Fundamentals of Magnetism – 2

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Ireland.

4. Magnetism of the electron
5. The multi-electron atom
6. The single-electron atom
7. Ions in solids

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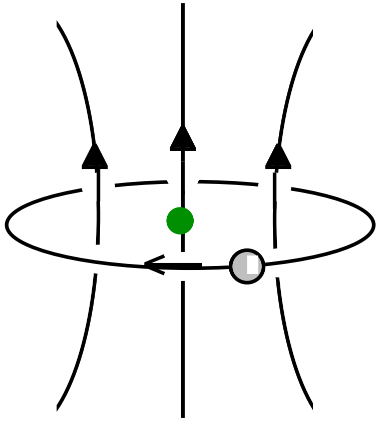
Lecture 2 covers the origin of magnetism in solids, in the spin and orbital moments of the electron. Paramagnetism of non-interacting electrons is discussed in the localized limit. The multi-electron atom is analysed, and the influence of the local crystalline environment and ligand field on its paramagnetism is explained. Finally, magnetic ordering is discussed, in terms of molecular field theory.

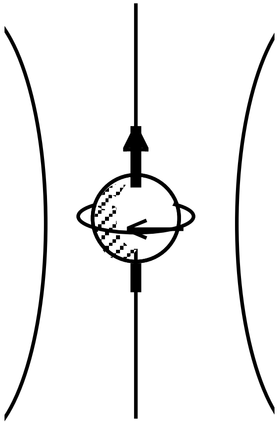
An elementary knowledge of atomic physics, and quantum mechanics is assumed.

4. Magnetism of the electron

Orbital and Spin Moment



(a)



(b)

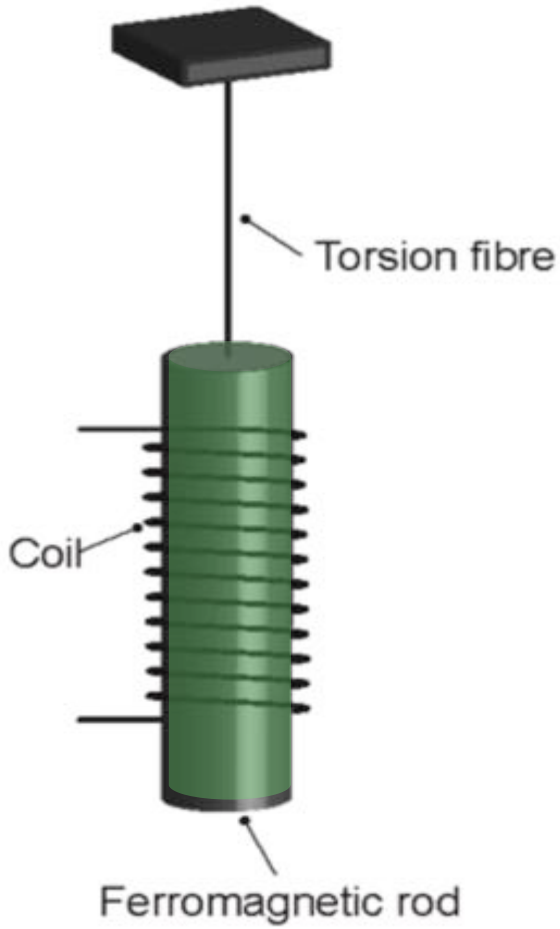
Magnetism in solids is due to the *angular momentum* of the atomic electrons.

Two contributions to the electron moment:

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

Einstein-de Hass Experiment

Demonstrates the relation between magnetism and angular momentum.



A ferromagnetic iron rod is suspended on a torsion fibre.

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

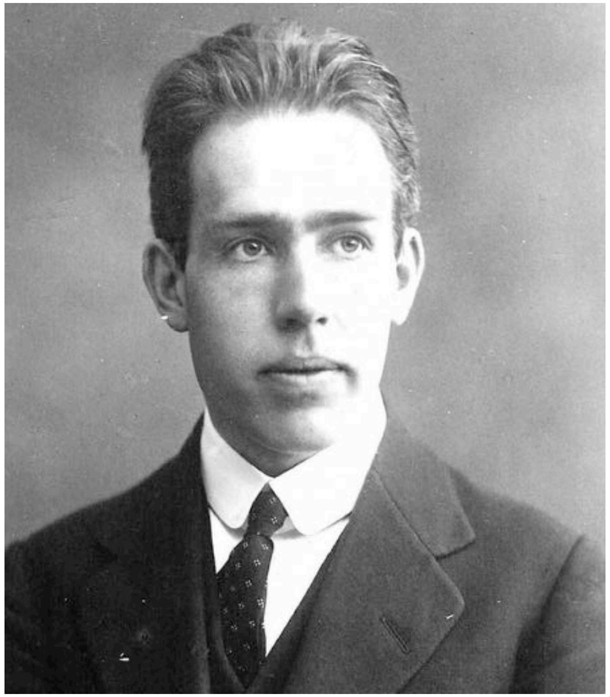
An angular impulse is delivered due to the reversal of the angular momentum of the electrons- conservation of angular momentum.

Fe has 26 electrons, moment per Fe is that of 2.2e

Paradigm shift was needed to explain

1) Amperian Currents
2) Weiss field
3) Bohr - van Leewen theorem.

Bohr-van Leeuwen Theorem



A famous and disconcerting result od classical statistical mechanics;

At any finite temperature, and in all finite electric or magnetic fields, the net magnetization of a collection of electrons in thermal equilibrium vanishes identically!

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*

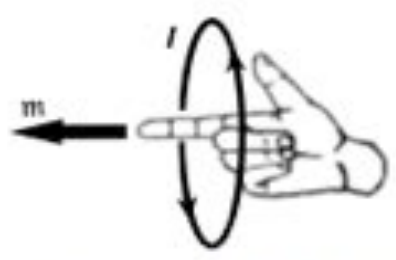
Dirac and Heisenberg in red *B. Cabrera in yellow*

The electron

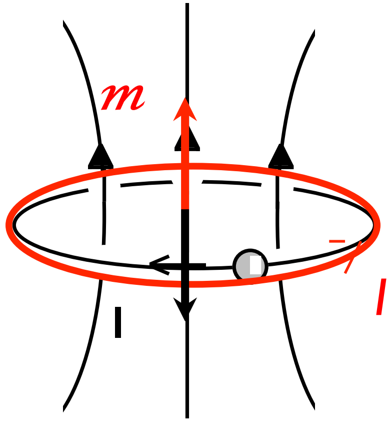
The magnetic properties of molecules and solids derive essentially from the magnetism of their electrons. (Nuclei also possess magnetic moments, but they are ≈ 1000 times smaller).

An electron is a point particle with:

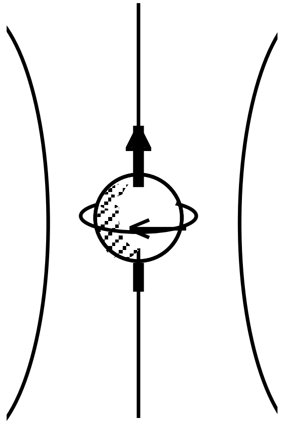
mass	$m_e = 9.109\ 10^{-31}$ kg
charge	$-e = -1.602\ 10^{-19}$ C
intrinsic angular momentum *(spin)*	$\frac{1}{2}\hbar = 0.527\ 10^{-34}$ J s



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



Orbital moment



Spin

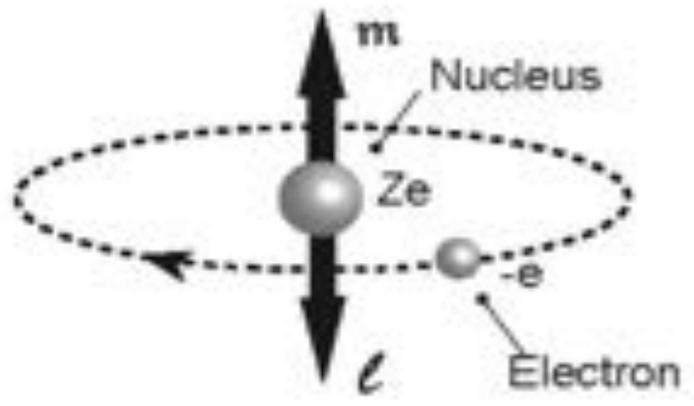
The same magnetic moment, the Bohr Magneton,

$$\boxed{\mu_B = e\hbar/2m_e = 9.27\ 10^{-24}\ \mathrm{Am}^2}$$

is associated with ½ħ of spin angular momentum or ħ 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

Orbital moment



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

The moment* is $\mathfrak{m} = IA \quad \mathfrak{m} = -evr/2$

Bohr: orbital angular momentum ℓ is quantized in units of ħ; h is Planck's constant = $6.626\ 10^{-34}$ J s; ħ = h/2π = $1.055\ 10^{-34}$ J s. $|\ell| = n\hbar$

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

Orbital quantum number ℓ, $\ell_z = m_l\hbar \quad m_l = 0, \pm 1, \pm 2, \ldots, \pm\ell$ so $\mathfrak{m}_z = -m_l(e\hbar/2m_e)$

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

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

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

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

g-factor; Bohr radius; energy scale

The *g-factor* is defined as the ratio of magnitude of m in units of μ_B to magnitude of ℓ in units of $\hbar$.

$g = 1$ 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

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

Spin moment

Spin is a relativistic effect.

Spin angular momentum $\boldsymbol{s}$

Spin quantum number s — s = ½ for electrons

Spin magnetic quantum number m_s — $m_s = \pm½$ for electrons

$$\boxed{s_z = m_s\hbar} \qquad m_s = \pm½ \text{ for electrons}$$

$$\boxed{\mathcal{m}_z = -(e/m_e)m_s\hbar = \pm\mu_B} \qquad \boldsymbol{\mathcal{m}} = -(e/m_e)\boldsymbol{s}$$

For spin moments of electrons we have gyromagnetic ratio and g-factor:

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

More accurately, after higher order corrections: $g = 2.0023$ $\mathcal{m}_z = 1.00116\mu_B$

An electron will usually have both orbital and spin angular momentum

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

Quantized mechanics of spin

In quantum mechanics, we represent physical observables by operators – differential or matrix.

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

n magnetic basis states ⇒ n x n Hermitian matrix, $A_{ij}=A^*_{ji}$

Pauli spin matrices

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

Spin operator (for s = ½)

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

Electron: $s = ½ \Rightarrow m_s=\pm½$ i.e spin down and spin up states

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

$$\boxed{\boldsymbol{s}\,|\uparrow\rangle = -\tfrac{1}{2}\hbar\,|\uparrow\rangle\,; \quad \boldsymbol{s}|\downarrow\rangle = \tfrac{1}{2}\hbar|\downarrow\rangle}$$

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

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

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

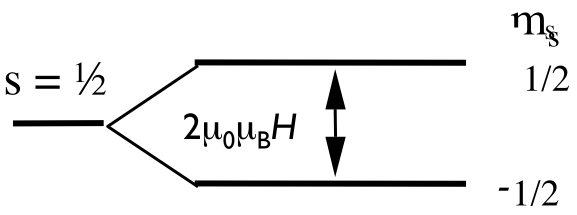
$$[\hat{\boldsymbol{s}}_x, \hat{\boldsymbol{s}}_y] = i\hbar\hat{\boldsymbol{s}}_z, \quad [\hat{\boldsymbol{s}}_y, \hat{\boldsymbol{s}}_z] = i\hbar\hat{\boldsymbol{s}}_x, \quad [\hat{\boldsymbol{s}}_z, \hat{\boldsymbol{s}}_x] = i\hbar\hat{\boldsymbol{s}}_y.$$

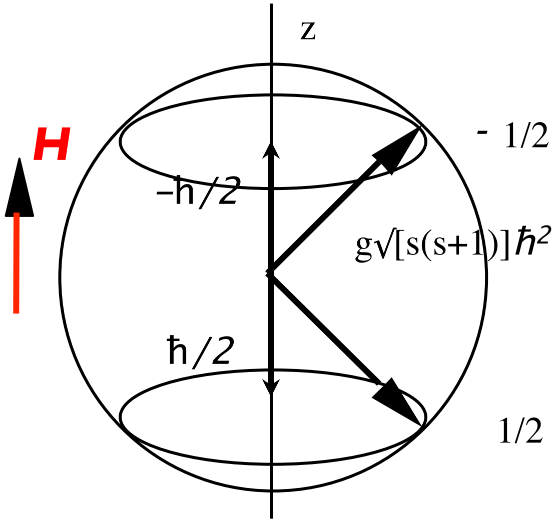
or

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

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 = -½) and ‘spin down’ (↓, m_s = ½), which correspond to two possible orientations of the spin moment relative to the applied field.

Spin magnetization of localized electrons

Populations of the energy levels are given by Boltzmann statistics; $\propto \exp\{-E_i/k_BT\}$. The thermodynamic average $\langle m \rangle$ is evaluated from these Boltzmann populations.

$$\langle m \rangle = \frac{[\mu_B \exp(x) - \mu_B \exp(-x)]}{[\exp(x) + \exp(-x)]}$$

where $x = \mu_0 \mu_B H/k_B T$.

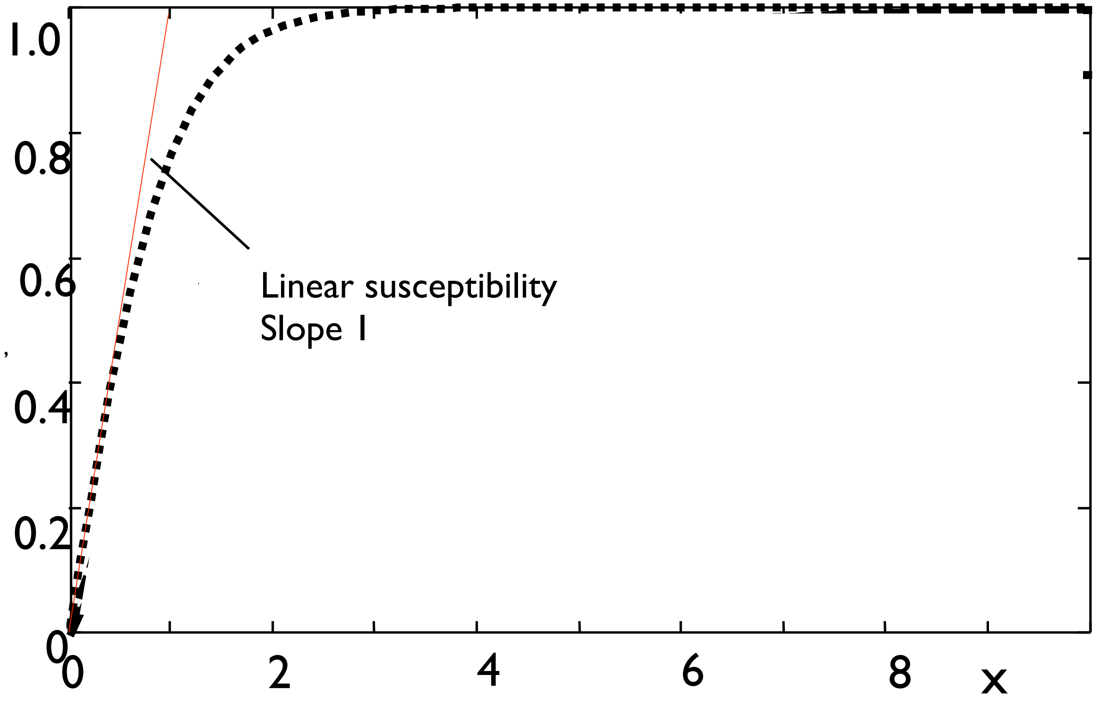
$$\boxed{\langle m \rangle = \underline{\mu_B}\tanh(x)}$$

Note that to approach saturation $x \approx 2$

At T = 300 K, $\mu_0 H$. = 900 T

At T = 1K , $\mu_0 H$. = 3 K.

Useful conversion 1 Tμ_B = 0.672 (μ_B/k_B)



Curie-law susceptibility of localized electrons

In small fields, tanh(x) ≈ x, hence the susceptibility

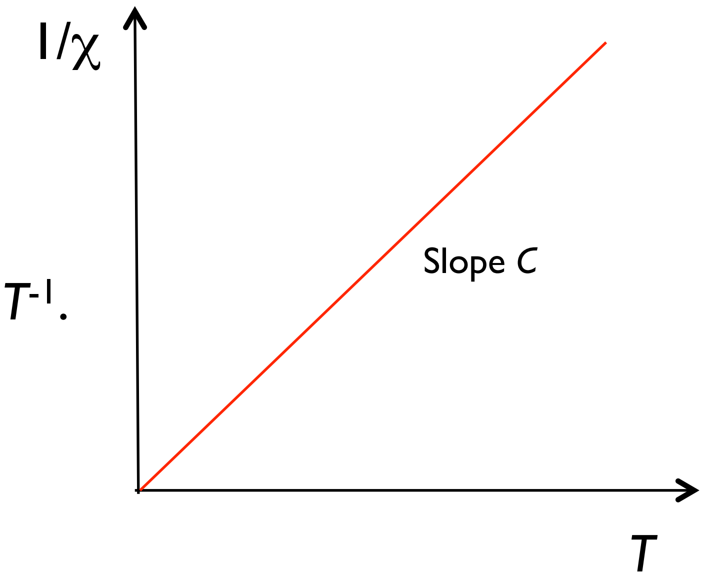
$$\chi = N\langle m\rangle/H \quad (N \text{ is no of electrons m}^{-3})$$

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

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

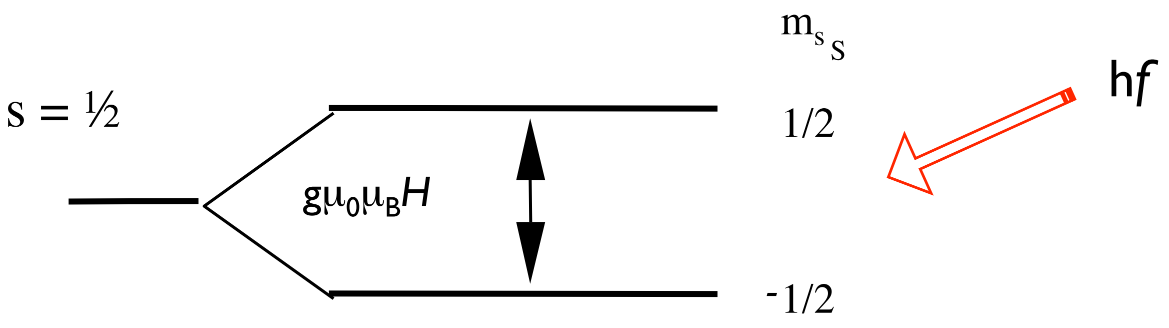
In other terms

$$\chi = C/T, \quad \text{where} \quad \boxed{C = \mu_0 N \mu_B^2/k_B}$$



C is the Curie constant with dimensions of temperature;
Assuming an electron density N of 6 10^{28} m^{-3} gives a Curie constant $C \approx 0.5$ K.
The Curie law susceptibility at room temperature is of order 10^{-3}.

Electrons in a field; paramagnetic resonance



At room temperature there is a very slight difference in thermal populations of the two spin states (hence the very small spin susceptibility of 10^{-3}). The relative population difference is $x = g\mu_0\mu_B H/2k_B T$

At resonance, energy is absorbed from the rf field until the populations are equalized.

