Magnetic Properties

Fundamentals and structural correlations

1

Magnetism References

- A. F. Orchard, “Magnetochemistry”.
- Drago, “Physical Methods in Chemistry”, Chapter 11.
- C. J. O’Connor, *Prog. Inorg. Chem.,* **1982,** *29,* 203.
- R. L. Carlin, “Magnetochemistry”, Springer-Verlag, Berlin, **1986.**
- F. E. Mabbs and D. L. Machin, “Magnetism and Transition Metal Complexes”, Chapman and Hall, London, **1973.**
- W. E. Hatfield, *Magnetic Measurements*, Chapter 4 in “Solid State Chemistry: Techniques”, A. K. Cheetham and P. Day, Eds., Clarendon Press, Oxford, **1987**.
- B. N. Figgis, M. A. Hitchman, “Ligand Field Theory and its Applications”, Chapter 9.

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Definitions

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}$$

$$\frac{B}{H} = 1 + 4\pi\frac{M}{H} = 1 + 4\pi\chi_{\mathrm{v}}$$

χ_{v}: volume susceptibility (dimensionless)

χ_{g}: gram susceptibility ($\mathrm{cm}^3\ \mathrm{g}^{-1}$):

$$\chi_{\mathrm{g}} = \frac{\chi_{\mathrm{v}}}{\rho} \quad \leftarrow \text{density}$$

χ_{m}: molar susceptibility ($\mathrm{cm}^3\ \mathrm{mol}^{-1}$):

$$\chi_{\mathrm{m}} = \chi_{\mathrm{g}} \bullet \mathrm{M}$$

(Technically, $\chi_{\mathrm{v}} = \frac{\partial M}{\partial H}$, which is important when dealing with magnetically-ordered materials where M is not proportional to H.)

- B is the flux density inside a sample, H is the applied field, and M is the induced magnetization.

$\therefore$ χ is a measure of the sample's 'susceptibility' to being magnetized, per unit applied field.

- Strictly, **M** doesn't have to be parallel to **H**, and then χ is a matrix.

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Energy relationships

$$E = \frac{HB}{8\pi} \quad (\text{erg/cm}^3)$$

$$E = \frac{H\left(1+4\pi\chi_{\text{v}}\right)H}{8\pi} = \left(\frac{1}{8\pi} + \frac{\chi_{\text{v}}}{2}\right)H^2$$

In a vacuum, $E_{\text{vac}} = \frac{H^2}{8\pi} \quad (\chi_v = 0)$

$$E - E_{\text{vac}} = \frac{\chi_{\text{v}}}{2}H^2$$

or, choosing E_{vac} to be the zero of energy

$$E = \frac{\chi_{\text{v}}}{2}H^2$$

$$F_z = \frac{dE}{dz} = \chi_{\text{v}}\left(H\frac{dH}{dz}\right)$$

- $HB/8\pi$ is the magnetic energy 'stored' in any medium. (Seems weird, but if you integrate $HB/8\pi$ over all space with no sample present, you obtain the energy that was needed to magnetize the magnet!)

F_z is the force that a volume element of the sample 'feels' as it moves in an inhomogeneous magnetic field (i.e., in or out of the field of a magnet along the z-direction).

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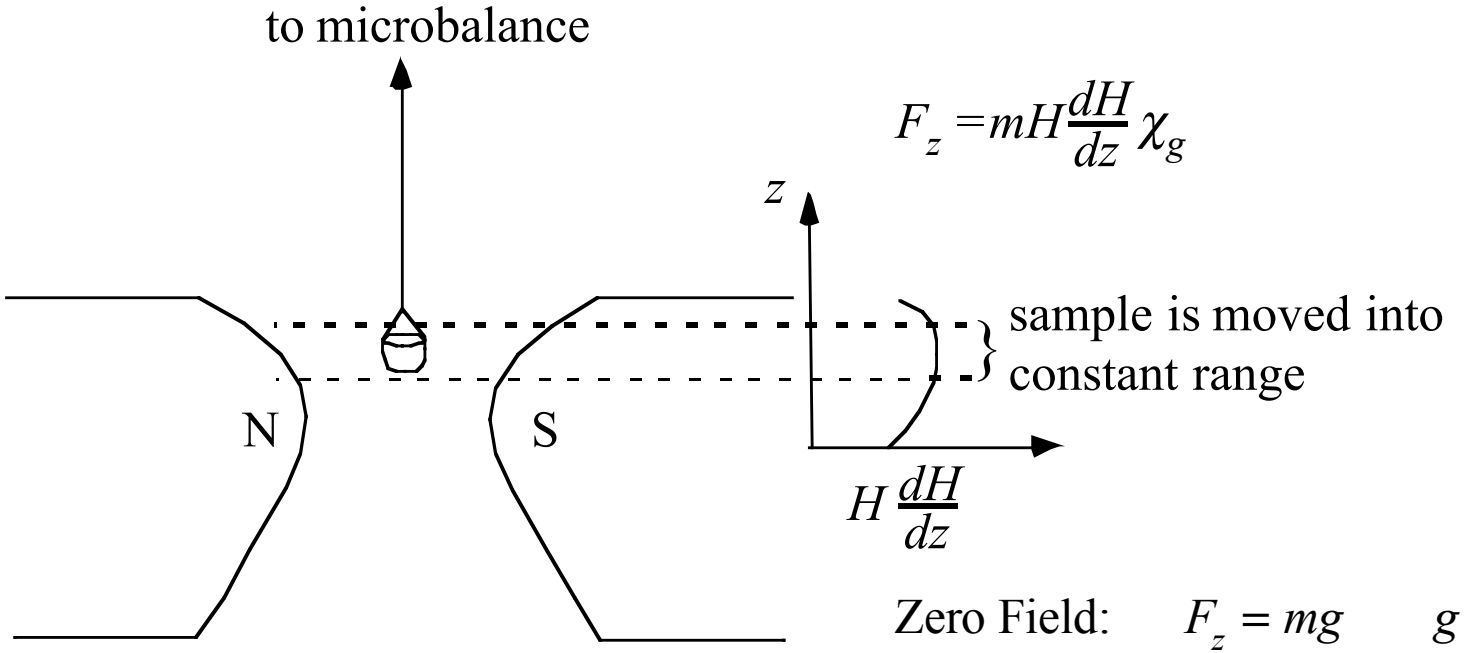
χ measurement; Faraday method

