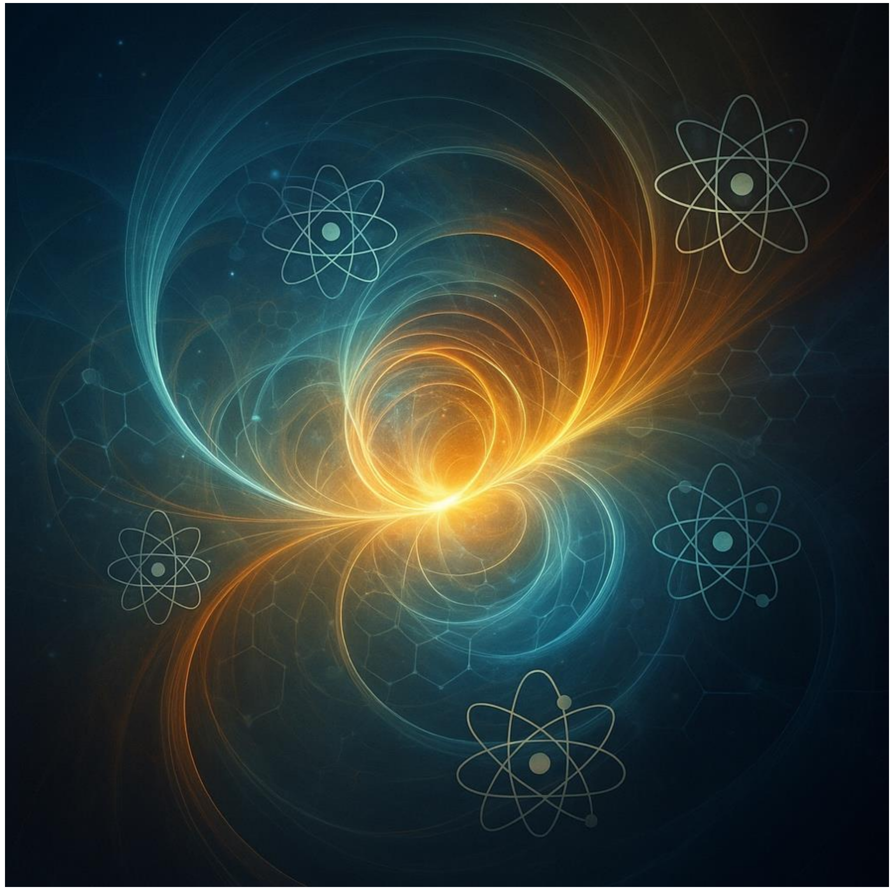
ΧΗΜΕΙΑ
ΠΑΝΕΠΙΣΤΗΜΙΟ
ΠΑΤΡΩΝ
UNIVERSITY OF PATRAS
CHEMISTRY

Introduction to Molecular and Solid-State Magnetism



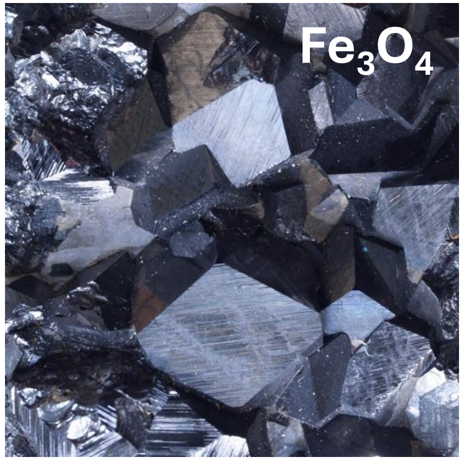
Dimitris I. Alexandropoulos

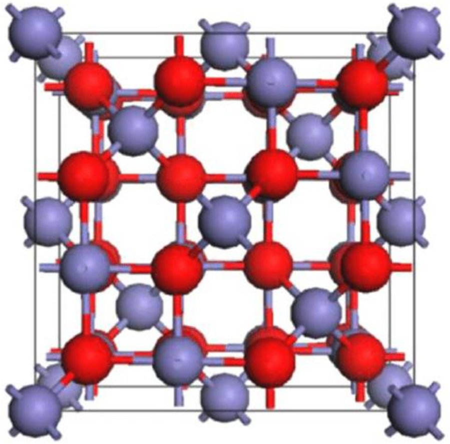
Department of Chemistry, University of Patras, 26504 Rio, Greece

Email: dimalexandrop@upatras.gr

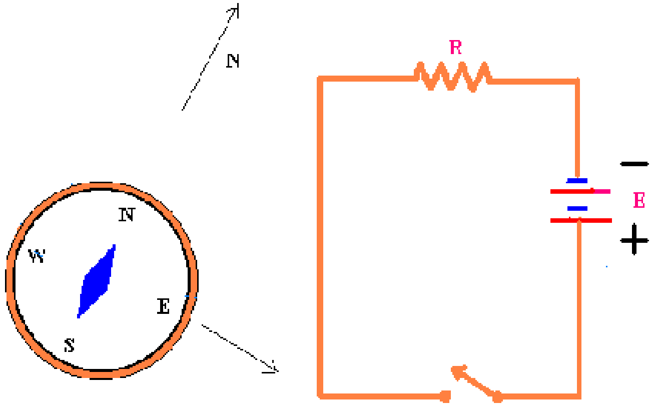
Magnetism

Magnetite

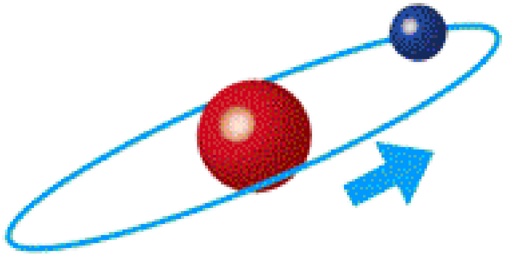




Electromagnetic theory

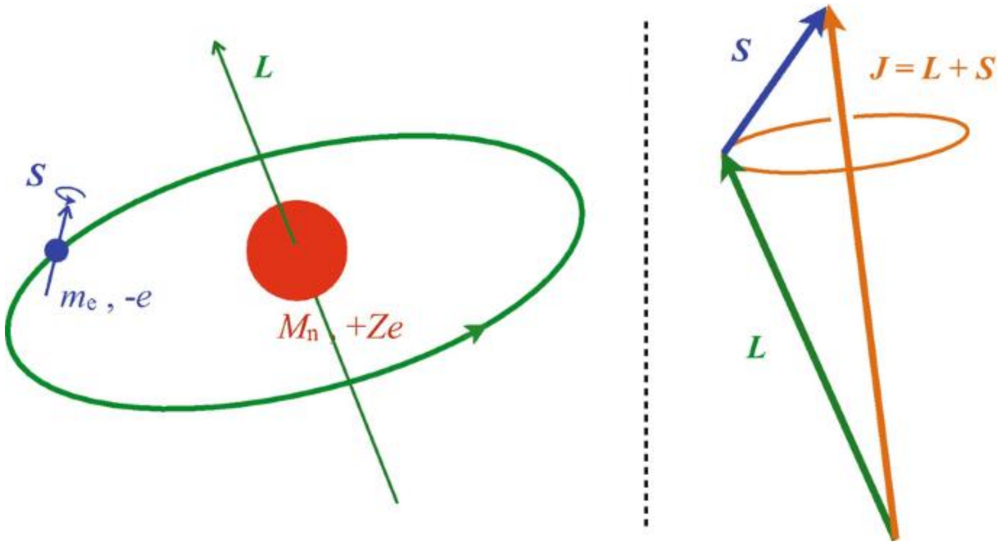


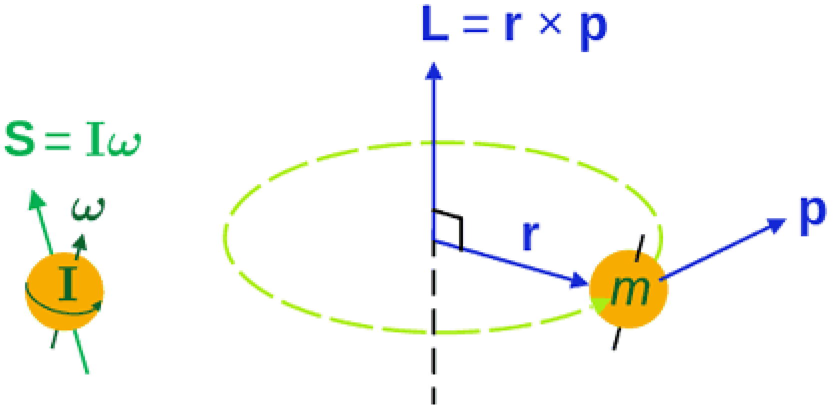
Atomic View



Ancient Times → 19th Century → Modern Era

Magnetic Moment





I = moment of inertia

ω = angular frequency

r = position (radius) vector

p = linear momentum

Spin Angular Momentum, S

Orbital angular momentum, L

Total angular momentum, J

J is derived from vector coupling of S and L

In general: J = L + S

S, L and J are quantised

Magnetic Moment

$$\hat{\mu} = \hat{\mu}_L + \hat{\mu}_S$$

$$\hat{\boldsymbol{\mu}}_L = -\frac{e}{2m_e}\hat{\mathbf{L}} \qquad\qquad \hat{\boldsymbol{\mu}}_S = -g_s\frac{e}{2m_e}\hat{\mathbf{S}}$$

$$\Downarrow \qquad \mu_B = \frac{e\hbar}{2m_e} \qquad \hbar = \frac{h}{2\pi} \qquad \Downarrow$$

$$\hat{\boldsymbol{\mu}}_L = -\mu_B\frac{\hat{\mathbf{L}}}{\hbar} \qquad\qquad \hat{\boldsymbol{\mu}}_S = -g_s\,\mu_B\frac{\hat{\mathbf{S}}}{\hbar}$$

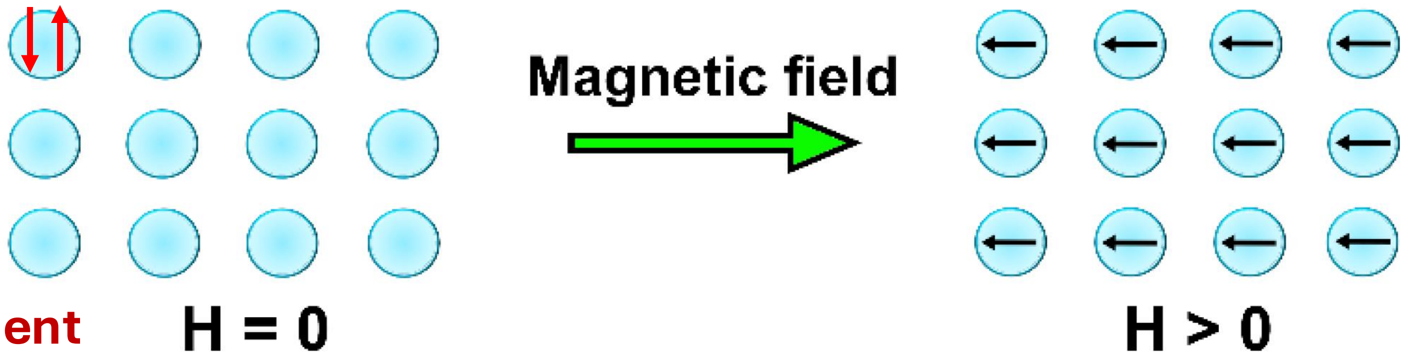
$$\hat{\mu} = -\mu_B\left(\frac{\hat{\mathbf{L}}}{\hbar} + g_s\frac{\hat{\mathbf{S}}}{\hbar}\right)$$

$$\boxed{\mu = -\mu_B\left(L + g_s S\right)}$$

Bulk Magnetic Materials

Measure material's magnetization response to an external magnetic field or its magnetic susceptibility , χ (dimensionless)

Diamagnetic material

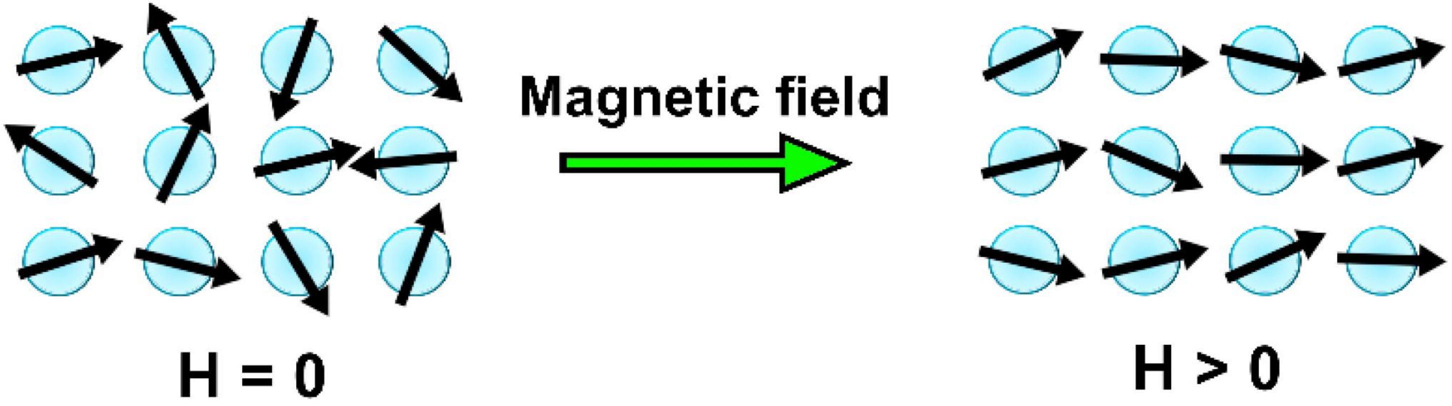


no permanent magnetic moments

induced magnetic moments that are *opposite* to the applied field

$\chi < 0$

Paramagnetic material



random directions

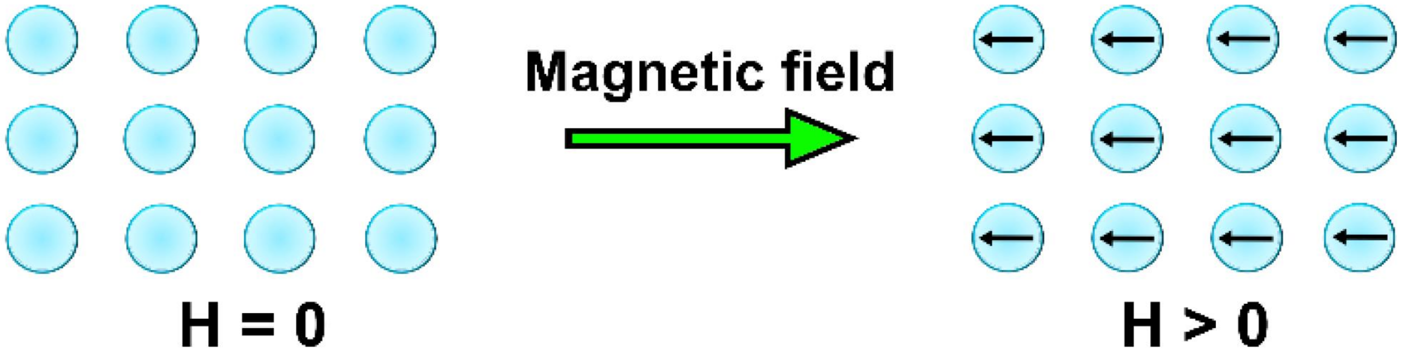
net magnetization in the same direction as the field

$\chi > 0$

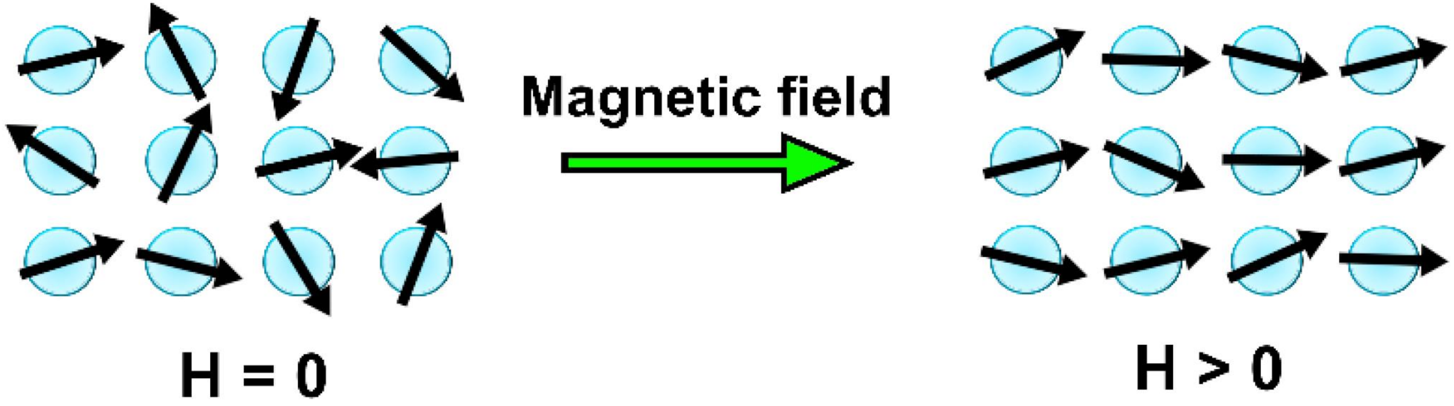
Bulk Magnetic Materials

Measure material's magnetization response to an external magnetic field or its magnetic susceptibility , χ (dimensionless)

Diamagnetic material



Paramagnetic material



Magnetic Susceptibility

$$\chi_v = \frac{M}{H} \qquad \chi_g = \frac{\chi_v}{\rho}$$

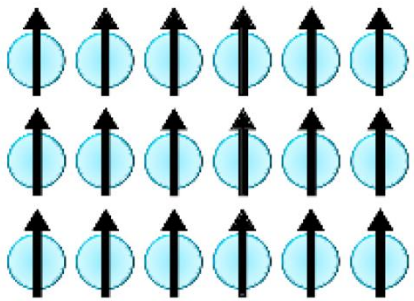
$$\chi_M = M_r \cdot \chi_g = M_r \cdot \frac{\chi_v}{\rho}$$

Curie law

$$\chi_M = \frac{C}{T} \quad , \; C = \frac{N_A \mu_\beta^2 g^2 S(S+1)}{3k_B}$$

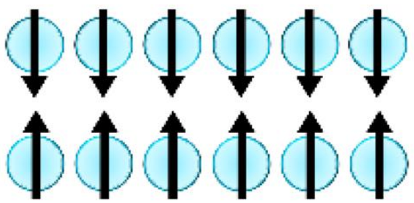
Bulk Magnetic Materials

Measure material’s magnetization response to an external magnetic field or its magnetic susceptibility , χ (dimensionless)



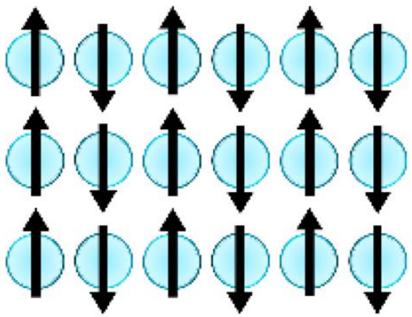
Ferromagnetism
(FM)

Example: Fe, Co, Ni



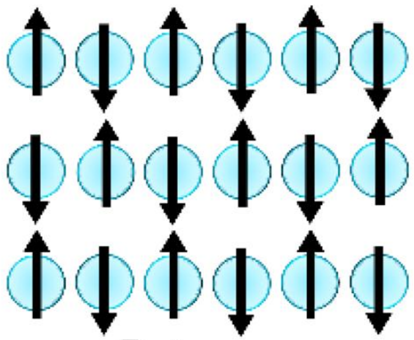
A-type
Antiferromagnetism
(A-type AFM)

$LaMnO_3$



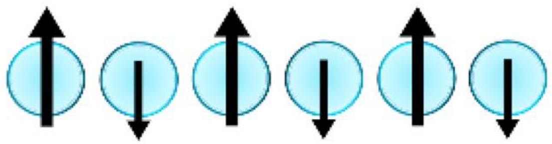
C-type
Antiferromagnetism
(C-type AFM)

$CdMnO_3$



G-type
Antiferromagnetism
(G-type AFM)

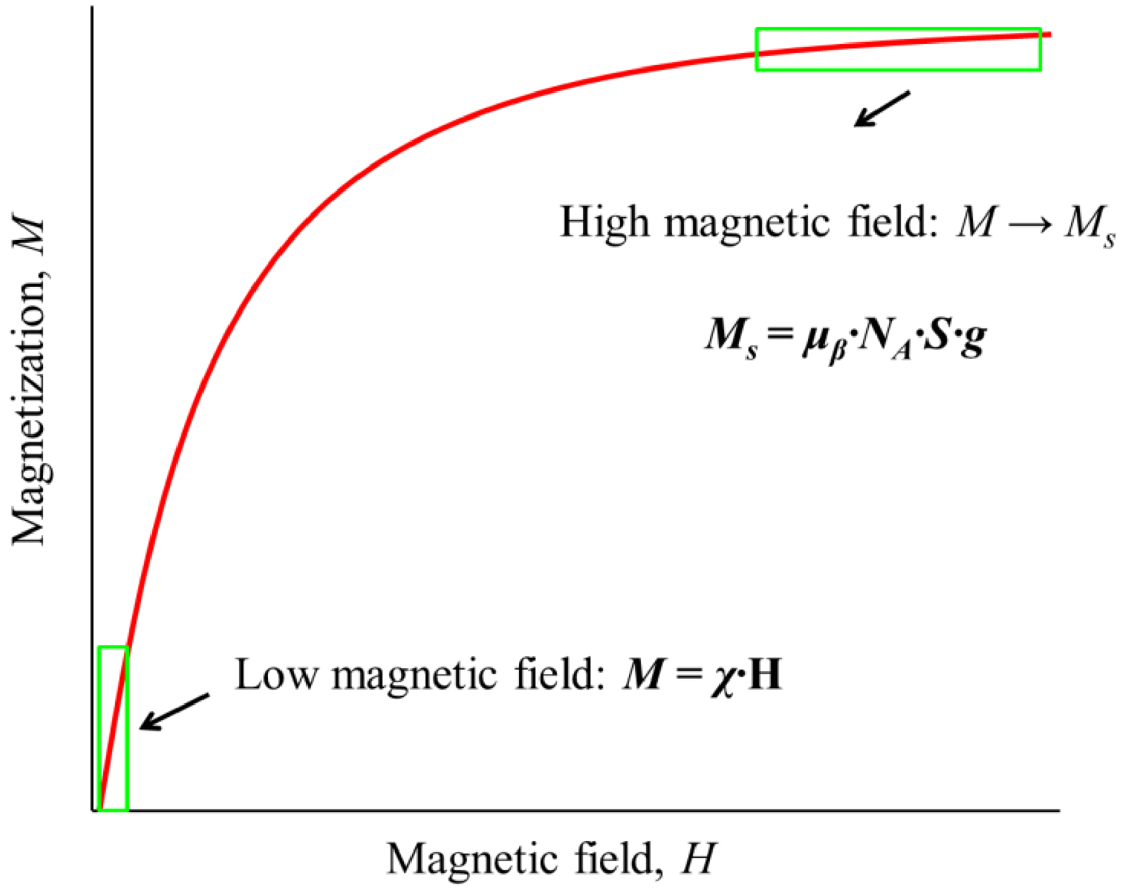
MnO



Ferrimagnetism

Fe_3O_4

Bulk Magnetic Materials



High magnetic field: $M \rightarrow M_s$

$$M_s = \mu_\beta \cdot N_A \cdot S \cdot g$$

Low magnetic field: $M = \chi \cdot \mathbf{H}$

$$M_s = \mu_\beta \cdot N_A \cdot S \cdot g \rightarrow \boxed{\frac{M_s}{\mu_\beta N_A}} = S \cdot g = n$$