The resonance condition is $h\nu = g\mu_0\mu_B H$

$$\nu/\mu_0 H = g\mu_B/h \qquad [= ge\hbar/2m_e h = e/2\pi m_e]$$

Spin resonance frequency $f = \nu/2\pi$ is 28 GHz T^{-1}

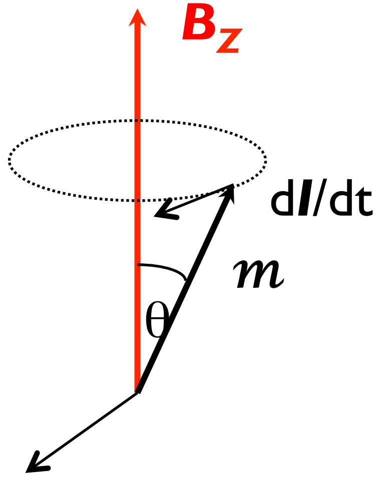
Electrons in a field - Larmor precession

$\boldsymbol{m} = \gamma \boldsymbol{l} \quad [\gamma = -e/m_e]$

$\Gamma = \boldsymbol{m} \times \mathbf{B}$

$\Gamma = d\boldsymbol{l}/dt$ (Newton's law)

$$\boxed{d\boldsymbol{m}/dt = \gamma\, \boldsymbol{m} \times \mathbf{B}}$$



$\Gamma = \boldsymbol{m} \times \mathbf{B}$

$$= \gamma \begin{vmatrix} \mathbf{e}_x & \mathbf{e}_y & \mathbf{e}_z \\ m_x & m_y & m_z \\ 0 & 0 & B_z \end{vmatrix}$$

$dm_x/dt = \gamma m_y B_z \quad dm_y/dt = -\gamma m_x B_z \quad dm_z/dt = 0$

Solution is $\boldsymbol{m}(t) = \boldsymbol{m}\,(\sin\theta \cos\omega_L t, \sin\theta \sin\omega_L t, \cos\theta)$

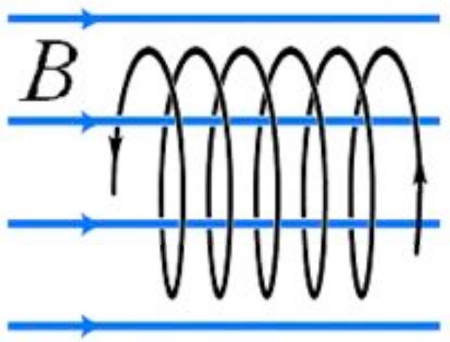
where $\omega_L = \gamma B_z$

Magnetic moment precesses at the Larmor precession frequency $\boxed{f_L = \gamma B/2\pi}$

$d\boldsymbol{M}/dt = \gamma \boldsymbol{M} \times \mathbf{B} - \alpha \mathbf{e}_M \times d\boldsymbol{M}/dt$

28 GHz T^{-1} for spin

Electrons in a field – Cyclotron resonance



Free electrons follow cyclotron orbits in a magnetic field.
Electron has velocity $\boldsymbol{v}$ then it experiences a Lorentz force

$$\boxed{\boldsymbol{F} = -e\boldsymbol{v} \times \boldsymbol{B}}$$

The electron executes circular motion about the direction of $\boldsymbol{B}$ (tracing a helical path if $v_{||} \neq 0$)

Cyclotron frequency $f_c = v_\perp/2\pi r$

$$\boxed{f_c = eB/2\pi m_e}$$

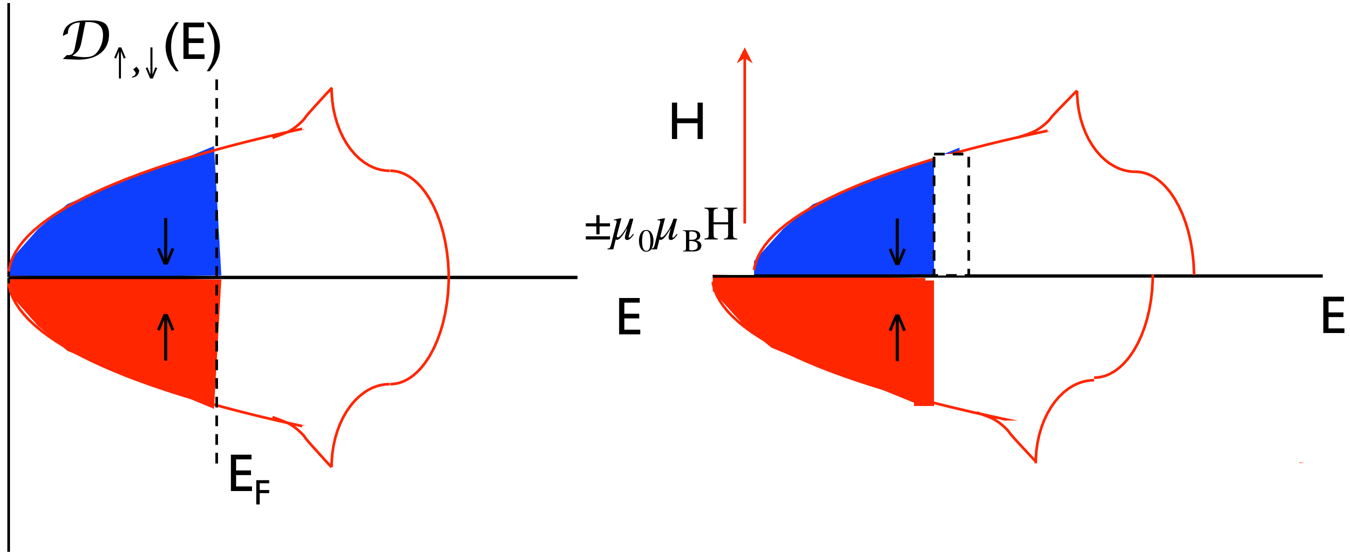
Electrons in cyclotron orbits radiate at the cyclotron frequency

Example: — Microwave oven

Since $\gamma_e = -(e/m_e)$, the cyclotron and Larmor and epr frequencies are all the *same* for electrons; 28.0 GHz T^{-1}

Pauli susceptibility

We now show the ↑ and ↓ density of states separately. They split in a field $B = \mu_0 H$



The splitting is really very small, ~ 10^{-5} of the bandwidth in a field of 1 T.

$M = \mu_B(N_\uparrow - N_\downarrow)/V$ Note M is magnetic moment per unit volume

At T = 0, the change in population in each band is $\Delta N = \frac{1}{2}\mathcal{D}(E_F)\mu_0\mu_B H$

$M = 2\mu_B \Delta N = \mathcal{D}(E_F)\mu_0\mu_B^2 H$ The dimensionless susceptibility $\chi = M/H$

$$\boxed{\chi_{Pauli} = \mathcal{D}(E_F)\mu_0\mu_B^2}$$ It is ~ 10^{-5} and independent of T

Landau diamagnetism

In the free-electron model, $\mathcal{D}(E_F) = (3/2)n/E_F$

Hence $\chi_{\mathrm{Pauli}} = \{3n\mu_0\mu_B^2/2E_F\}[1 + cT^2 + \ldots]$ (Compare Curie law $n\mu_0\mu_B^2/k_BT$)

The ratio of electronic specific heat coefficient to Pauli susceptibility in the nearly-free, independent electron approximation should be a constant $\mathcal{R}$.

Free electron model was used by Landau to calculate the orbital diamagnetism of conduction electrons. The result is:

$$\boxed{\chi_L = -n\mu_0\mu_B^2/2k_BT_F}$$

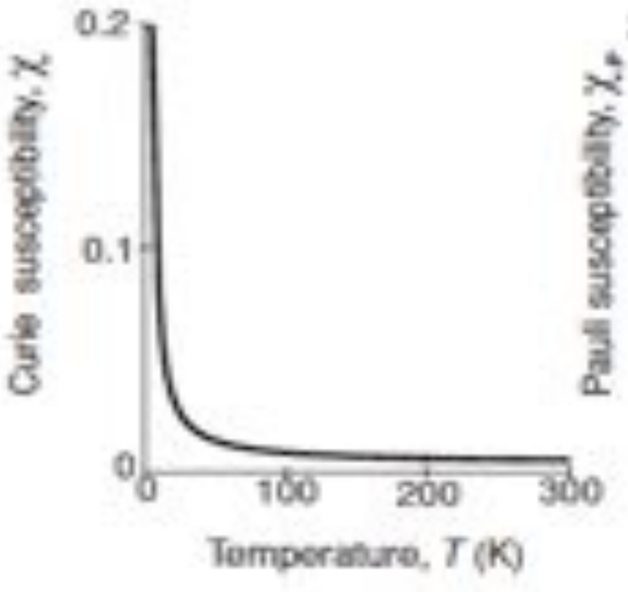
exactly one third of the Pauli susceptibility, and opposite in sign.

The real band structure is taken into account in an approximate way by renormalizing the electron mass. Replace m_e by an effective mass m*

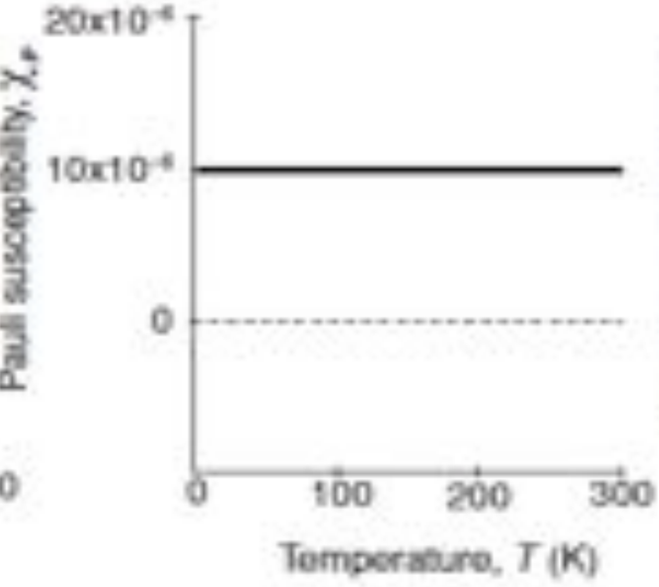
Then $\chi_L = -(1/3)(m_e/m^*)\,\chi_P$

In some semimetals such as graphite or bismuth, m* can be $\approx 0.01\ m_e$, hence the diamagnetism of the conduction electrons may sometimes be the dominant contribution to the susceptibility. ($\chi_L = -4\ 10^{-4}$ for graphite)

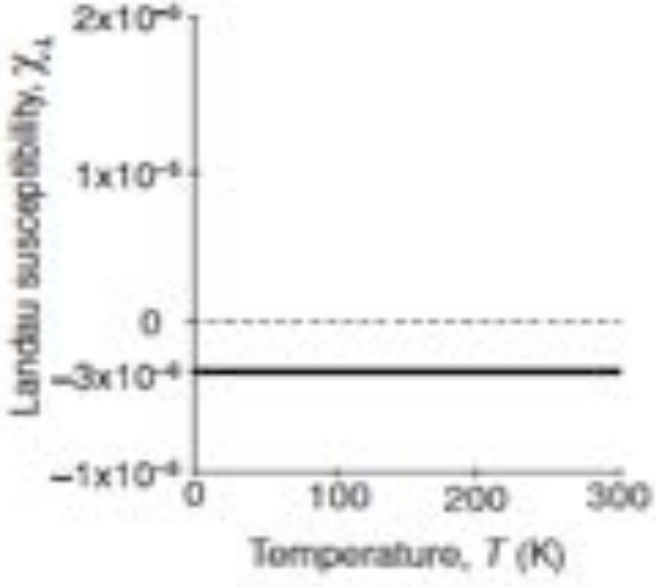
Susceptibility of electrons; summary



Curie



Pauli

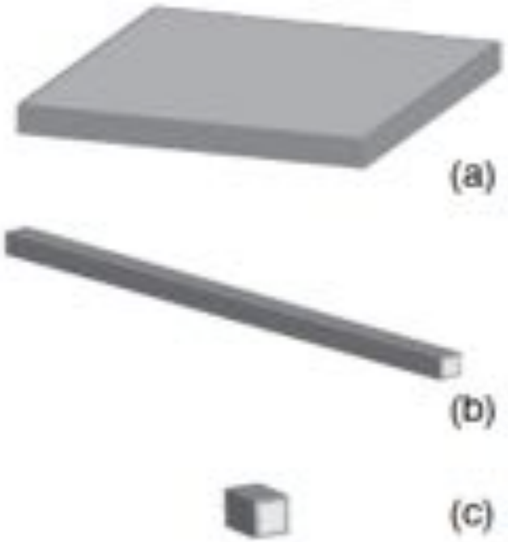


Landau

Density of states in other dimension

3-d solid

$\mathcal{D}(\varepsilon) \propto \varepsilon^{1/2}$



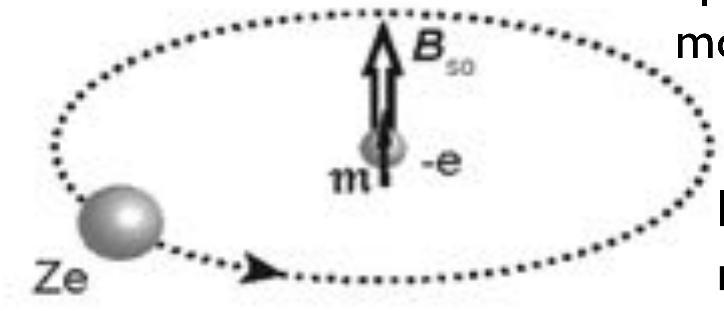
Confinement of the free-electron gas: (a) in two dimensions, (b) in one dimension – a quantum wire, and (c) in zero dimensions – a quantum dot.

$\mathcal{D}(\varepsilon) = \text{constant}$

$\mathcal{D}(\varepsilon) \propto \varepsilon^{-1/2}$

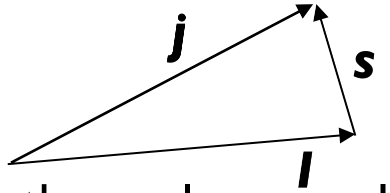
Discreet levels

Spin-Orbit Coupling



Spin and angular momentum coupled to create total angular momentum $\boldsymbol{j}$. $\boldsymbol{J} = \boldsymbol{l} + \boldsymbol{s}$

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



From the electron's point of view, the nucleus revolves round it with speed v ⇒ current loop. It is a relativistic effect

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

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

$$B_{so} = \mu_0 Zev/4\pi r^2 \quad [\sim 10\,\mathrm{T} \text{ for B or C}]$$

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

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

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

The spin – orbit Hamiltonian for a single electron is of the form:

$$\boxed{\mathcal{H}_{so} = \lambda \hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{s}}.}$$

in general $\mathcal{H}_{so} = (1/2m_e{}^2c^2r)dV/dr\ \boldsymbol{l.s}$

Here the two ħs have been assimilated into λ, making it an energy (c.f. exchange)

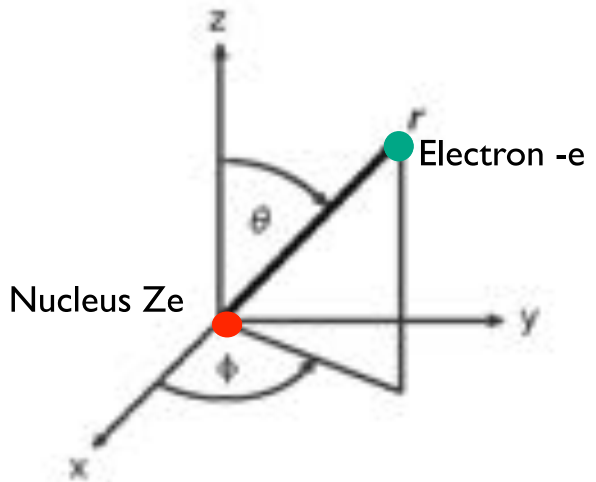
Orbital angular momentum

The orbital angular momentum operators also satisfy the commutation rules:

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

Spherical polar coordinates

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



$$\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p} = -i\hbar(y\partial/\partial z - z\partial/\partial y)\mathbf{e}_x - i\hbar(z\partial/\partial x - x\partial/\partial z)\mathbf{e}_y - i\hbar(x\partial/\partial y - y\partial/\partial x)\mathbf{e}_z.$$

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

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

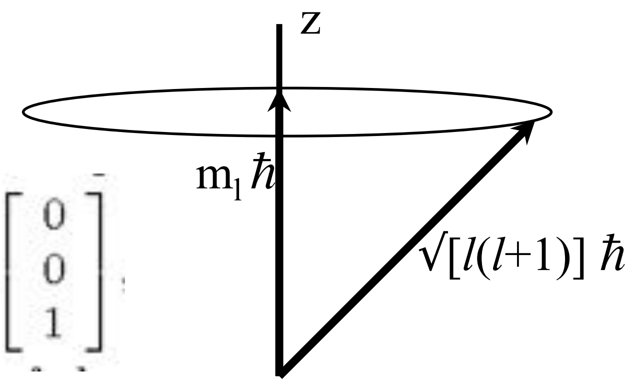
5. The Single-electron Atom

Orbital angular momentum operators

Eigenvalues of $\boldsymbol{l}^2$:

$$\boxed{l(l+1)\hbar^2}$$

l is the orbital angular momentum quantum number



l = 1 case

$m_l = 1, 0, -1$ corresponds to the eigenvectors $\begin{bmatrix}1\\0\\0\end{bmatrix}, \begin{bmatrix}0\\1\\0\end{bmatrix}, \begin{bmatrix}0\\0\\1\end{bmatrix}$

$\boldsymbol{l}_x$, $\boldsymbol{l}_y$ and $\boldsymbol{l}_z$ 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

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

Solution of Schrodinger's equation

Schrodinger's equation:

$$\boxed{\mathcal{H}\psi_i = \varepsilon_i\psi_i.}$$

$$\left[-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{1}{\hbar^2 r^2}\hat{l}^2\right)-\frac{Ze^2}{4\pi\epsilon_0 r}\right]\psi_i=\varepsilon_i\psi_i.$$

$$\varepsilon_n=\frac{-Zme^4}{8\epsilon_0^2h^2n^2}=\frac{-ZR_0}{n^2}$$

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

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

And the combined angular parts are $\boxed{Y_\ell^{m_\ell}(\theta,\phi)\propto P_\ell^{m_\ell}(\theta)e^{im_\ell\phi}.}$ *(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	$Y_2^{\pm2}=\sqrt{15/32\pi}\sin^2\theta\exp(\pm2i\phi)$	
f	$Y_3^{\pm2}=\sqrt{105/32\pi}\sin^2\theta\cos\theta\exp(\pm2i\phi)$	$Y_3^{\pm3}=\pm\sqrt{35/64\pi}\sin^3\theta\exp(\pm3i\phi)$

One-electron hydrogenic states

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)

	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

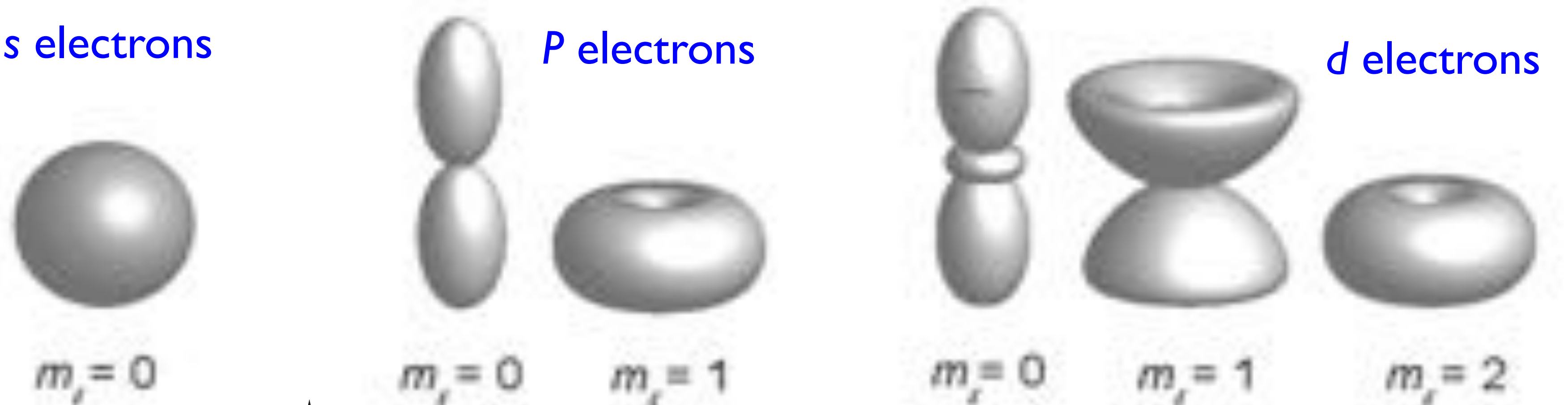
*The Pauli exclusion principle: No two electrons can have the same four quantum numbers.
⇒ Two electrons in the same orbital must have opposite spin.