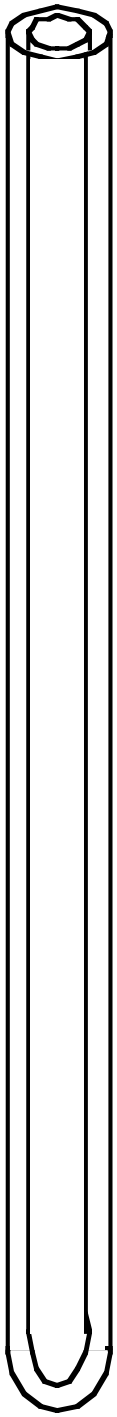


$$F_z = mH\frac{dH}{dz}\chi_g$$

Zero Field: $F_z = mg$ g - gravitationalal constant

With Field: $F_z = \frac{dE}{dz} = m\left[g + \left(H\frac{dH}{dz}\right)\chi_g\right]$

- Pole pieces shaped to yield field gradient requirements (or "shaping coils" mounted to faces of the magnet).
- Advantages: good sensitivity; no 'packing error'; Small sample allows good thermostatting of sample
- Disadvantage: magnetic anisotropies difficult to measure.



χ measurement; Evans (solution) NMR method

Evans, *J. Chem. Soc.,* **1959,** 2003.
Oatfeld & Cohen, *J. Chem. Ed.,* **1972,** *49,* 829.

- Two, concentric, NMR tubes are used.
- Inner tube: internal standard, dissolved in solvent
- Outer tube: internal standard, dissolved in solvent, *plus* paramagnetic solution species to be measured.

The presence of paramagnetic ions in the outer tube shifts the field felt by the standard molecules in the outer tube.

shift of resonance field $\rightarrow \dfrac{\Delta H}{H} = \dfrac{2\pi}{3}\Delta\chi_{\mathrm{v}}$

where $\Delta\chi_{\mathrm{v}}$ is the difference in the volume susceptibilities of the liquids

gram susceptibility of paramagnetic substance:

$$\chi_{\mathrm{g}} = \chi_0 \underbrace{\underbrace{\left(1 + \frac{\rho_0 - \rho_S}{m}\right)}_{\text{correction for density changes}}}_{\text{accounts for solvent displaced}} + \frac{3}{2\pi m}\frac{\Delta\nu}{\nu}$$

$\leftarrow$ frequency shift (Hz)

$\leftarrow$ resonance frequency (Hz)

$m =$ grams of paramagnetic solute / ml solution

$\rho_0 =$ solvent density

$\rho_S =$ solution density

$\chi_0 =$ gram susceptibility of solvent

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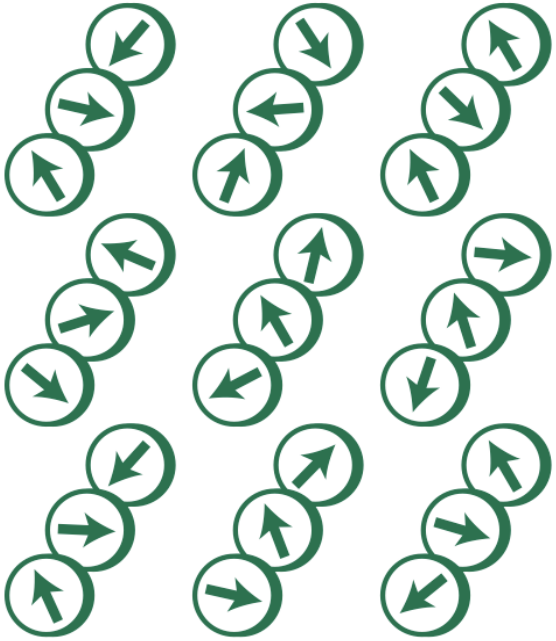
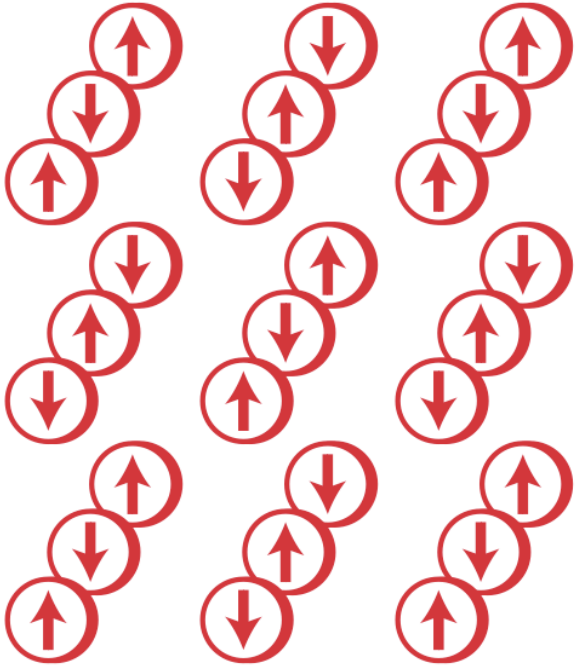
The Basic Schemes