Reduced magnetization

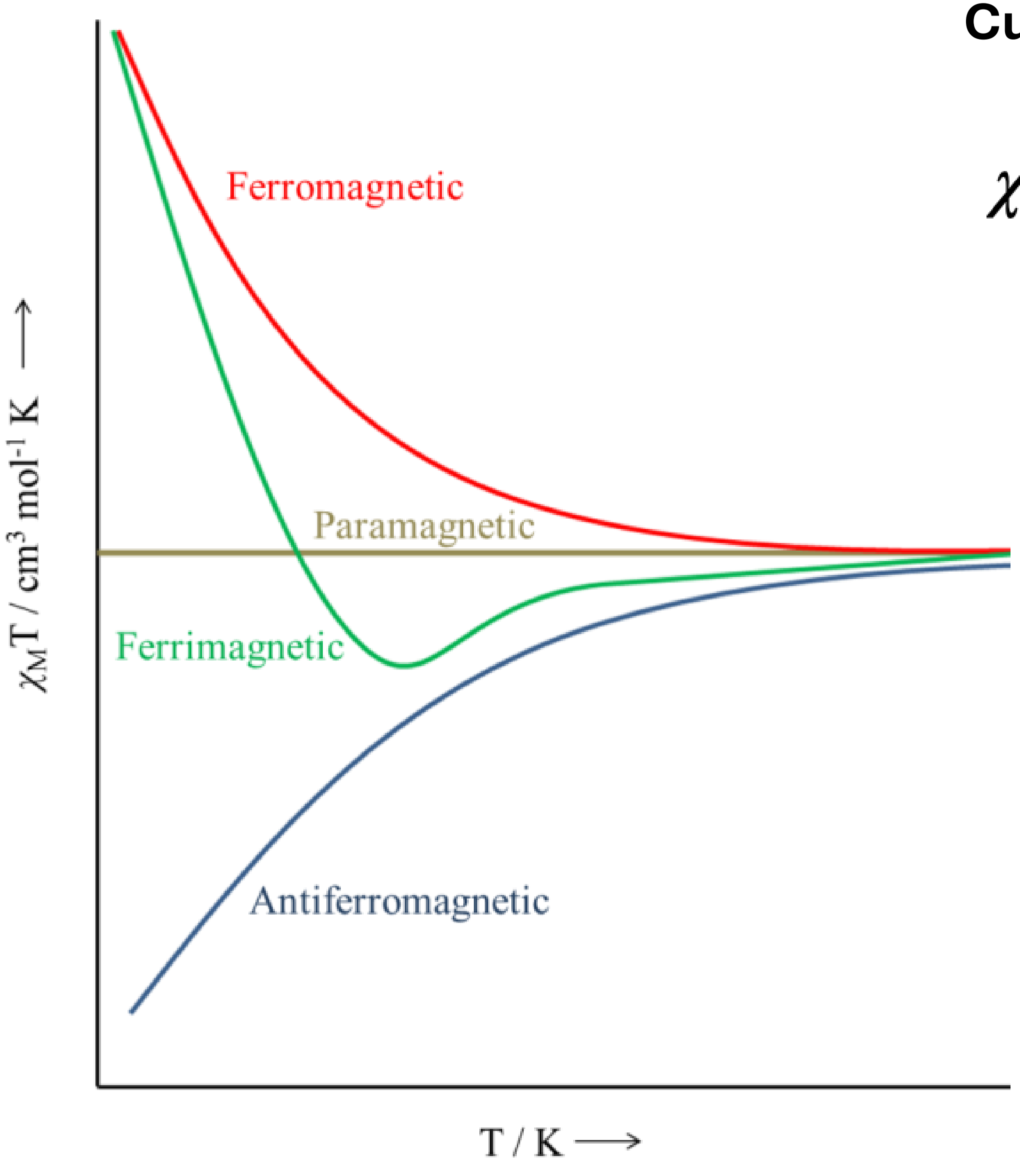
Curie’s Law

Temperature dependence of susceptibility

$$\chi_M = \frac{C}{T}$$

Bulk Magnetic Materials

Curie's Law



$$\chi_M = \frac{C}{T} \Longrightarrow C = \frac{N_A \mu_{\text{eff}}^2}{3k_B}$$

$$\chi_M = \frac{N_A \mu_{\text{eff}}^2}{3k_B T} \Longrightarrow \chi_M T = \frac{N_A \mu_{\text{eff}}^2}{3k_B}$$

$$\mu_{\text{eff}} \approx 2\sqrt{S(S+1)}\,\mu_B$$

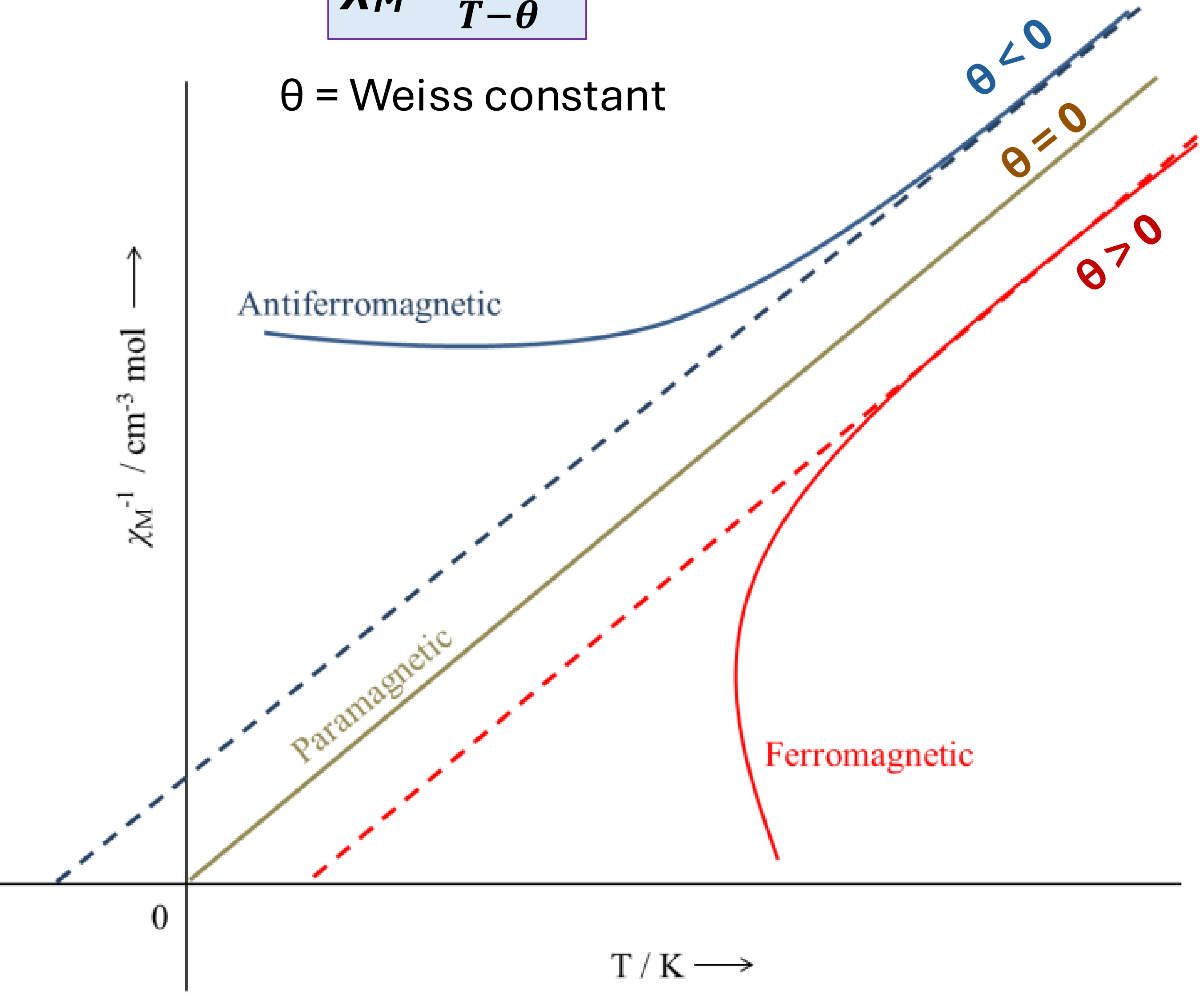
$$\mu_{\text{eff}} \approx \sqrt{n(n+2)}\,\mu_B$$

Bulk Magnetic Materials

Curie-Weiss Law

$$\chi_M = \frac{C}{T-\theta}$$

θ = Weiss constant



➢ **Curie temperature T_C**

A ferromagnet loses its spontaneous magnetization and becomes paramagnetic.

- **$T < T_C$: FM ordering**
- **$T > T_C$: paramagnetic, Curie-Weiss law**

➢ **Néel temperature T_N**

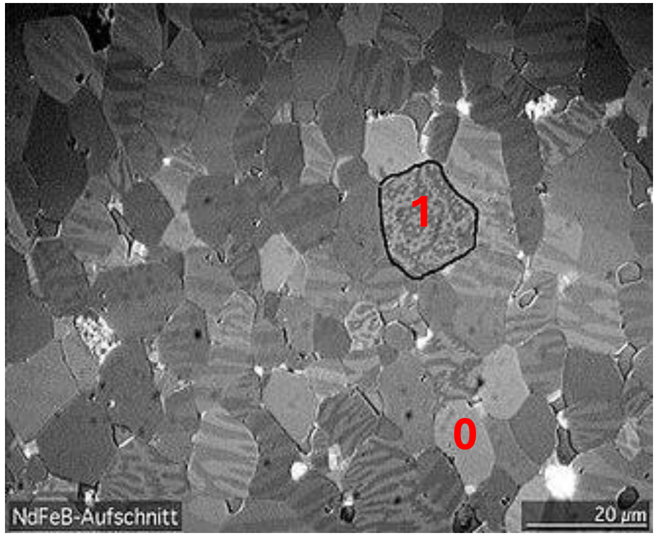
An antiferromagnet loses its antiferromagnetic order and becomes paramagnetic.

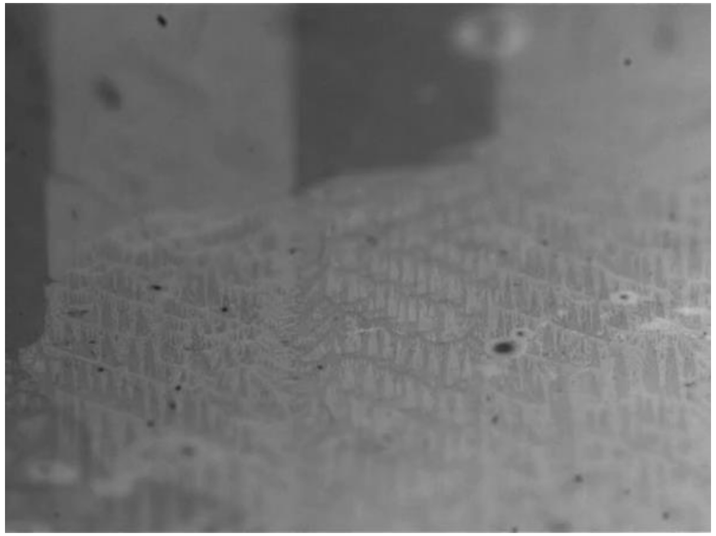
- **$T < T_N$: AFM ordering**
- **$T > T_N$: paramagnetic, Curie–Weiss**

Ferrimagnets?

Traditional Technology


Hard disk drive (HDD)

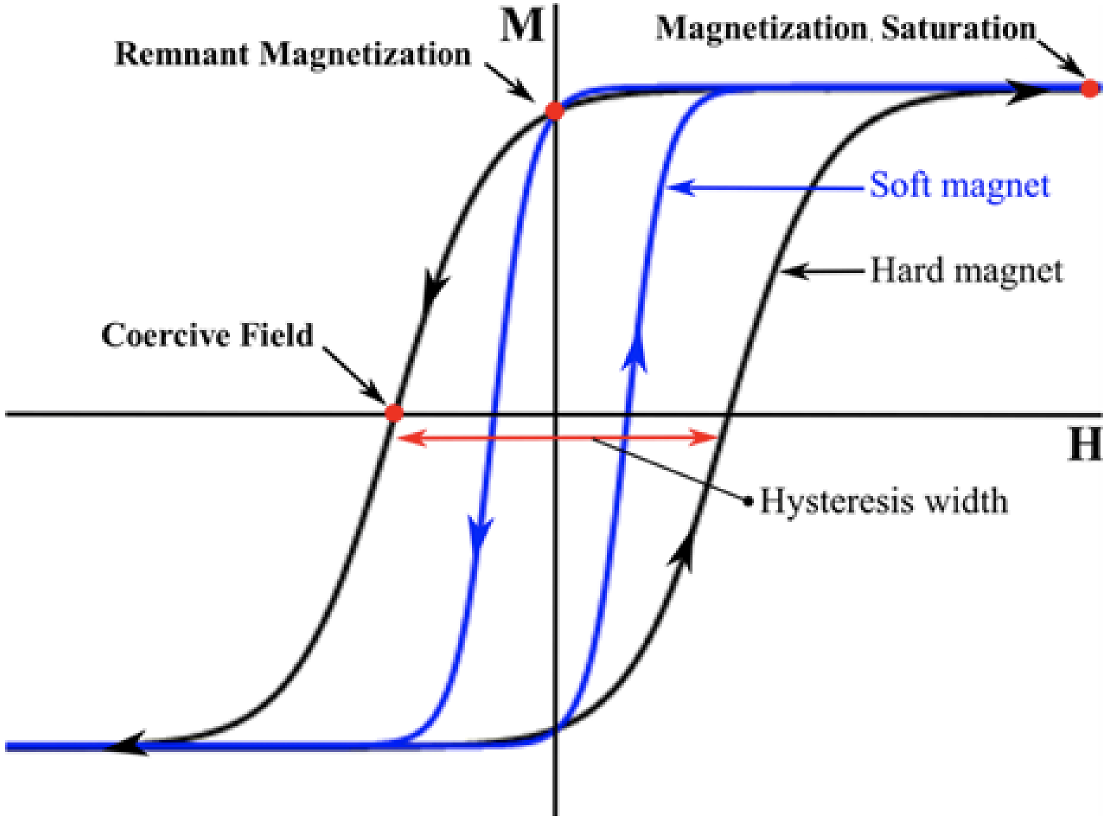

Microstructure of NdFeB

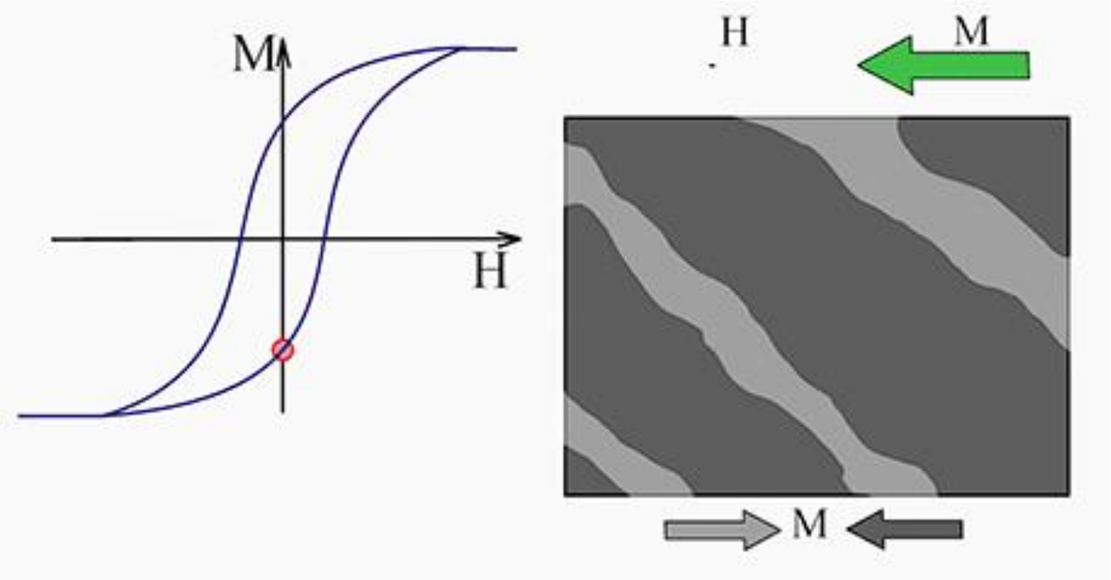

Magnetic domains

Atoms need to “talk” to each other (exchange interaction) to form a stable domain. If we keep shrinking bits/domains, eventually there are not enough atoms to keep the magnetization stable, and we hit the superparamagnetic limit for magnetic storage.

Bulk Magnetic Materials

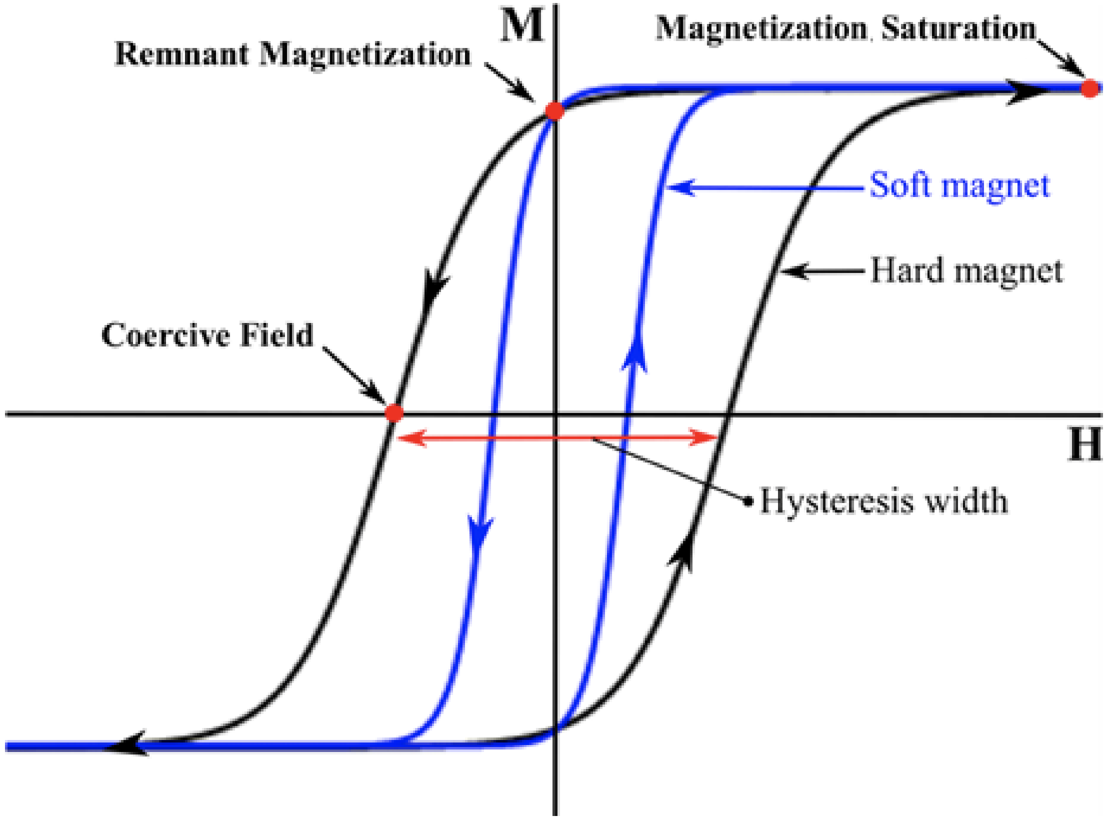
Magnetic Hysteresis

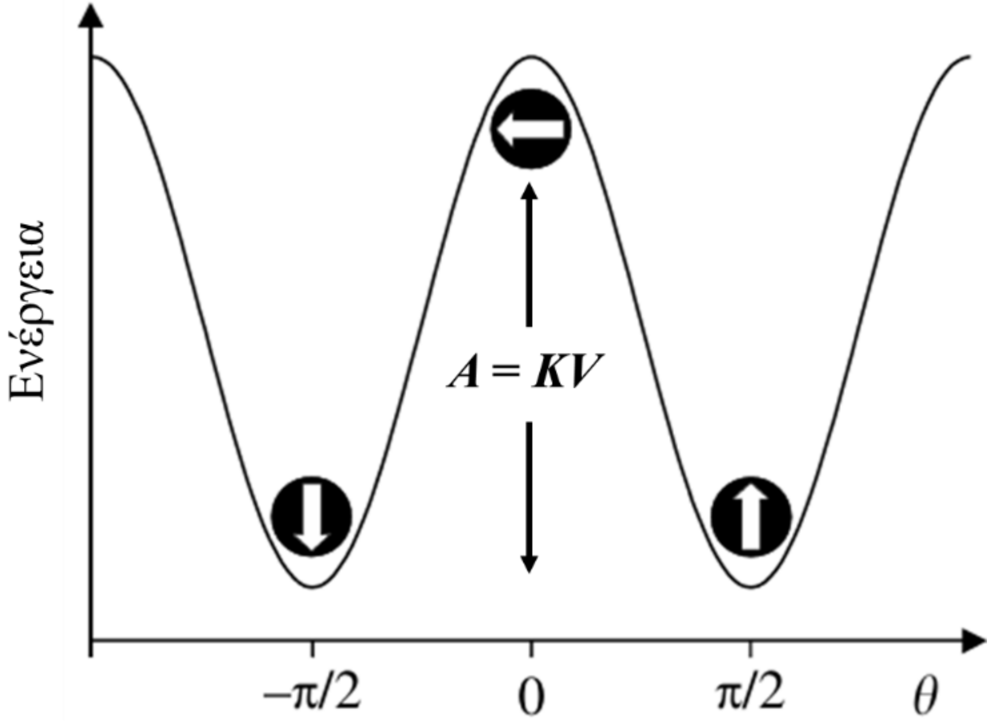




Bulk Magnetic Materials

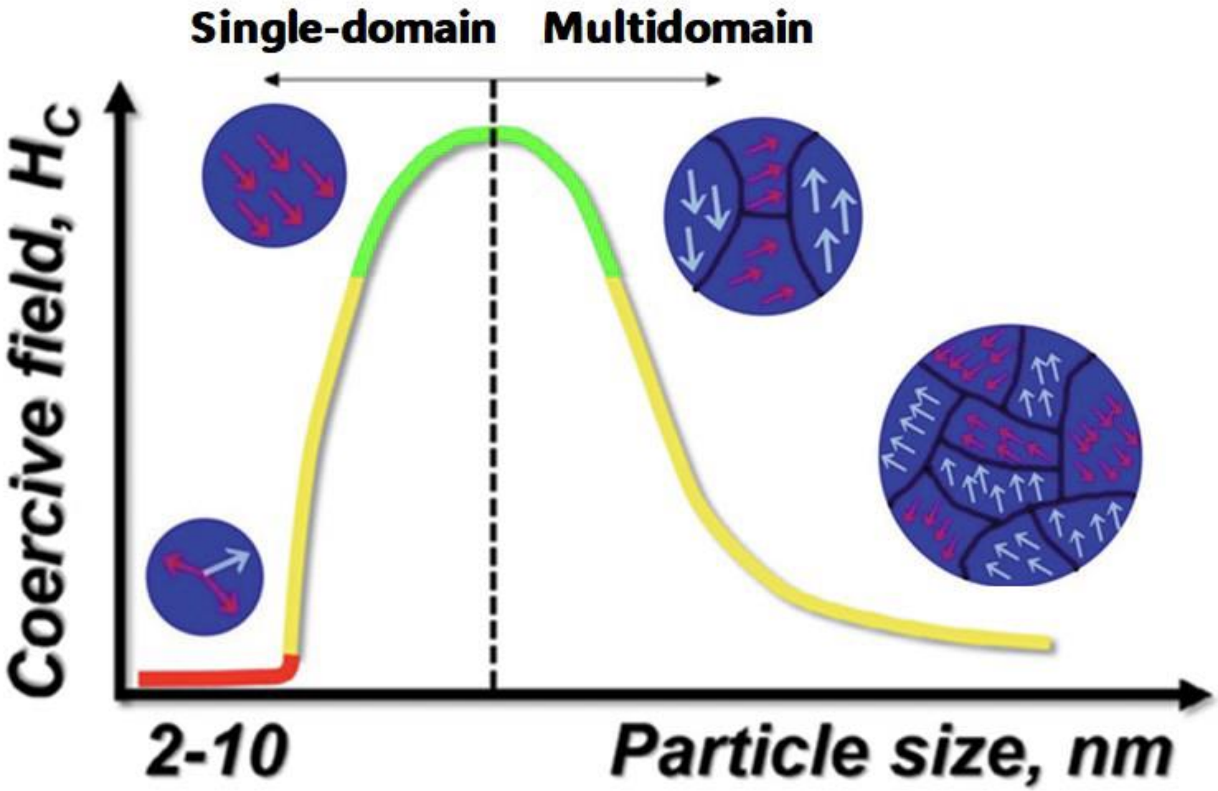
Magnetic Hysteresis

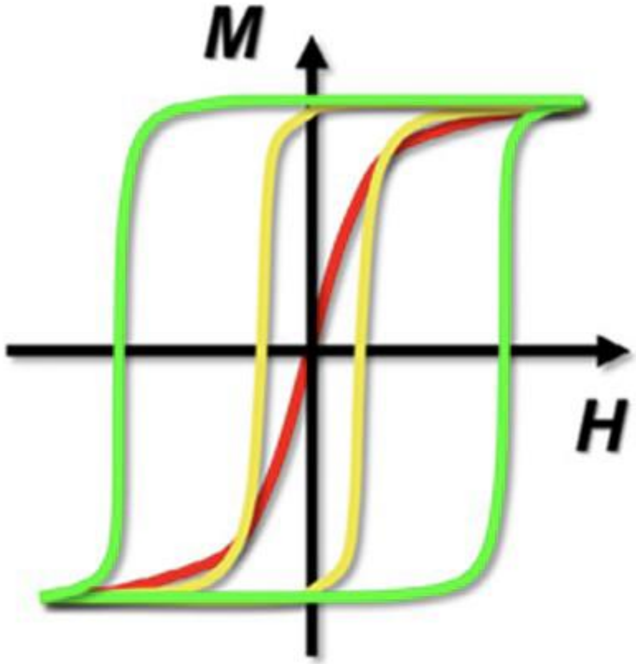




Bulk Magnetic Materials

Magnetic Hysteresis





Magnetic Materials: From Bulk to Molecules

Macroscopic ⟷ Nanoscopic

Permanent magnets	Micron particles	Nanoparticles	Clusters	Molecular clusters	Individual spins