Single-electron orbitals

s electrons

P electrons

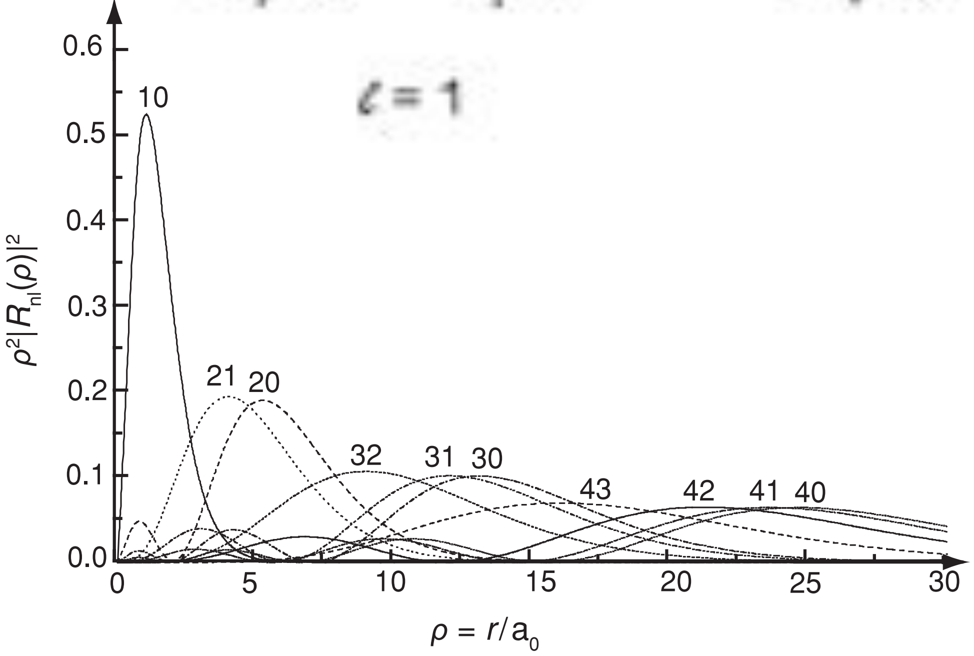
d electrons



$\ell = 0$

$\ell = 1$

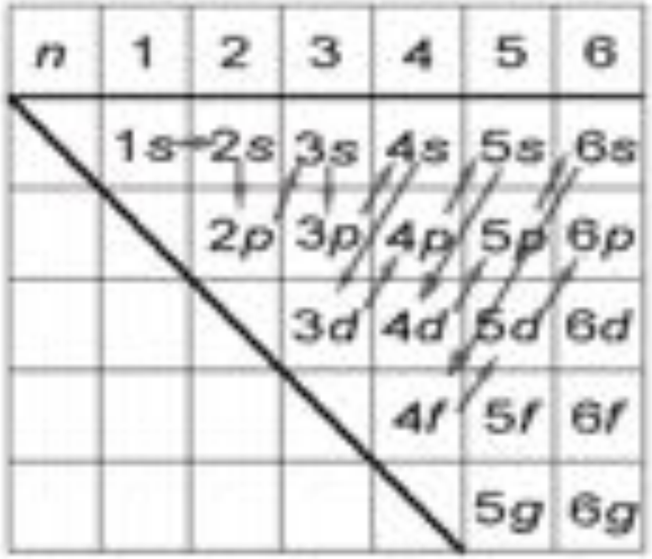
$\ell = 2$



6. The Multi-electron Atom

The many-electron atom

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

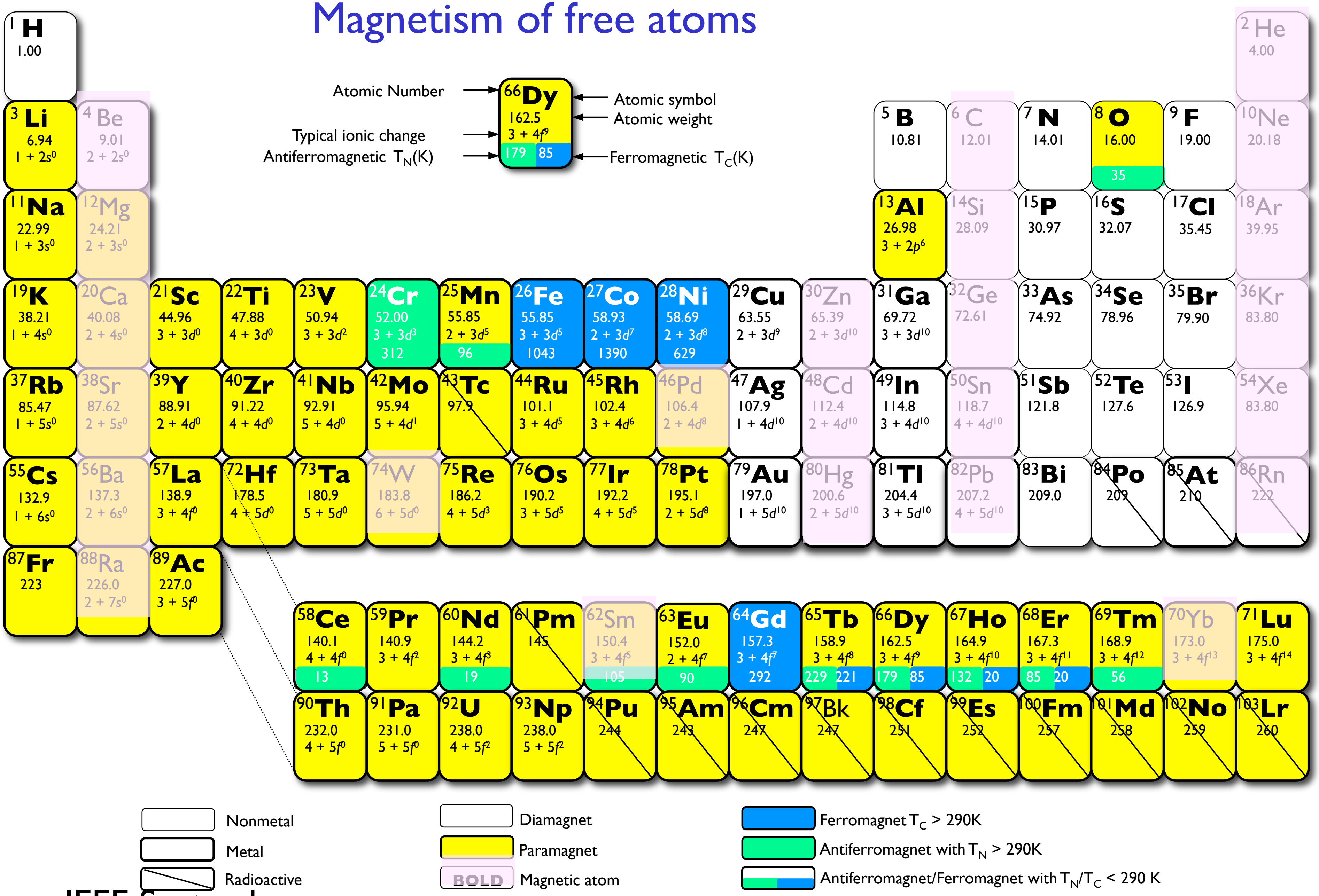


n	1	2	3	4	5	6
	1s	2s	3s	4s	5s	6s
		2p	3p	4p	5p	6p
			3d	4d	5d	6d
				4f	5f	6f
					5g	6g

Hartree-Fock 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.

Magnetism of free atoms



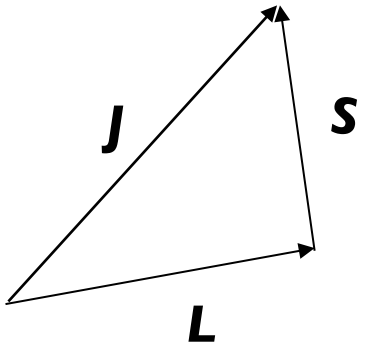
Atomic Number	Atomic symbol	Atomic weight	Typical ionic change	Antiferromagnetic T_N(K)	Ferromagnetic T_C(K)
1	H	1.00			
2	He	4.00			
3	Li	6.94	1 + $2s^{0}$		
4	Be	9.01	2 + $2s^{0}$		
5	B	10.81			
6	C	12.01			
7	N	14.01			
8	O	16.00		35	
9	F	19.00			
10	Ne	20.18			
11	Na	22.99	1 + $3s^{0}$		
12	Mg	24.21	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	132.9	1 + $6s^{0}$		
56	Ba	137.3	2 + $6s^{0}$		
57	La	138.9	3 + $4f^{0}$		
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 + $4f^{14}$		
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 + $5f^{0}$		
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

IEEE Santander

79 out of the 103 first elements are magnetic as free atoms Moments << $Z\mu_B$

Addition of angular momenta



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

$$\boxed{\mathbf{J} = \mathbf{L} + \mathbf{S}} \qquad |L-S| \leq J \leq |L+S|$$

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

To determine the ground-state of a multi-electron atom/ion.

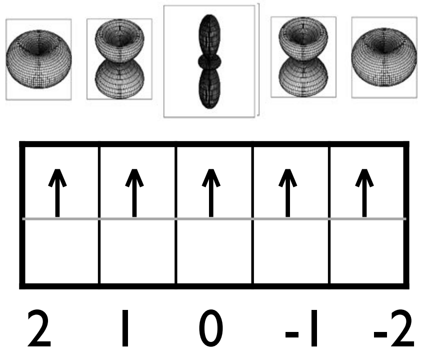
1) Maximize S
2) Maximize *L* consistent with *S*.
3) Couple *L* and *S* to form *J*.
   - Less than half full shell $J = L-S$
   - More than half full shell $J = L+S$

Hund’s rules; examples

Fe^{3+} $3d^5$

$S = 5/2$ $L = 0$ $J = 5/2$

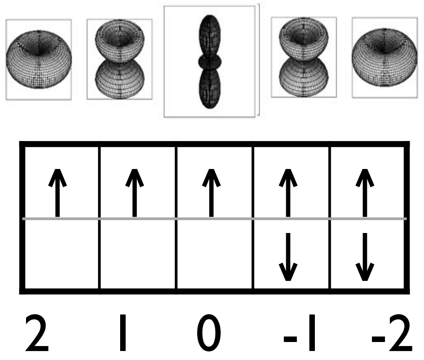
$^6S_{5/2}$



Note; Maximizing S is equivalent to maximizing $M_s = \Sigma m_{si}$, since $M_s \leq S$

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

$S = 3/2$ $L = 3$ $J = 9/2$



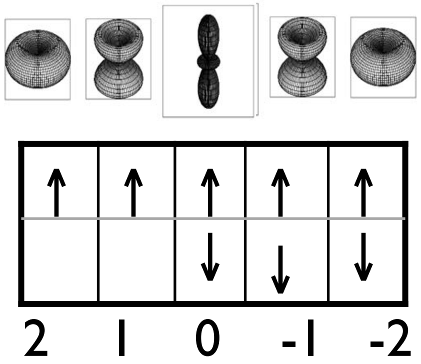
$^4F_{9/2}$

Note; Maximizing L is equivalent to maximizing $M_L = \Sigma m_{li}$, since $M_L \leq L$

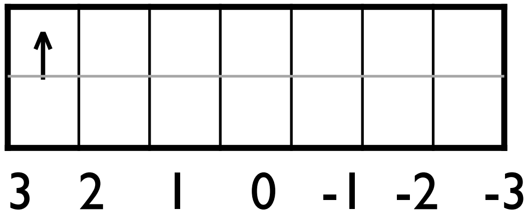
Ni^{2+} $3d^8$

$S = 1$ $L = 3$ $J = 4$

$^3F_4$



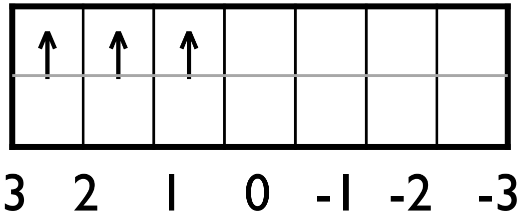
Ce^{3+} $4f^1$



S = 1/2   L = 3   J = 5/2

$^2F_{5/2}$

Nd^{3+} $4f^3$

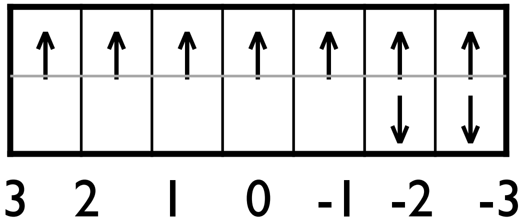


$S = 3/2$ $L = 6$ $J = 9/2$

$^4I_{9/2}$

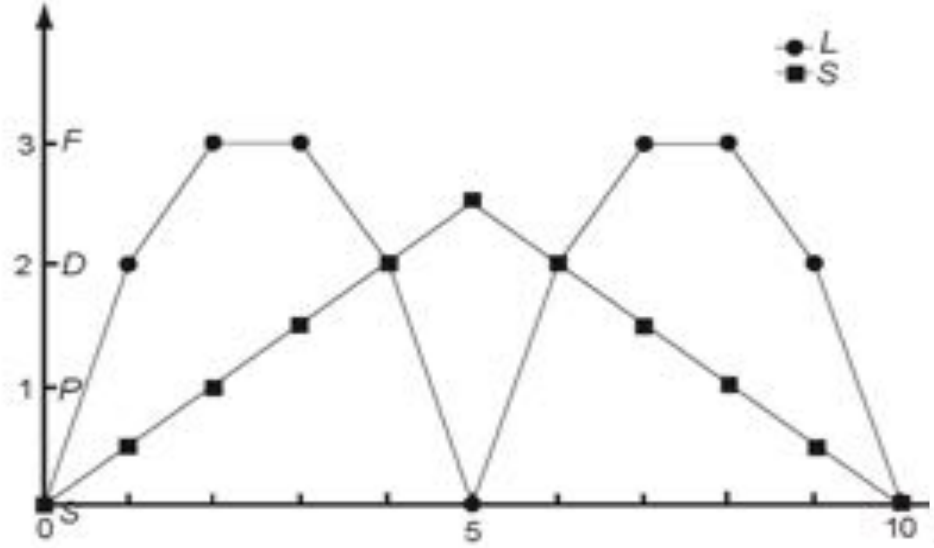
Dy^{3+} $4f^9$

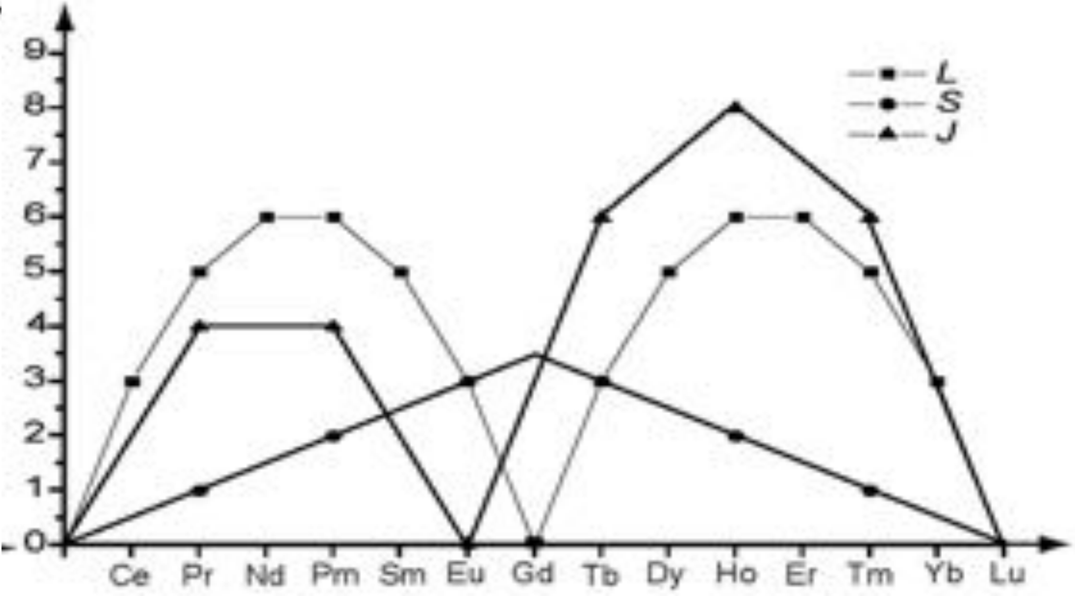
$S = 5/2$ $L = 5$ $J = 15/2$



$^6H_{15/2}$

Hund’s rules 3*d* and 4*f*





Spin-Orbit Coupling

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

Λ Is atomic 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. (for Hund's 3rd rule)

Compare single-electron atom case: $\mathcal{H}_{so} = \lambda \mathbf{l.s}$

$\boxed{\Lambda = \pm \lambda/2S}$

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

	ion	Λ (K)
$3d^1$	Ti^{3+}	124
$3d^2$	Ti^{2+}	88
$3d^3$	V^{2+}	82
$3d^4$	Cr^{2+}	85
$3d^6$	Fe^{2+}	-164
$3d^7$	Co^{2+}	-272
$3d^8$	Ni^{2+}	-493

Zeeman Interaction

The magnetic moment of an ion is represented by the expression $\boldsymbol{m} = -(\boldsymbol{L} + 2\boldsymbol{S})\mu_B/\hbar$

The Zeeman Hamiltonian for the magnetic moment in a field **B** along $\mathbf{e}_z$ is $\mathcal{H}_{\text{Zeeman}} = -\boldsymbol{m}.\mathbf{B}$

$$\boxed{\mathcal{H}_{\text{Zeeman}} = (\mu_B/\hbar)(\boldsymbol{L}_z + 2\boldsymbol{S}_z)B_z}$$

For a particular J-multiplet the matrix elements of $\boldsymbol{L} + 2\boldsymbol{S}$ are proportional to those of $\boldsymbol{J}$ (Wigner Eckart theorem)

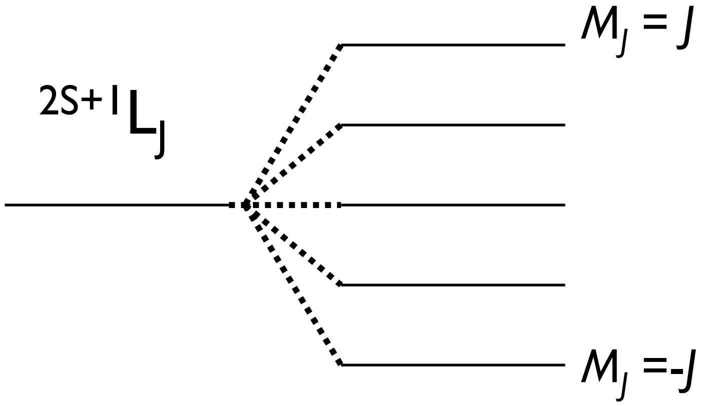
$\langle LSJM_J|\, \boldsymbol{L} + 2\boldsymbol{S}\, |LSJM_J\rangle = g_J\langle LSJM_J|\, \boldsymbol{J}\, |LSJM_J\rangle$ g_J is the Landé g-factor

$$(\boldsymbol{L} + 2\boldsymbol{S}) = g_J\boldsymbol{J}$$

$$\boldsymbol{m}_z = g_J\boldsymbol{J}_z\mu_B/\hbar$$

$$\boxed{\mathcal{H}_{\text{Zeeman}} = g_J\boldsymbol{J}_z B(\mu_B/\hbar)}$$

$$\mathcal{H}_{\text{Zeeman}}\psi_{LSJM} = g_J\,\mu_B\,M_J B\,\psi_{LSJM}$$



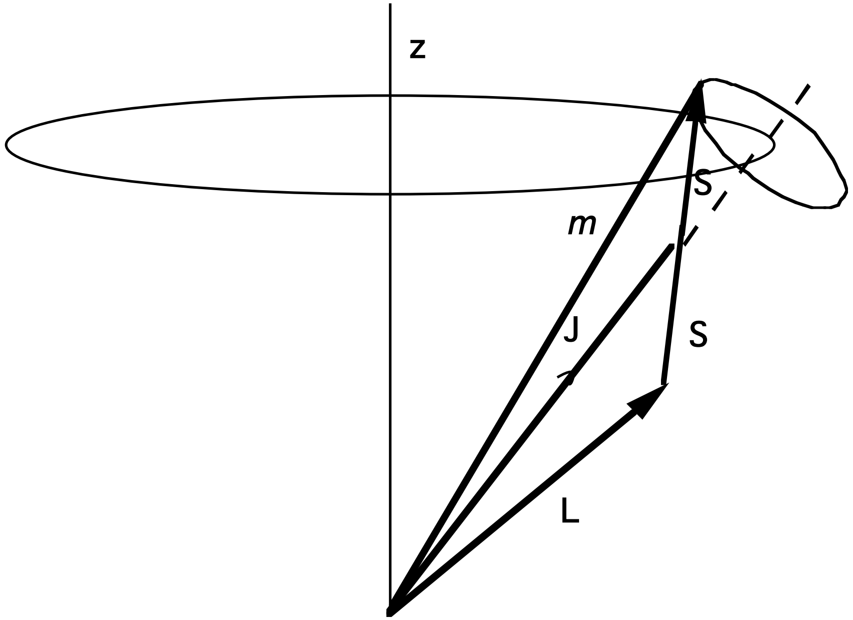
Landé g-factor

The vector model of the atom, including magnetic moments. First project $\mathcal{m}$ onto ***J***. ***J*** then precesses around **z**.

The g-factor for the atom or ion is the ratio of the component of magnetic moment along ***J*** in units of μ_B to the magnitude of the angular momentum in units of $\hbar$.