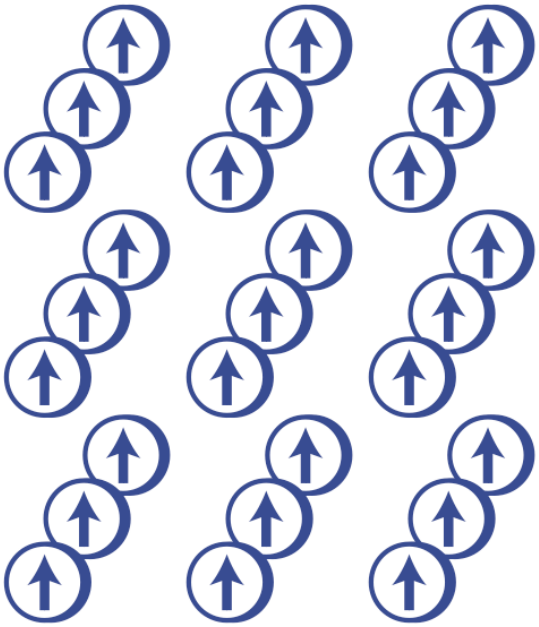


Paramagnet

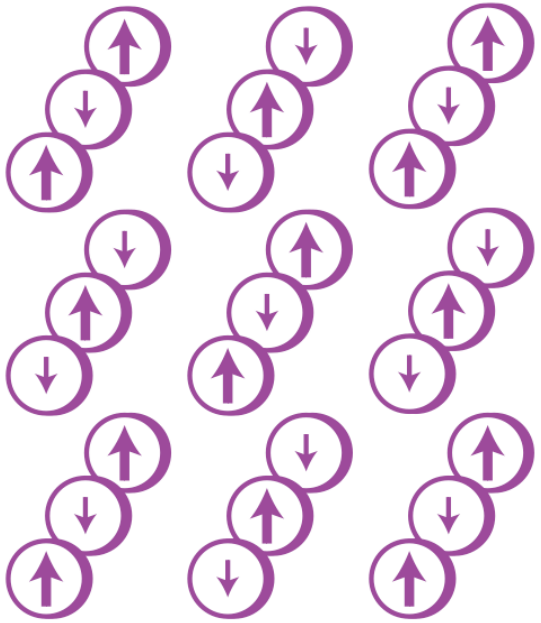


Antiferromagnet

Zero temperature ‘snapshots’ of magnetic moments in each paramagnetic (zero field), ferromagnetic, antiferromagnetic, and ferrimagnetic materials.



Ferromagnet



Ferrimagnet

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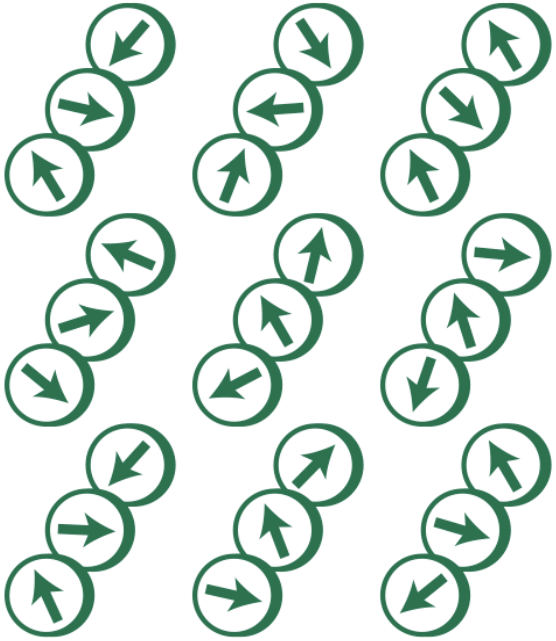


Paramagnet

$\chi_{\text{dia}} \sim 10^{-6}$ - present in all matter

T independent

Very weakly destabilizing in H

$\chi_{\text{para}} \sim 10^{-3} - 10^{-2}$ - unpaired spins

$1/T$ dependence

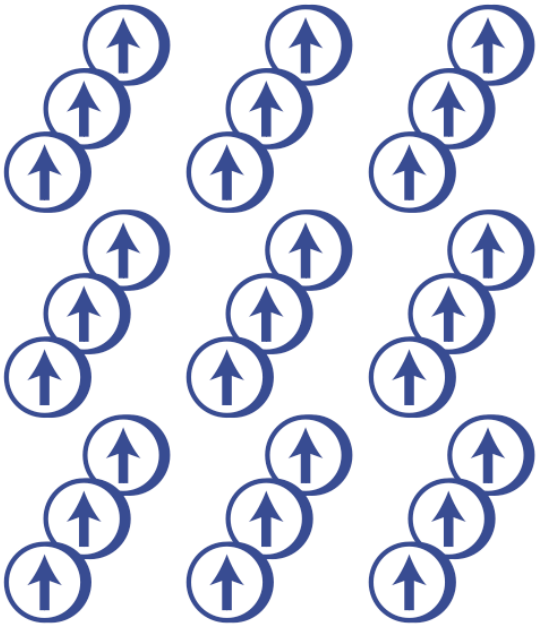
weakly stabilizing in H

Antiferromagnet

$\chi_{\text{anti}} \sim \chi_{\text{dia}}$ at $T = 0$

if exactly stoiciometric

slowly rises with T until T_N

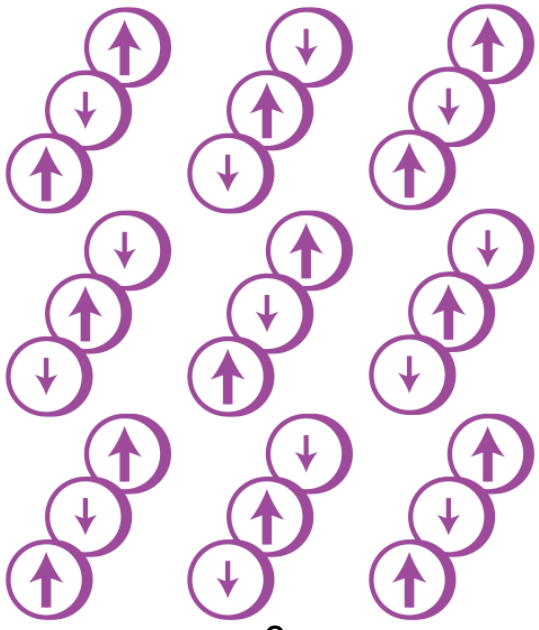


Ferromagnet

$\chi_{\text{ferro}} \sim$ up to 10^6

slowly decreases with T until near T_C

stabilizing in H



Ferrimagnet

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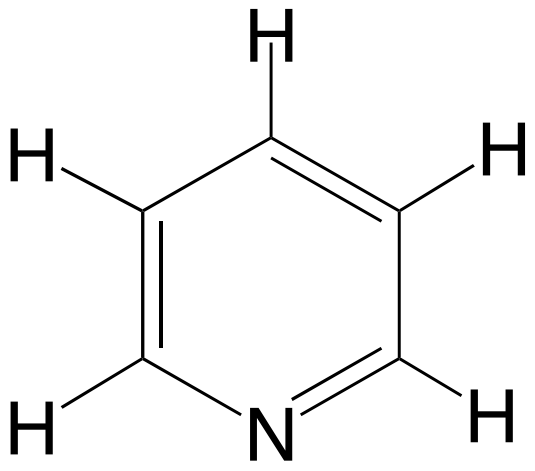
Diamagnetism – Pascal's Constants



All paramagnetic measurements should be corrected for diamagnetism:

$$\chi_{obs} = \chi_{para} + \chi_{dia}$$

(+) (–)

These can be estimated using Pascal's constants (from atomic/ionic susceptibilities)

$5 \times \text{C(ring)} = 5 \times (-6.24 \times 10^{-6}) = -31.2 \times 10^{-6}$