$S = 10^{20}$ 10^{10} 10^{8} 10^{6} 10^{5} 10^{4} 10^{3} 10^{2} 10 1

Multidomain

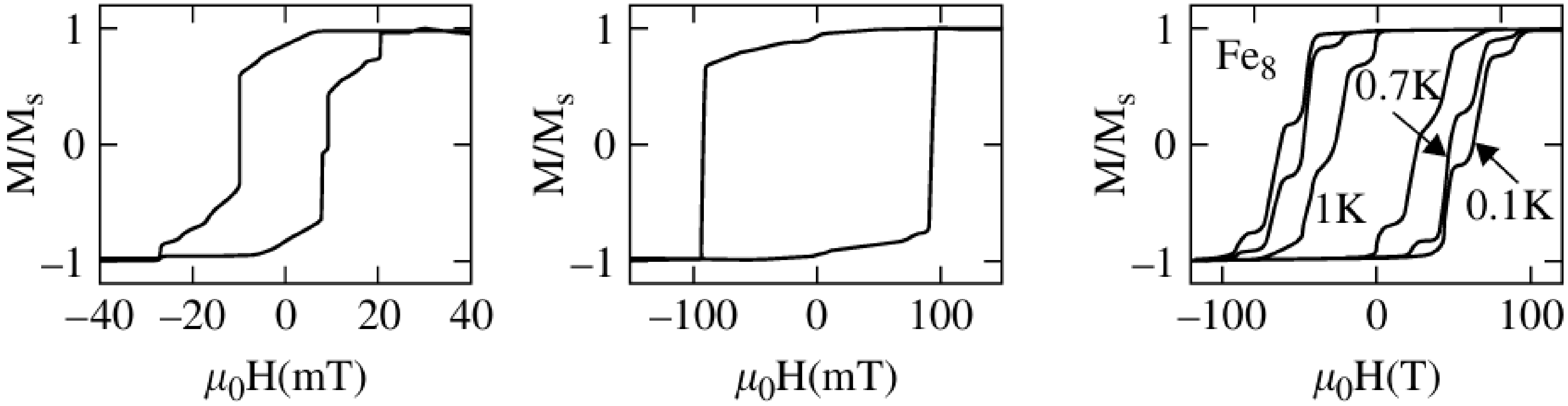
Nucleation, propagation and annihilation of domain walls

Single domain

Uniform rotation curling

Magnetic moment

quantum tunnelling, quantization, Quantum interference



The magnetism of spin-only ions

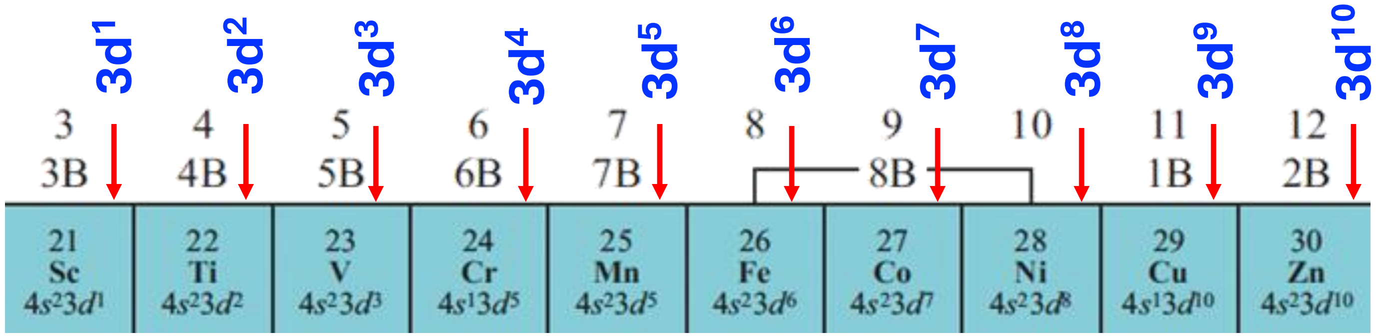
- Contributions to the magnetic moment: S, L and J
- Resume of coordination chemistry: d-orbital splitting, Δ and P
- The ‘spin-only’ approach
- The Zeeman effect (application of a magnetic field) and the Brillouin function
- Saturation magnetisation (M_{sat}) and magnetic susceptibility (χ)
- The temperature dependence of c: Curie behaviour

→ Deviations from Curie-behaviour: Curie-Weiss paramagnets

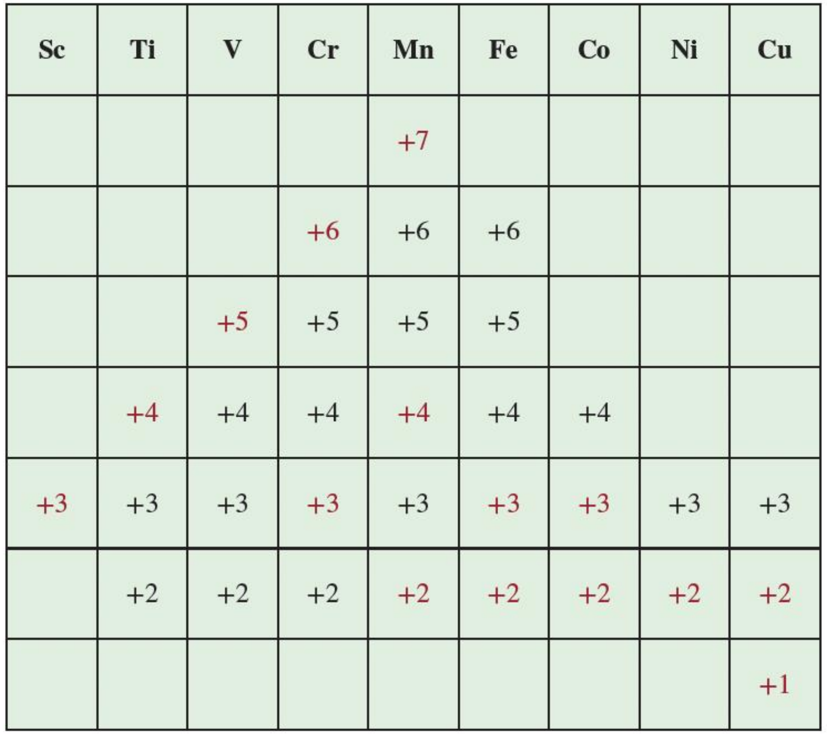
- *The effect of anisotropy: zero field splitting*
- *Spin-Orbit Coupling*
- *Magnetic Exchange coupling*

8. ΟΙ ΠΕΡΙΟΔΙΚΕΣ ΣΧΕΣΕΙΣ ΜΕΤΑΞΥ ΤΩΝ ΣΤΟΙΧΕΙΩΝ

Οι ηλεκτρονιακές απεικονίσεις κατιόντων μετάλλων μετάπτωσης



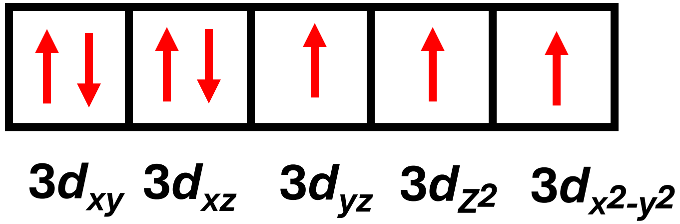
$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
3	4	5	6	7	8	9	10	11	12
3B	4B	5B	6B	7B	8B			1B	2B
21 Sc $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr $4s^1 3d^5$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu $4s^1 3d^{10}$	30 Zn $4s^2 3d^{10}$



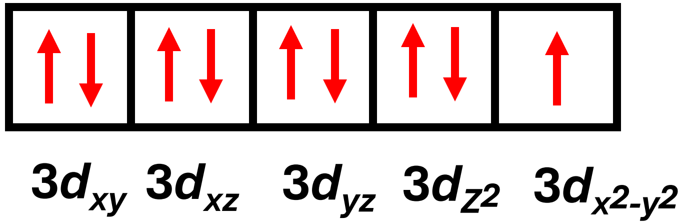
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
				+7				
			+6	+6	+6			
		+5	+5	+5	+5			
	+4	+4	+4	+4	+4	+4		
+3	+3	+3	+3	+3	+3	+3	+3	+3
	+2	+2	+2	+2	+2	+2	+2	+2
								+1

$Z = 27 \rightarrow \text{Co}: \underbrace{1s^2 2s^2 2p^6 3s^2 3p^6}_{Z = 18 \rightarrow \text{Ar}} 4s^2 3d^7 \Rightarrow [\text{Ar}]3d^7 4s^2$

Co^{2+}: $[\text{Ar}]3d^7$



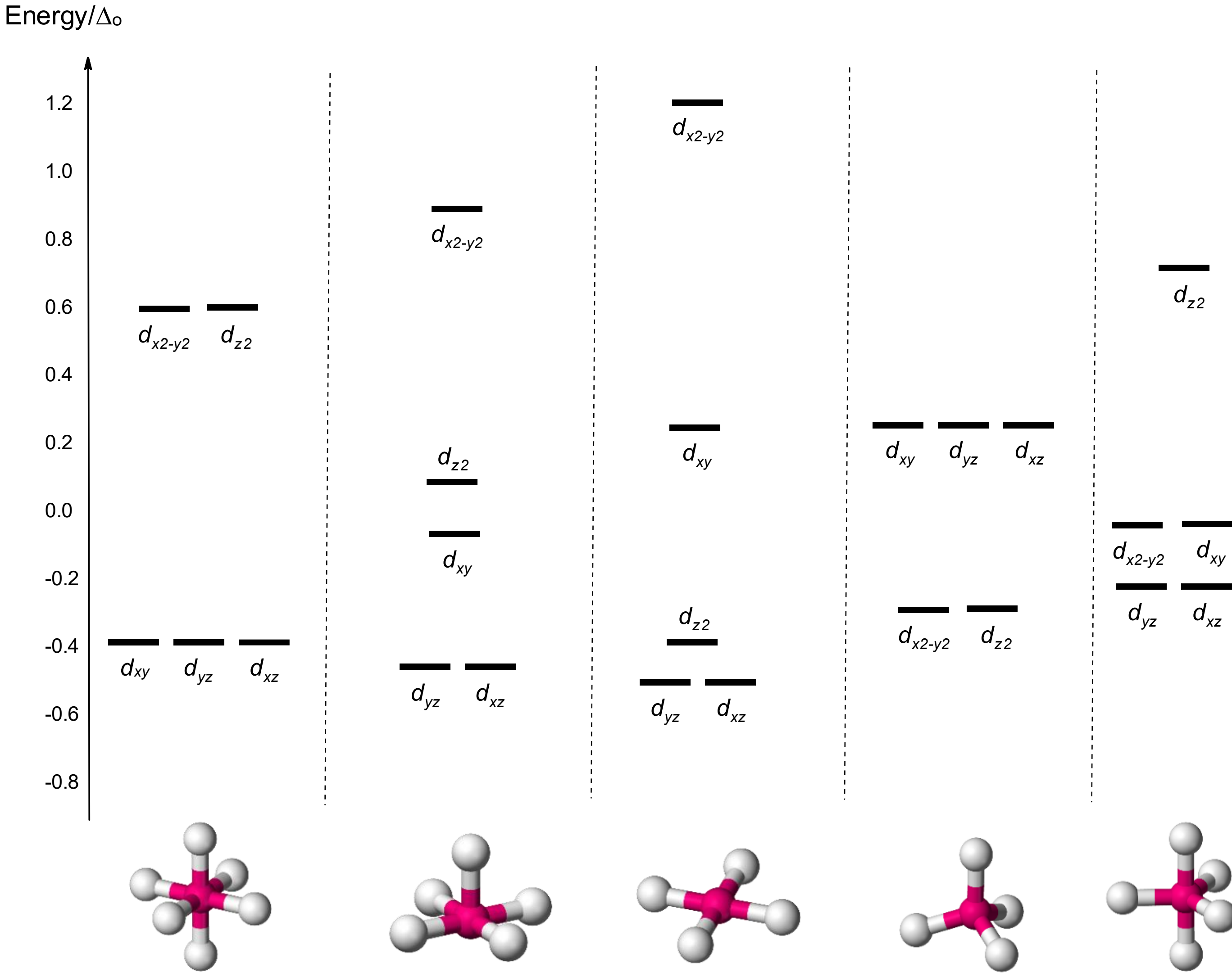
Cu^{2+}: $[\text{Ar}]3d^9$



The magnetism of spin-only ions

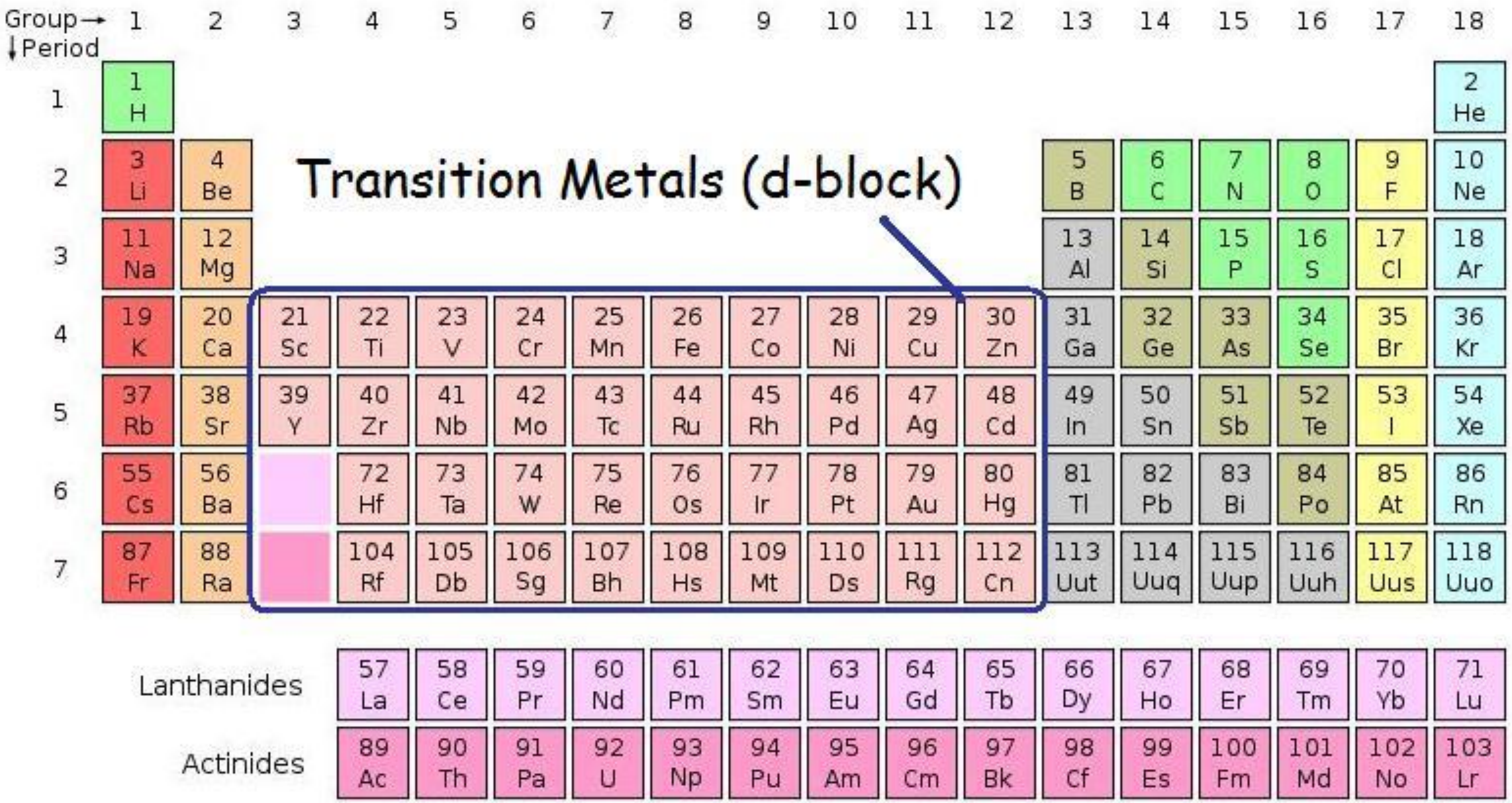
The magnetism of T.M. ions typically depends upon:

- **The metal**
- **Its oxidation state**
- **The coordination geometry**
- **The magnitude of the crystal field splitting, Δ**
- **The magnitude of the inter-electron repulsion, P**



- **For simple O_h and T_d complexes we have: ‘High spin’ P > Δ or ‘Low spin’ Δ > P**
- **For more complex geometries we can have ‘intermediate spin’ e.g. square-pyramidal $[Fe(S_2CNEt_2)_2Cl]$ (d^5)**

The magnetism of spin-only ions



Transition Metals (d-block)

Group→ ↓Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
Lanthanides				57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides				89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Examples:

- $Cr(NH_3)_6^{3+}$
- $Pd(CN)_4^{2-}$
- $MoCl_4(PPh_3)_2$

d^n configuration for transition metal ions

Determine total number of valence electrons (*s* and *d*): *n*

Determine oxidation state: *o*

Number of *d*-electrons = *n* - *o*

The magnetism of spin-only ions

Useful trends for transition metals

Magnitude of D and P

D depends upon the strength of metal-ligand bonding which depends on:

- **Energy match**
- **orbital overlap**
- **symmetry**

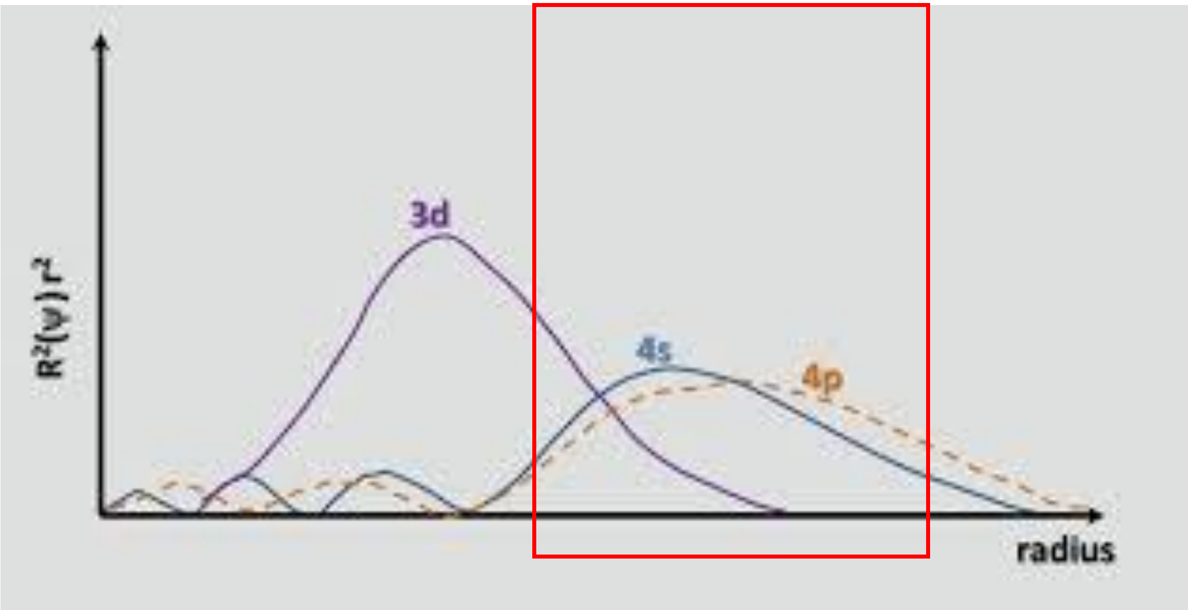
- **For 3d transition metals, metal-ligand interactions are dominated by interaction of ligands with the valence 4s,4p orbitals.**
- **Descending a group: the *d*-orbitals become more expanded**

D(5*d*)	>	D(4*d*)	>	D(3*d*)
~30,000 cm^{-1}		~20,000 cm^{-1}		~10,000 cm^{-1}

- **As the *d*-orbitals become more expanded then inter-electron repulsion (P) is reduced**
- **On descending a triad D increases, P decreases so most second and third row metals are low spin.**

The magnetism of spin-only ions

Useful trends for transition metals



Radial distribution function

(probability of finding e^- at distance *r* from nucleus)

Valence 4s, 4p are radially expanded.