$g_J\boldsymbol{J} = (\boldsymbol{L} + 2\boldsymbol{S})$ Take scalar product with ***J***

$g_J = -(\mathcal{m}.\boldsymbol{J}/\mu_B)/(\boldsymbol{J}^2/\hbar) = -\mathcal{m}.\boldsymbol{J}(\hbar/\mu_B)/[J(J+1)]$



$\mathbf{J}^2 = J(J+1)\hbar^2$; $\mathbf{J}_z = M_J\hbar$

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

$-(\mu_B/\hbar)\{(\boldsymbol{L}^2 + 3\boldsymbol{L}.\boldsymbol{S} + 2\boldsymbol{S}^2)\}$

$-(\mu_B/\hbar)\{(\boldsymbol{L}^2 + 2\boldsymbol{S}^2 + (3/2)(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2)\}$ since $\boldsymbol{J}^2 = \boldsymbol{L}^2 + \boldsymbol{S}^2 + 2\,\boldsymbol{L}\cdot\boldsymbol{S}$

$-(\mu_B/\hbar)\{((3/2)\boldsymbol{J}^2 - (1/2)\boldsymbol{L}^2 + (1/2)\boldsymbol{S}^2)\}$

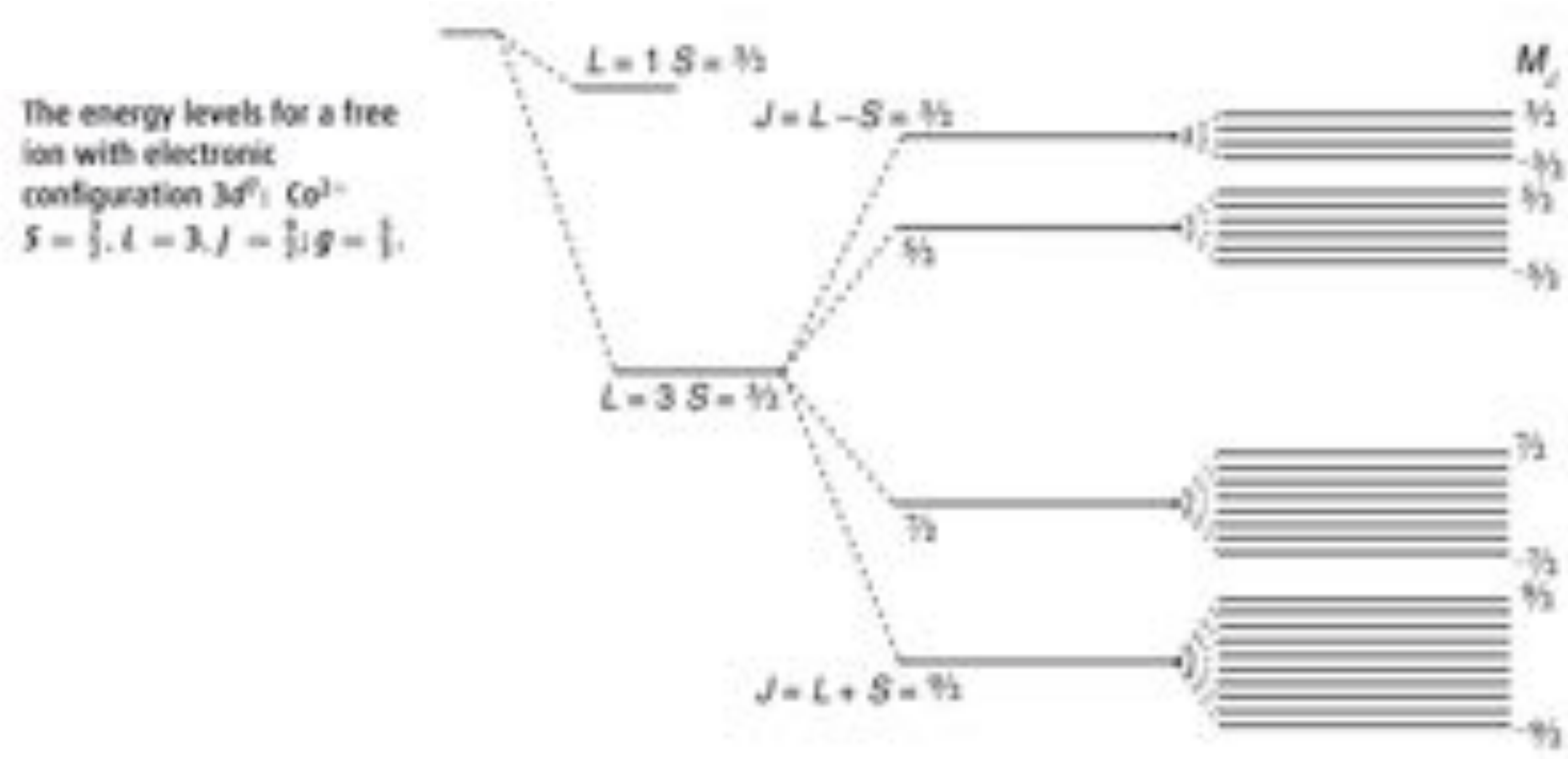
$-(\mu_B/\hbar)\{((3/2)J(J+1) - (1/2)L(L+1) + (1/2)S(S+1)\}$

hence

$$\boxed{g = 3/2 + \{S(S+1) - L(L+1)\}/2J(J+1)}$$

Check; $g_S = 2$, $g_L = 1$

Co^{2+} free ion



The energy levels for a free ion with electronic configuration $3d^7$: Co^{2+} $S = \frac{3}{2}, L = 3, J = \frac{9}{2}; g = \frac{4}{3}$.

Paramagnetic susceptibility - Brillouin theory

Curie law $\boxed{\chi = C / T}$

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

The thermodynamic average of the moment:

$$\langle \mathrm{m} \rangle = \frac{\sum_i \mathrm{m}_i \exp(-\varepsilon_i / k_B T)}{\sum_i \exp(-\varepsilon_i / k_B T)}$$

$\boldsymbol{B} = B_z$
$E = - \boldsymbol{m}.\boldsymbol{B}$

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

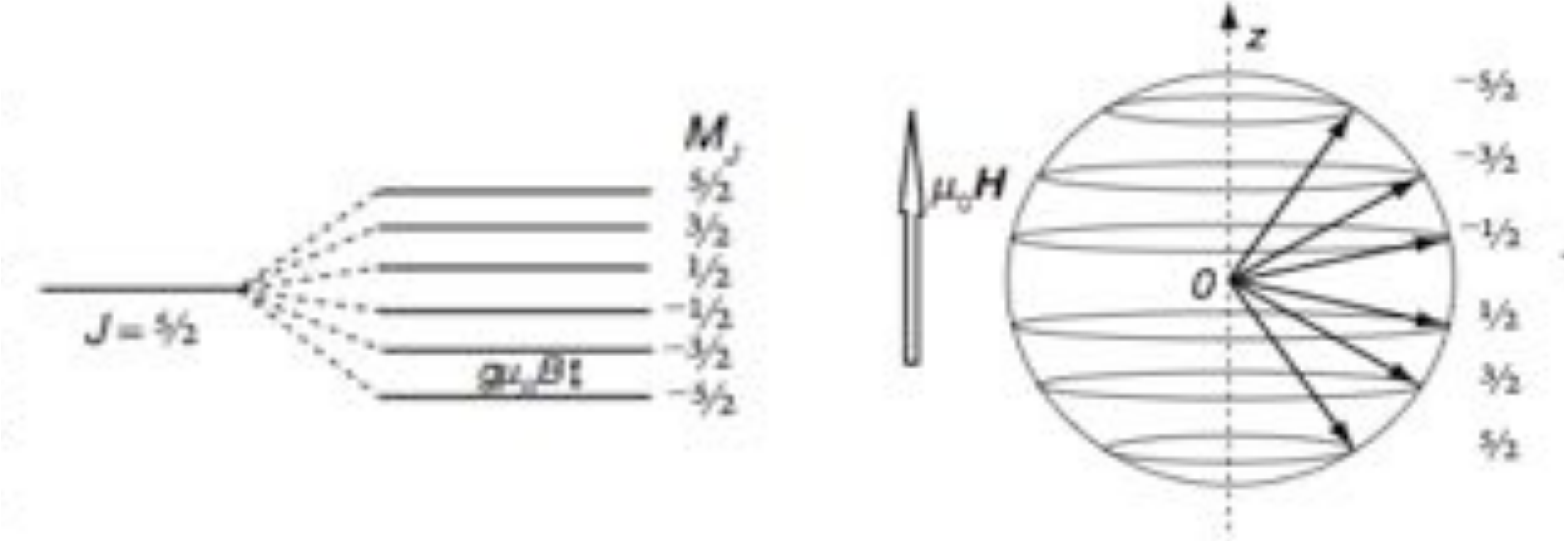
Using the identities:

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

and the fact that $\chi = n\langle m \rangle / H$ (*n* is the number density of atoms/ions)

we find

$$\boxed{C = \frac{\mu_0 n g^2 \mu_B^2 J(J+1)}{3k_B}.} \qquad \chi = \mu_0 n m_{eff}^2 \mu_B^2 / 3k_B T$$



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

4f ions

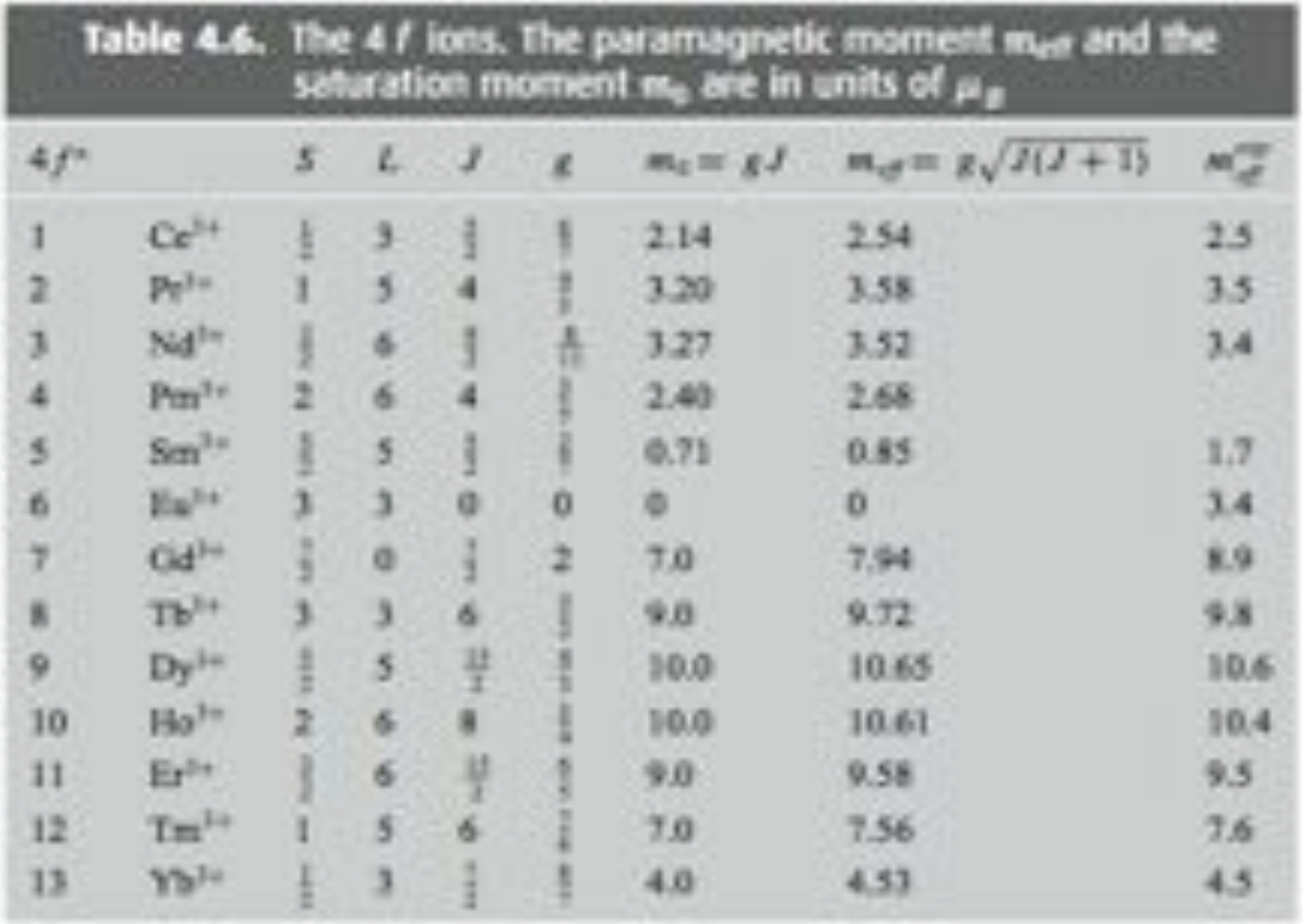


Table 4.6. The 4 *f* ions. The paramagnetic moment m_{eff} and the saturation moment m_0 are in units of μ_B

$4f^n$		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

J is a good quantum number

3d ions

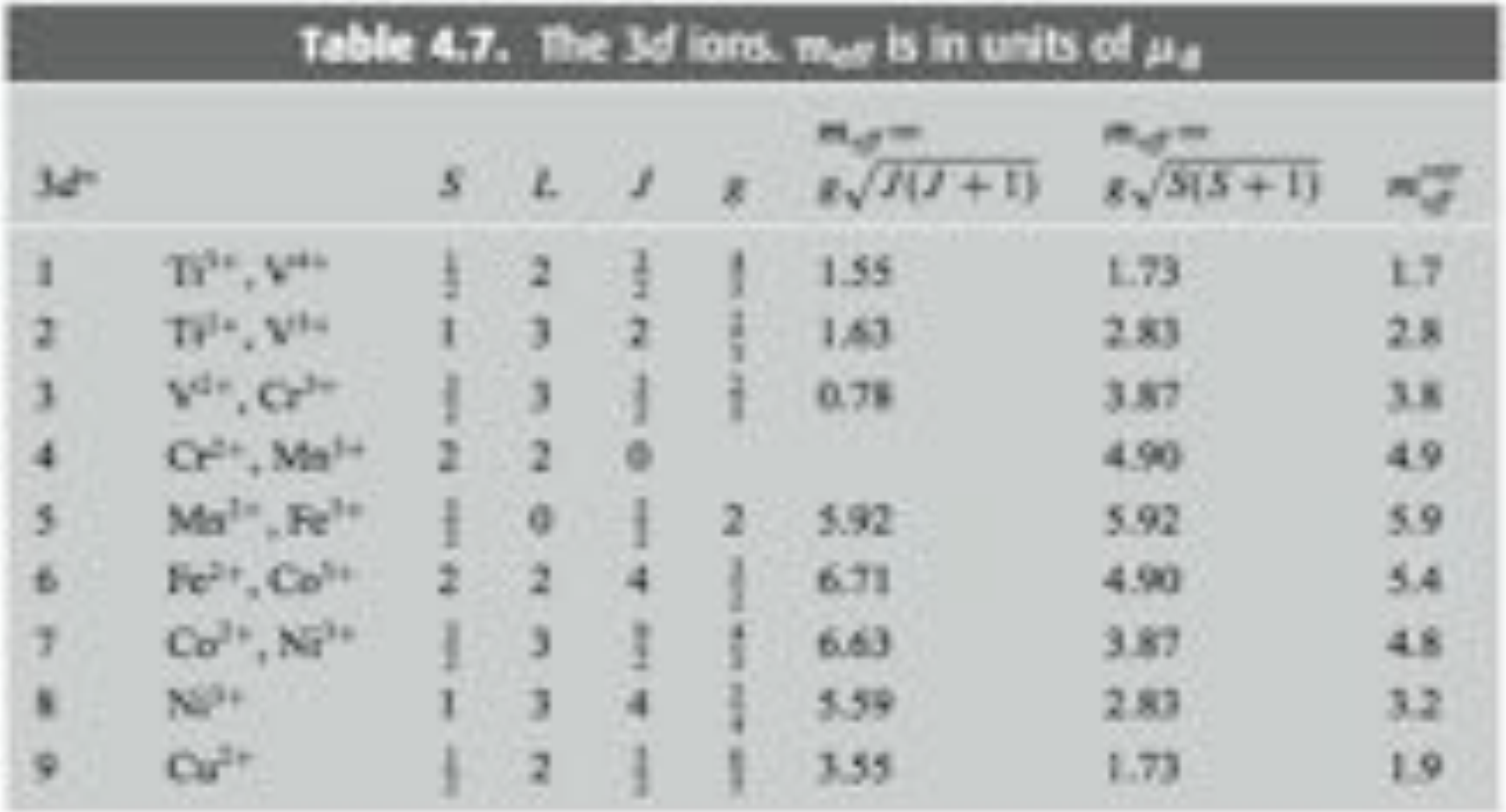


Table 4.7. The 3d ions. m_{eff} is in units of μ_B

$3d^n$		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^{2+}	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

S is a good quantum number
L is ‘quenched’

Magnetization curve - Brillouin theory

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

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

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

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

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

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

multiply top and bottom by $\exp\{y/2\}$

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

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

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

Paramagnetism - Brillouin theory

setting x = *J*y, we obtain

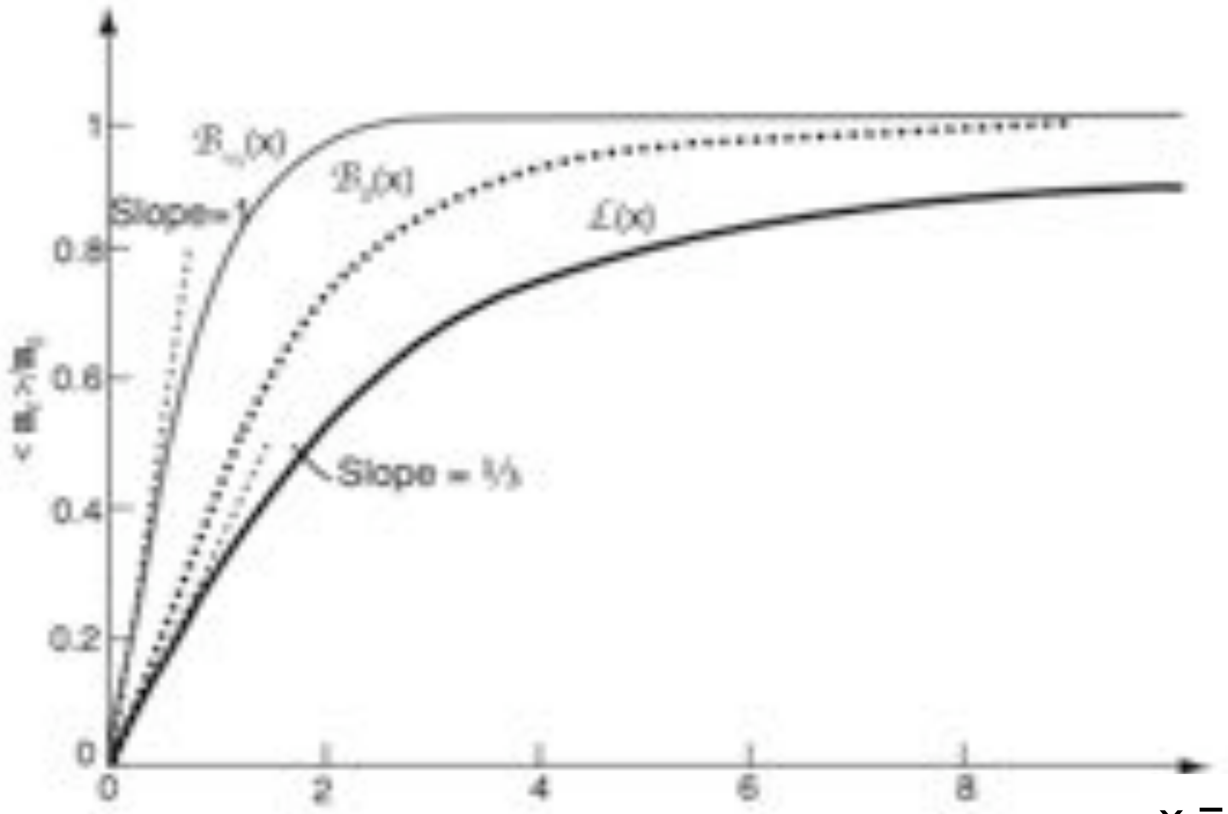
$$\boxed{\langle \mathrm{m}_z \rangle = \mathrm{m}_0 \mathcal{B}_J(x)}$$

where $\mathcal{B}_\mathrm{J}$(x) *is* the Brillouin function { }

$$\langle \mathrm{m}_z \rangle = \mathrm{m}_0 \left\{ \frac{2J+1}{2J} \coth \frac{2J+1}{2J} x - \frac{1}{2J} \coth \frac{x}{2J} \right\}$$

This reduces to $\langle m \rangle$ = μ_B tanh(x) in the limit *J* = ½, g = 2.
and $\langle m \rangle$ = $\mathcal{L}$(x) *is* the Langevin function {coth x - 1/x} in the large-*J* limit.