$5 \times \text{H} = 5 \times (-2.93 \times 10^{-6}) = -14.6 \times 10^{-6}$

$1 \times \text{C(ring)} = -4.6 \times 10^{-6}$

Total: -50.4×10^{-6} $\text{cm}^3\ \text{mol}^{-1}$ (or emu mol^{-1})

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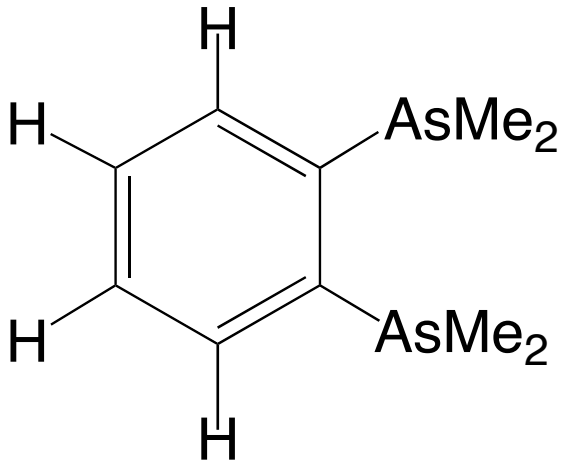
Pascal's Constants not perfect

	calc.	exptl.
pyridine:	-50.4×10^{-6}	-49×10^{-6}
	-147×10^{-6}	-194×10^{-6}



Fortunately, it is usually the case that $|\chi_{para}| >> |\chi_{dia}|$ and errors like this can be tolerated. Nevertheless, if diamagnetic complexes analogous to paramagnetic species can be measured, they yield better estimates.

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Statistical Thermodynamics

Magnetic susceptibility measurements are “bulk property” measurements, and results are averages over the so-called ‘ensemble’ of molecules in the system.

Probability the an energy level with energy ε_i is occupied

$$p_i = \frac{g_i e^{-\varepsilon_i / k_B T}}{\sum_i g_i e^{-\varepsilon_i / k_B T}}$$ where g_i is the degeneracy of the i^{th} level.

The 'thermal average' of property A one will measure for a system in equilibrium:

$$\langle \mathrm{A} \rangle = \sum_i p_i A_i = \frac{\sum_i A_i g_i e^{-\varepsilon_i / k_B T}}{\sum_i g_i e^{-\varepsilon_i / k_B T}}$$; where A_i is the value of property A in the i^{th} state

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Magnetization of an Ideal Paramagnet

If we call $\bar{\mu}$ the average magnetic moment of a paramagnetic molecule, then $N_A\bar{\mu}$ is the molar magnetization the compound in question.

If we apply a magnetic field along the z-axis to a sample of *noninteracting* molecules, each molecule will experience Zeeman splitting of its energy levels.

$\bar{\mu}$ is given by substituting into the formula we have have just presented as follows

$$\langle A \rangle = \frac{\sum_i A_i g_i e^{-\varepsilon_i/k_B T}}{\sum_i g_i e^{-\varepsilon_i/k_B T}} \quad \Rightarrow \quad \bar{\mu} = \frac{\sum_{M_J=-J}^{J} \mu_{M_J} e^{-E_{M_J}/k_B T}}{\sum_{M_J=-J}^{J} e^{-E_{M_J}/k_B T}} = \frac{\sum_{M_J=-J}^{J} M_J g_J \mu_B e^{M_J g_J \mu_B H/k_B T}}{\sum_{M_J=-J}^{J} e^{M_J g_J \mu_B H/k_B T}}$$

What do all the symbols mean?

- J is the total angular momentum, but in many cases, $J \simeq S$.
- M_J is the z-component of J, so that in spin-only cases, $M_J = M_S$.
- μ_{M_J} is the z-component of the magnetic moment for each Zeeman level, so $\mu_{M_J} = M_J g_J \mu_B$. (We can ignore x and y components since they cancel each out when averaged over all molecules.)
- E_{M_J} is the energy of each Zeeman level, so , $E_{M_J} = -\boldsymbol{\mu}_{M_J} \cdot \mathbf{H} = -M_J g_J \mu_B H$

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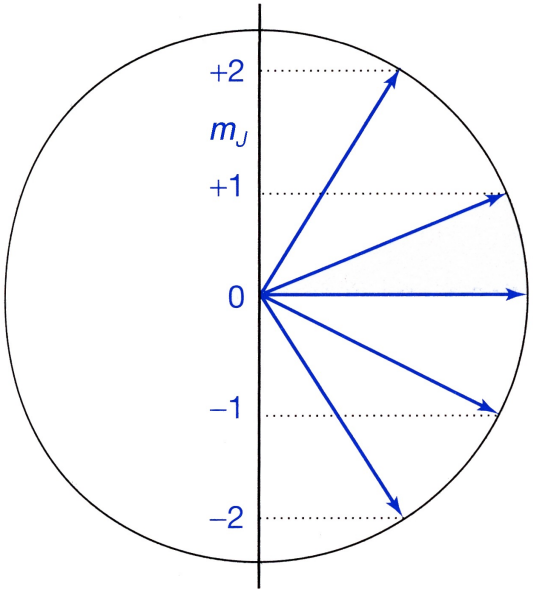
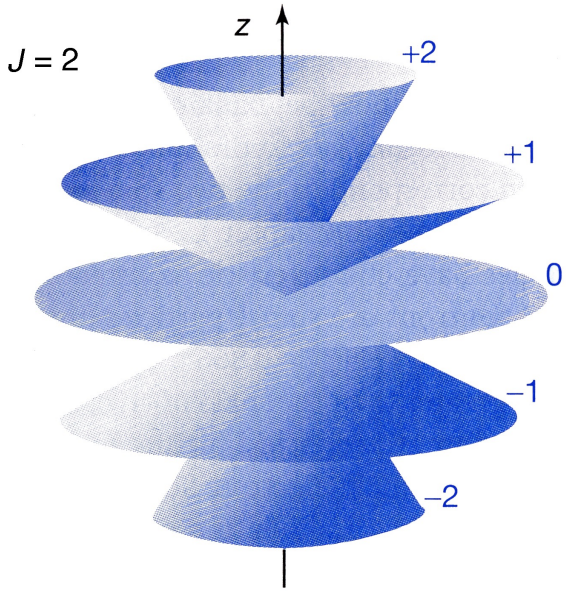
Pictorial View