Best M-L overlap occurs here

Bonding to *3d* orbitals therefore inefficient

D is a reflection of bonding interaction between metal *d* and ligand orbitals

The magnetism of spin-only ions

Spectrochemical Series

Small D Large D

$\mathrm{I^- < Br^- < \underline{SCN^-} < Cl^- < F^- < OH^- < H_2O < \underline{NCS^-} < py < NH_3 < en < bipy < NO_2^- < PPh_3 < CN^- \approx CO}$

p-donors s-donors p-acceptors

Group VII Group VI Group V Group IV

Examples:

- $Fe(CN)_6^{3-}$
- $Ni(H_2O)_6^{2+}$
- $Fe(bipy)_2(NCS)_2$
- $NiBr_2(PEt_3)_2$

- Higher oxidation states have more radially contracted (smaller) d-orbitals but they are also lowered in energy.
- Since the overlap is already poor then the change in energy is more important.
- The lower orbital energies give better energy match and larger splitting; NiF_6^{4-} is high spin, NiF_6^{3-} is low spin

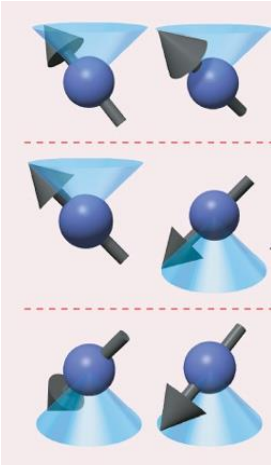
The magnetism of spin-only ions

The electron is defined by a spin m_S which can be

+ ½ or – ½

There is efficient communication between the unpaired electrons on an individual metal atom so that their spins are strongly correlated and act together as a net spin $S = \Sigma m_S$

The spin multiplicity is given by 2S+1, i.e. there are (2S+1) M_S states ranging from –S to +S in integer values.

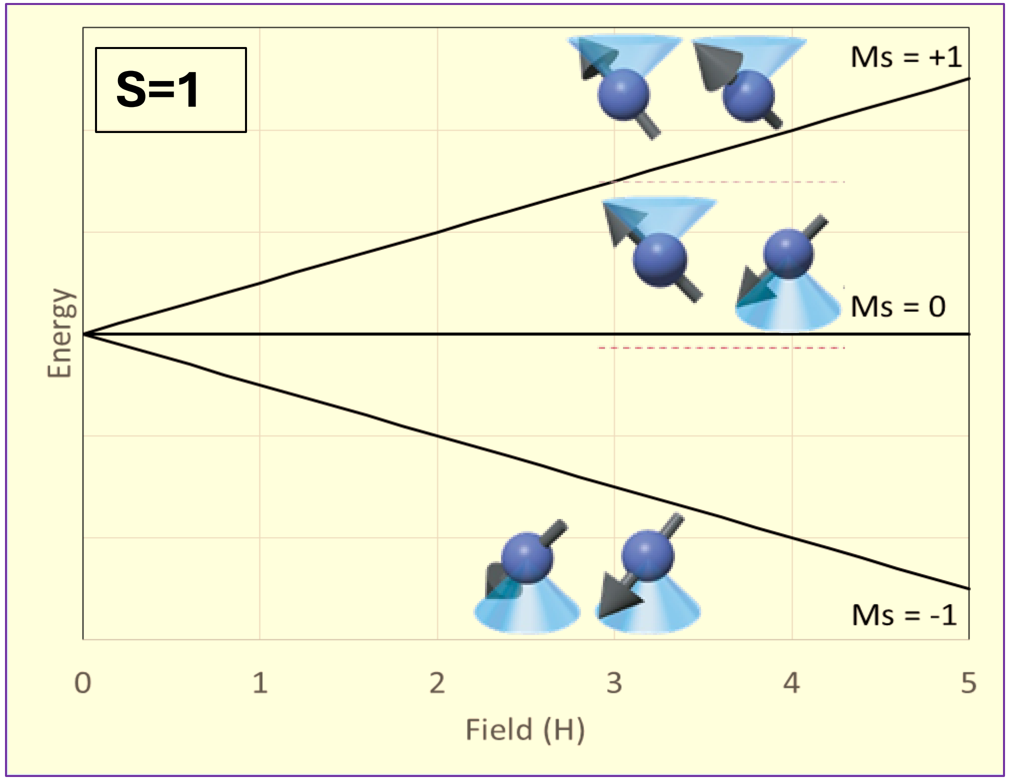


$M_S = +1$

$M_S = 0$

$M_S = -1$

The magnetism of spin-only ions



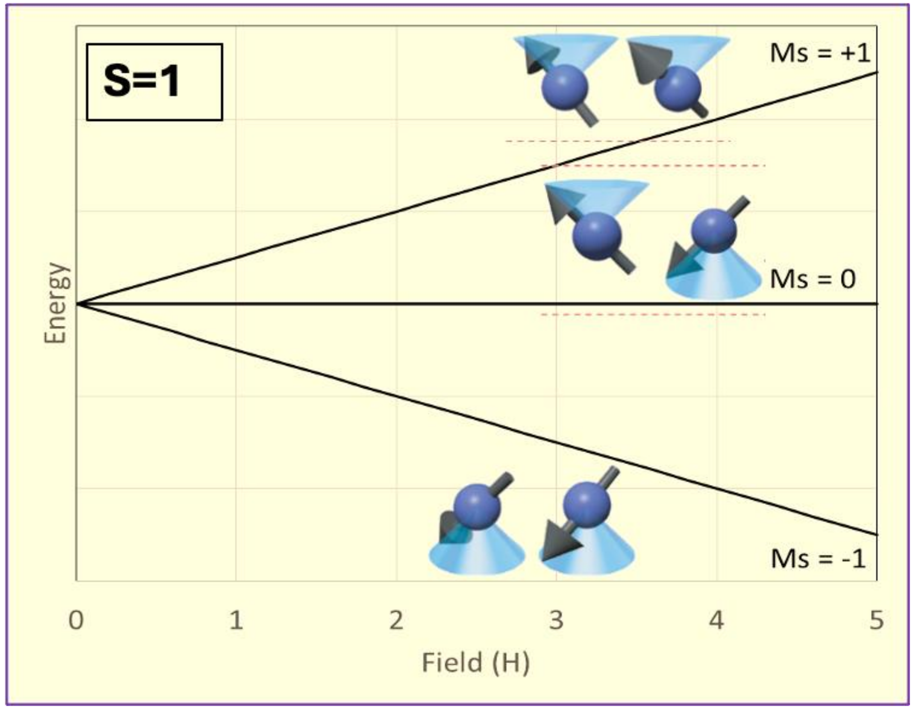
In zero-field these M_S states are degenerate.

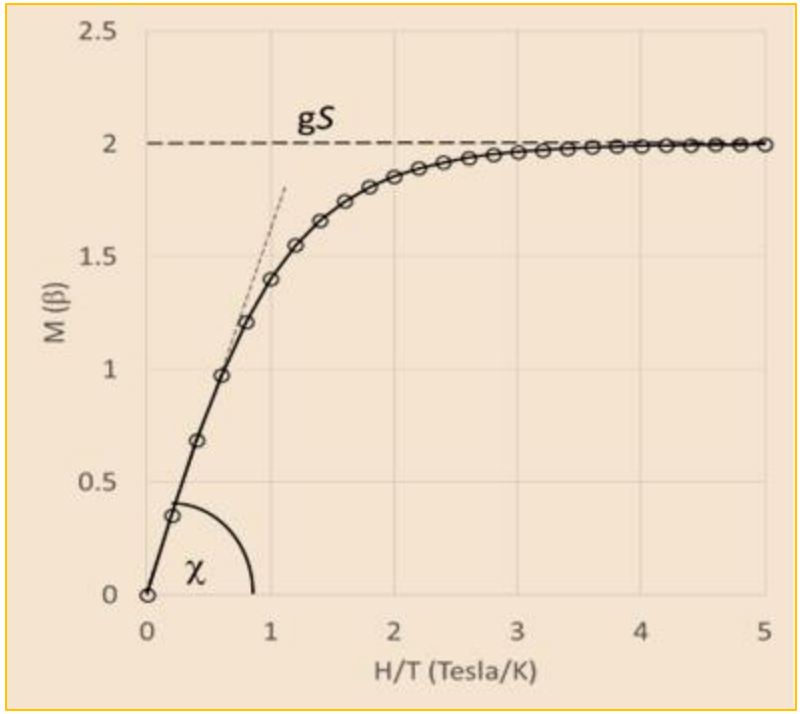
However, when a magnetic field is applied the degeneracy is lost. This is known as the electron-Zeeman interaction. The energy of the M_S states is given by:

$$E(M_S) = g\mu_B B M_S$$

g is the g-factor (~2.0) for spin-only ions, b is the Bohr magneton, H is the applied magnetic field.

The magnetism of spin-only ions

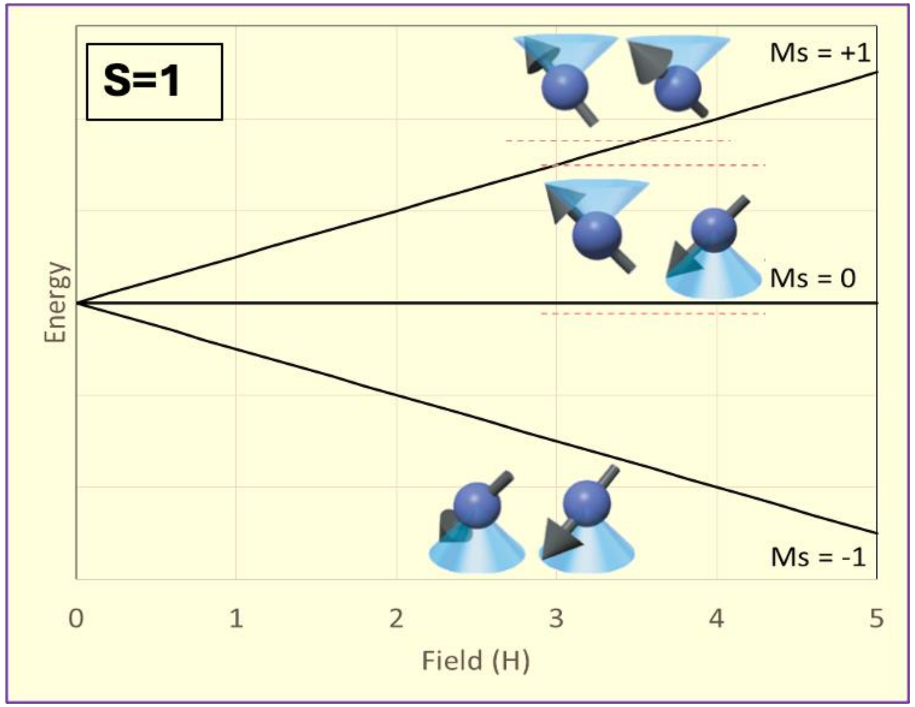


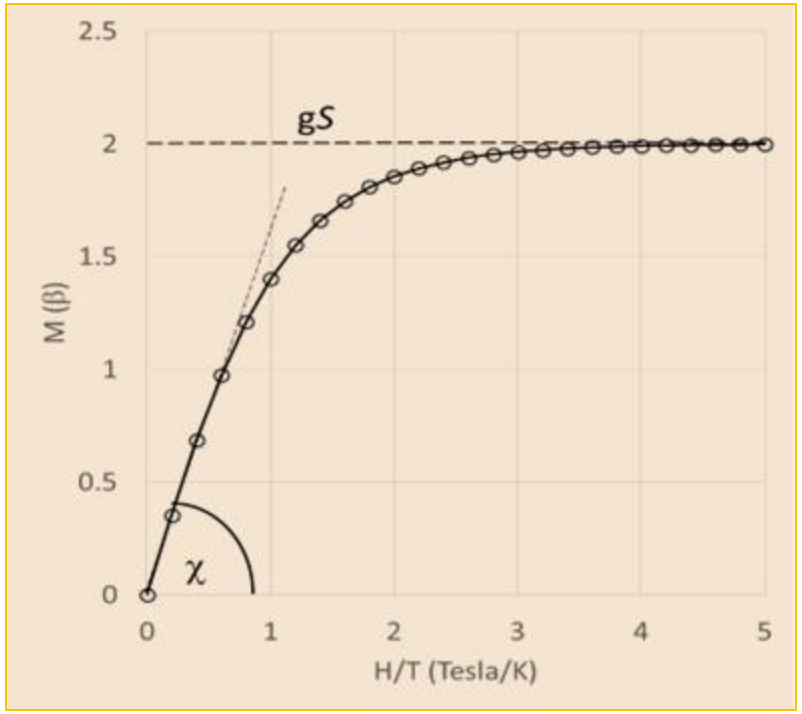


<u>In zero field</u> the populations of the M_S states are equal and <u>there is no net magnetic moment</u> (as many 'spin up' as 'spin down' electrons).

The spin states M_S interact through the electron-Zeeman interaction (the Zeeman term just means what happens when we apply a field)

The magnetism of spin-only ions





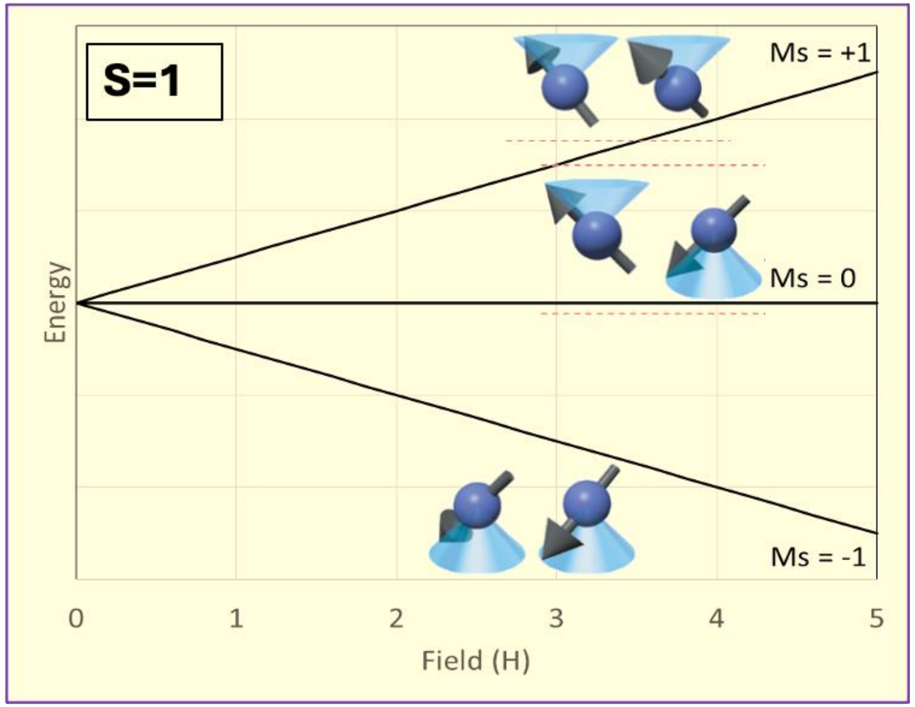
In an applied field (H) the energies of the M_S states are no longer degenerate and follow:

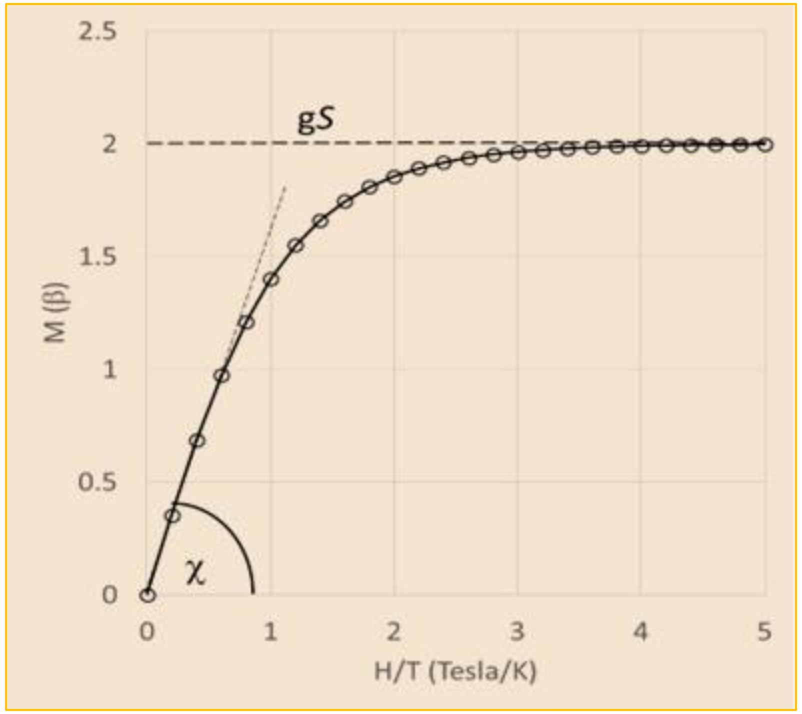
$$E(M_S) = g\mu_B B M_S$$

The populations of these states are determined by a Boltzmann distribution.

- **As the field increases the population difference between M_S = +1 and -1 increases, so there is a larger magnetization (M) induced in the sample.**
- **As the temperature decreases the population of the higher energy M_S states is reduced and again the magnetisation increases.**

The magnetism of spin-only ions





At very large fields and at low temperature only the ground state is populated, and the magnetisation becomes 'saturated', M_{sat} = gS (Bohr Magnetons)

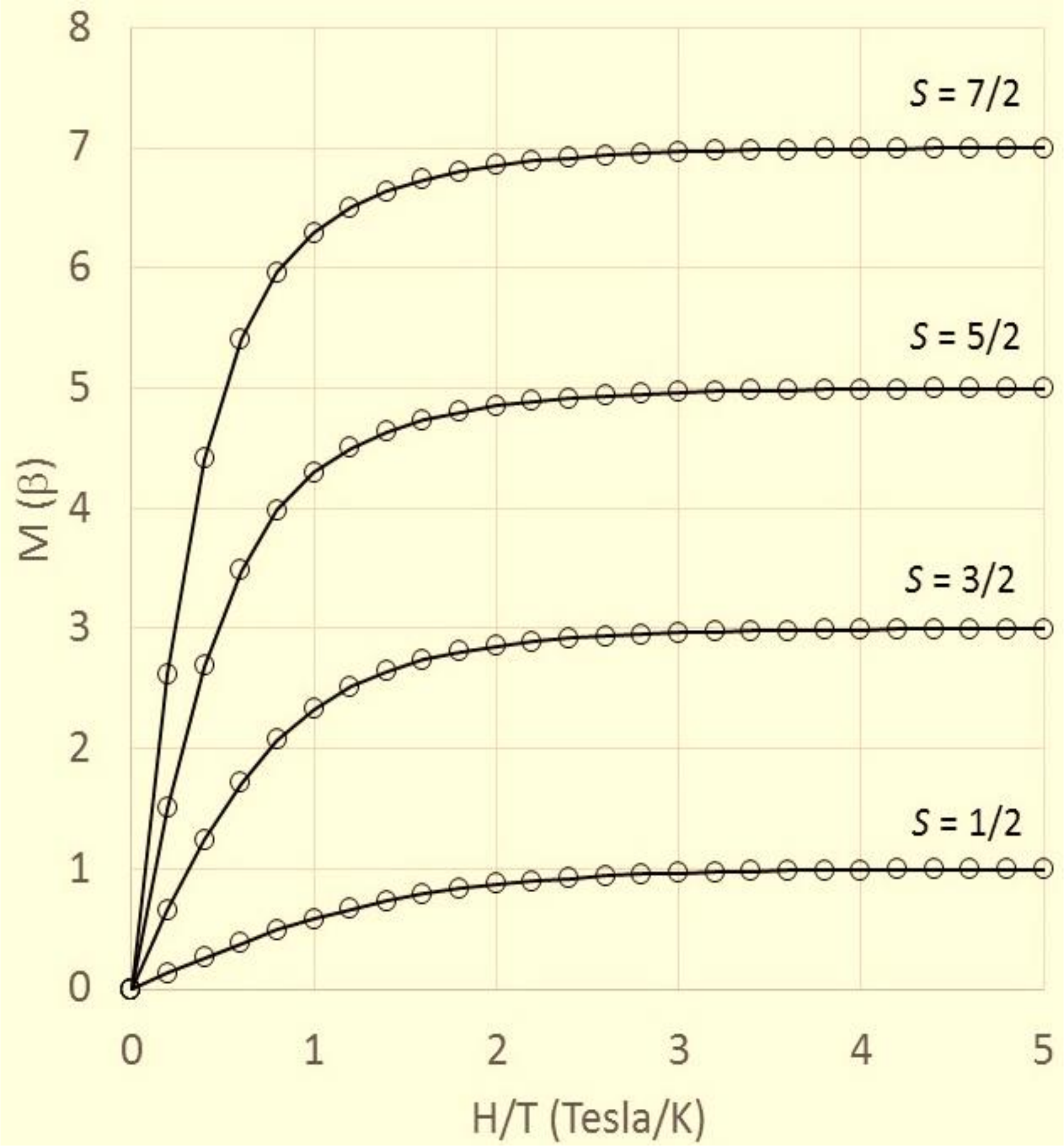
Bohr magneton is a non-SI unit, 1 μ_B = 5585 emu·mol^{-1}

μ_B is also written Nβ or in older texts, BM

<u>This is our first method for determining S</u>

Note for spin-only ions g ~ 2.0

The magnetism of spin-only ions



Identify which ions exhibit the curves shown left:

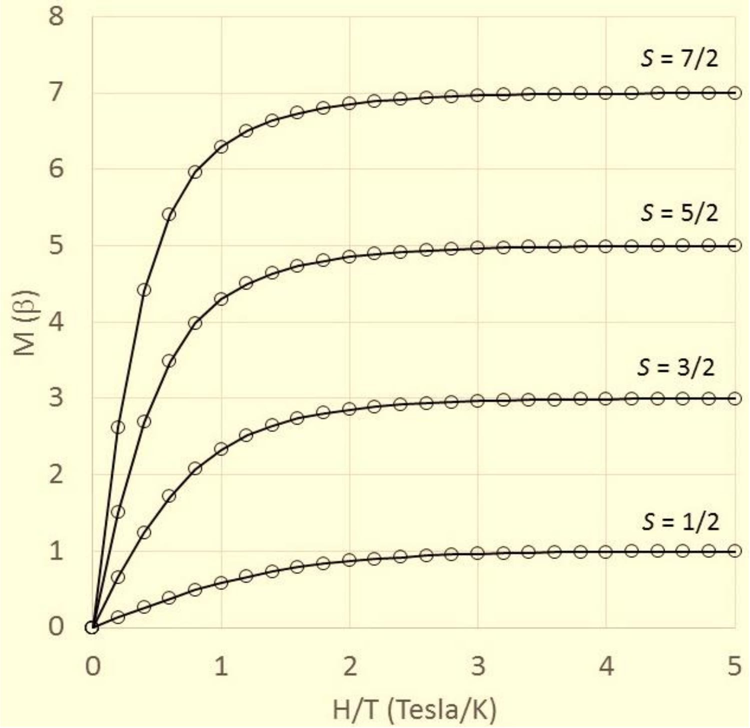
- $Gd(H_2O)_9^{3+}$
- $Ni(H_2O)_6^{2+}$
- $Cr(H_2O)_6^{3+}$
- $Mn(H_2O)_6^{2+}$
- $Cu(H_2O)_6^{2+}$
- $Cr(H_2O)_6^{2+}$

The magnetism of spin-only ions

The saturation magnetisation reaches a maximum value of gS Bohr magnetons (μ_B) so increases linearly with S.

In many cases we may not reach saturation (H is not large enough or T is too high to depopulate all excited states).