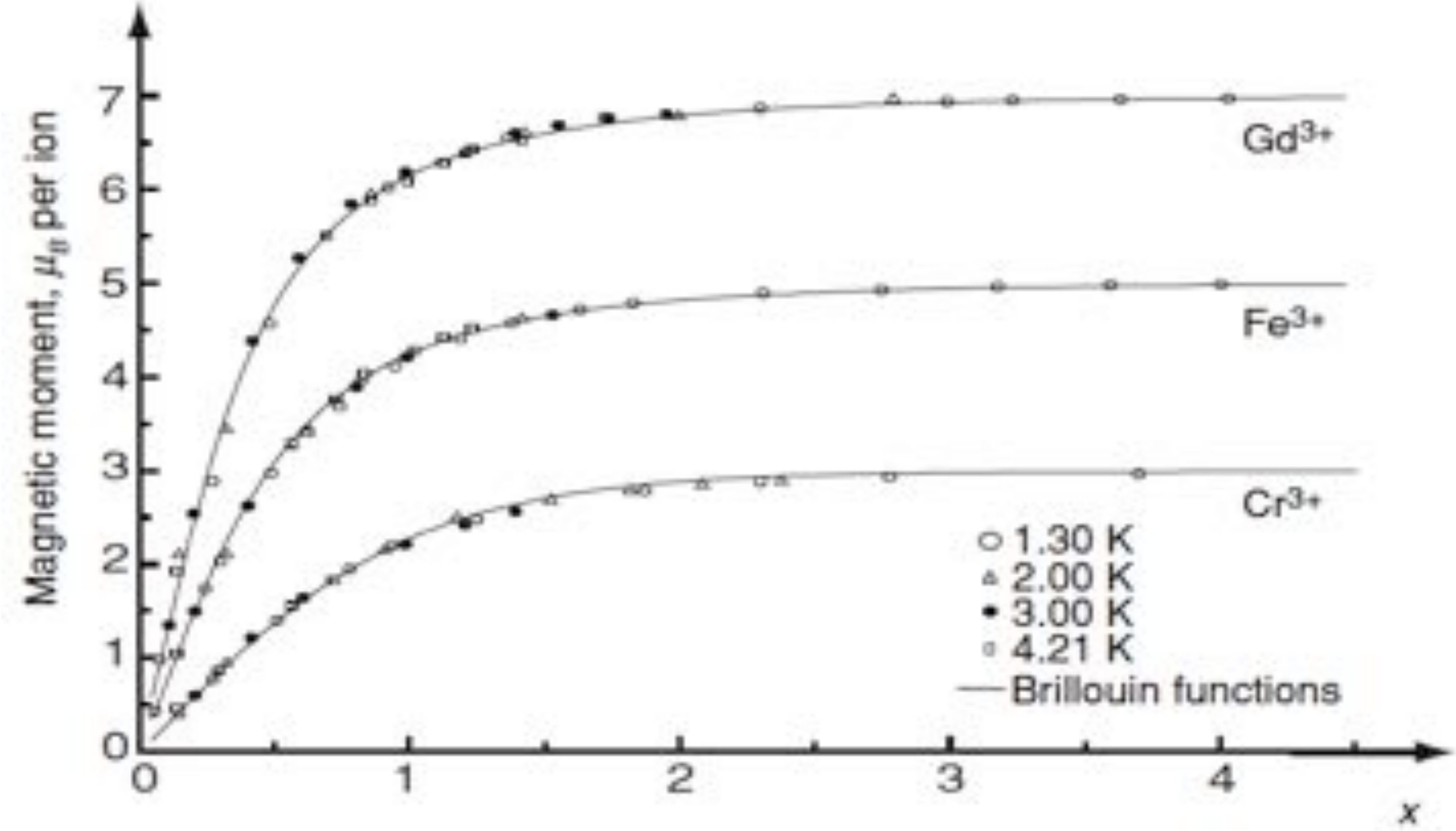
Magnetization curves for paramagnetic ions



$x = g J \mu_B B / k_B T$

Comparison of the Brillouin functions for s = ½, J = 2 and the Langevin function (J = ∞)

Experimental confirmation



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

Mean field theory of ferromagnetism

Weiss (1907) supposed that in addition to any externally applied field $\boldsymbol{H}$, there is an internal 'molecular' field in a ferromagnet proportional to its magnetization.

$$\boxed{\boldsymbol{H}^{\mathrm{i}} = n_W \boldsymbol{M}}$$

$\boldsymbol{H}^{\mathrm{i}}$ must be immense in a ferromagnet like iron to be able to induce a significant fraction of saturation at room temperature; $n_W \approx 10 - 1000$. The origin of these huge fields remained a mystery until Heisenberg introduced the idea of the *exchange interaction* in 1928.

Magnetization is given by the Brillouin function,

$$<m> = m\,\mathcal{B}_J(x)$$

where now $x = \mu_0 m H^i / k_B T$.

The magnetization at zero temperature, $M_0 = Nm$ where $m = g\mu_B J$. At nonzero temperature $M_s = N<m>$

Mean field theory of ferromagnetism

In zero external field, we have $M_s/M_0 = \mathcal{B}_J(x)$ (1)

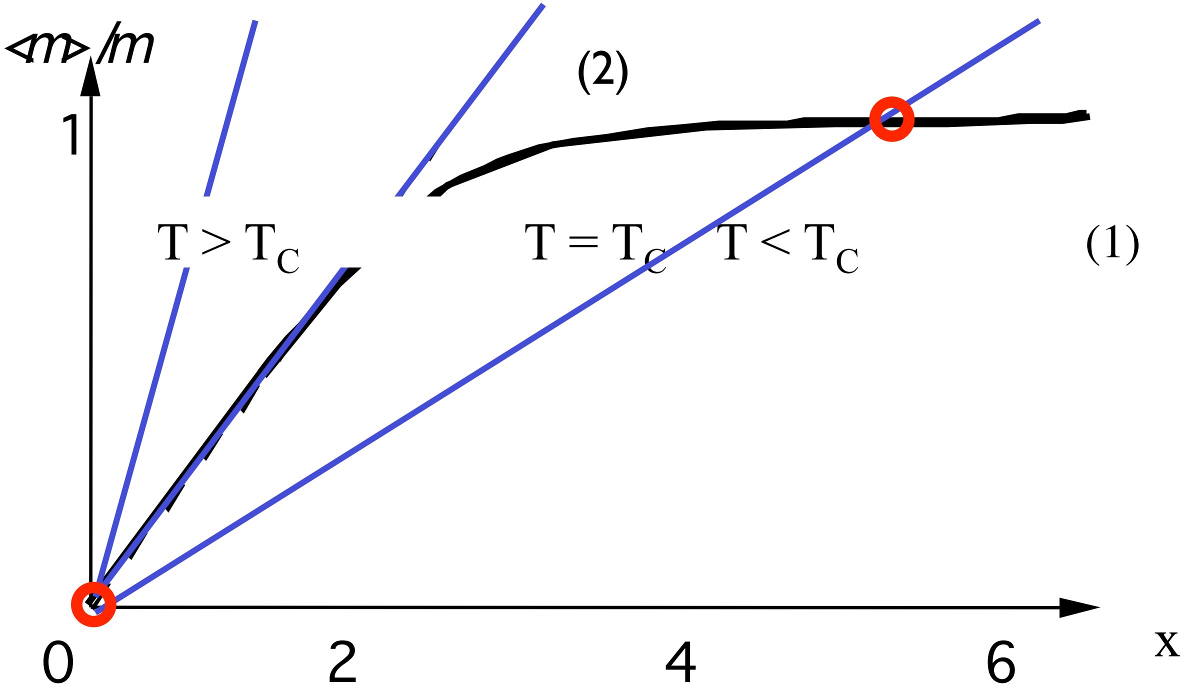
Also by eliminating H^i from the expressions for H^i ($H^i = n_W M_s$) and x ($H^i = k_B T x/\mu_0 m$); since $M_0 = Nm$

$$M_s/M_0 = (Nk_B T/\mu_0 M_0^2 n_W)x$$

which can be rewritten in terms of the Curie constant $C = \mu_0 N g^2 \mu_B^2 J(J+1)/3k_B$

$$M_s/M_0 = [T(J+1)/3CJn_W]x \qquad (2)$$

The simultaneous solution of (1) and (2) is found *graphically*, or they can be solved numerically.



Graphical solution of (1) and (2) to find the spontaneous magnetization M_s when $T < T_C$. in blue for $T < T_C$, $T = T_C$ and $T > T_C$.

Mean field theory of ferromagnetism

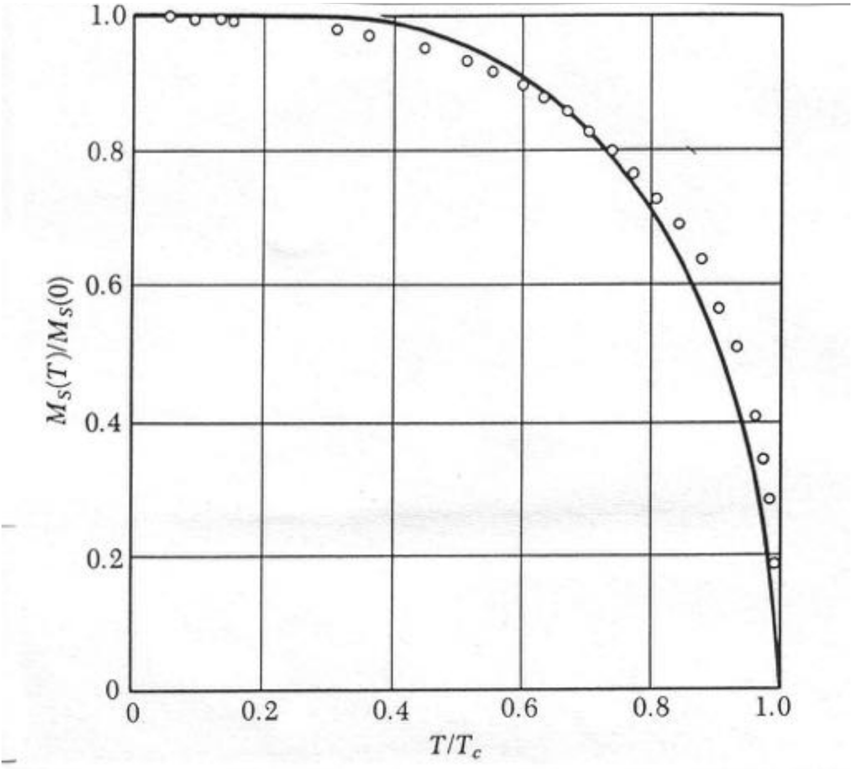
At the Curie temperature, the slope of (2) is equal to the slope at the origin of the Brillouin function

For small x. $\mathcal{B}_J(x) \approx [(J+1)/3J]x + \ldots$

hence $\boxed{T_C = n_W C}$

where the Curie constant $C = \mu_0 N g^2 \mu_B{}^2 J(J+1)/3k_B$.
In practice, T_C is used to determine n_W.

The spontaneous magnetization for nickel, together with the theoretical curve for S = ½ from the mea field theory. The theoretical curve is scaled to give correct values at either end.



Exchange

Heisenberg and Dirac explained the origin of magnetism in solids in terms of the exchange interaction. It is short-range interaction, coupling the *spins* of nearest-neighbour atoms.
It is not due to magnetic dipolar interactions; those fields are ~ 1 T, and far too weak.
Nor is there any real 'molecular field' inside the sample. Since $\nabla.\boldsymbol{B} = 0$, it would be observed outside as well.
It is due to interelectronic Coulomb interactions, subject to the symmetry constraints of quantum mechanics.

Interatomic exchange $\boxed{\mathcal{H}_{Heis} = -2\,\mathcal{J}\,\mathbf{S}_i.\mathbf{S}_j}$

$\mathcal{J} > 0$; ferromagnetic interatomic interaction
$\mathcal{J} < 0$; antiferromagnetic interatomic interaction

Relation between $\mathcal{J}$ and H^i $\mathcal{H}_i = -2(\Sigma_j \mathcal{J}\mathbf{S}_j).\mathbf{S}_i \approx -\mu_0 H^i m_i = -\mu_0 H^i g\mu_B S_i = -\mu_0 n_W M g\mu_B S_i$

$$T_C = \mu_0 N n_W g^2 \mu_B^2 S(S+1)/3k_B = 2Z\mathcal{J}S(S+1)/3k_B$$

Number of nearest-neighbours in Σ_i

Summary – so far

- Filled electronic shells are not magnetic (the spins are paired; $m_s = \pm 1/2$)
- Only partly-filled shells may possess a magnetic moment
- The magnetic moment is given by $\mathfrak{m} = g_J \mu_B \mathbf{J}$, where $\hbar\mathbf{J}$ represents the total angular momentum. For a given configuration the values of J and g_j in the ground state are given by Hund's rules

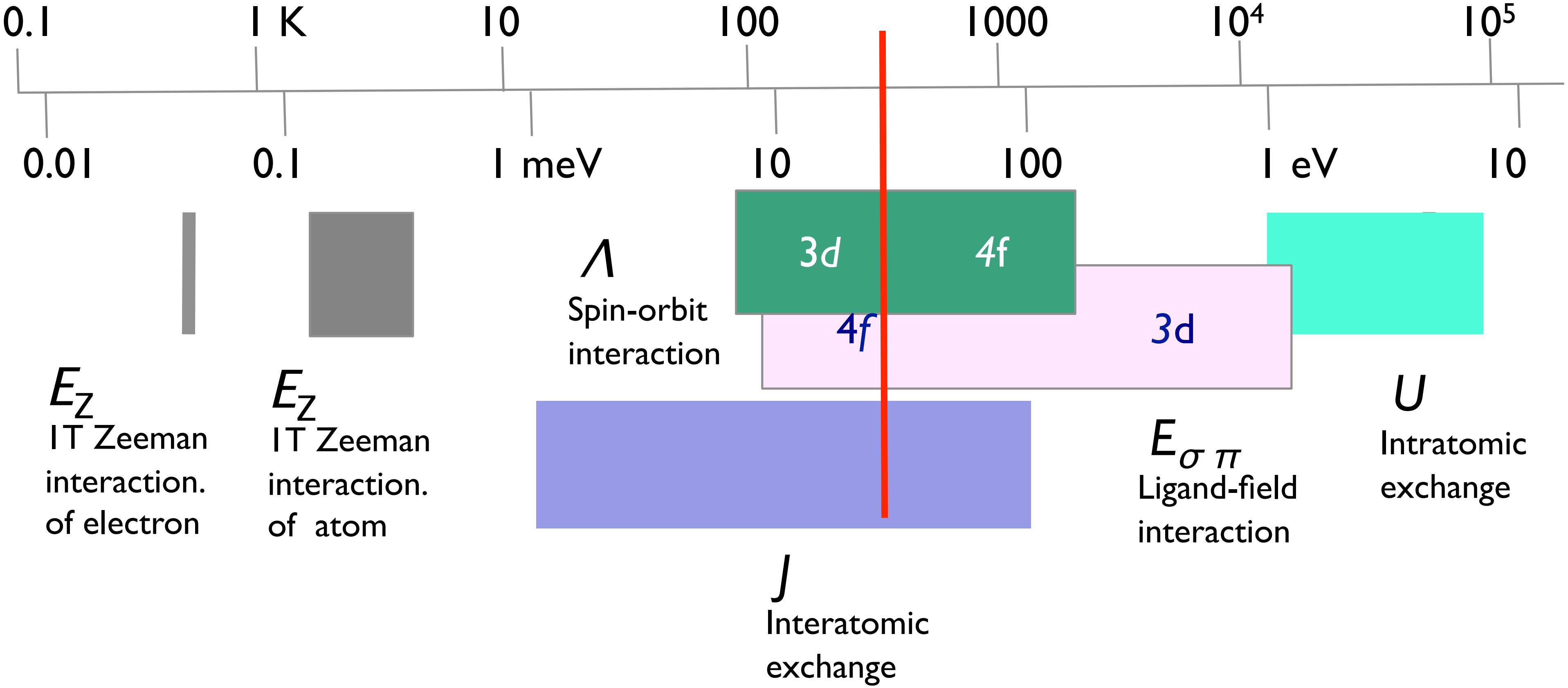
* * *

When the ion is embedded in a solid, the crystal field interaction is important. This is the electrostatic Coulomb interaction of an ion with its surroundings.
The third point is modified:

- Orbital angular momentum for 3*d* ions is *quenched*. The spin only moment is $\mathfrak{m} \approx g\mu_B\mathbf{S}$, with g = 2.
- Magnetocrystalline anisotropy appears, making certain crystallographic axes easy directions of magnetization.

7. Ions in Solids

Energy scales



E_Z
1T Zeeman interaction. of electron

E_Z
1T Zeeman interaction. of atom

Λ
Spin-orbit interaction

J
Interatomic exchange

$E_{\sigma\,\pi}$
Ligand-field interaction

U
Intratomic exchange

Magnitudes of the interactions

The Hamiltonian is now

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{so} + \mathcal{H}_{cf} + \mathcal{H}_Z$$

Typical magnitudes of energy terms (in K)

	$\mathcal{H}_0$	$\mathcal{H}_{so}$	$\mathcal{H}_{cf}$	$\mathcal{H}_Z$ in 1 T
3*d*	**1 - 5 10^4**	**10^2 -10^3**	**10^4**	**1**
4*f*	**1 - 6 10^5**	**1 - 5 10^3**	**≈3 10^2**	**1**

$\mathcal{H}_{so}$ must be considered before $\mathcal{H}_{cf}$ for 4*f* ions, and the converse for 3*d* ions. Hence J is a good quantum number for 4*f* ions, but S is a good quantum number for 3*d* ions. The 4*f* electrons are generally localized, and 3*d* electrons are localized in oxides and other ionic compounds.

Magnitudes of the interactions

$$\mathcal{H}_i = \mathcal{H}_0 + \mathcal{H}_{so} + \qquad \mathcal{H}_Z$$

Coulomb interactions $|L,S\rangle$

spin-orbit interaction $\Lambda \boldsymbol{L}.\boldsymbol{S}$ $|J\rangle$

Zeeman interaction $g\mu_B \boldsymbol{B}.\boldsymbol{J}/\hbar$ $|M_J\rangle$

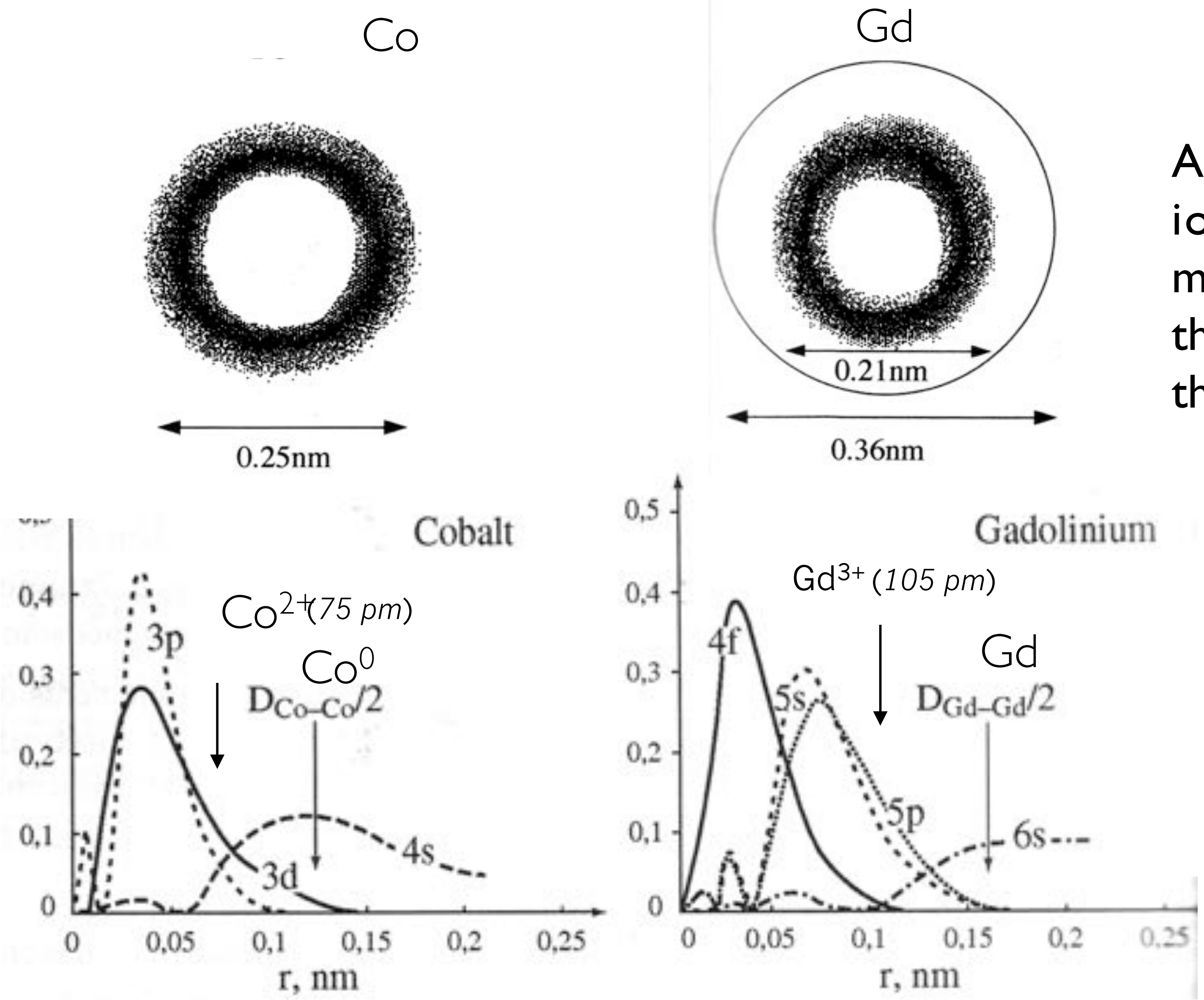
Crystal field interaction $\int \rho_0(\mathbf{r})\varphi_{cf}(\mathbf{r})d^3r$

	ion	Λ
$3d^1$	Ti^{3+}	124
$3d^2$	Ti^{2+}	88
$3d^3$	V^{2+}	82
$3d^4$	Cr^{2+}	85
$3d^6$	Fe^{2+}	-164
$3d^7$	Co^{2+}	-272
$3d^8$	Ni^{2+}	-493

$4f^1$	Ce^{3+}	920
$4f^2$	Pr^{3+}	540
$4f^3$	Nd^{3+}	430
$4f^5$	Sm^{3+}	350
$4f^8$	Tb^{3+}	-410
$4f^9$	Dy^{3+}	-550
$4f^{10}$	Ho^{3+}	-780
$4f^{11}$	Er^{3+}	-1170
$4f^{12}$	Tm^{3+}	-1900
$4f^{13}$	Yb^{3+}	-4140

	$\mathcal{H}_0$	$\mathcal{H}_{so}$	$\mathcal{H}_{cf}$	$\mathcal{H}_Z$ in 1 T
3*d*	$1 - 5\ 10^4$	$10^2 - 10^3$	10^4	1
4*f*	$1 - 6\ 10^5$	$1 - 5\ 10^3$	$\approx 3\ 10^2$	1

3*d* and 4*f* compared



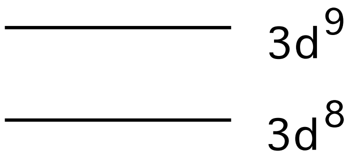
As metallic atoms or ions the transition metals occupy one third of the volume of the rare earths.

