, compared with Brillouin function predictions

Basic Concepts in Magnetism

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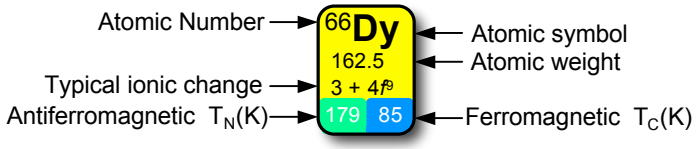
Ireland.

1. Magnetostatics
2. Magnetism of multi-electron atoms
3. Crystal field
4. Magnetism of the free electron gas
5. Dilute magnetic oxides

Comments and corrections please: jcoey@tcd.ie

www.tcd.ie/Physics/Magnetism

Magnetic Periodic Table



1 **H** 1.00																	2 He 4.00
3 **Li** 6.94 $1+2s^0$	4 Be 9.01 $2+2s^0$											5 **B** 10.81	6 C 12.01	7 **N** 14.01	8 **O** 16.00 35	9 **F** 19.00	10 Ne 20.18
11 **Na** 22.99 $1+3s^0$	12 Mg 24.21 $2+3s^0$											13 **Al** 26.98 $3+2p^6$	14 Si 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 Ar 39.95
19 **K** 38.21 $1+4s^0$	20 Ca 40.08 $2+4s^0$	21 **Sc** 44.96 $3+3d^0$	22 **Ti** 47.88 $4+3d^0$	23 **V** 50.94 $3+3d^2$	24 **Cr** 52.00 $3+3d^3$ 312	25 **Mn** 55.85 $2+3d^5$ 96	26 **Fe** 55.85 $3+3d^5$ 1043	27 **Co** 58.93 $2+3d^7$ 1390	28 **Ni** 58.69 $2+3d^8$ 629	29 **Cu** 63.55 $2+3d^9$	30 Zn 65.39 $2+3d^{10}$	31 **Ga** 69.72 $3+3d^{10}$	32 Ge 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 Kr 83.80
37 **Rb** 85.47 $1+5s^0$	38 Sr 87.62 $2+5s^0$	39 **Y** 88.91 $2+4d^0$	40 **Zr** 91.22 $4+4d^0$	41 **Nb** 92.91 $5+4d^0$	42 **Mo** 95.94 $5+4d^1$	43 **Tc** 97.9	44 **Ru** 101.1 $3+4d^5$	45 **Rh** 102.4 $3+4d^6$	46 Pd 106.4 $2+4d^8$	47 **Ag** 107.9 $1+4d^{10}$	48 Cd 112.4 $2+4d^{10}$	49 **In** 114.8 $3+4d^{10}$	50 Sn 118.7 $4+4d^{10}$	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 Xe 83.80
55 **Cs** 13.29 $1+6s^0$	56 Ba 137.3 $2+6s^0$	57 **La** 138.9 $3+4f^0$	72 **Hf** 178.5 $4+5d^0$	73 **Ta** 180.9 $5+5d^0$	74 W 183.8 $6+5d^0$	75 **Re** 186.2 $4+5d^3$	76 **Os** 190.2 $3+5d^5$	77 **Ir** 192.2 $4+5d^5$	78 **Pt** 195.1 $2+5d^8$	79 **Au** 197.0 $1+5d^{10}$	80 Hg 200.6 $2+5d^{10}$	81 **Tl** 204.4 $3+5d^{10}$	82 **Pb** 207.2 $4+5d^{10}$	83 **Bi** 209.0	84 **Po** 209	85 **At** 210	86 Rn 222
87 **Fr** 223	88 Ra 226.0 $2+7s^0$	89 **Ac** 227.0 $3+5f^0$															

58 **Ce** 140.1 $4+4f^0$ 13	59 **Pr** 140.9 $3+4f^2$	60 **Nd** 144.2 $3+4f^3$ 19	61 **Pm** 145	62 Sm 150.4 $3+4f^5$ 105	63 **Eu** 152.0 $2+4f^7$ 90	64 **Gd** 157.3 $3+4f^7$ 292	65 **Tb** 158.9 $3+4f^8$ 229 221	66 **Dy** 162.5 $3+4f^9$ 179 85	67 **Ho** 164.9 $3+4f^{10}$ 132 20	68 **Er** 167.3 $3+4f^{11}$ 85 20	69 **Tm** 168.9 $3+4f^{12}$ 56	70 Yb 173.0 $3+4f^{13}$	71 **Lu** 175.0 $3+4f^{14}$
90 **Th** 232.0 $4+5f^0$	91 **Pa** 231.0 $5+5f^0$	92 **U** 238.0 $4+5f^2$	93 **Np** 238.0 $5+5f^2$	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 Bk 247	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 259	103 **Lr** 260

Nonmetal
Metal
Radioactive

Diamagnet
Paramagnet
BOLD Magnetic atom

Ferromagnet T_C > 290K
Antiferromagnet with T_N > 290K
Antiferromagnet/Ferromagnet with T_N/T_C < 290 K