In such cases magnetic data can be fitted to the <u>Brillouin function</u>. The Brillouin function describes how M changes with H and T: $M = Ng\mu_B S\, B_S(x)$



$$B_S(x) = \frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S}\coth\left(\frac{x}{2S}\right)$$

coth = υπερβολική συνεφαπτομένη

$$x = \frac{g\mu_B SH}{k_B T}$$

(Zeeman energy of the magnetic moment / thermal energy)

Weak field / high T: $B_S(x) \approx \frac{S+1}{3S}x \Longrightarrow M \approx N\frac{g^2\mu_B^2 S(S+1)}{3k_B T}H$

$$\boxed{\chi_M = \frac{M}{H} = \frac{N_A g^2\mu_B^2 S(S+1)}{3k_B T}}$$

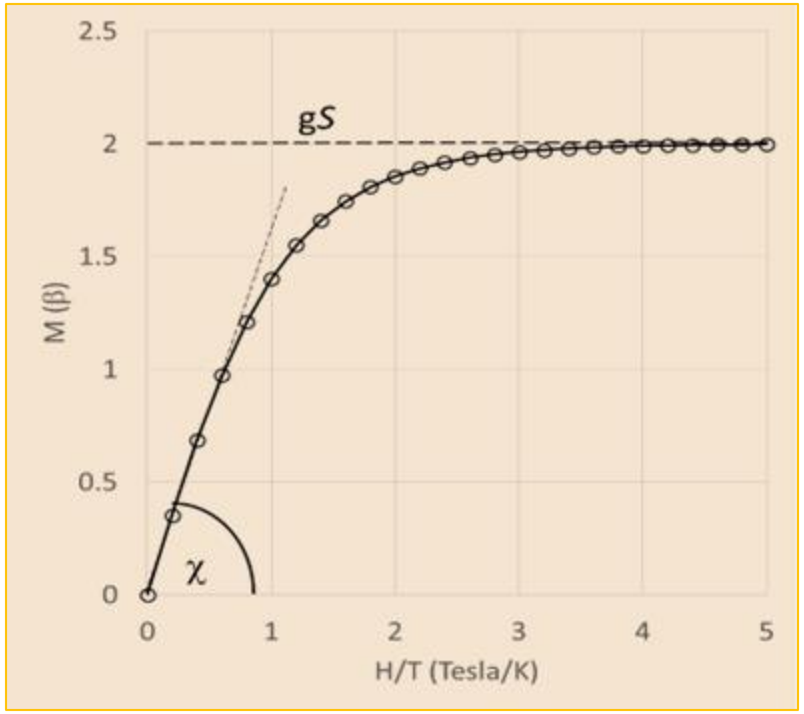
The magnetism of spin-only ions

Magnetic Susceptibility

- The magnetic susceptibility (c) is defined as $\partial M/\partial H$
- In small fields the gradient ($\partial M/\partial H$) ~ constant and we approximate: $\chi = M/H$
- As chemists we measure χ in emu/mol (or cm^3/mol)

∂ = μερική παράγωγος

gradient = κλίση



Experimental note: We apply a field and measure the induced magnetization. We want to use as large a field as possible (to observe a strong response) but need to ensure we are still in the linear region!

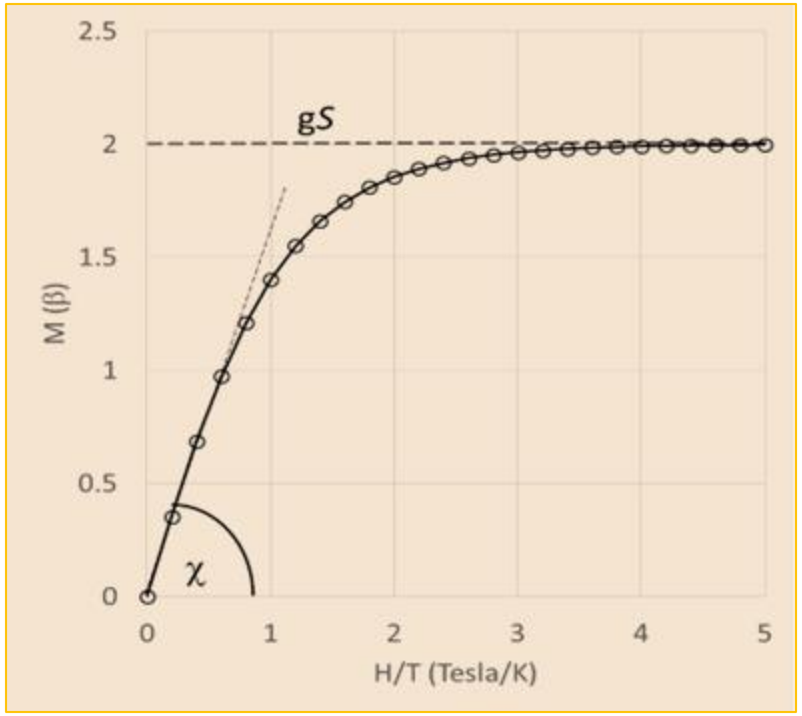
The magnetism of spin-only ions

Other forms of magnetic susceptibility

- $\chi = \chi_v$ = volume magnetic susceptibility (dimensionless, i.e., no units)
- χ_v is independent of the magnetic field but only if the field is weak
- $\chi_g = \chi_v$ / density = χ per gram (units: cm^3/g)
- $\chi_m = \chi_g \cdot MW = \chi$ per mole (units: cm^3/mol)
- Magnetic fields: 1 G = 1 Oe and 1 T = 10^4 G = 10^4 Oe
- Energies are usually expressed as cm^{-1} or Kelvin (K), where:

$$1\ cm^{-1} = 1.4388\ K$$

- Sometimes you see "emu" = electromagnetic unit = cm^3



The magnetism of spin-only ions

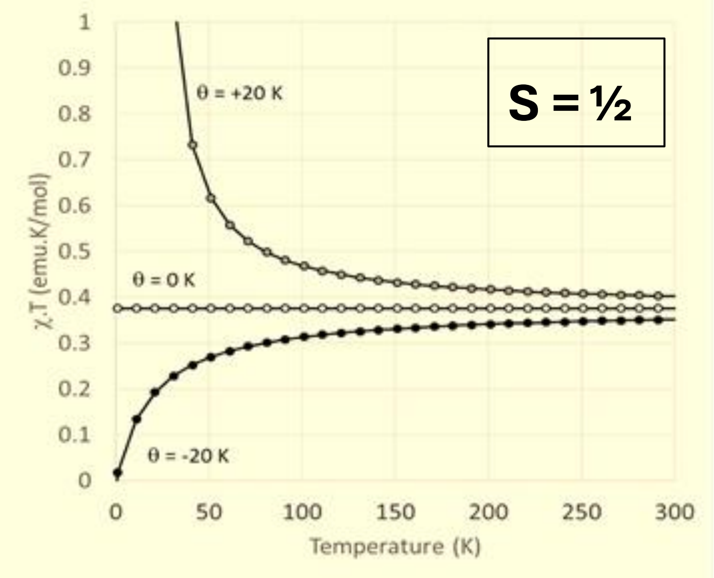
Origin of Curie-Weiss behaviour

There are multiple origins for deviation from pure Curie behaviour. Some of these include:

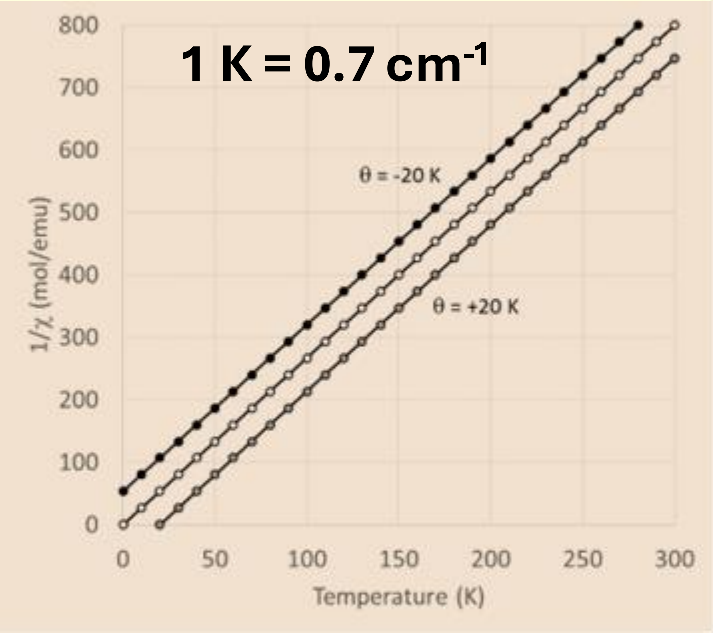
- Zero field splitting (typically small θ, say |θ| < 2 K but can be 10-20 K in exceptional circumstances)
- Spin-orbit coupling (can be larger θ, say |θ| < 20 K)
- Magnetic exchange coupling (in polynuclear complexes) (|θ| can be 100’s of K or just a few K!!)

Often a combination of all these factors may occur!

In order to try and deduce the origin of the Weiss constant we need to consider each of these factors in more detail.



S = ½



1 K = 0.7 cm^{-1}

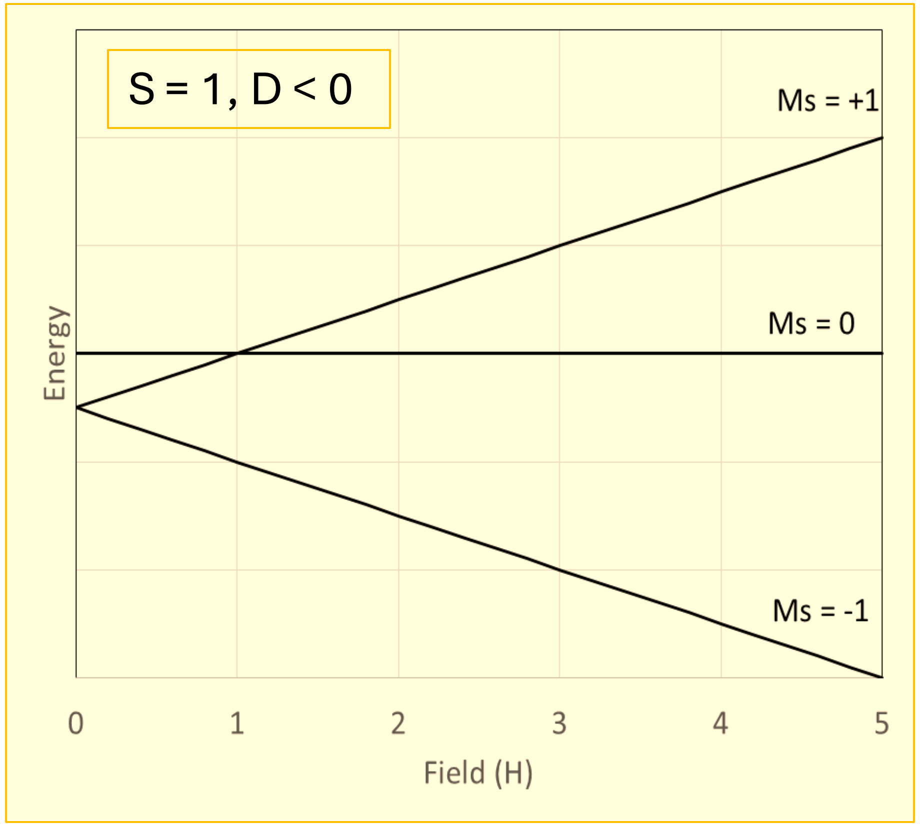
The magnetism of spin-only ions

Zero-field splitting (D)

The effect of zero-field splitting is to do ‘what it says on the label’ i.e. split the degeneracy of the M_S states in zero field.

The zero field splitting parameter D defines the strength of the zero field splitting (D can often be < 1 cm^{-1} but can be as high as 20 – 30 cm^{-1} or so).

$$E(M_S) = g\beta H M_S + D M_S^2$$



The magnetism of spin-only ions

Zero-field splitting (D)

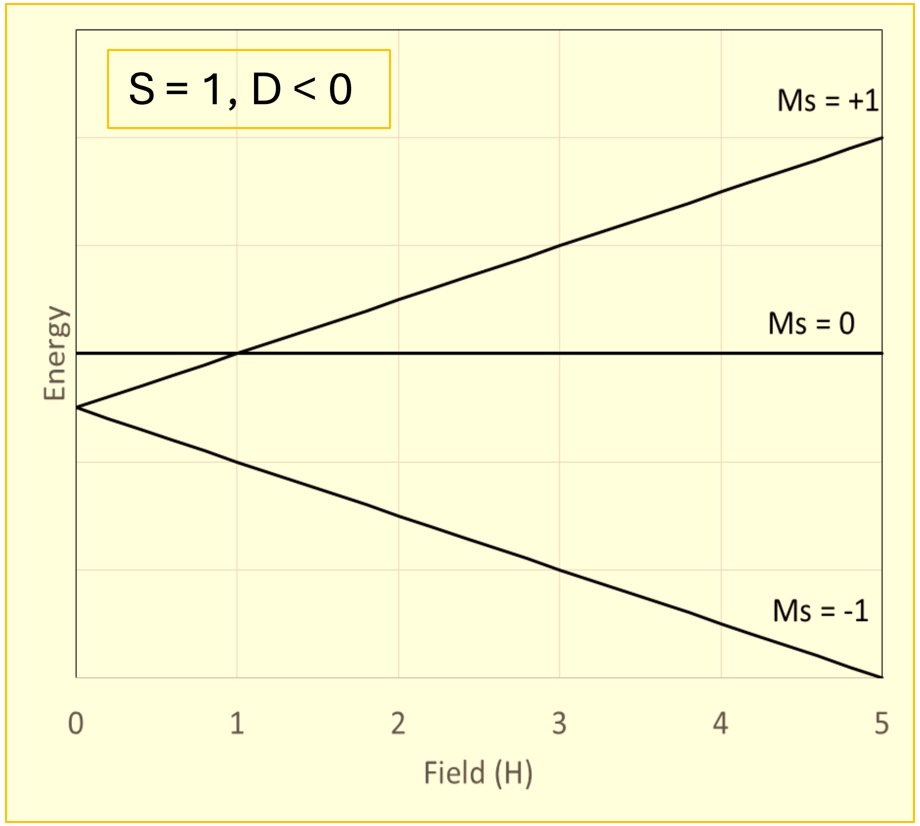
$$E(M_S) = g\beta H M_S + D M_S^2$$

The origin of D arises through anisotropy/chemical environment.

If D = 0 the spin system is described as a **'Heisenberg'** spin and there is no preferred spin orientation.

If $D < 0$ then the $M_S = \pm S$ states lie lower in energy. There is a preference for the spin to align coparallel or antiparallel to the applied field and it is described as an **'Ising' spin**.

If $D > 0$ then the $M_S = 0$ state lies lowest in energy and the spin orientation prefers to lie perpendicular to the applied field, known as an **'XY'-spin system**.



The magnetism of spin-only ions

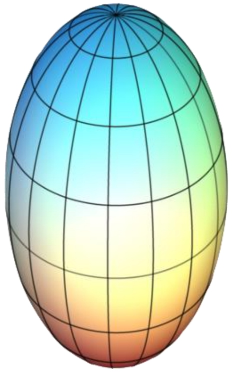
Zero-field splitting (D)

Zero field splitting reflects some inherent anisotropy in the sample which differentiates the magnetism parallel or perpendicular to the applied field. We will focus here on axial anisotropy (D) which distinguishes *z* from the *xy* plane, but recognise that we can also have what is termed a ‘transverse anisotropy’ (E) which reflects anisotropy between *x* and *y*.

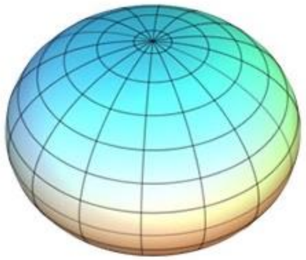
$$0 < |E/D| < 1/3$$

The origin of zero field splitting is:

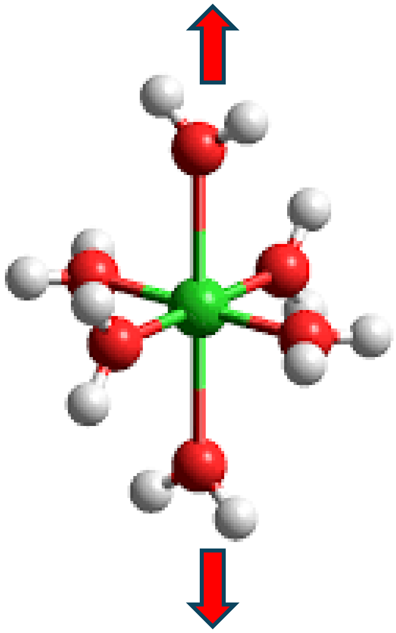
- Local anisotropy at the metal centre, e.g. *trans*-ML_4X_2
- Anisotropy arising from differences in the chemical environment beyond the first coordination sphere.
- Spin-orbit coupling!!!



Oblate shape



Prolate shape

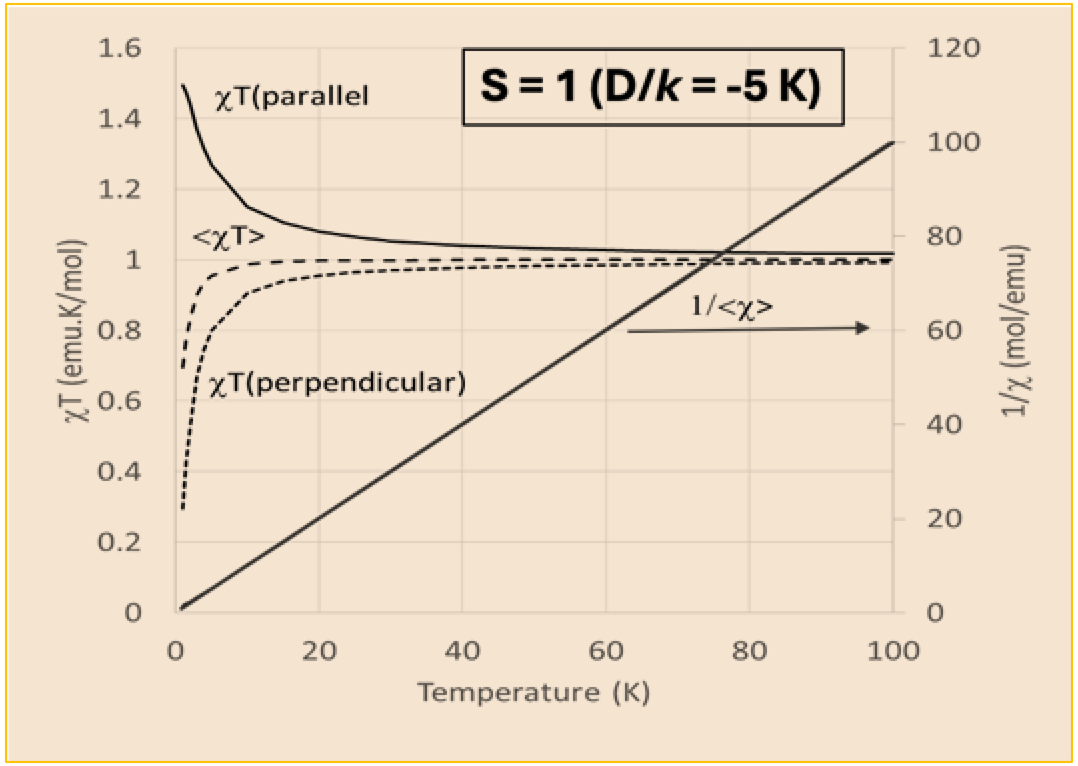


The magnetism of spin-only ions

The effect of zero-field splitting (ZFS)

The anisotropy associated with ZFS leads to an inequivalence between z and the xy plane, often referred to as parallel and perpendicular directions.

The magnetic response in these directions is also anisotropic and we refer to the susceptibilities in terms of $\chi_{||}$ and $\chi_{\perp}$



The average susceptibility of the sample is:

$$\langle\chi\rangle = \frac{\chi_{\|} + 2\chi_{\perp}}{3}$$

Note: we see a decrease in <χT> upon cooling consistent with θ < 0 due to ZFS irrespective of whether D < 0 or D > 0. Even for relatively large values of D the deviation in <χT> is only evident at low temperature (< 10 K).

The magnetism of spin-only ions

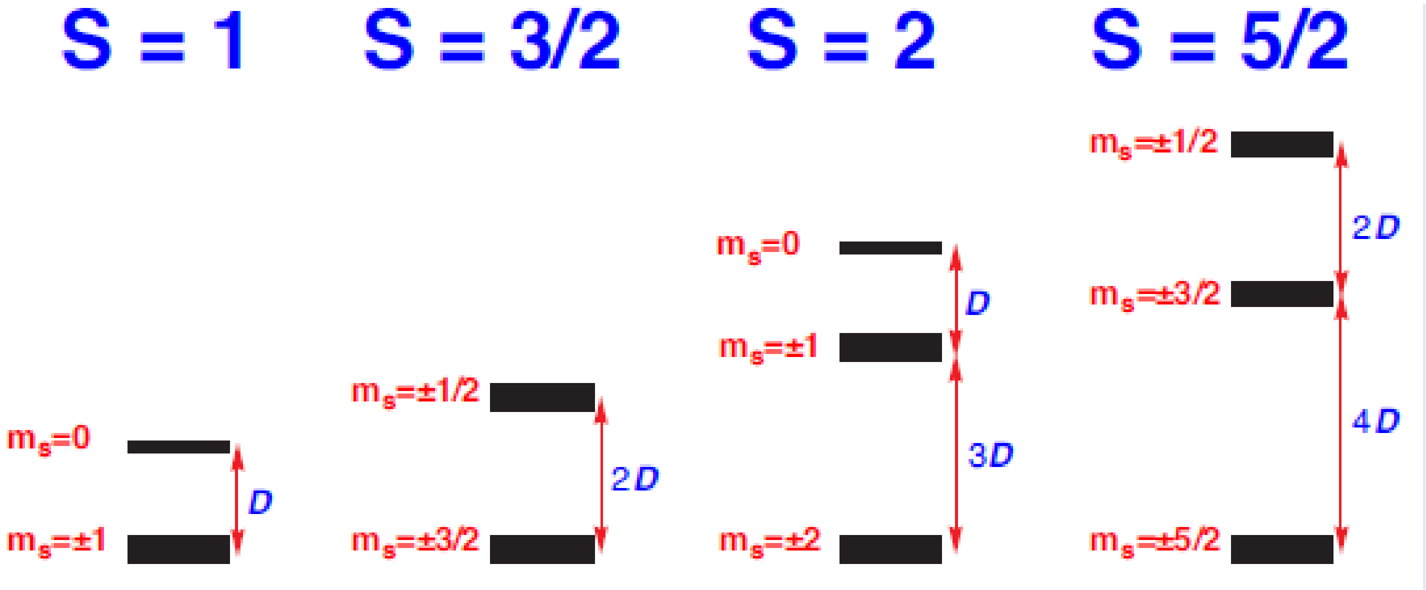
The effect of zero-field splitting (ZFS)

- ZFS is the removal of spin microstate degeneracy for systems with $S > 1/2$ in the absence of an applied field. That is, the degeneracy is removed as a consequence of molecular electronic structure and/or spin density distribution (i.e., the electron density of the singly occupied molecular orbital (SOMO)).
- For odd-electron systems, axial ZFS (the "*D*" ZFS parameter) removes the microstate degeneracy and produces Kramer's doublets. Rhombic ZFS (the "*E*" ZFS parameter) splits the Kramer's doublets.
- Zero-field splitting causes magnetic anisotropy and has profound effects on magnetic *properties*. For example, magnetic hardness (≈ the width of a hysteresis loop) is related to the magnetoanisotropy.
- At the molecular level, understanding ZFS is essential for rational design of single-molecule magnets since the energy barrier separating the $+m_s$ and $–m_s$ microstates is equal to $S^2|D|$.

The magnetism of spin-only ions

Energy level splitting for $S = 1$ to $5/2$ for $D < 0$

$E(m_s) = m_s^2D$



Orbital angular momentum can be of primary contributor to zfs, and can make the zfs quite large (≈1-10 cm^{-1}) compared to spin-dipolar contributions (≈10^{-3} - 10^{-1} cm^{-1}).

There are two scenarios in which orbital angular momentum manifests itself in zfs:

in-state orbital angular momentum (*e.g.*, orbital T states in O_h symmetry),

out-of-state orbital angular momentum (*e.g.*, mixing of excited states with the ground state).