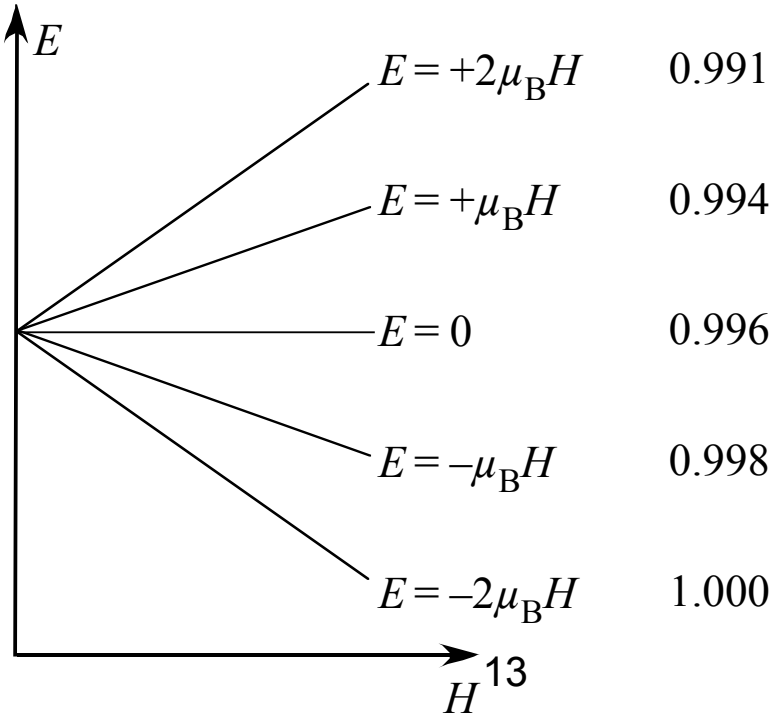
$$\bar{m} = \frac{\sum_{M_J=-J}^{J} \mu_{M_J} e^{-E_{M_J}/k_B T}}{\sum_{M_J=-J}^{J} e^{-E_{M_J}/k_B T}} = \frac{\sum_{M_J=-J}^{J} M_J g_J \mu_B e^{M_J g_J \mu_B H/k_B T}}{\sum_{M_J=-J}^{J} e^{M_J g_J \mu_B H/k_B T}}$$

$\mu_B H = 0.4574 \text{ cm}^{-1}$ for $H = 1.0$ T (10,000 G)

$\frac{\mu_B H}{k_B} = 0.6581 \text{ K}$ for $H = 1.0$ T (10,000 G)



relative populations at 298 K, $H = 1.0$ T



Magnetization and Susceptibility

$M_J g_J \mu_B H / k_B T \ll 1$ at temperatures over a few K. Therefore, we can expand

$$e^{M_J g_J \mu_B H / k_B T} \simeq 1 + M_J g_J \mu_B H / k_B T$$

$$\bar{m} = \frac{\sum_{M_J=-J}^{J} M_J g_J \mu_B e^{M_J g_J \mu_B H / k_B T}}{\sum_{M_J=-J}^{J} e^{M_J g_J \mu_B H / k_B T}} \simeq g_J \mu_B \frac{\sum_{M_J=-J}^{J} M_J \left(1 + M_J g_J \mu_B H / k_B T\right)}{\sum_{M_J=-J}^{J} \left(1 + M_J g_J \mu_B H / k_B T\right)}$$

$$= \frac{g_J^2 \mu_B^2 H}{k_B T} \frac{\sum_{-J}^{J} M_J^2}{\sum_{M_J=-J}^{J} (1)} \quad \Rightarrow \quad \boxed{\bar{m} = \frac{g_J^2 \mu_B^2 H}{3 k_B T} J(J+1)}$$

math notes: $e^x \simeq 1 + x$ for $x \ll 1$

$\sum_{-J}^{J} x = 0$; $\sum_{-J}^{J} (1) = 2J + 1$

$\sum_{-J}^{J} x^2 = \frac{1}{3} J(J+1)(2J+1)$

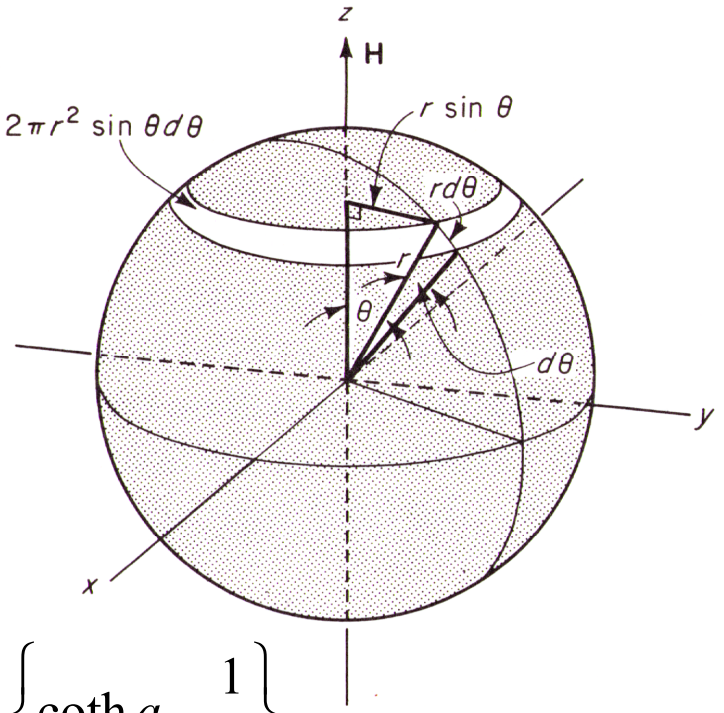
The molar bulk magnetization, M, is then $M = N_A \bar{m} = \frac{N_A}{3 k_B T} \left[g_J^2 J(J+1) \mu_B^2 \right] H$

The molar magnetic susceptibility is then,

$$\boxed{\chi_m = \frac{\partial M}{\partial H} = \frac{N_A}{3 k_B T} \mu_{eff}^2 \quad ; \quad \text{and} \quad \mu_{eff} = g_J \sqrt{J(J+1)} \mu_B}$$