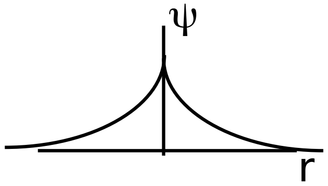
LOCALIZED MAGNETISM

Integral number of 3*d* or 4*f* electrons on the ion core; Integral number of unpaired spins; Discreet energy levels.

Ni^{2+} $3d^8$ $m = 2\ \mu_B$

$m = 0.6\ \mu_B$





$\psi \approx \exp(-r/a_0)$

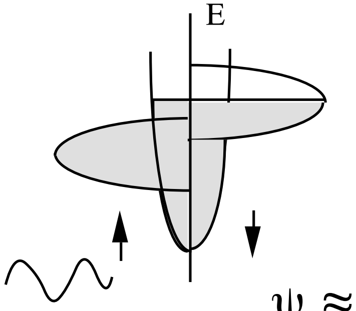
Boltzmann statistics

DELOCALIZED MAGNETISM

Nonintegral number of unpaired spins per atom.

Spin-polarized energy bands with strong correlations.

Ni $3d^{9.4}4s^{0.6}$



$\psi \approx \exp(-i\mathbf{k}.\mathbf{r})$

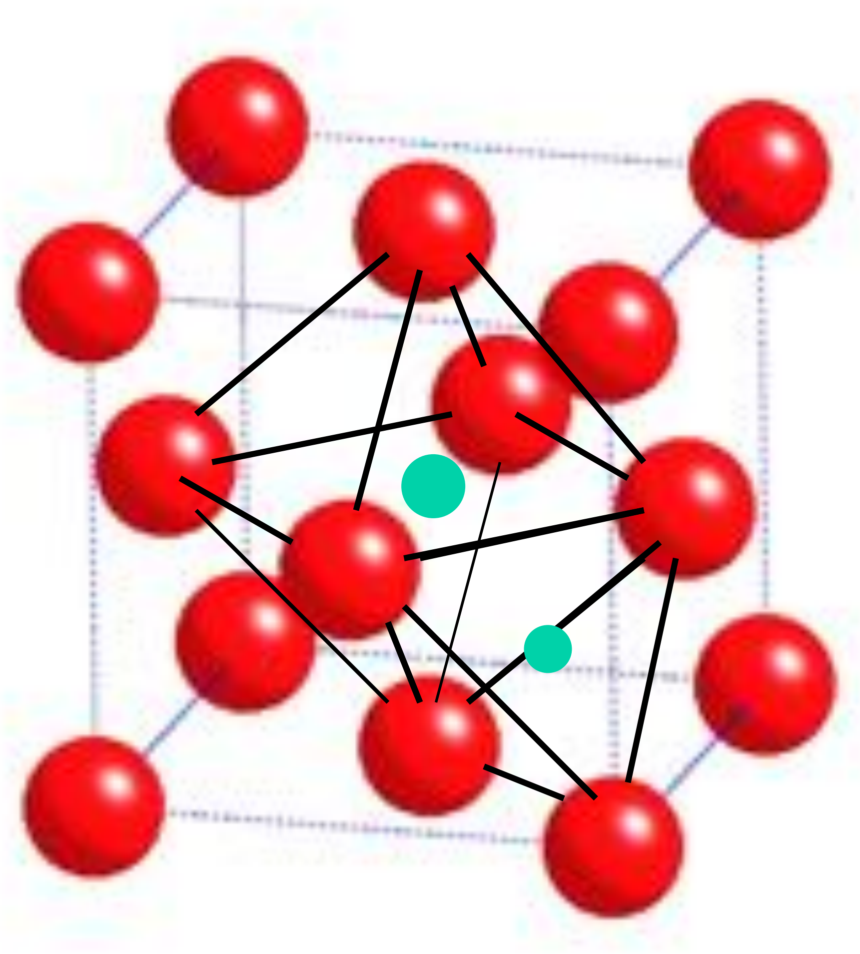
Fermi-Dirac statistics

4*f* metals	*localized electrons*
4*f* compounds	*localized electrons*
3*d* compounds	*localized/delocalized electrons*
3*d* metals	*delocalized electrons.*

Above the ferromagnetic Curie temperature, the moments do not disappear, they just become disordered in a paramagnetic state when $T > T_C$.

Oxides

Oxides are usually insulating. Structures are based on dense-packed O^{2-} arrays, with cations in interstitial sites.



Octahedral and tetrahedral sites are common in transition metal oxides and other compounds.

Both have *cubic* symmetry if undistorted

$R_{oct} = (2^{1/2} - 1)r_O = 58$ pm

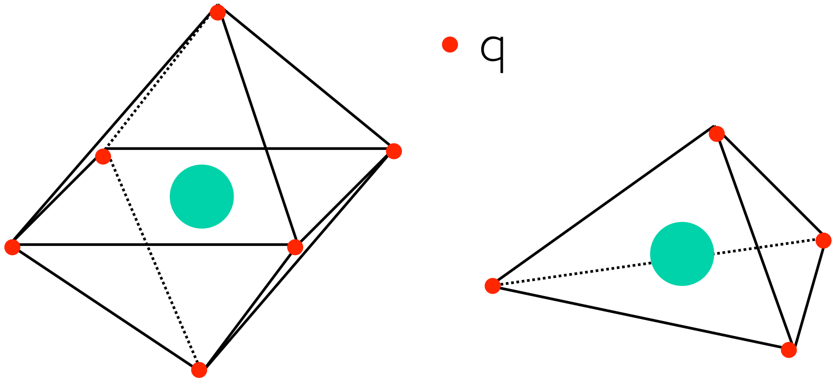
$R_{tet} = ((3/2)^{1/2} - 1)r_O = 32$ pm

Cation radii in oxides: low spin values are in parentheses.

4-fold tetrahedral	pm	6-fold octahedral	pm	6-fold octahedral	pm	12-fold substitutional	pm
Mg^{2+}	53	Cr^{4+} $3d^2$	55	Ti^{3+} $3d^1$	67	Ca^{2+}	134
Zn^{2+}	60	Mn^{4+} $3d^3$	53	V^{3+} $3d^2$	64	Sr^{2+}	144
Al^{3+}	42			Cr^{3+} $3d^3$	62	Ba^{2+}	161
Fe^{3+} $3d^5$	52	Mn^{2+} $3d^5$	83	Mn^{3+} $3d^4$	65	Pb^{2+}	149
		Fe^{2+} $3d^6$	78 (61)	Fe^{3+} $3d^5$	64	Y^{3+}	119
		Co^{2+} $3d^7$	75 (65)	Co^{3+} $3d^6$	61 (56)	La^{3+}	136
		Ni^{2+} $3d^8$	69	Ni^{3+} $3d^7$	60	Gd^{3+}	122

The radius of the O^{2-} anion is 140 pm

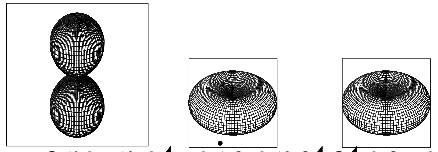
Orbital moment quenching is a cubic crystal field



To demonstrate quenching of orbital angular momentum, consider the 2p states ψ^0, ψ^1, ψ^{-1} corresponding to *l* = 1, $m_l = 0, \pm 1$.

$$\psi^0 = R(r)\cos\theta$$

$$\psi^{\pm 1} = R(r)\sin\theta\exp\{\pm\iota\phi\}$$



The functions are eigenstates in the central potential V (r) but they are not eigenstates of H_{cf}. Suppose the oxygens can be represented by point charges q at their centres, then for the octahedron,

$$\mathcal{H}_{cf} = V_{cf} = D(x^4 + y^4 + z^4 - 3y^2z^2 - 3z^2x^2 - 3x^2y^2)$$

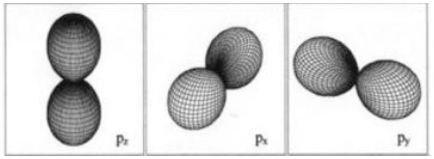
where $D \approx eq/4\pi\varepsilon_o a^6$. But $\psi^{\pm 1}$ are *not* eigenfunctions of $V_{cf,}$ e.g. $\int\psi_i^* V_{cf}\psi_j dV \neq \delta_{ij}$, where i,j = -1, 0, 1.

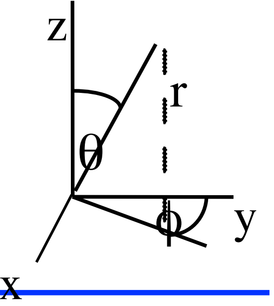
We seek linear combinations that are eigenfunctions, namely

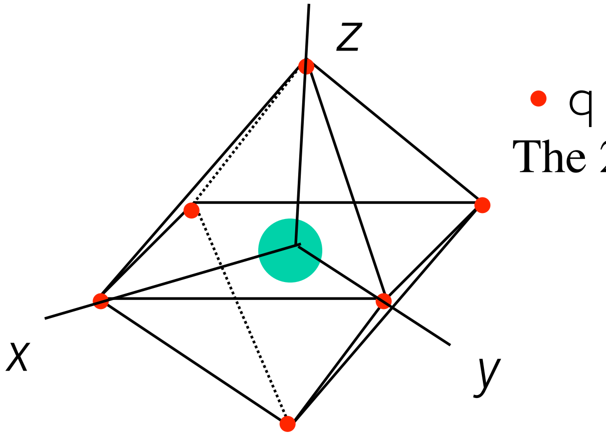
$$\psi^0 = R(r)\cos\theta = zR(r) = p_z$$

$$(1/\surd 2)(\psi^1 + \psi^{-1}) = R'(r)\sin\theta\cos\phi = yR(r) = p_y$$

$$(1/\surd 2)(\psi^1 - \psi^{-1}) = R'(r)\sin\theta\sin\phi = xR(r) = p_x$$







The 2*p* eigenfunctions are degenerate in an undistorted cubic environment

$$\psi^0 = R(r)\cos\theta = zR(r) = p_z$$
$$(1/\sqrt{2})(\psi^1 + \psi^{-1}) = R'(r)\sin\theta\cos\phi = yR(r) = p_x$$
$$(1/\sqrt{2})(\psi^1 - \psi^{-1}) = R'(r)\sin\theta\sin\phi = xR(r) = p_y$$

p_x p_y p_z

Note that the z-component of angular momentum; $\mathbf{l}_z = i\hbar/\partial\phi$ is *zero* for these wavefunctions. Hence the orbital angular momentum is quenched.

The same is true of the 3*d* eigenfunctions, which are

$d_{x^2-y^2}$, d_{z^2}

$$d_{xy} = (1/\sqrt{2})(\psi^2 - \psi^{-2}) = R'(r)\sin^2\theta\sin 2\phi \approx xyR(r)$$
$$d_{yz} = (1/\sqrt{2})(\psi^1 - \psi^{-1}) = R'(r)\sin\theta\cos\theta\sin\phi \approx yzR(r)$$
$$d_{zx} = (1/\sqrt{2})(\psi^1 + \psi^{-1}) = R'(r)\sin\theta\cos\theta\cos\phi \approx zxR(r)$$
$$d_{x^2-y^2} = (1/\sqrt{2})(\psi^2 + \psi^{-2}) = R'(r)\sin^2\theta\cos 2\phi \approx (x^2-y^2)R(r)$$
$$d_{3z^2-r^2} = \psi^0 = R'(r)(3\cos^2\theta - 1) \approx (3z^2-r^2)R(r)$$

t_{2g} *orbitals*

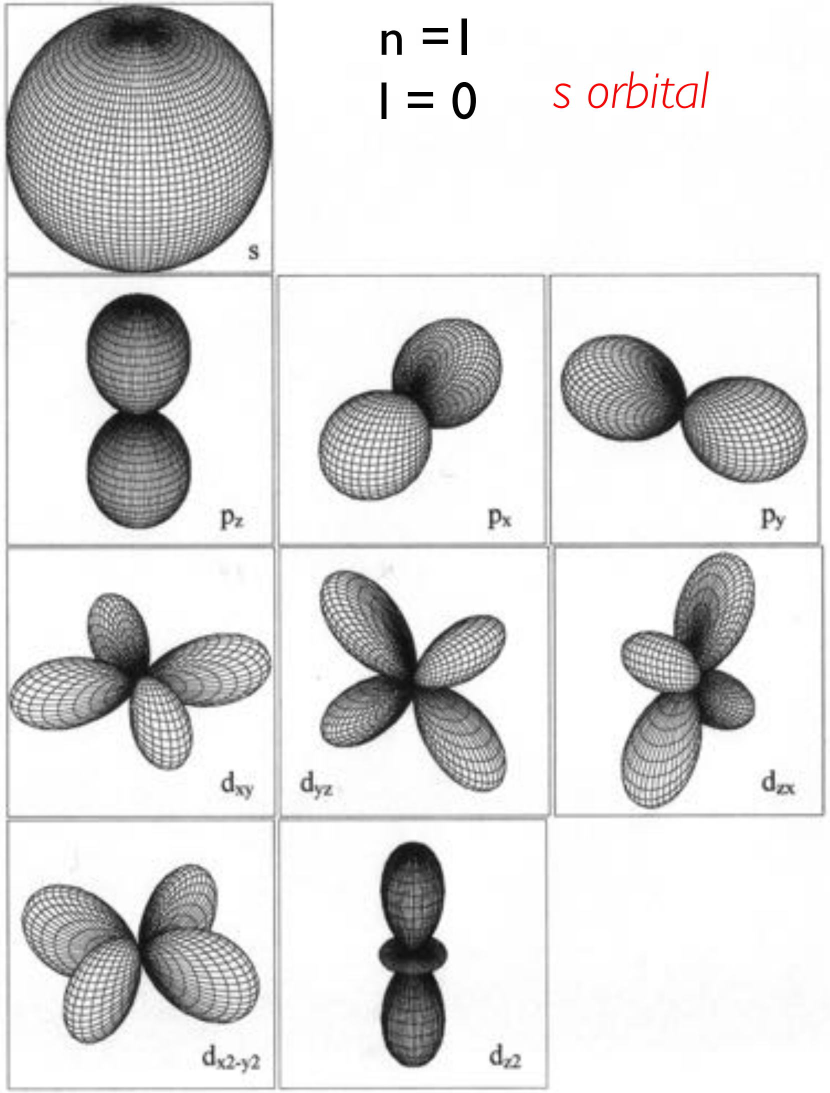
e_g *orbitals*

d_{xy} d_{yz} d_{zx}

The 3*d* eigenfunctions split into a set of three and a set of two in an undistorted cubic environment

Notation; *a* or *b* denote a nondegenerate single-electron orbital, *e* a twofold degenerate orbital and *t* a threefold degenerate orbital. Capital letters refer to multi-electron states. *a*, *A* are nondegenerate and symmetric with respect to the principal axis of symmetry (the sign of the wavefunction is unchanged), *b*. *B* are antisymmetric with respect to the principal axis (the sign of the wavefunction changes). Subscripts *g* and *u* indicate whether the wavefunction is symmetric or

Orbitals in a cubic crystal field



$n = 1$
$l = 0$ *s orbital*

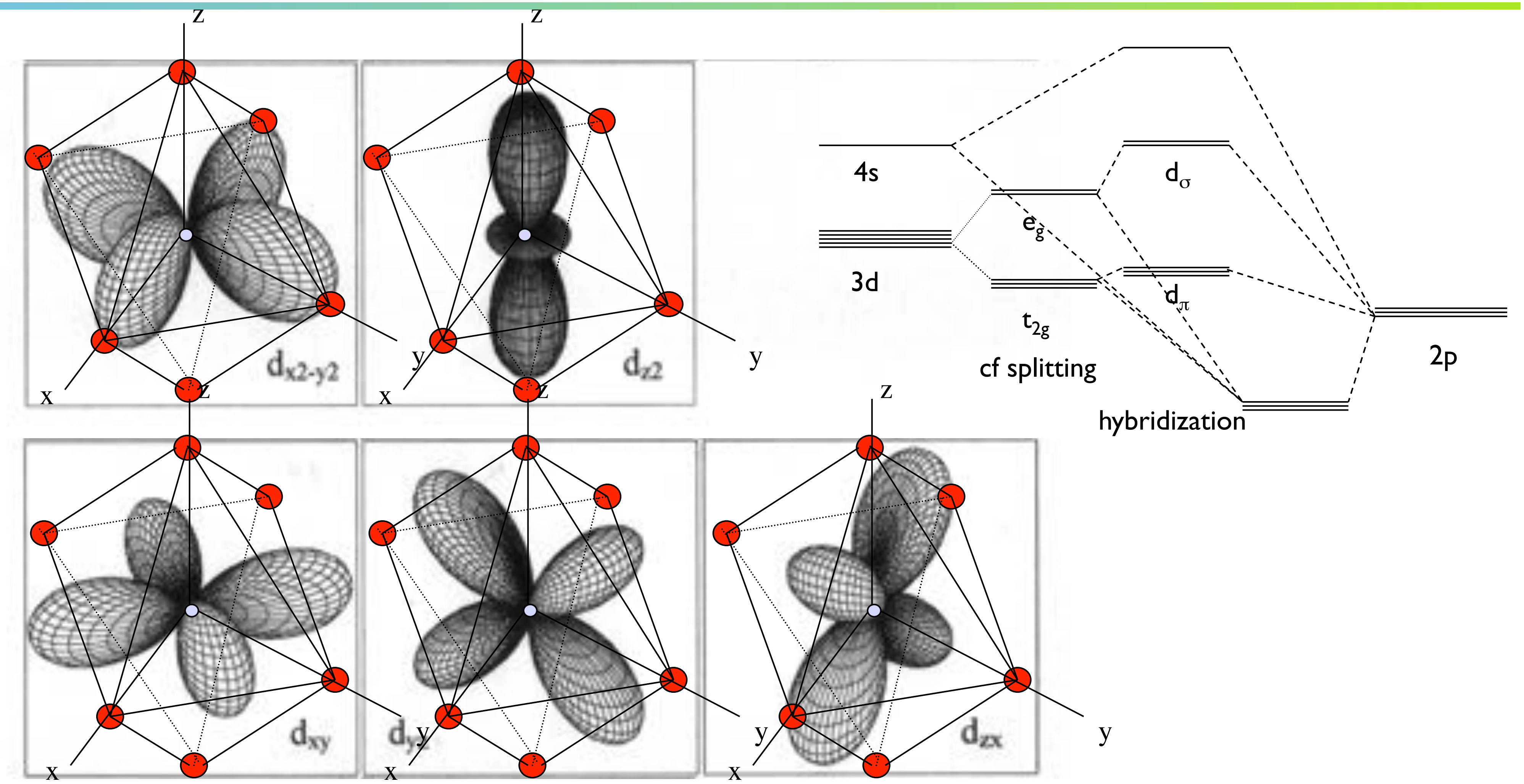
$n = 2$
$l = 1$ *p orbitals*

t_{2g}

$n = 3$
$l = 2$ *d orbitals*

e_g

Orbitals in the crystal field



Crystal-field theory regards the splitting of the 3*d* orbitals in octahedral oxygen, for example, as an electrostatic interaction with neighbouring point charges (oxygen anions). In reality the 3*d* and 2*p* orbitals of oxygen overlap to form a partially covalent bond. The oxygens bonding to the 3*d* metals are the *ligands*. The overlap is greater for the e_g than the t_{2g} orbitals in octahedral coordination.

The overlap leads to mixed wavefunctions, producing bonding and antibonding orbitals, whose splitting increases with overlap. The hybridized orbitals are

$$\phi = \alpha\psi_{2p}+\beta\psi_{3d}$$

where $\alpha^2 + \beta^2 = 1$.

For 3*d* ions the splitting is usually 1- 2eV, with the ionic and covalent contributions being of comparable magnitude

The *spectrochemical series* is the sequence of ligands in order of effectiveness at producing crystal/ligand field splitting.