The magnetism of spin-only ions

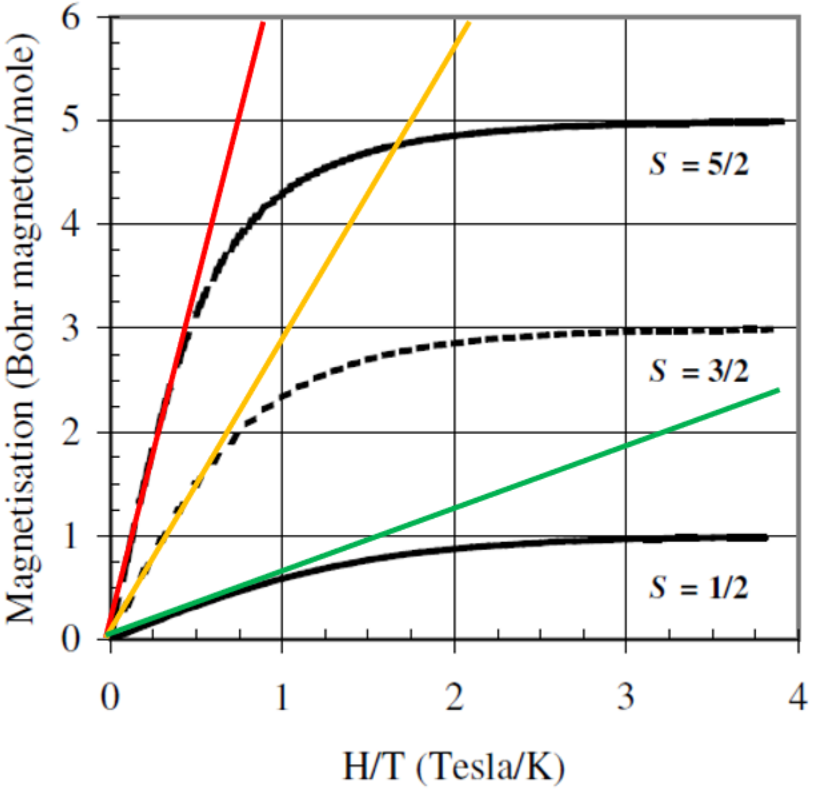
The Zeeman effect

- The application of an applied magnetic field is known as the Zeeman effect.
- The applied field lifts the degeneracy of the M_S sub-levels of the S state according to:

$$E(M_S) = g\mu_\beta H M_S$$

The population of the $M_S = -½$ is greater than that of $M_S = +½$

- A magnetization is induced in the sample

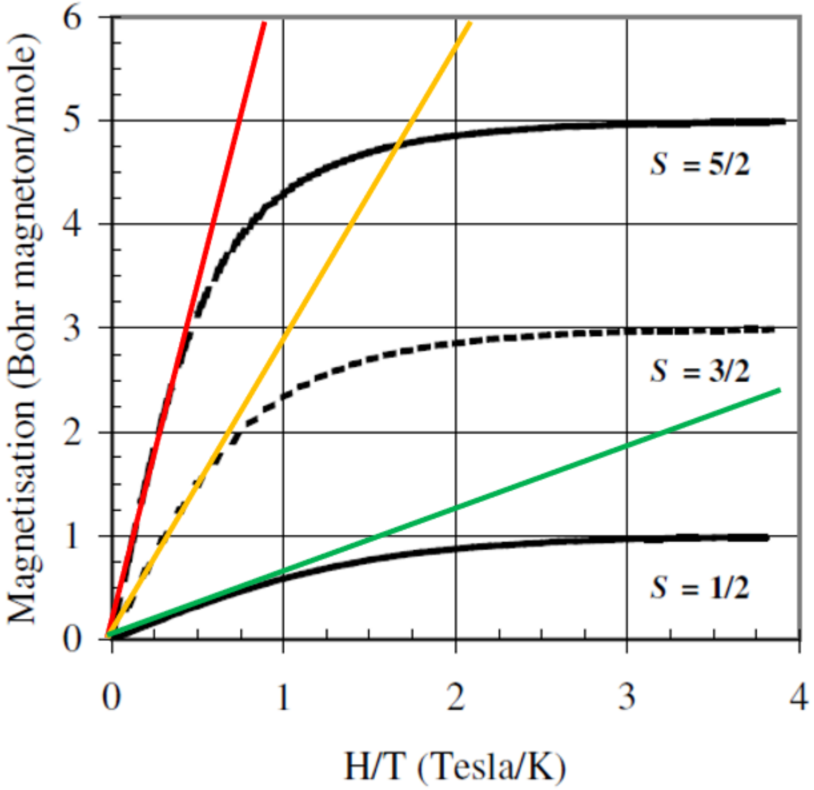


The magnetism of spin-only ions

The Zeeman effect

The magnetic susceptibility is defined as: $\chi = dM/dH$

<u>In small fields:</u> $dM/dH \sim M/H = \chi$



Experimentally we use a small applied field H in the region where M/H is linear (well away from saturation)

But a large enough field H that M is easy to measure.

The magnetisation induced in the sample depends on:

(a) Temperature

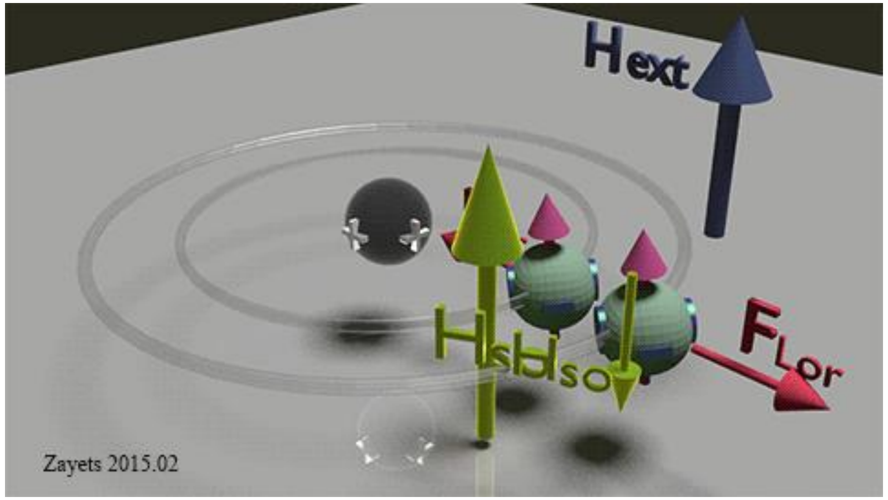
(b) Applied field (DE between M_S states)

The magnetism of spin-only ions

Orbital angular momentum and spin-orbit coupling

- **What is orbital angular momentum?**
- **Energy terms relevant to magnetism:**
- ***Crystal field splitting***
- ***Jahn-Teller splitting***
- ***Inter-electron repulsion***
- ***Spin-orbit coupling***
- ***Temperature***
- **Perturbation Theory**
- **Magnetism of Lanthanides: λ > D**
- **Magnetism of Transition metals: D > λ**

Term Symbols as a convenient shorthand for electronic configurations



The magnetism of spin-only ions

Energy Terms we are interested in as magnetochemists…

- Crystal field splitting, Δ
- Inter-electron repulsion, P
- Jahn-Teller distortion, d
- Spin-orbit coupling constant, λ
- Zero field splitting parameter, D
- Magnetic exchange, J

Bad news…. The order of magnitude of these parameters differs depending on what system we look at ☹

Good news… There are some common rules of thumb about which perturbations to apply first depending on what you are looking at…

- These all need to be considered in relation to thermal energy kT !!!!

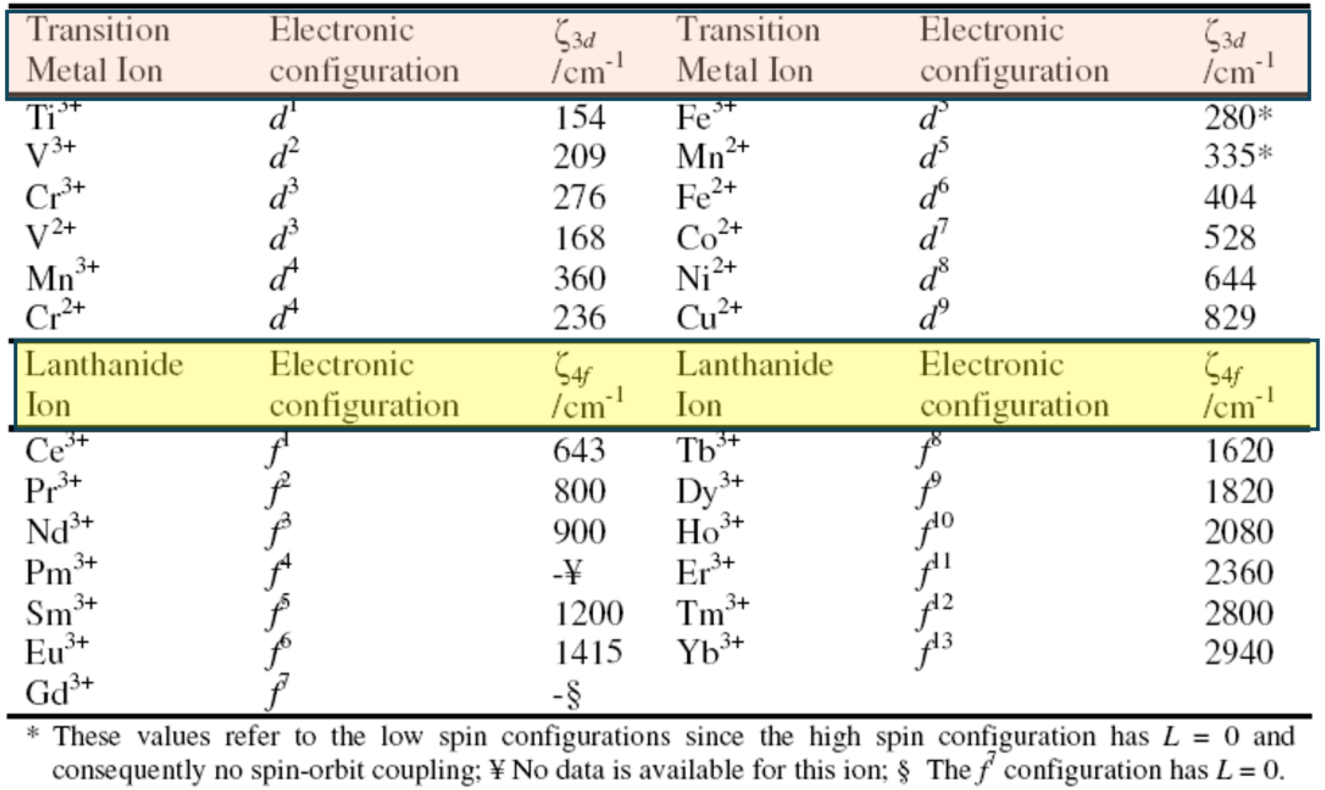
The magnetism of spin-only ions

Energy Terms we are interested in as magnetochemists…

Spin-orbit coupling constant, $\lambda = \pm\zeta/2S$

ζ = one-electron spin-orbit coupling constant ($\zeta \propto Z^4$)

S = spin quantum number.



Transition Metal Ion	Electronic configuration	ζ_{3d} /cm^{-1}	Transition Metal Ion	Electronic configuration	ζ_{3d} /cm^{-1}
Ti^{3+}	d^1	154	Fe^{3+}	d^5	280*
V^{3+}	d^2	209	Mn^{2+}	d^5	335*
Cr^{3+}	d^3	276	Fe^{2+}	d^6	404
V^{2+}	d^3	168	Co^{2+}	d^7	528
Mn^{3+}	d^4	360	Ni^{2+}	d^8	644
Cr^{2+}	d^4	236	Cu^{2+}	d^9	829
Lanthanide Ion	Electronic configuration	ζ_{4f} /cm^{-1}	Lanthanide Ion	Electronic configuration	ζ_{4f} /cm^{-1}
Ce^{3+}	f^1	643	Tb^{3+}	f^8	1620
Pr^{3+}	f^2	800	Dy^{3+}	f^9	1820
Nd^{3+}	f^3	900	Ho^{3+}	f^{10}	2080
Pm^{3+}	f^4	-¥	Er^{3+}	f^{11}	2360
Sm^{3+}	f^5	1200	Tm^{3+}	f^{12}	2800
Eu^{3+}	f^6	1415	Yb^{3+}	f^{13}	2940
Gd^{3+}	f^7	-§			

* These values refer to the low spin configurations since the high spin configuration has $L = 0$ and consequently no spin-orbit coupling; ¥ No data is available for this ion; § The f^7 configuration has $L = 0$.

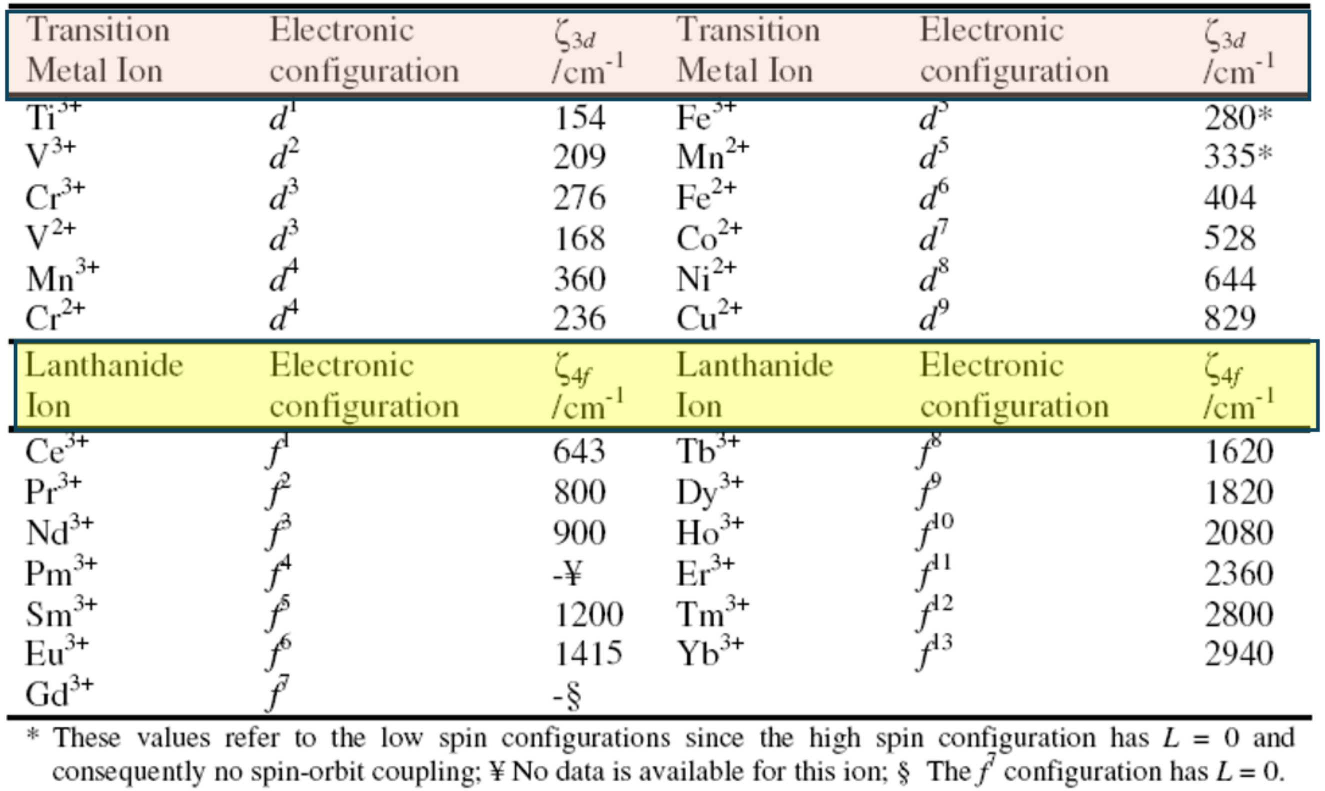
Since ζ scales with the atomic number Z^4:

- **λ negligible for non-metals (C,N,O etc)**
- **λ small for 1st row transition metals ($\lambda < kT$)**
- **λ large for lanthanides ($\lambda > kT$)**

Remember kT ~ 200 cm^{-1} at RT

The magnetism of spin-only ions

Energy Terms we are interested in as magnetochemists…



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* These values refer to the low spin configurations since the high spin configuration has $L = 0$ and consequently no spin-orbit coupling; ¥ No data is available for this ion; § The f^7 configuration has $L = 0$.

A further note on spin-orbit coupling

In transition metal complexes metal-ligand covalency spreads some of the unpaired electron density onto the ligand (typically C,N,O-based).

These ligand atoms have some small spin-orbit coupling constants so in a real complex $\lambda_{obs} < \lambda_{free\ ion}$.

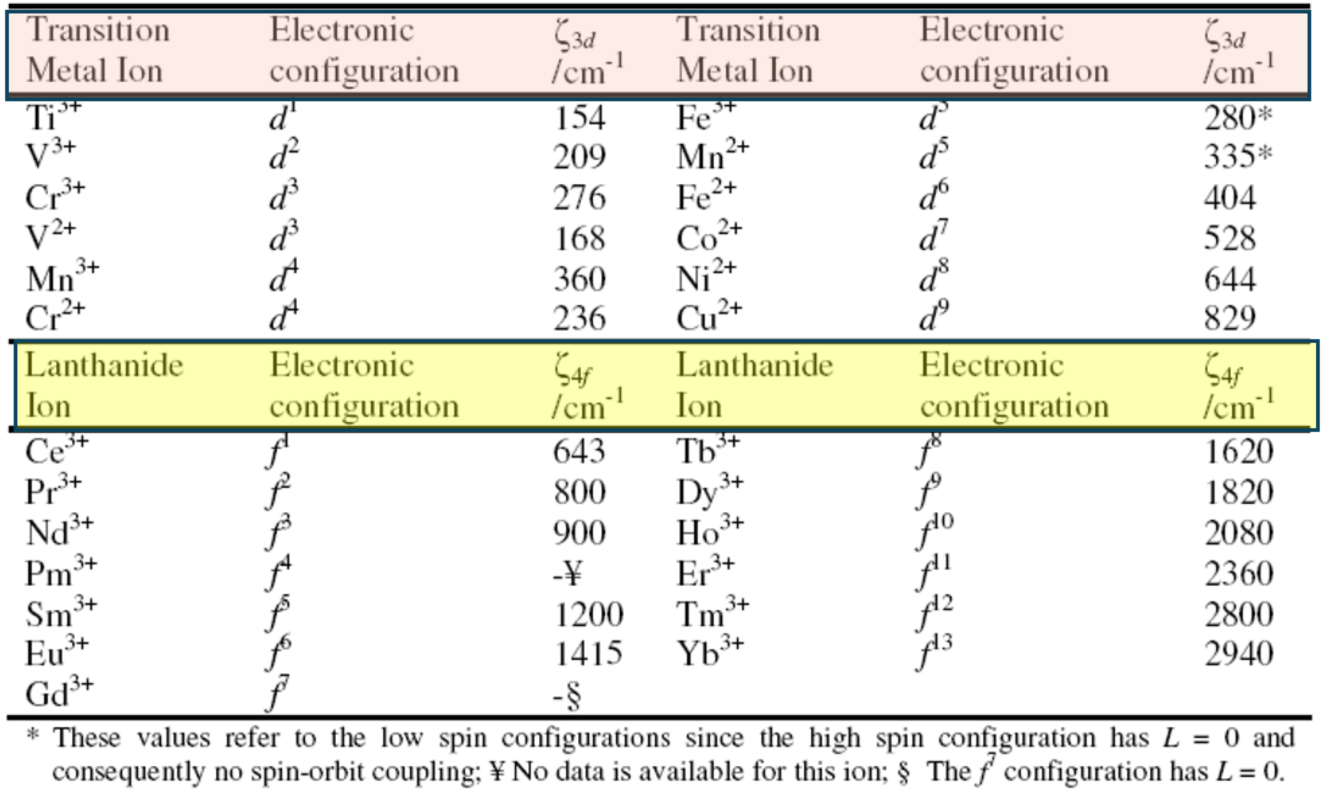
In some texts an orbital reduction factor *k* is included ($0 < k < 1$) such that the experimental spin-orbit coupling is given by $k\lambda$ (Typically $0.6 < k < 0.8$).

The magnetism of spin-only ions

Magnetism of Ln^{3+}

While kT > Δ then

we can neglect Δ



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* These values refer to the low spin configurations since the high spin configuration has $L = 0$ and consequently no spin-orbit coupling; ¥ No data is available for this ion; § The f^7 configuration has $L = 0$.

At 300 K:

$$\lambda \; > \; kT \; > \; \Delta$$

$$(10^3) \quad (10^2) \quad (10^1 - 10^2)$$

Approach to understanding the electronic structure:

a) Neglect the crystal field (except at low temp)

a) But must consider spin-orbit coupling

At low temperature kT → 10^1 or 10^0 then the effect of Δ may become important

The magnetism of spin-only ions

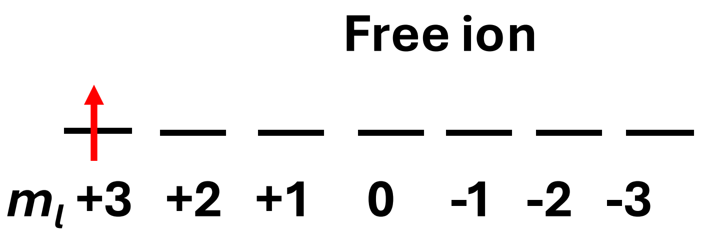
Magnetism of Ln^{3+} ions

The Ln^{3+} oxidation state is most common for all lanthanides (both Ln^{2+} and Ln^{4+} are rare)

Ln^{3+} configurations are all $6s^0 4f^n$

Since the *f*-orbitals are so radially contracted there is no significant splitting of the *f*-orbitals when they form complexes so their magnetism approximates very well to 'the free ion'.

Example Ce^{3+}


Free ion

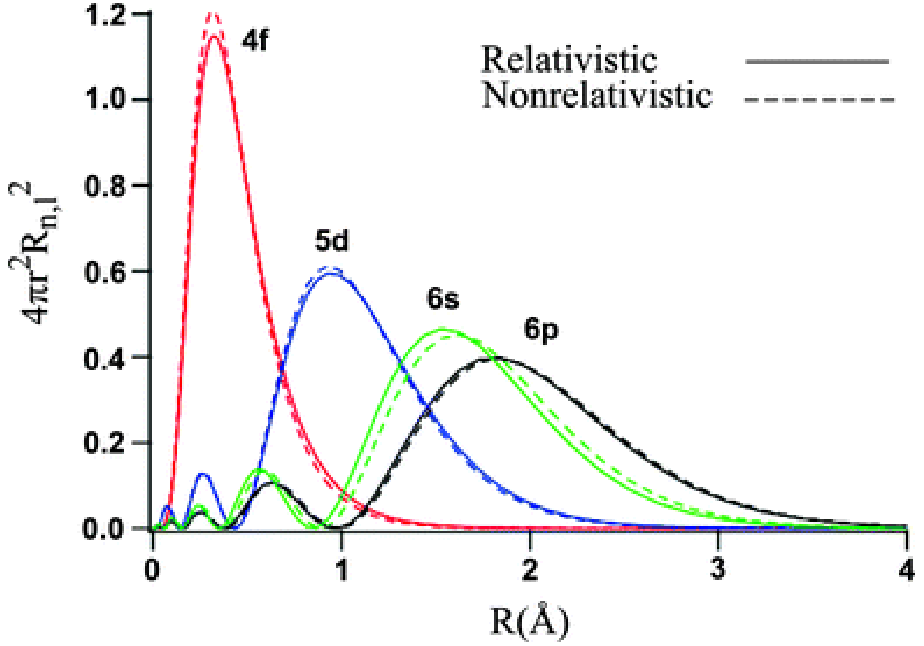
m_l +3 +2 +1 0 -1 -2 -3

$S = \Sigma m_s = ½$

$L = \Sigma m_L = 3$

Term Symbol: ^2F

Radial distribution function for Ln ion valence orbitals



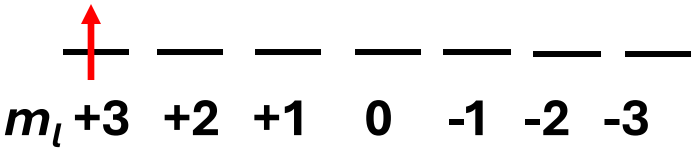
Need to consider both spin (S) and orbital (L) angular momenta

The magnetism of spin-only ions

Magnetism of Ln^{3+} ions ($\lambda >> \Delta$)

Example Ce^{3+}

Free ion



$S = \Sigma m_s = ½$

$L = \Sigma m_L = 3$

Term Symbol: ^2F

$J = |L + S|, |L + S - 1|...|L - S| = 7/2$ or $5/2$

If we wish to include the effect of spin-orbit coupling in our term symbol we place it as a subscript:

$^2F_{5/2}$ and $^2F_{7/2}$

Start with the most important energy term: spin-orbit coupling, λ:

What does spin-orbit coupling do?