Curie Law derived

Classical Result



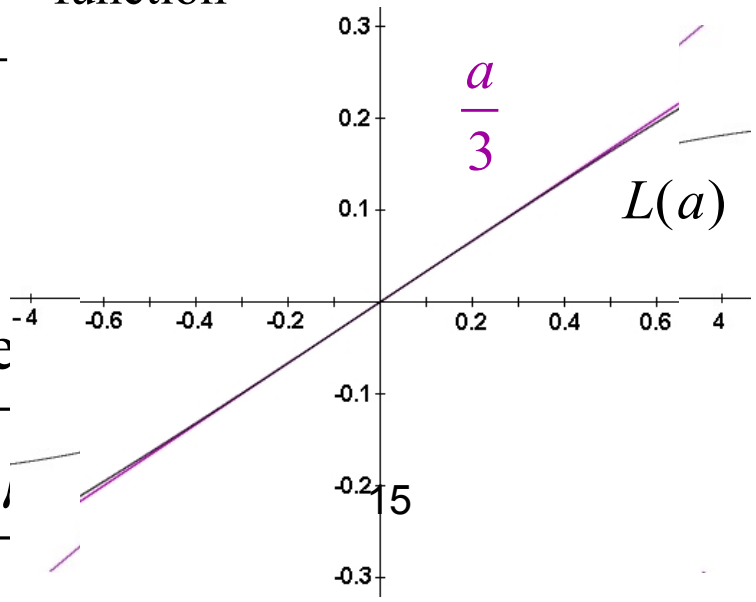
$$\underbrace{\left(x=\cos\theta\ ;\ dx=\sin\theta d\theta\right)\qquad\left(a=\frac{\mu H}{k_B T}\right)}$$

$$N_A\bar{m}=\frac{N_A\int_0^{\pi}\mu\cos\theta e^{\mu H\cos\theta/k_BT}\sin\theta d\theta}{\int_0^{\pi}e^{\mu H\cos\theta/k_BT}\sin\theta d\theta}=N_A\mu\frac{\int_{-1}^{1}xe^{ax}dx}{\int_{-1}^{1}e^{ax}dx}=N_A\mu\underbrace{\left\{\coth a-\frac{1}{a}\right\}}_{L(a)}$$

Langevin function

Normally, $a\ll 1\ \left(\mu H\ll k_BT\right)$, $\therefore$ use $\coth a-\frac{1}{a}=\frac{a}{3}-\frac{a^3}{45}+$

$$\bar{\mu}=N_A\mu L(a)\simeq N_A\frac{\mu a}{3}=N_A\frac{\mu^2 H}{3k_BT}$$



Comparison of the Q.M. result with the

$$\boxed{N_A\bar{m}_{classical}=\frac{N_A\mu}{3k_BT}H}\qquad k_BT\gg\mu H$$

Curie's Law

Empirical form: $\boxed{\chi_m = \frac{C}{T}}$

$$\boxed{\chi_m = \frac{C}{T} \;\; ; \quad \text{and} \quad C = \frac{N_A \mu_{eff}^2}{3k_B} \simeq 0.125 g_J^2 J(J+1)}$$

NOTE: $$\frac{N_A \mu_B^2}{3k_B} = \frac{(6.023\times10^{23}\ \text{mol}^{-1})\left(9.2740\times10^{-21}\ \frac{\text{erg}}{\text{G}}\right)^2}{3\left(1.3807\times10^{-16}\ \frac{\text{erg}}{\text{K}}\right)} \simeq 0.125\ \frac{\text{erg}}{\text{G}^2}\ \text{K mol}^{-1} = 0.125\ \text{K mol}^{-1}$$

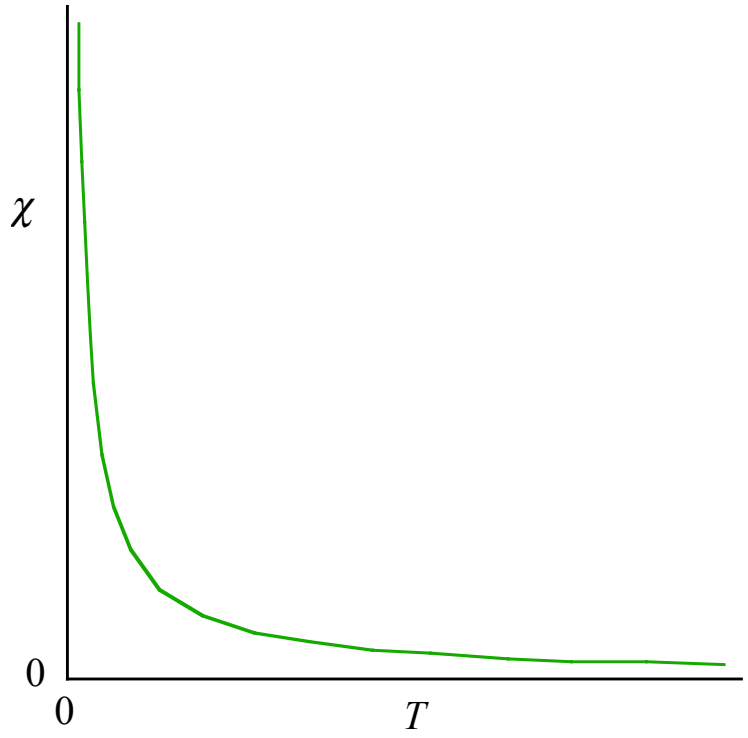
BUT (!): $$\frac{N_A \mu_B^2}{3k_B} = \frac{(6.023\times10^{23}\ \text{mol}^{-1})\left(9.2740\times10^{-24}\ \frac{\text{J}}{\text{T}}\right)^2}{3\left(1.3807\times10^{-23}\ \frac{\text{J}}{\text{K}}\right)} \simeq 1.25\ \frac{\text{J}}{\text{T}^2}\ \text{K mol}^{-1} = 0.125\ \text{K mol}^{-1}$$?