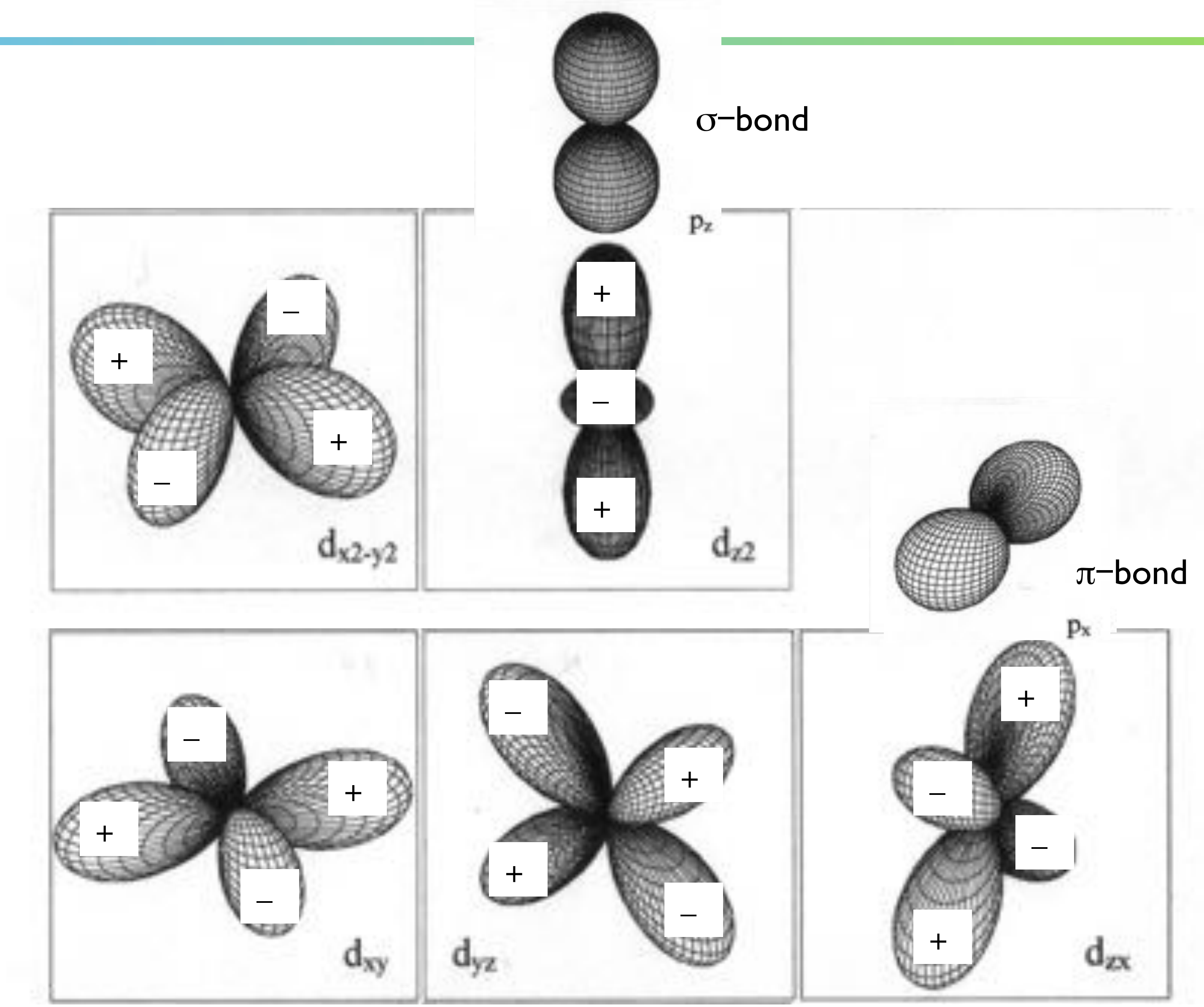
$$Br^- < Cl^- < F^- < OH^- < CO^{2-}_3 < O^{2-} < H_2O < NH_3 < SO^{2-}_3 < NO^-_2 < S^{2-} < CN^-$$

The bond is mostly ionic at the beginning of the series and covalent at the end.

Covalency is stronger in tetrahedral coordination but the crystal field splitting is

$$\Delta_{tet} = (3/5)\Delta_{oct}$$

Ligand field interaction



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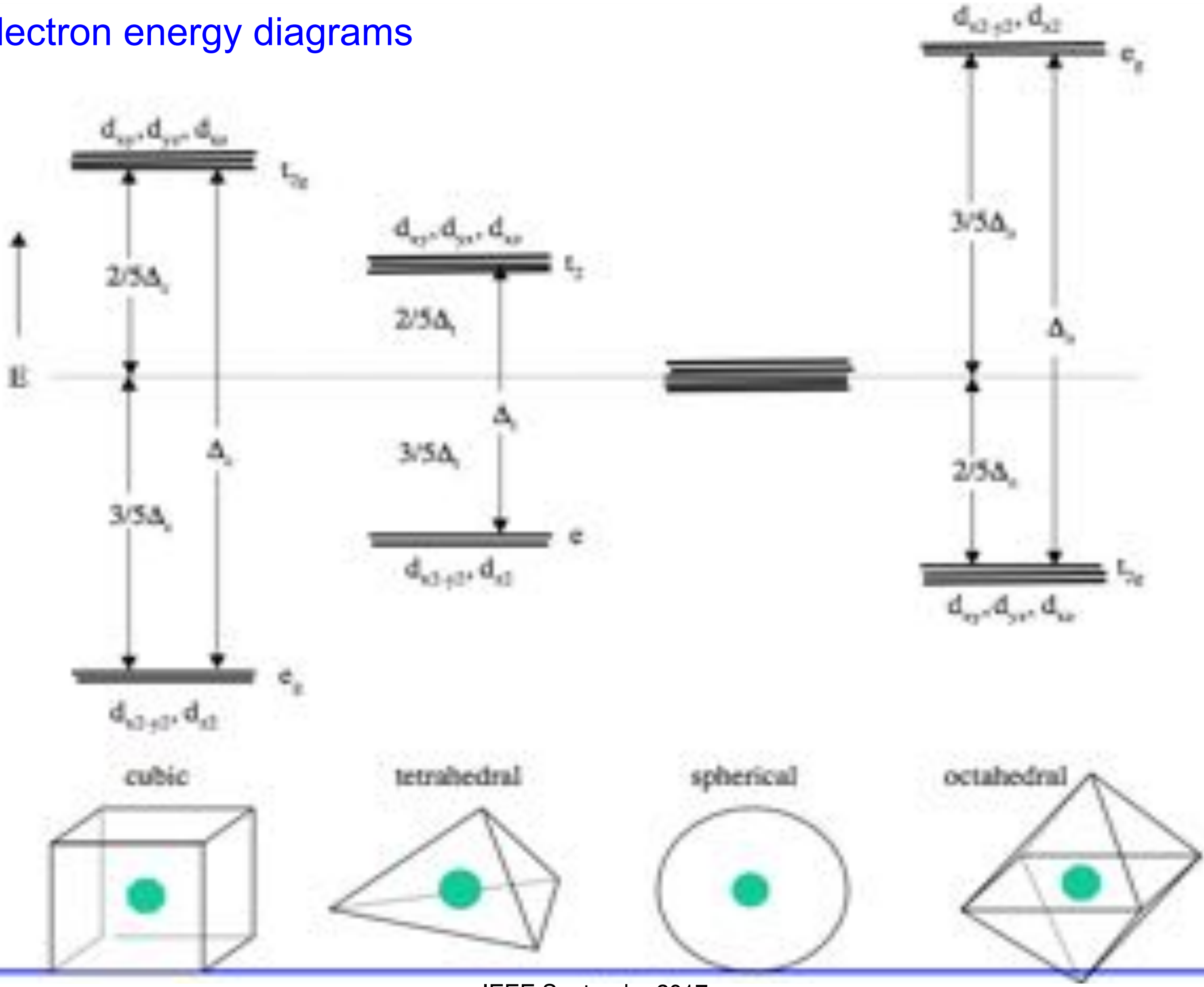
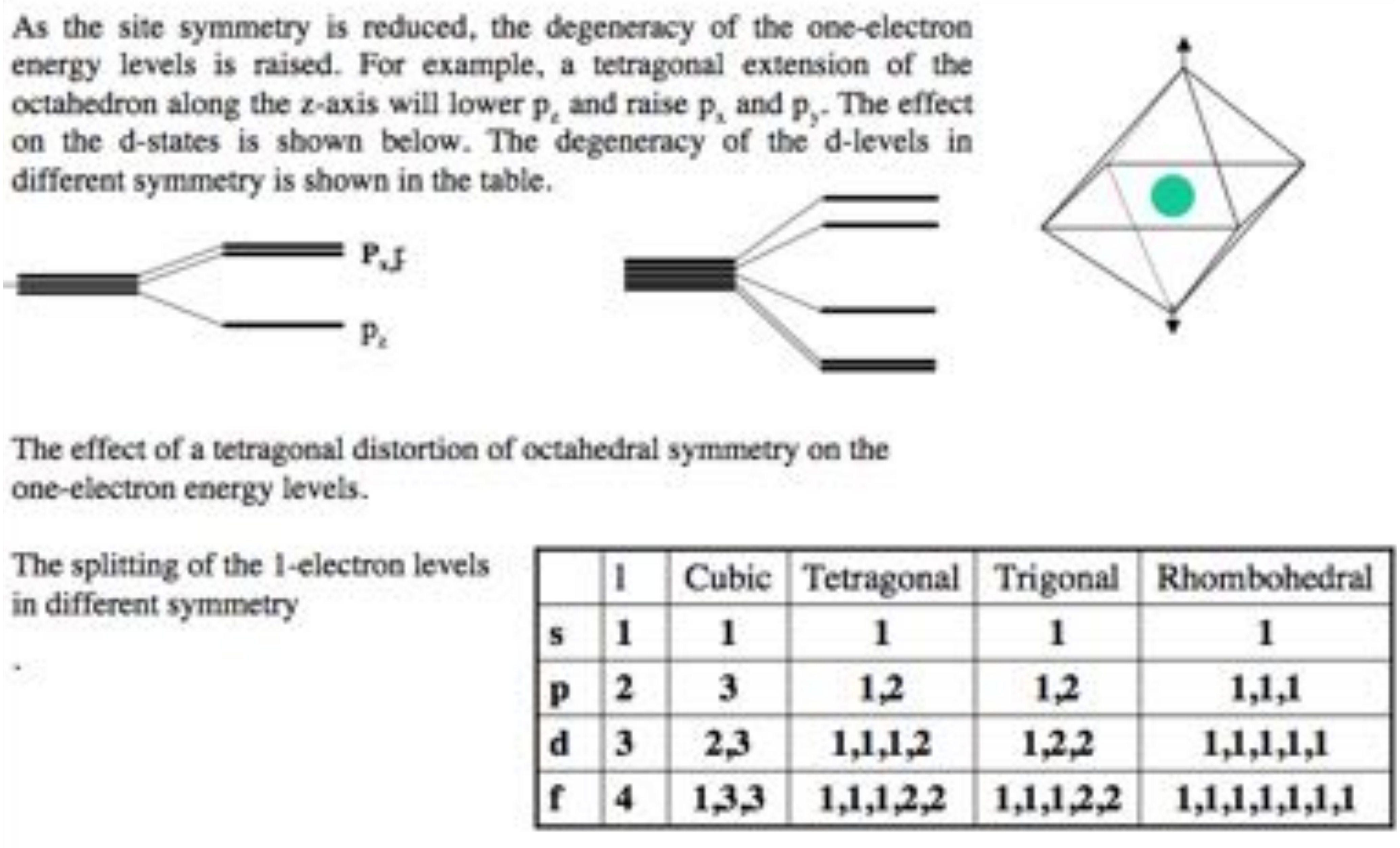
One-electron energy diagrams



Lower symmetry

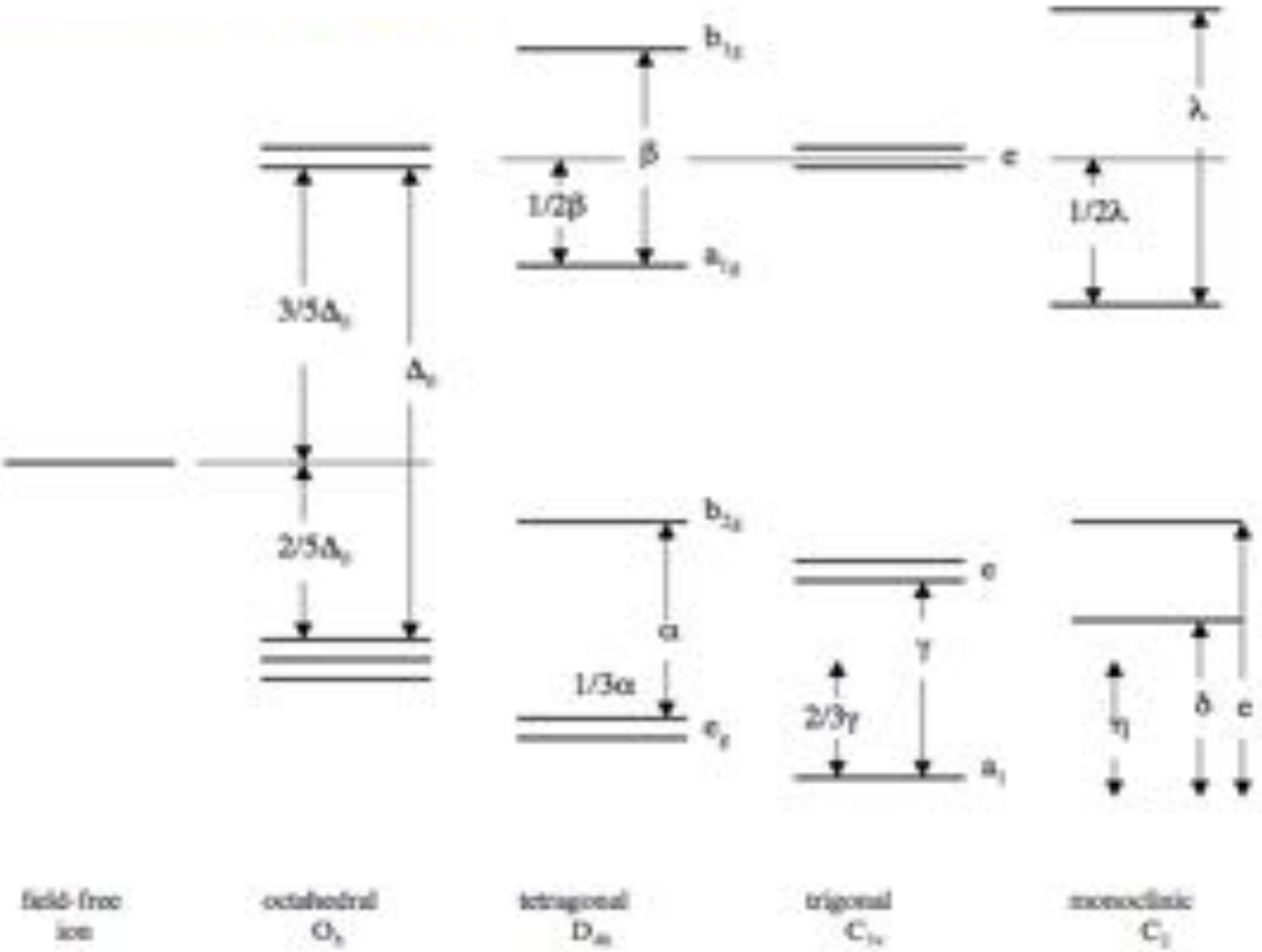


As the site symmetry is reduced, the degeneracy of the one-electron energy levels is raised. For example, a tetragonal extension of the octahedron along the z-axis will lower p_z and raise p_x and p_y. The effect on the d-states is shown below. The degeneracy of the d-levels in different symmetry is shown in the table.

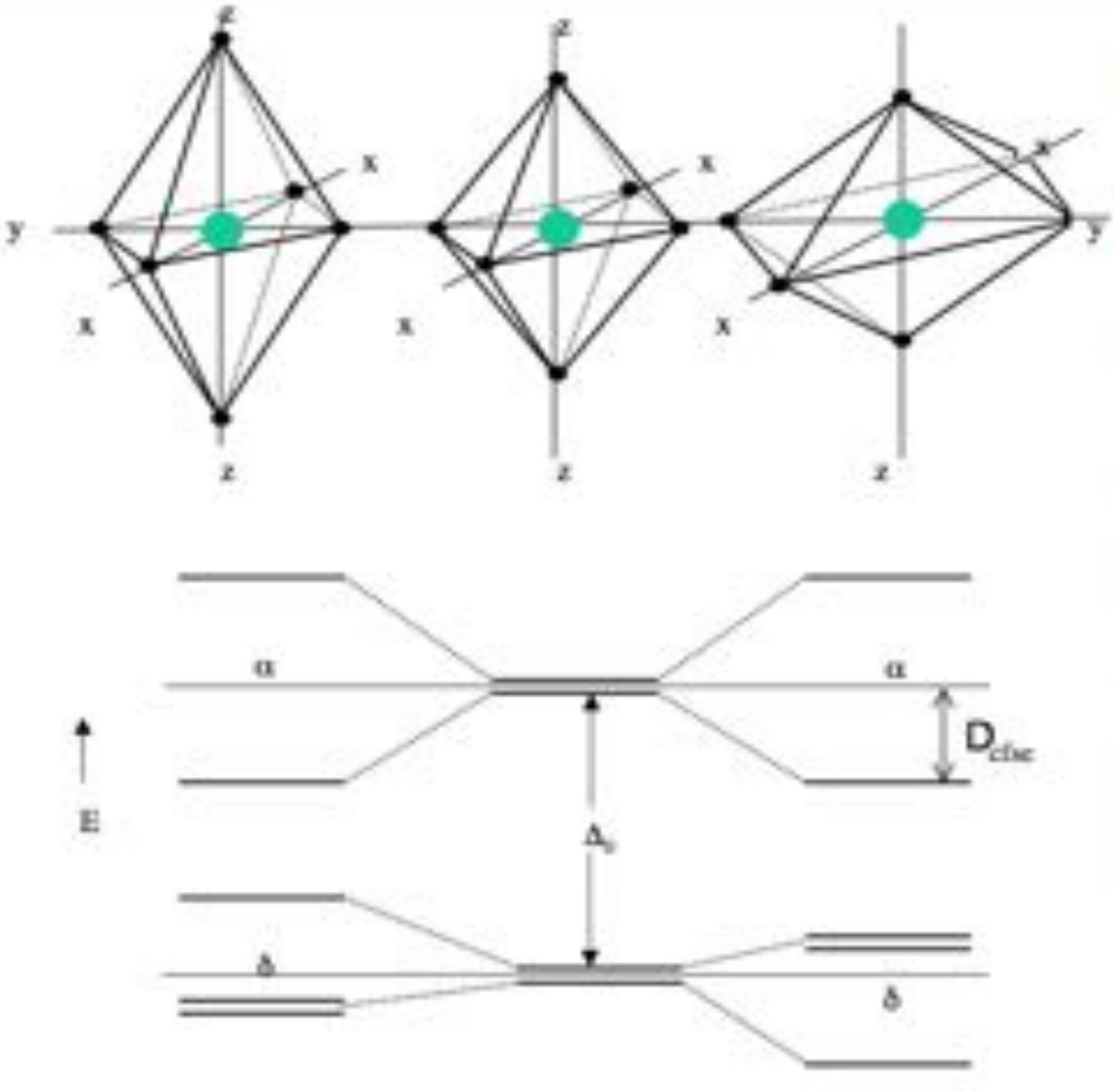
The effect of a tetragonal distortion of octahedral symmetry on the one-electron energy levels.

The splitting of the 1-electron levels in different symmetry

	l	Cubic	Tetragonal	Trigonal	Rhombohedral
s	1	1	1	1	1
p	2	3	1,2	1,2	1,1,1
d	3	2,3	1,1,1,2	1,2,2	1,1,1,1,1
f	4	1,3,3	1,1,1,2,2	1,1,1,2,2	1,1,1,1,1,1,1


b1g
β
1/2β
a1g
3/5Δo
Δo
2/5Δo
b2g
α
1/3α
eg
e
λ
1/2λ
e
γ
2/3γ
a1
η
δ
e
field-free ion
octahedral Oh
tetragonal D4h
trigonal C3v
monoclinic C2

The Jahn-Teller effect



- A system with a single electron (or hole) in a degenerate level will tend to distort spontaneously.

- The effect is particularly strong for d^4 and d^9 ions in octahedral symmetry (Mn^{3+}, Cu^{2+}) which can lower their energy by distorting the crystal environment- this is the *Jahn-Teller* effect.