It does what it says on the box; it permits the spin angular momentum S and the orbital angular momentum L to couple (interact).

This gives rise to the total angular momentum J

J can take all possible integer values between |L + S | and |L - S |

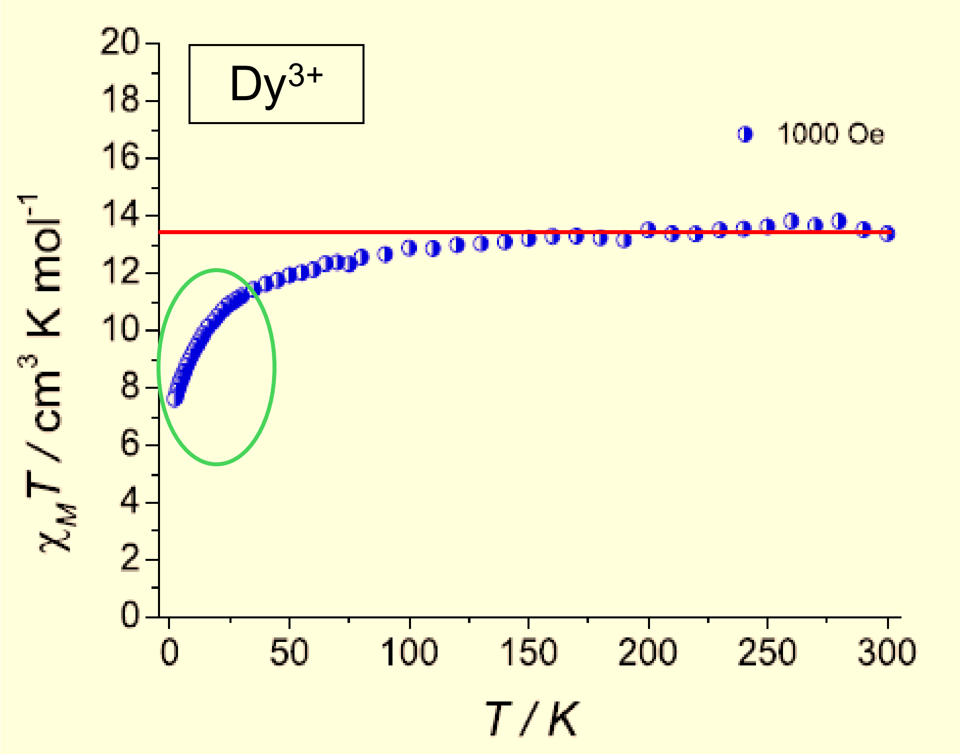
The magnetism of spin-only ions

Magnetism of Ln^{3+} ions ($\lambda >> \Delta$)

- $\lambda >> kT >> \Delta$
- **We evaluate S and L and invoke spin-orbit coupling to determine J and evaluate the spin ground term (S, L, J).**
- **In most cases $\lambda J >> kT$ and the magnetism reflects the spin ground state and is (nearly) temperature independent.**

$$\chi = \frac{Ng_J^2\mu_B^2 J(J+1)}{3kT}$$

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$



Downturn in χT due to effect of the crystal field ($\Delta > kT$ at low temperature).

The magnetism of spin-only ions

Magnetism of Ln^{3+} ions ($\lambda >> \Delta$)

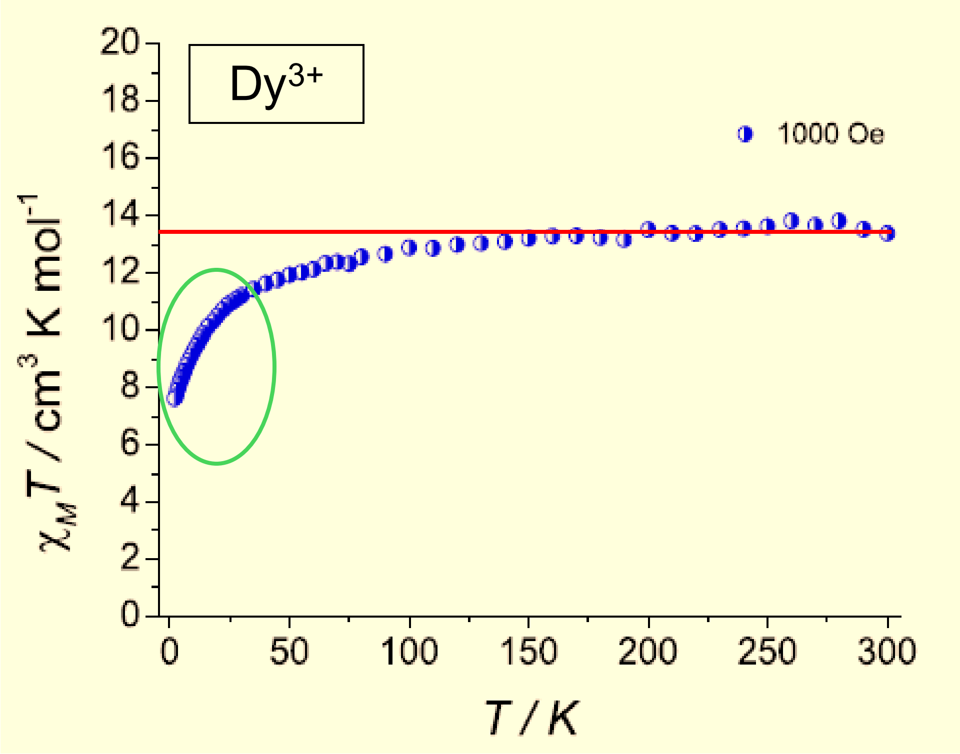
$$\chi = \frac{N g_J^2 \mu_B^2 J(J+1)}{3kT}$$

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Warning:

At low T $\Delta > kT$ and Δ then becomes significant.

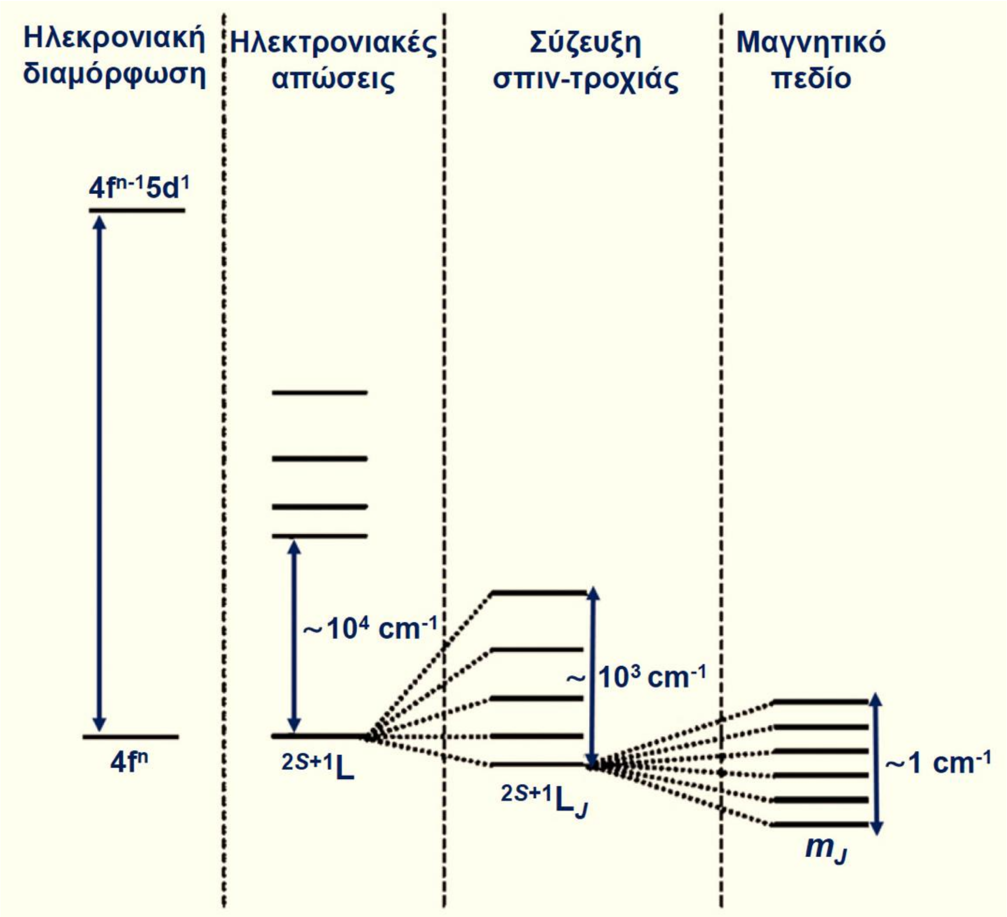
The effect of Δ is to split the degeneracy of the $^{2S+1}L_J$ ground state (which is 2J +1 degenerate) and we start to see temperature dependent effects at low temperature.

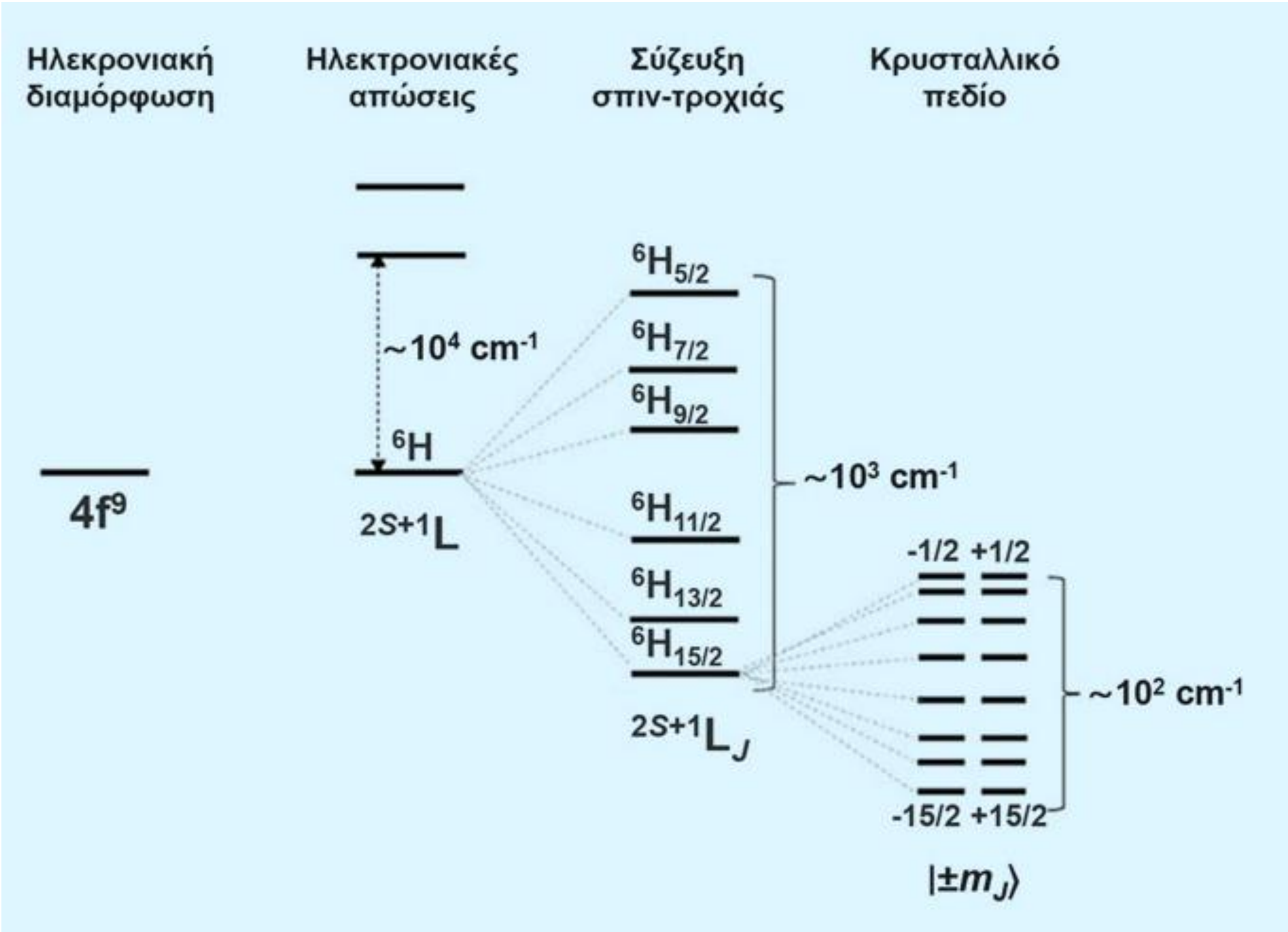


Downturn in χT due to effect of the crystal field (Δ > *k*T at low temperature).

The magnetism of spin-only ions

Magnetism of Ln^{3+} ions ($\lambda >> \Delta$)



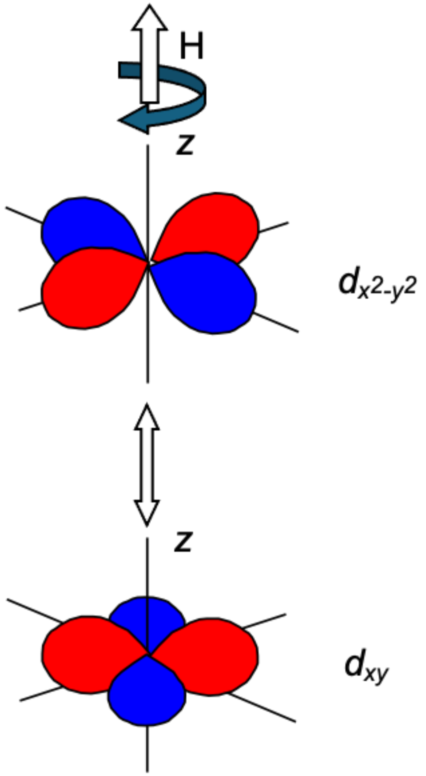


The magnetism of spin-only ions

Magnetism of transition metal ions: L

Free Ion: The five *d*-orbitals are degenerate

The d^1 configuration gains orbital angular momentum about the z axis due to the symmetry and degeneracy of the d_{xy} and $d_{x^2-y^2}$ orbitals.



Orbital angular momentum about an axis (x, y or z) arises from the movement of an electron by rotation about the axis to a symmetry equivalent and degenerate orbital which does not contain an electron with the same spin.

The magnetism of spin-only ions

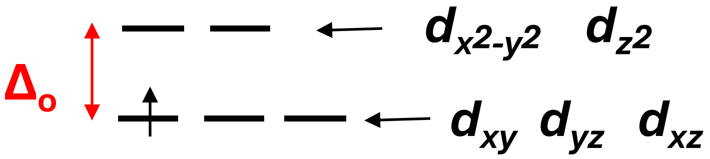
Magnetism of transition metal ions: L

Free Ion: The five *d*-orbitals are degenerate

The d^1 configuration gains orbital angular momentum about the z axis due to the symmetry and degeneracy of the d_{xy} and d_{x2-y2} orbitals.

O_h complex: The *d*-orbitals are split

Now the d_{xy} and d_{x2-y2} orbitals are no longer degenerate. A substantial energy barrier (D) exists which quenches orbital angular momentum arising from motion of the electron between d_{xy} and d_{x2-y2} orbitals



For first row TM: Δ_o ~ 10,000 cm^{-1}

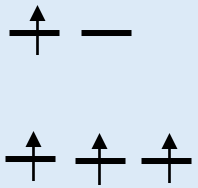
(>> *k*T)

The magnetism of spin-only ions

Magnetism of 1^{st} row transition metal ions

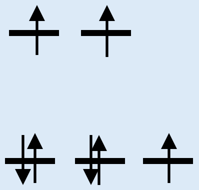
- Evaluate d^n configuration and appropriate d-orbital splitting (O_h, T_d etc) and whether you expect high or low spin.
- Draw the expected ground state configuration (based on Δ and P)
- Determine the term symbol and hence whether it retains orbital angular momentum or is 'spin-only'

Mn^{3+}



'Spin only'

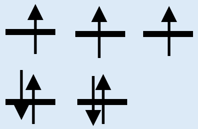
Co^{2+}



Orbital angular momentum 'partially quenched'

(not equal occupancy of t_{2g})

Co^{2+}



'Spin only'

Magnetism depends on d^n configuration and geometry!

The magnetism of spin-only ions

Magnetism of ‘spin-only’ ions (A and E terms)

- **If all the orbital angular momentum is quenched then to first order, L = 0 and J = S [Recall J = |L + S|, |L + S -1|…. |L – S|]**
- **As we discussed for ‘spin-only ions’:**

$$\chi_M = \frac{M}{H} = \frac{N_A g^2 \mu_B^2 S(S+1)}{3k_B T}$$

Where g ~ 2.0

“The spin-only approximation”

The magnetism of spin-only ions

Second Order Effects: A and E terms

The ground state gains a bit of excited state character (i.e. a bit of an orbital contribution to g) which permits g to deviate from the spin-only value (2.0).

If the excited state is high in energy then the perturbation from spin-only is small.

If the excited state is low in energy then the perturbation from spin-only is large.

The deviation from spin-only due to spin-orbit coupling depends on |λ|

The degree of deviation of g from the spin only value is given by:

$$g = 2\left(1 - \frac{\alpha k \lambda}{\Delta}\right)$$

Transition metals with less than a half-filled shell: $\lambda > 0$ and $g < 2.0$

Transition metals with a greater than half-filled shell: $\lambda < 0$ and $g > 2.0$

The magnetism of spin-only ions

Summary

For transition metals Δ >> kT ~ λ ~ δ. For many configurations the crystal field is efficient at quenching the orbital angular momentum and many transition metal ions exhibit temperature independent spin-only values

$$\chi T = \frac{Ng^2\beta^2 S(S+1)}{3k}$$

$$g = 2\left(1 - \frac{\alpha k \lambda}{\Delta}\right)$$

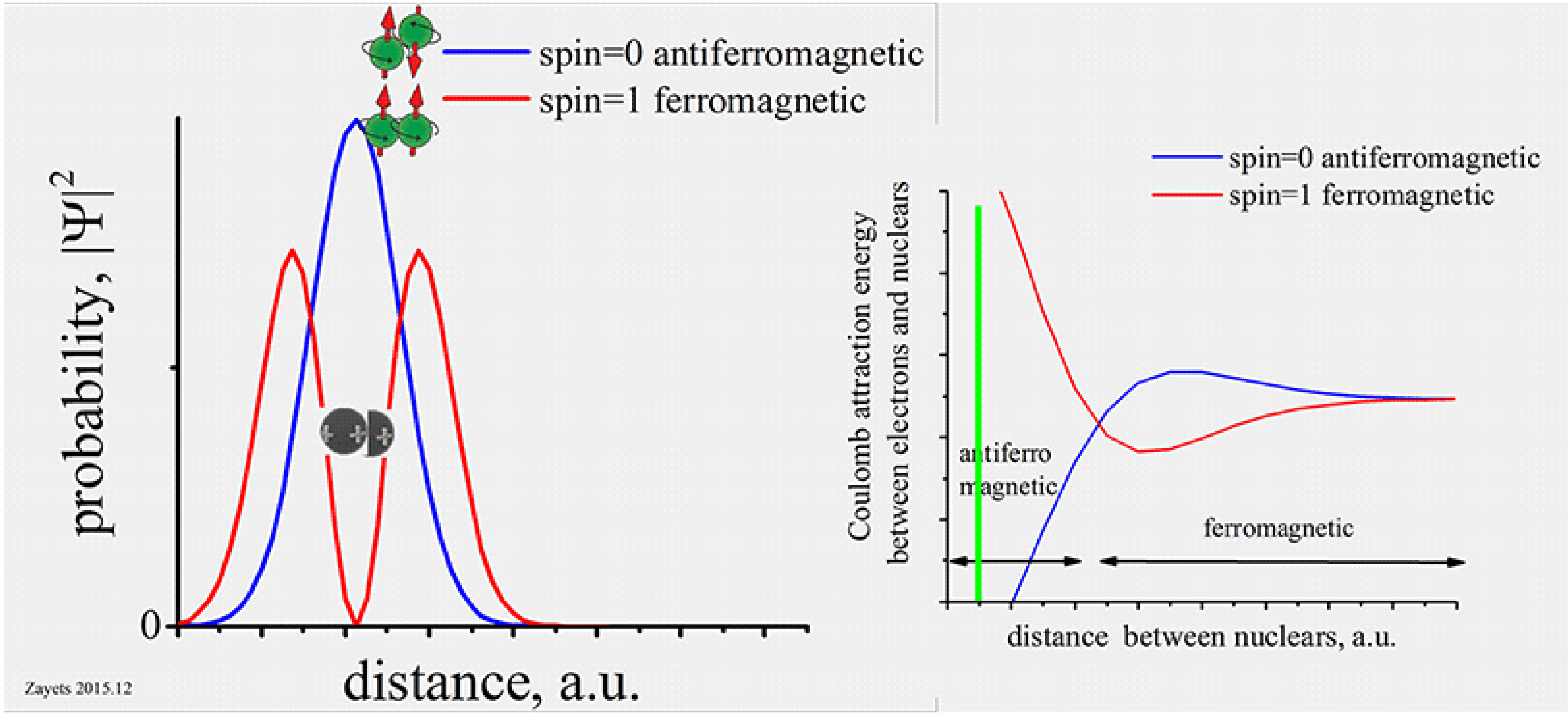
For lanthanides l >> kT > D, the magnetic behaviour down to low temperature typically follows free ion behaviour

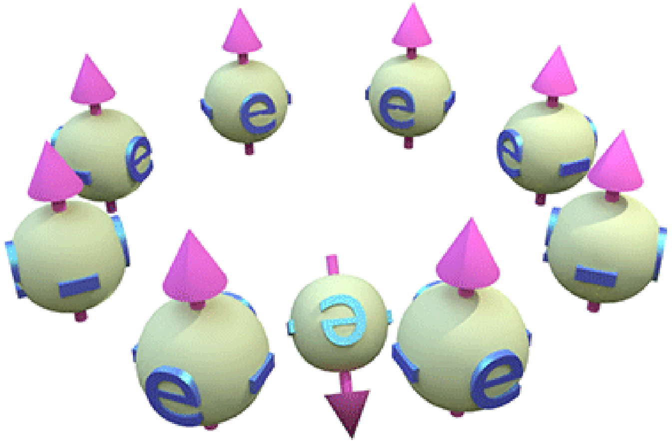
$$\chi T = \frac{Ng_J^2\beta^2 J(J+1)}{3k}$$

For transition metal configurations with residual orbital angular momentum, the magnetism is complex due to competition between kT and λ and δ and strongly temperature dependent. At high temperature kT > λ it often approximates to spin-only but with g > 2 whereas at low temperature a Kramers doublet is the ground state with S_{eff} = ½ and g >> 2

Magnetic exchange interactions

- **Direct approach**
- **Superexchange mechanism**





Magnetic exchange interactions

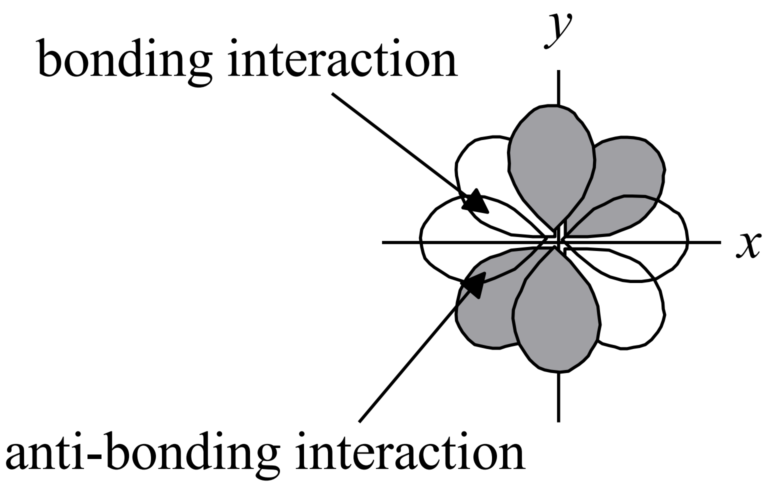
Ferromagnetic (coparallel) alignment

Let us look at how we fill a set of d-orbitals in the gas phase (though the argument is applicable to p and f orbitals too)

Electrons repel each other so prefer to occupy separate orbitals

Hund's rules of maximum multiplicity indicate that electrons in separate orbitals prefer to align coparallel.