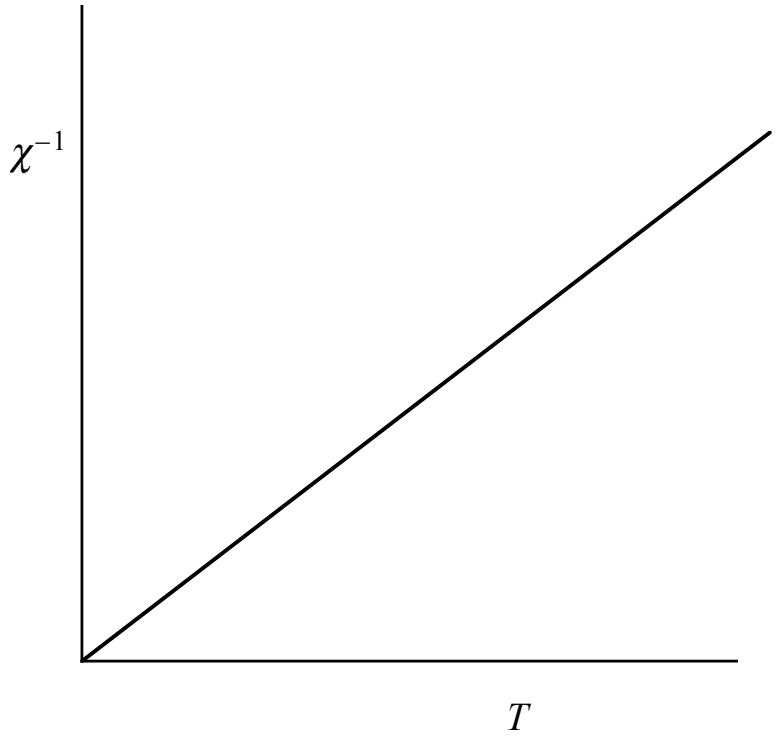
Why? $1\ \text{G}^2 = 1\ \text{erg}$, BUT $1\ \text{T}^2 = 10\ \text{J}$

Using SI units throughout for C: $$\mu_0 \frac{N_A \mu_B^2}{3k_B} \simeq \left(4\pi\times10^{-7}\ \frac{\text{N}}{\text{A}^2}\right)\left(1.25\ \frac{\text{J}}{\text{T}^2}\ \text{K mol}^{-1}\right) = 1.57\times10^{-6}\ \text{m}^3\ \text{K mol}^{-1}$$

χ and χ^{-1}

$$\chi_m = \frac{C}{T} \quad ; \quad \text{and} \quad C = \frac{N_A \mu_{eff}^2}{3k_B} \simeq 0.125 g_J^2 J(J+1)$$





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Spin-Only Magnetism

$$\chi_m = \frac{C}{T} = \frac{N_A}{3k_B T}\mu_{eff}^2 \quad ; \quad \text{and} \quad \mu_{eff} = 2\sqrt{S(S+1)}\mu_B = \sqrt{n(n+2)}\mu_B$$

(assumes $g_e = 2$) $n =$ # of unpaired electrons

n	S	μ_{eff}
1	$^1/_2$	1.73
2	1	2.83
3	$^3/_2$	3.87
4	2	4.90
5	$^5/_2$	5.92
6	3	6.93
7	$^7/_2$	7.94

Note:

The high-T *slope* of a χ^{-1} vs. $1/T$ plot is a more reliable measure of μ_{eff} than the direct use of the Curie formula from a single measurement at a fixed temperature.

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Table 5.3 μ_{eff} data (~ 300 K) for selected compounds of d^3 and d^5 ions.

d^3	$CrCl_3$	3.90	$K_3[Cr(ox)_3].3H_2O$	3.62
	$[Cr(NH_3)_6]Br_3$	3.77	$KCr(SO_4)_2.12H_2O$	3.84
	$[Cr(en)_3]Br_3$	3.82	$K_3[MoCl_6]$	3.79
	$[Cr(bpy)_3]Cl_3$	3.81	$K_2[MnCl_6]$	3.84
	$K_3[Cr(CN)_6]$	3.87	$[V(en)_3]Br_2$	3.81
	$K_3[Cr(NCS)_6].4H_2O$	3.79	$[V(bpy)_3]Cl_2$	3.67
	$K_3[Mo(NCS)_6].4H_2O$	3.70	$[Mo(bpy)_3]Cl_3$	3.66
	$(N^nBu_4)_3[Cr(N_3)_3]_6$	3.76	$K_4[V(CN)_6]$	3.78
d^5	$MnCl_2$	5.79	$FeCl_3$	5.73
	$MnBr_2$	5.82	$(Et_4N)[FeCl_4]$	5.88
	$(NH_4)_2Mn(SO_4)_2.6H_2O$	5.88	$(NH_4)Fe(SO_4)_2.12H_2O$	5.89
	$[Mn(NH_3)_6]Cl_2$	5.92	$K_3[Fe(ox)_3].3H_2O$	5.90
	$(Et_4N)_2[MnCl_4]$	5.94		

Spin-Only Examples

n	S	μ_{eff} (μ_B)
3	$^3/_2$	3.87
5	$^5/_2$	5.92

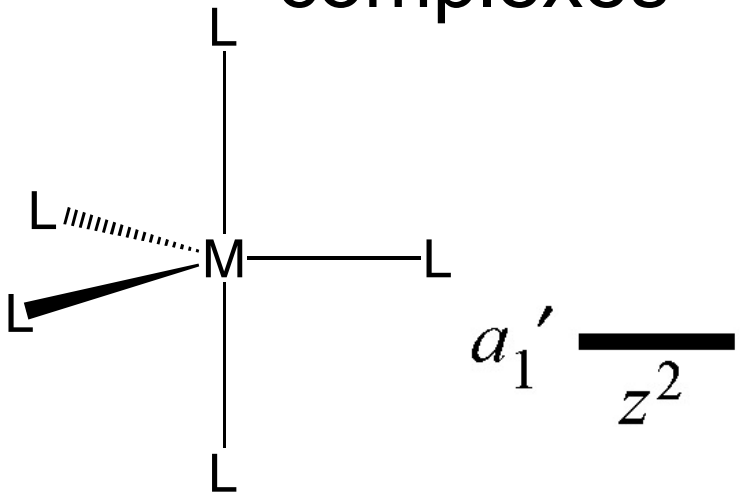
High-spin d^5- and d^3-complexes often behave as nearly ideal spin-only systems. In these cases, μ_{eff} obtained by assuming the Curie formula is correct and plugging in the temperature, 300K, gives good to excellent agreement with experiment. (Why?)

Table 5.8 m_{eff} data (/μ_B) at *ca.* 300 K for a selection of trigonal bipyramidal complexes.