- If the local strain is ε, the energy change is

$$\delta E = -A\varepsilon + B\varepsilon^2.$$

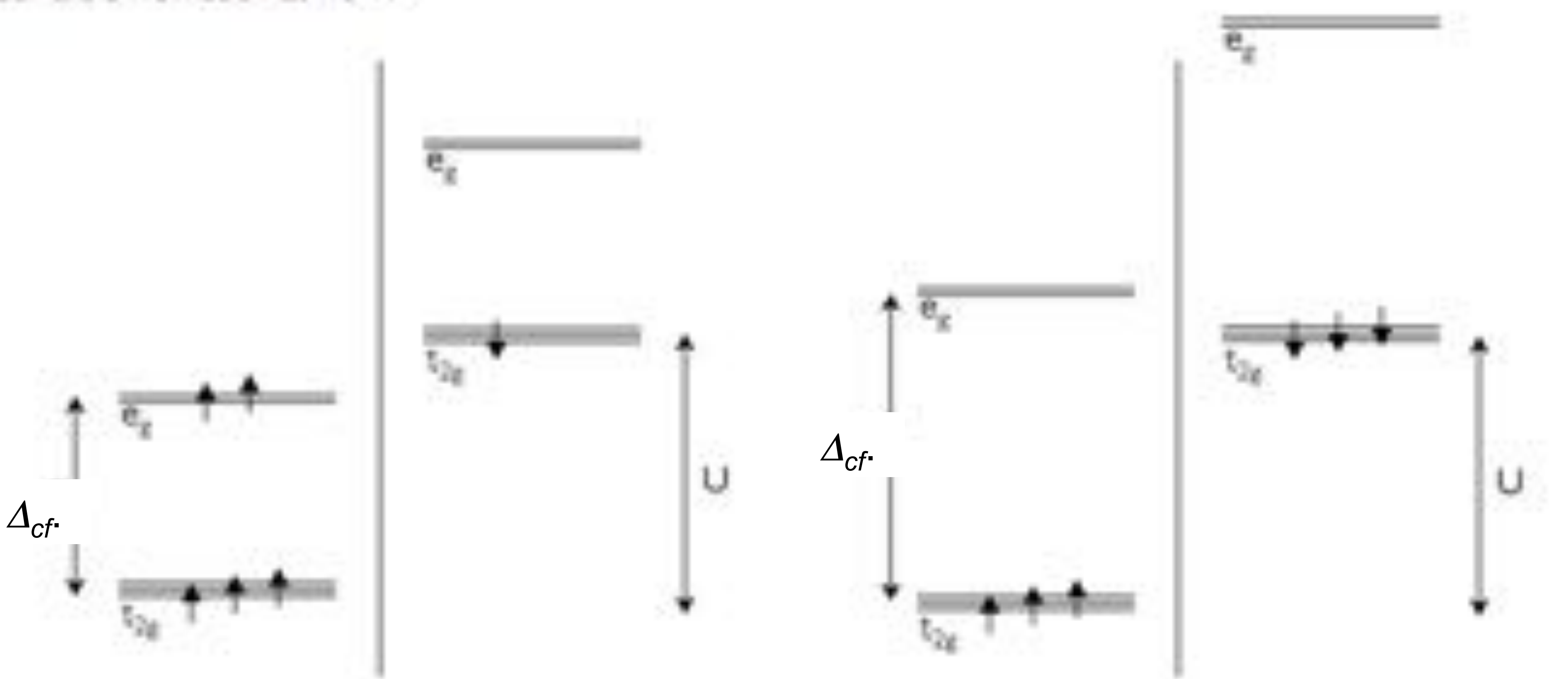
where the first term is the crystal field stabilization energy and the second term is the increased elastic energy.

- The Jahn-Teller distortion may be static or dynamic.

High and low spin states

An ion is in a high spin state or a low spin state depending on whether the Coulomb interaction
leading to Hund's first rule (maximize S) is greater than or less than the crystal field splitting Δ

Consider a 3d^5 ion such as Fe^{3+}.



$U_H > \Delta_{cf}$. gives a high-spin state, $S = 2$ e.g. FeCl$_3$ $U_H < \Delta_{cf}$. gives a low-spin state, $S = 0$ e.g. Pyrite FeS$_2$

Crystal Field Hamiltonian

$$\boxed{\mathcal{H}_{cf} = \int \rho_0(\boldsymbol{r})\varphi_{cf}(\boldsymbol{r})\mathrm{d}^3\boldsymbol{r}.}$$

Charge distribution of the ion

potential created by the crystal

$$\varphi_{cf}(\boldsymbol{r}) = \int \frac{\rho(\mathbf{r}')}{4\pi\epsilon_0|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}^3\boldsymbol{r}'.$$

Here $1/|r-r'|$ can be expanded spherical harmonics using spherical polar coordinates $r = (r, \theta, \phi)$ and $r' = (r', \theta', \phi')$:

$$\frac{1}{|r-r'|} = \frac{1}{r'}\sum_{n=0}^{\infty}\frac{4\pi}{(2n+1)}\left(\frac{r}{r'}\right)^n \sum_{m=-n}^{n}(-1)^m Y_n^{-m}(\theta', \phi')Y_n^m(\theta, \phi).$$

Hence

$$\varphi_{cf}(r, \theta, \phi) = \sum_{n=0}^{\infty}\sum_{m=-n}^{n} r^n \gamma_{nm} Y_n^m(\theta, \phi).$$

where

$$\gamma_{nm} = \frac{4\pi}{(2n+1)}\int \frac{\rho(r')(-1)^m Y_n^{-m}(\theta', \phi')}{r'^{n+1}}\mathrm{d}^3r'.$$

structural parameters

The approximation made so far is *terrible*.It ignores the screening of the potential by the outer shells of the 4*f* ion for example, and also the covalent contribution. *But it captures the symmetry of the problem.* We proceed with it, but treat the crystal field coefficients as empirical parameters.

It is useful to expand the charge distribution of a central *4f ion* in terms of the 2^n-pole moments of the charge distribution, n = 2, 4, 6

The quadrupole moment

$$Q_2 = \int \rho_{4f}(r)(3\cos^2\theta - 1)r^2 \mathrm{d}^3 r.$$

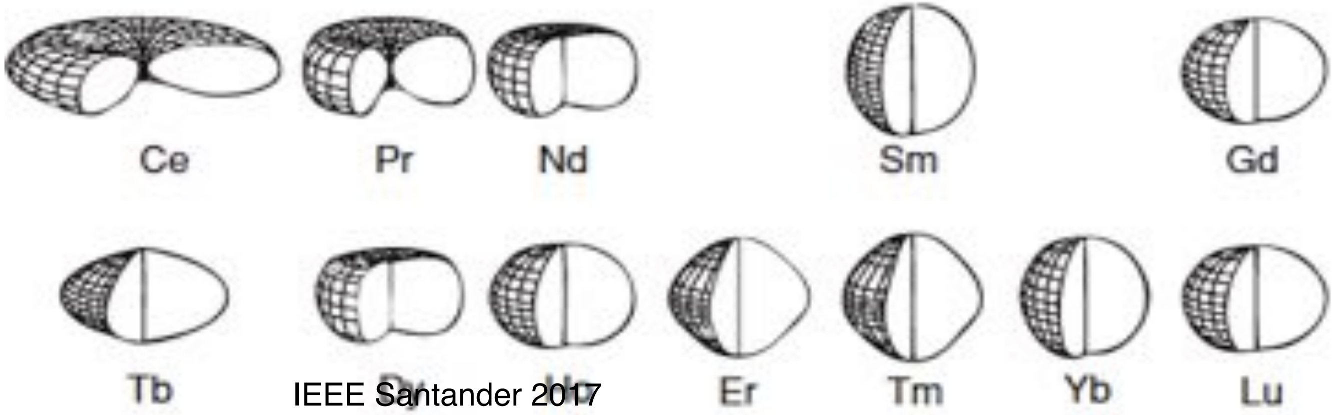
The hexadecapole moment

$$Q_4 = \int \rho_{4f}(r)(35\cos^4\theta - 30cos^2\theta + 3)r^4 \mathrm{d}^3 r,$$

The 64-pole moment

$$Q_6 = \int \rho_{4f}(r)(231\cos^6\theta - 315\cos^4\theta + 105\cos^2\theta - 5)r^6 \mathrm{d}^3 r.$$

Rare earth quadrupole moments



Single-ion anisotropy

Single-ion anisotropy is due to the electrostatic crystal field interaction + spin-orbit interaction. The 4f charge distribution $\rho_0(\mathbf{r})$ interacts with the crystal field potential $\varphi_{cf}(\mathbf{r})$ to stabilizes some particular orbitals; spin-orbit interaction $-\Lambda\boldsymbol{L}.\boldsymbol{S}$ then leads to magnetic moment alignment along some specific directions in the crystal.

The leading term in the crystal field interaction is

$$\varepsilon_a = (1/2)Q_2A_2^0(3\cos^2\theta - 1),$$

where A_2^0 is the uniaxial second-order crystal field parameter, which described the electric field gradient created by the crystal which interacts with the 4*f* quadrupole moment. Compare $\varepsilon_a = K_1\sin^2\theta$

The crystal field interaction can be expressed in terms of angular momentum operators, using the Wigner-Eckart theorem

$$\boxed{\mathcal{H}_{cf} = \sum_{n=0,2,4,6}\ \sum_{m=-n,\ldots,n} B_n^m\hat{\mathrm{O}}_n^m,}$$

cf coefficient

Stevens operators

Here $B_n^m = \theta_n \langle r_{4f}^n \rangle A_n^m$ and θ_n is different for each 4*f* ion, proportional to the 2^n-pole moment

$Q_2 = 2\,\theta_2 \langle r_{4f}^2 \rangle$ $Q_4 = 8\,\theta_4 \langle r_{4f}^4 \rangle$ $Q_6 = 16\,\theta_6 \langle r_{4f}^6 \rangle$

$A_n^m \sim \gamma_{nm}$ parameterises the crystal field produced by the lattice.

NB. $Q_2 \neq 0$ for J (or L) ≥ 1

$Q_4 \neq 0$ for J (or L) ≥ 2

$Q_6 \neq 0$ for J (or L) ≥ 3

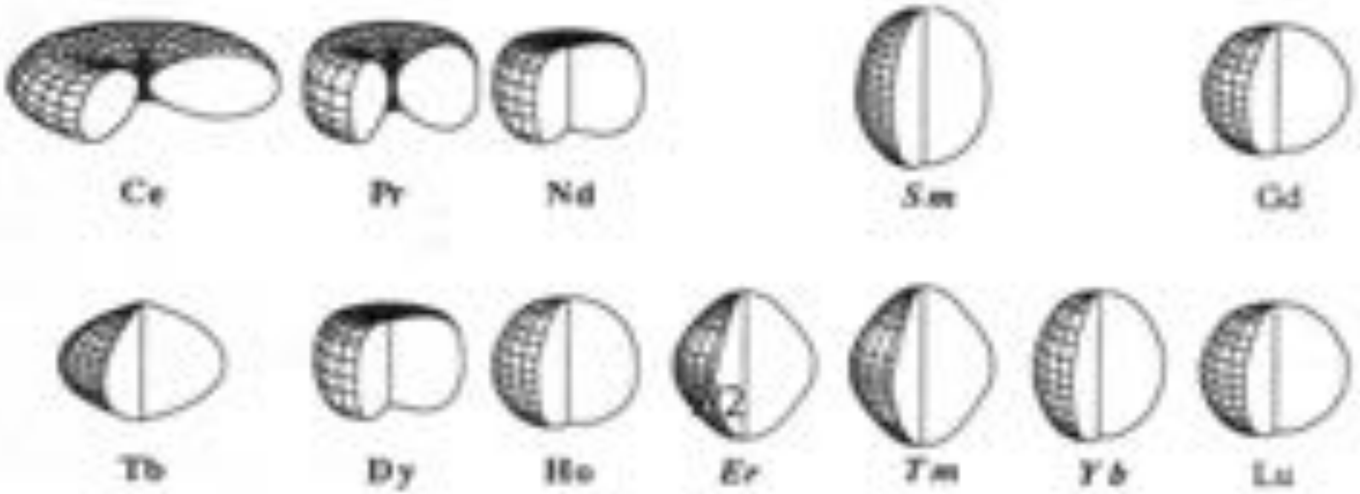
The Stevens operators are tabulated, as well as which ones feature in each point symmetry

e.g. The leading term in any uniaxial site is the one in O_2^0

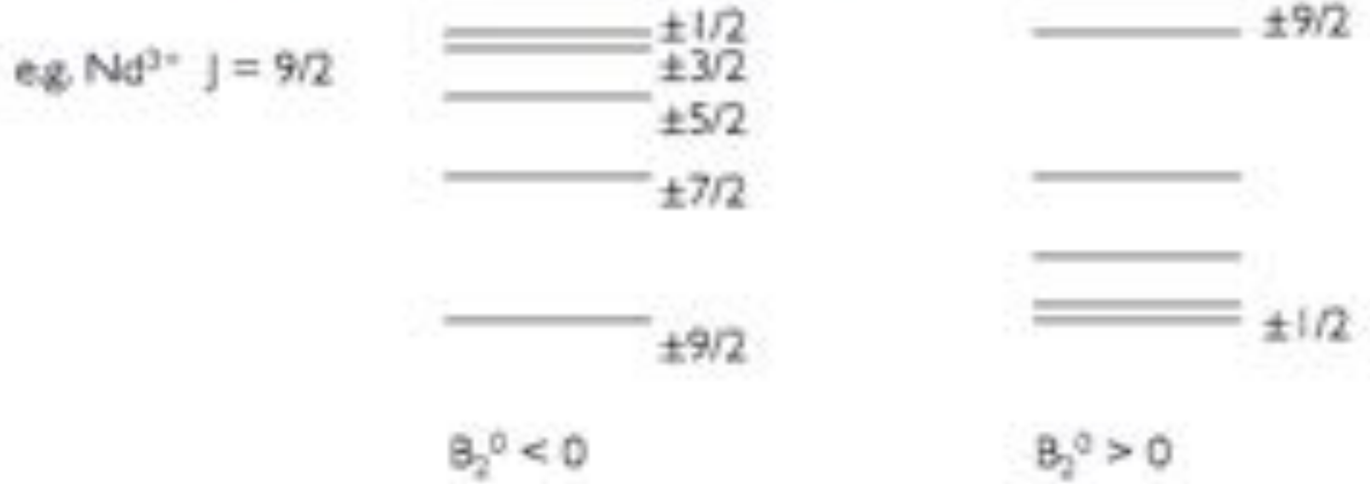
$$\hat{\mathbf{O}}_2^0 = [3\hat{J}_z^2 - J(J+1)].$$

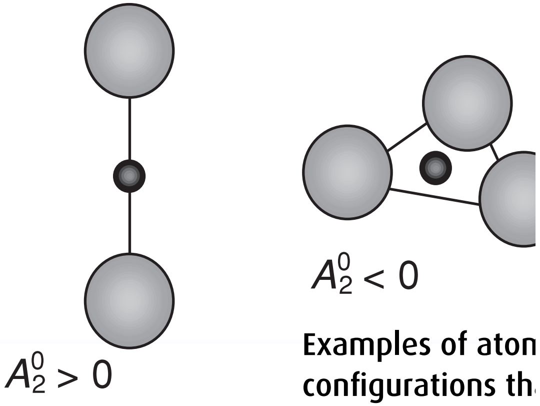
The complete second order (uniaxial) cf Hamiltonian is

$$\mathcal{H}_{cf} = \theta_2 \langle r_{4f}^2 \rangle \left[A_2^0 \hat{\mathbf{O}}_2^0 + A_2^2 \hat{\mathbf{O}}_2^{2(c)} \right]$$



Charge distributions of the rare-earth ions. Those with a positive quadrupole moment ($\theta_2 > 0$), italic typ distinguished from those with a negative quadrupole moment ($\theta_2 < 0$) bold type. Note the quarter-shell changes.





Examples of aton
configurations th
positive and nega
electric field grad
the central site.

The cf Hamiltonian for a site with cubic symmetry is

$$\mathcal{H}_{cf} = \theta_4 \langle r_{4f}^4 \rangle \left[A_4^0 \hat{O}_4^0 + 5 A_4^{4(c)} \hat{O}_2^{2(c)} \right] + \theta_6 \langle r_{4f}^6 \rangle \left[A_6^0 \hat{O}_6^0 - 21 A_6^0 \hat{O}_2^{2(c)} \right]$$

For 3*d* ions only the fourth-order terms exist; (l = 2)

For 3*d* ions the second-order term

$$\mathcal{H}_{cf} = \theta_2 \langle r_{4f}^2 \rangle \left[A_2^0 \hat{O}_2^0 + A_2^2 \hat{O}_2^{2(c)} \right]$$

Is often simplified to $\mathcal{H}_{\mathrm{cf}} = \mathrm{D}S_z^2$ Typically D ≤ 1 K

Kramer' s theorem

It follows from time-reversal symmetry that the cf energy levels of any ion with an odd number of electrons, and therefore half-integral angular momentum, must be at least 2-fold degenerate. These are the $|\pm M_J\rangle$ Kramers doublets.

When J is integral, there will be a $|0\rangle$ singlet (with no magnetic moment) and a series of doublets.

Summary 2

You should now know;

- Magnetism in solids is inextricably connected to angular momentum
- It arises from quantized spin and orbital angular momenta of the electrons
- Curie law paramagnetic susceptibility of localized electrons
- Pauli susceptibility of delocalized electrons
- Hund’s rules for calculating the ground state of a free ion
- Crystal fields in solids tend to quench orbital angilar momentum; spin survives
- Magnetic anisotropy − sources and magnitudes.
- Magnetic exchange interactions
- Ferromagnetic, ferrimagnetic and antiferromagnetic order.

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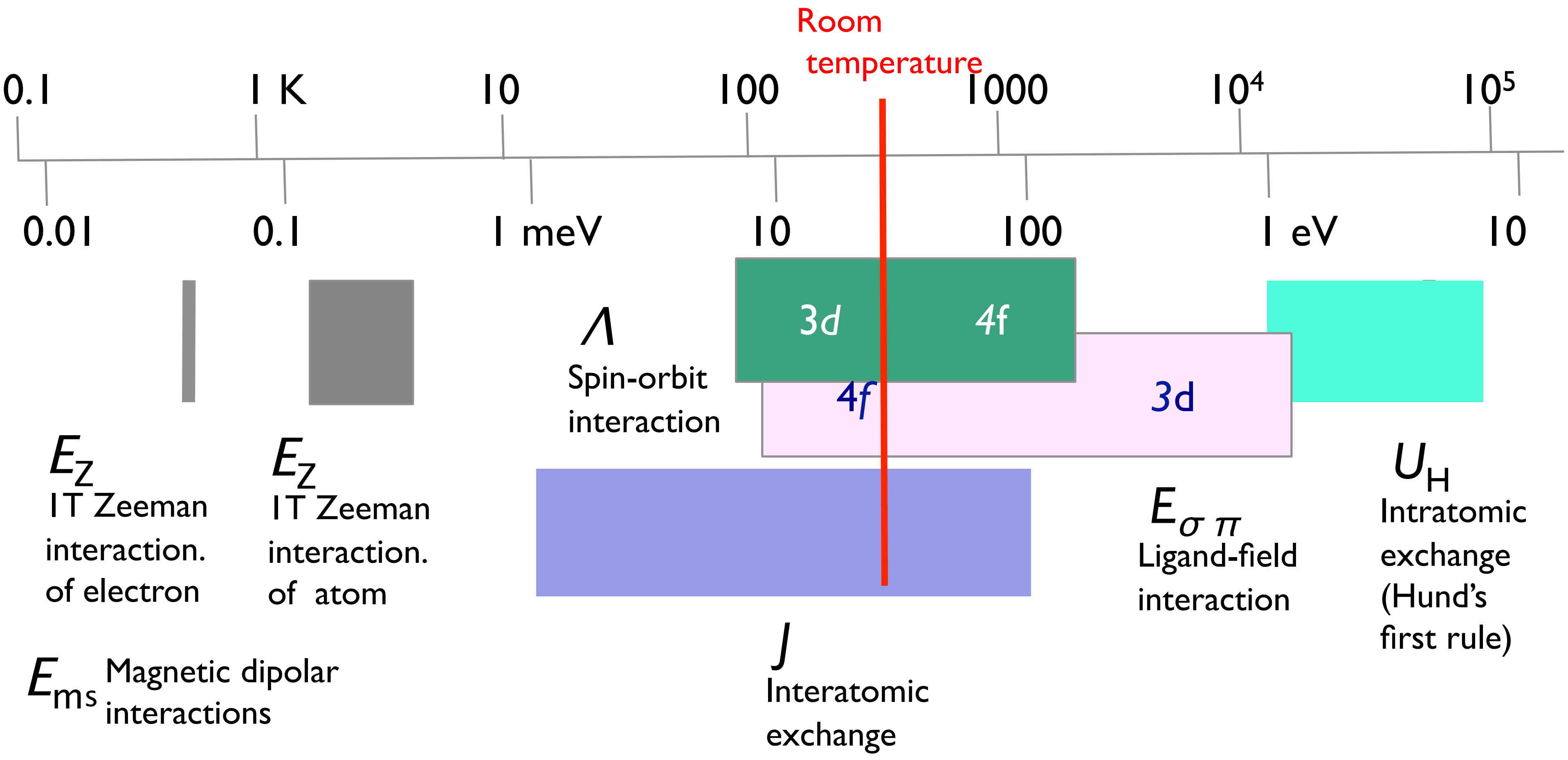
Energy scales



E_Z 1T Zeeman interaction. of electron

E_Z 1T Zeeman interaction. of atom

E_{ms} Magnetic dipolar interactions

Λ Spin-orbit interaction

J Interatomic exchange

$E_{\sigma\,\pi}$ Ligand-field interaction

U_H Intratomic exchange (Hund's first rule)