The coparallel arrangement (↑↑) is preferred over the antiparallel arrangement (↑↓) by an energy term 2K (where K is pretentiously known as the potential exchange correlation integral!)

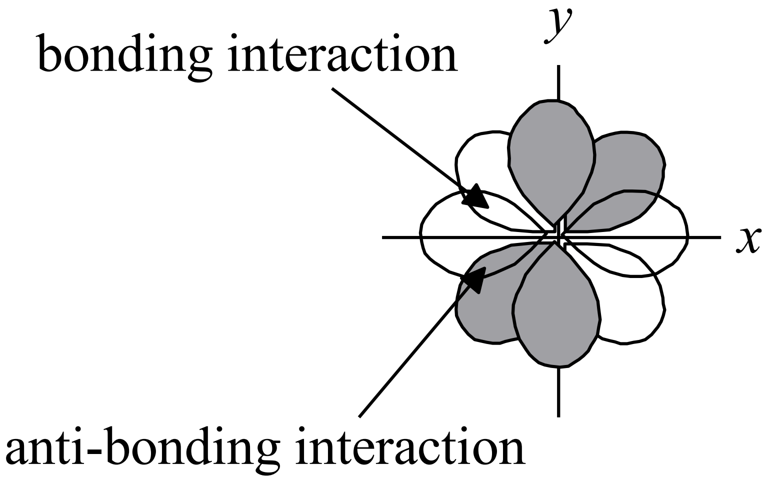


Orthogonal nature of d_{xy} and d_{x2-y2} orbitals

Magnetic exchange interactions

Ferromagnetic (coparallel) alignment

Here the *d*-orbitals overlap in space (they are on the same atom!) but they are described as being ***orthogonal*** to each other, i.e. the overlap integral is zero (there is no net bonding interaction between them).

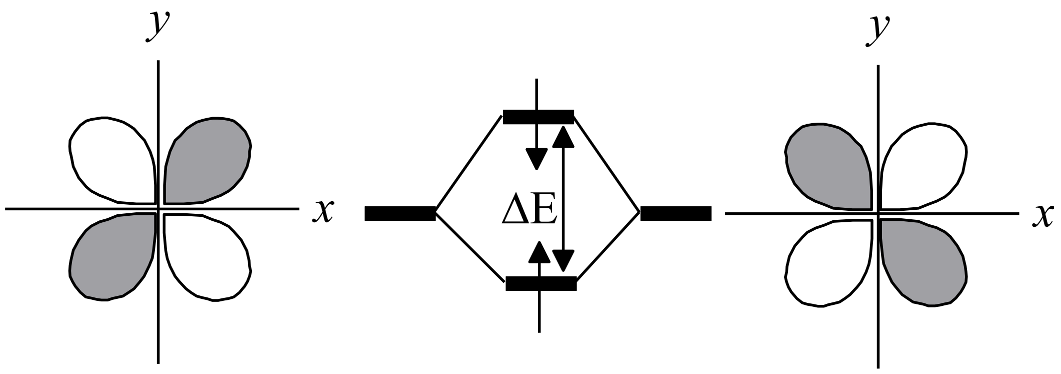


Orthogonal nature of d_{xy} and d_{x2-y2} orbitals

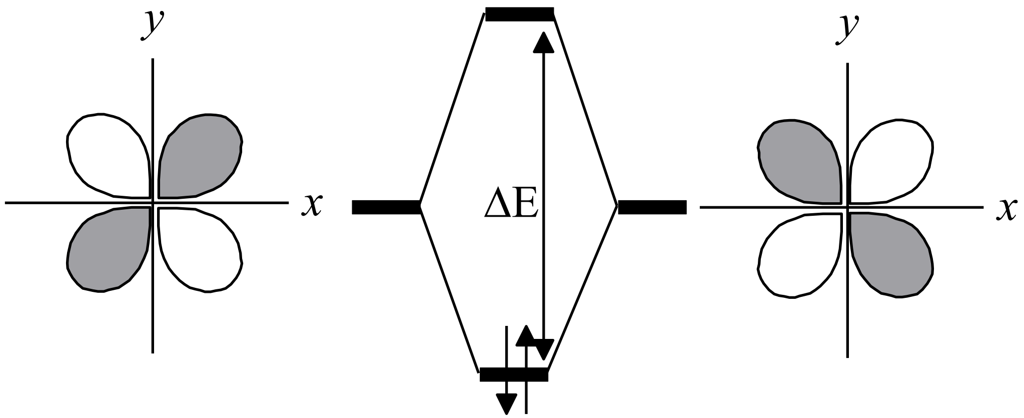
Unpaired electrons in orthogonal orbitals align coparallel

Magnetic exchange interactions

Antiferromagnetic (antiparallel) alignment



A very weak bonding interaction stabilises the antiferromagnetic state (ΔE < P).



A strong bonding interaction generates a closed shell singlet.

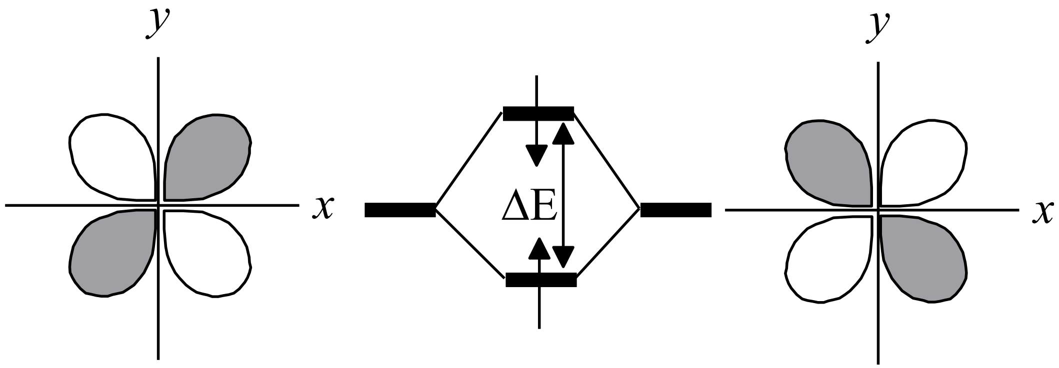
Now let us look at bonding interactions between electrons during bond formation.

When the orbitals overlap efficiently, we form a strong bonding MO and an antibonding MO. The two electrons become paired forming a singlet state ($S = 0$).

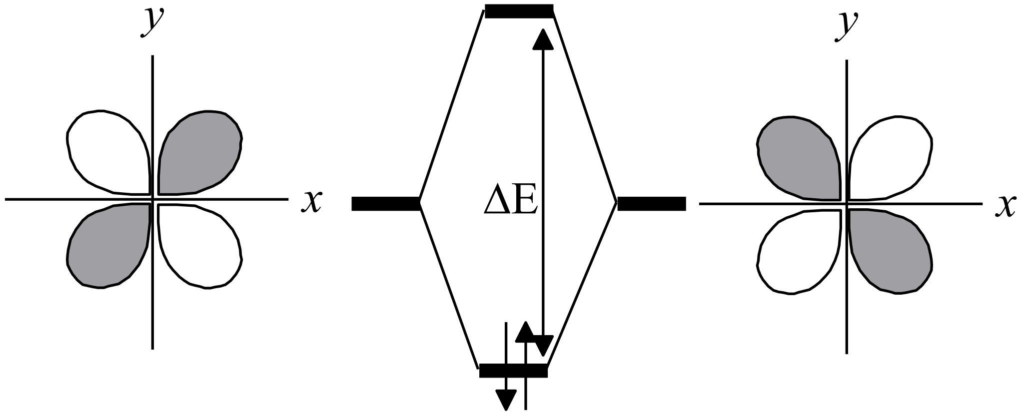
At longer separations, there is still overlap forming bonding and antibonding orbitals but with poor overlap the energy gap is small and less than the inter-electron repulsion term (P). We maintain two unpaired electrons with the closed shell bonding interaction higher in energy.

Magnetic exchange interactions

Antiferromagnetic (antiparallel) alignment



A very weak bonding interaction stabilises the antiferromagnetic state (ΔE < P).



A strong bonding interaction generates a closed shell singlet.

The ground state configuration can either be coparallel or antiparallel. The antiparallel arrangement (S = 0) is stabilised by mixing in with the excited singlet state.

The extent of stabilisation is given by the kinetic exchange integral -4St where S is the overlap integral and t the hopping integral associated with sharing the electron over two sites.

Magnetic exchange interactions

Electron-electron interactions: Overall behaviour

Orthogonal orbitals stabilise the ferromagnetic interaction via potential exchange integral (2K).

Weakly bonding orbitals stabilise the antiferromagnetic interaction via kinetic exchange integral (-4Sb).

The net effect is that the magnetic exchange coupling (J) between two spins is given by:

$2J = 2K - 4S\beta$ in other words.... $J_{obs} = J_F + J_{AF}$

$4S\beta$ reflects degree of covalency; S is the overlap integral and β the resonance integral

If $J > 0$ we have a ferromagnetic spin alignment

If $J < 0$ we have an antiferromagnetic alignment

Normally the term $4S\beta$ dominates unless we arrange the magnetic orbitals (orbitals containing an unpaired electron) carefully to generate strictly orthogonal orbitals such that $S = 0$.

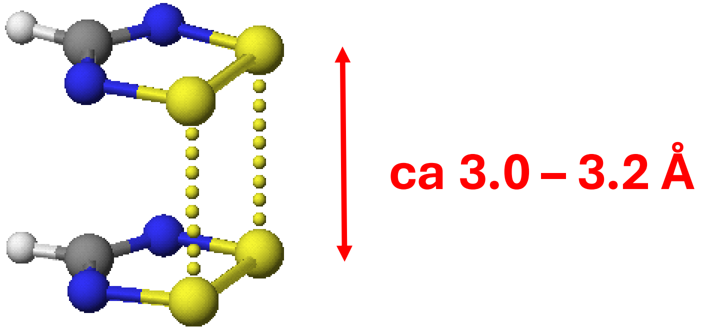
Magnetic exchange interactions

Direct Exchange

Direct exchange reflects the interactions between metals through direct overlap of *d*-orbitals.

This is relatively rare due to:

- **The contracted nature of the d-orbitals**
- **Bringing metals close together requires ligands which force metals close together without obstructing their close approach.**

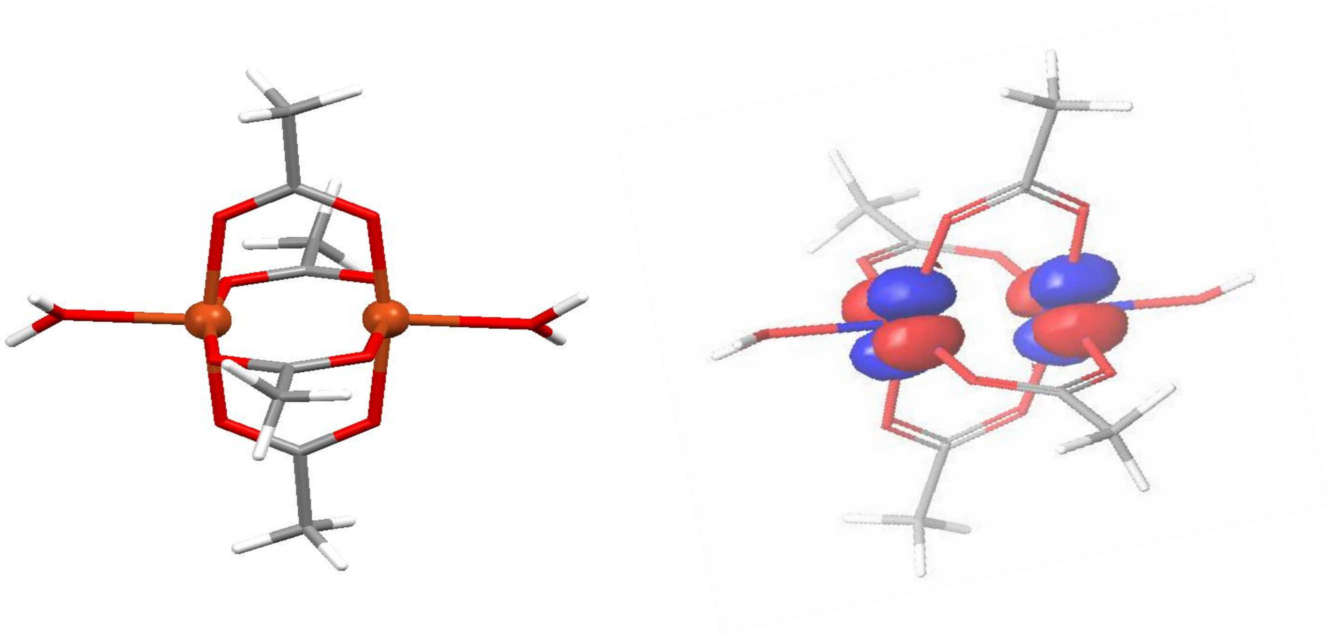


For many p-radicals close face-to-face approach of radical centres leads to a bonding interaction. At longer distances they can be considered as having open shell singlet character and some paramagnetism is often observed above ca. 200-250 K.

Direct exchange occurs (mainly) in bulk metals where the electrons on neighboring atoms change places

Magnetic exchange interactions

Direct Exchange



Copper paddlewheels such as $Cu_2(OAc)_4.2H_2O$ are argued to exhibit antiferromagnetic coupling via the face-to-face interaction between d_{x2-y2} orbitals

These orbitals are constrained to be aligned face-to-face favouring orbital overlap but the M…M distance is ca. 2.6Å

At temperatures below ca. 150 K $Cu_2(OAc)_4.2H_2O$ has χT = 0 emu.K/mol.

Magnetic exchange interactions

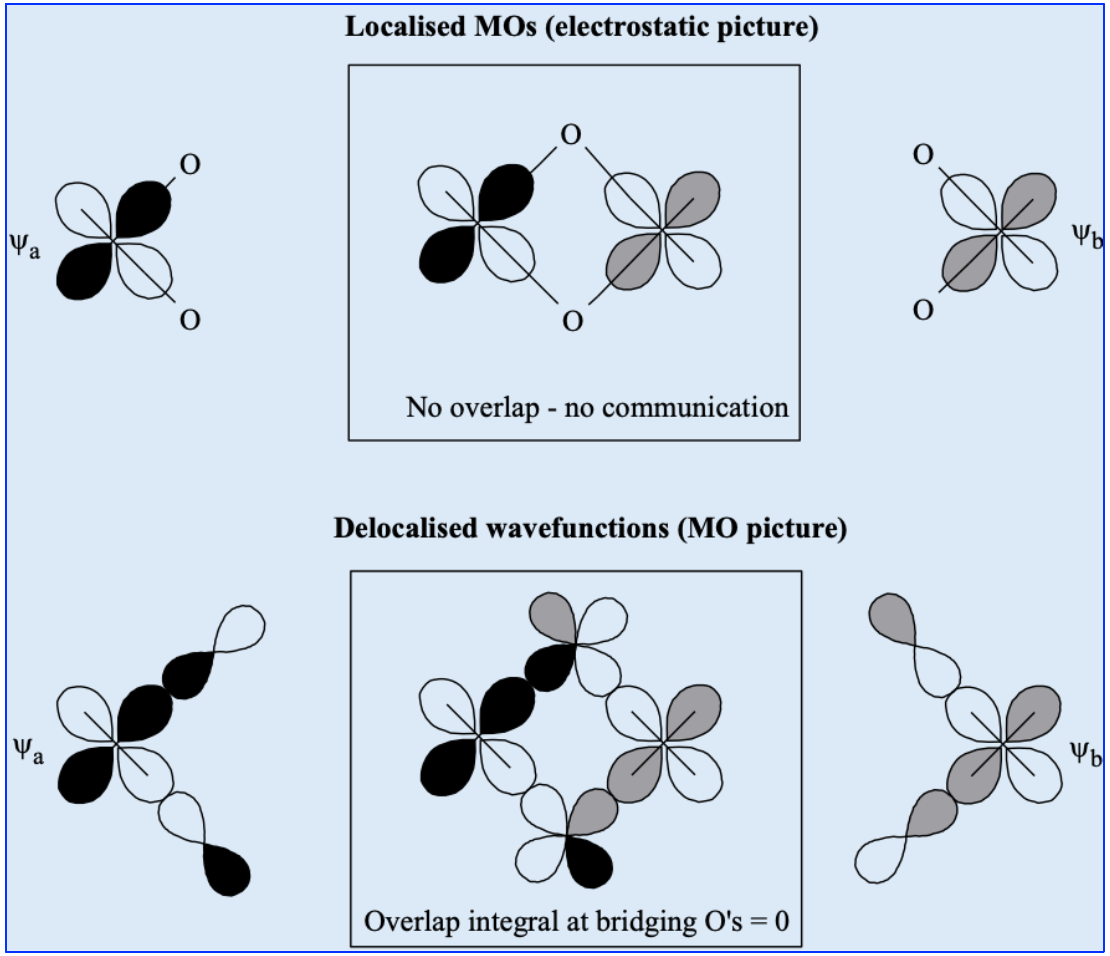
Superexchange

Superexchange is the most common mechanism for magnetic communication between transition metals.

In many cases the metal…metal separation is too large to facilitate direct orbital overlap. Yet we observe strong communication.

In superexchange, communication between metal centres is mediated via metal-ligand covalency to bridging ligands leading to overlap of electron density on the bridging atom(s).

<u>**We now consider overlap integrals and orbital orthogonality in the overlap region.**</u>



Magnetic exchange interactions

Goodenough-Kanamori Rules

The Goodenough-Kanamori rules are a set of empirical rules which explain the observed magnetic behaviour of many metal-oxo bridged systems when the coupling is *via* a 90° or 180° M-O-M bridge:

- **When the magnetic orbitals are arranged so as to afford a reasonable overlap integral ($S > 0$) the exchange is antiferromagnetic ($J < 0$).**
- **When the magnetic orbitals are arranged in such a way as to have no overlap integral ($S = 0$) then the exchange will be ferromagnetic ($J > 0$).**
- **Superexchange through the s framework tends to be more efficient than through the p framework.**

$$\boxed{2J = 2K - 4S\beta}$$

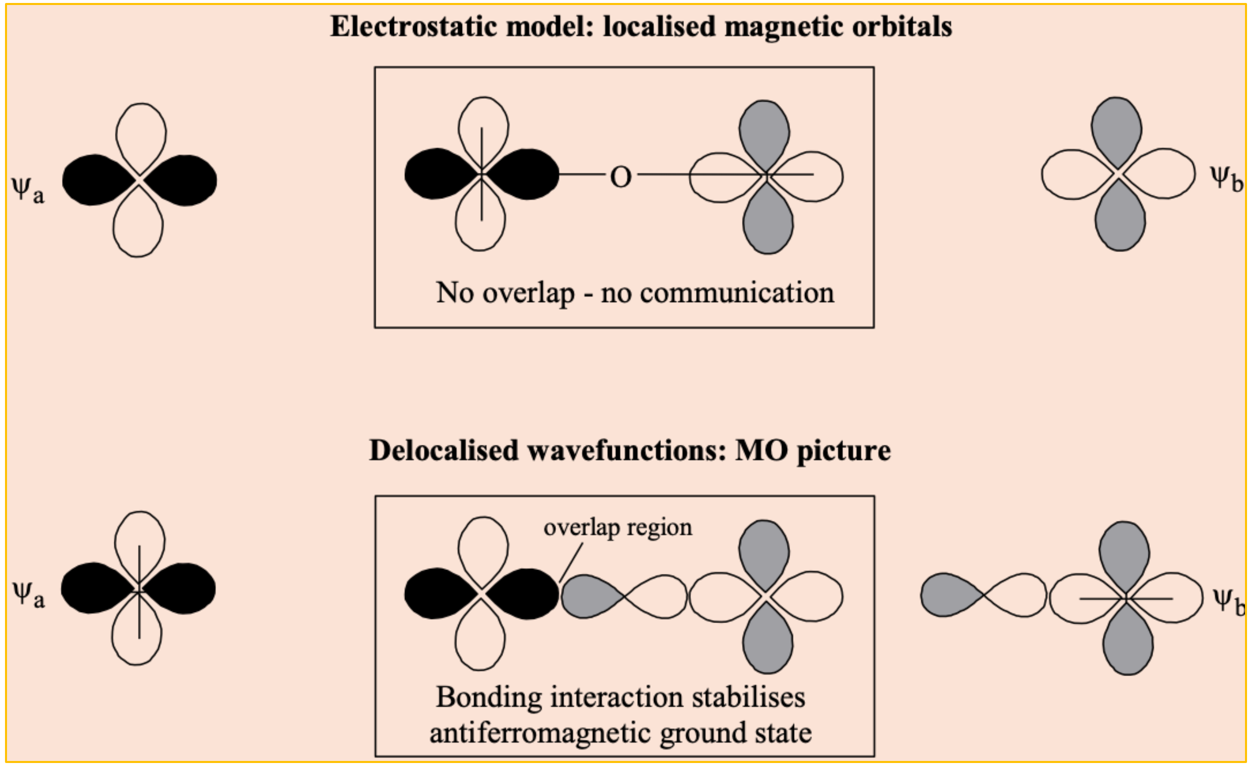
$2K$ = potential exchange integral (difference between ↑ ↑ and ↑ ↓)

$4S\beta$ reflects degree of covalency; S is the overlap integral and β the resonance integral.

Magnetic exchange interactions

Example: Linear Ni-O-Ni exchange (180º)

- In a purely ionic bonding model there is no delocalisation to the O^{2-} anion the Ni^{2+} ions are well separated and exchange is negligible.
- If we take into account some degree of metal-ligand covalency then the unpaired electron spends some time on the bridging ligand.
- In the current example the orbitals give a net overlap integral ($S > 0$) so $2J = 2K – 4St$
- The overlap integral is efficient so $2J < 0$
- Antiferromagnetic coupling is expected.



How do we interpret the magnetism of exchange-coupled clusters?

Qualitative Analysis

Limiting high temperature values of χT

At high temperature *k*T >> |*J*| so we neglect exchange coupling

System should behave like a set of independent ions

$$\chi T = n\,\frac{N_A g^2 \mu_B^2 S(S+1)}{3k}$$

Limiting low temperature limit of χT

At low temperature kT << J so we determine the expected spin ground state (S_T) for the molecule

$$\chi T = \frac{N_A g^2 \mu_B^2 S_T(S_T+1)}{3k}$$