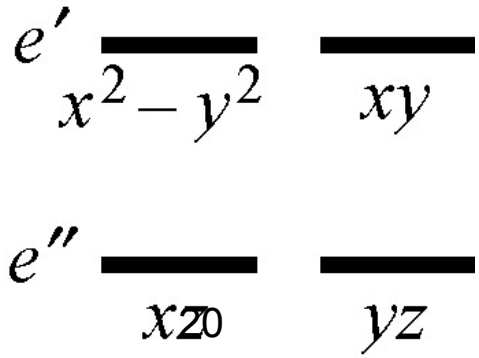
S = 0	$[Ni(CN)_5]^{3-}$, *t*-$Ni(PMe_3)_3(CN)_2$	0 (closed-shell d^8)		
	$[Mo(NO)(SPh)_4]^-$	0 (closed-shell d^4)		
S = 1/2	*t*-$Ti(NMe_3)_2Cl_3$	1.69 (d^1)	$[VCl_5]^-$	1.70 (d^1)
	t-$Co(PMe_3)_3Br_2$	2.10 (d^7)	$[CuCl_5]^{3-}$	1.89 (d^9)
S = 1	*t*-$V(PMe_3)_2Cl_3$	2.61 (d^2)	*t*-$Co(PMe_3)_2Cl_3$	3.05 (d^6)
	$[Ni(Me_6tren)Cl]^+$	3.42 (d^8)	$[Fe(QP)Cl]^+$	3.10 (d^6)
S = 3/2	*t*-$Cr(NMe_3)_2Cl_3$	3.88 (d^3)	*t*-$Fe(PMe_3)_2Cl_3$	4.22 (d^5)
	$[Co(Me_6tren)Cl]^+$	4.45 (d^7)	$[Co(Opy)_5]^{2+}$	4.56 (d^7)
S = 2	$[Cr(Me_6tren)Cl]^+$	4.85 (d^4)	*t*-$Mn(PMe_3)_2I_3$	4.80 (d^4)
	$[Fe(Me_6tren)Br]^+$	5.34 (d^6)		
S = 5/2	$[Mn(Me_6tren)I]^+$	5.95 (d^5)		

Me_6tren = *tris*-(2-dimethylaminomethyl)amine, $N(CH_2CH_2NMe_2)_3$
QP = *tris*-(2-diphenylphosphinophenyl)phosphine, $P(o\text{-}C_6H_4PPh_2)_3$
Opy = pyridine N-oxide, C_5H_5NO

Other coordination geometries: d^n Trigonal Bipyramidal complexes

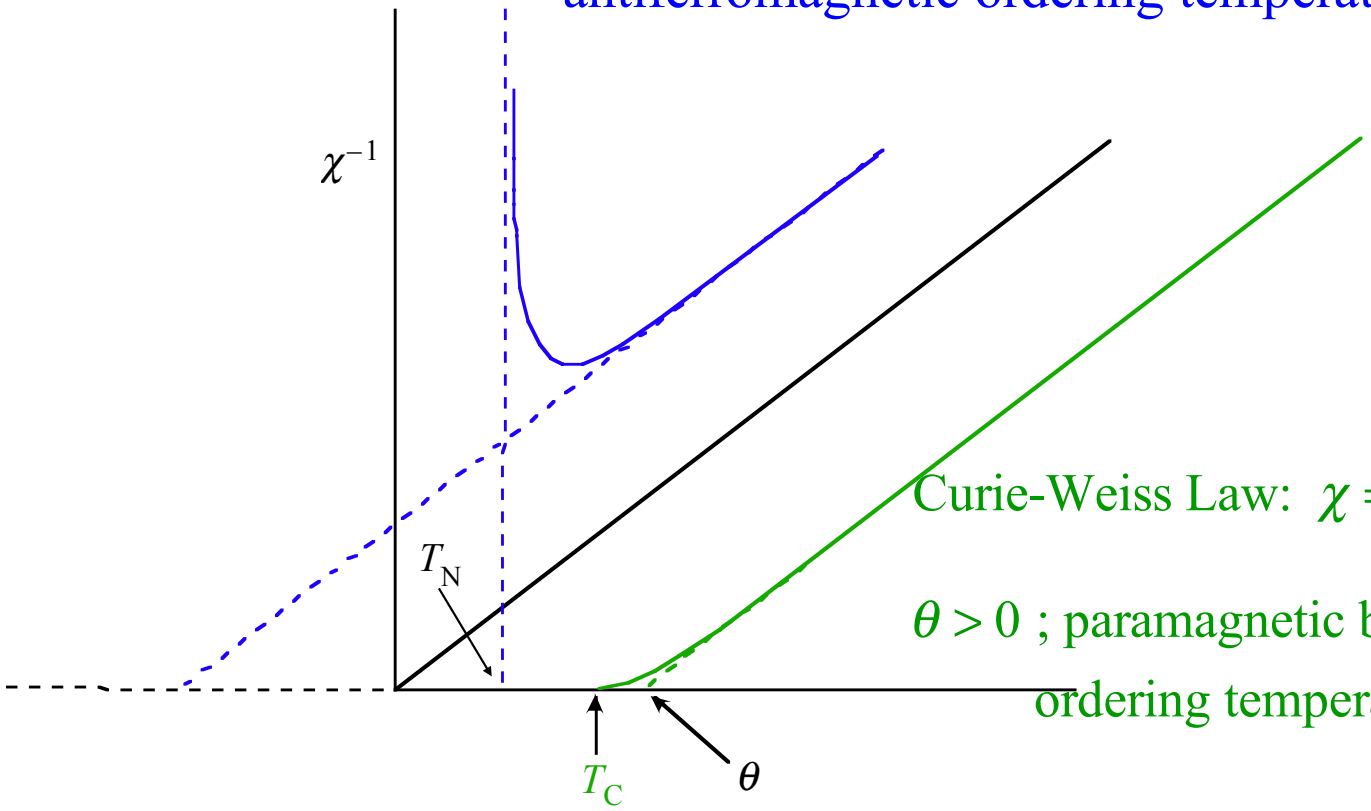


Spin states are determined by varying ligand field strengths in axial and equatorial ligands – see if you can discern trends.



Non-ideal Paramagnets: Curie-Weiss Law: $\chi = \dfrac{C}{T-\theta}$

$\theta < 0$; paramagnetic behavior well above antiferromagnetic ordering temperature (T_N)



Curie-Weiss Law: $\chi = \dfrac{C}{T-\theta}$; $\chi^{-1} = \left(\dfrac{1}{C}\right)T - \left(\dfrac{\theta}{C}\right)$

$\theta > 0$; paramagnetic behavior well above ferromagnetic ordering temperature (T_C). Applies only for $T > \theta$.

Curie Law: $\chi = \dfrac{C}{T}$; $\chi^{-1} = \left(\dfrac{1}{C}\right)T$

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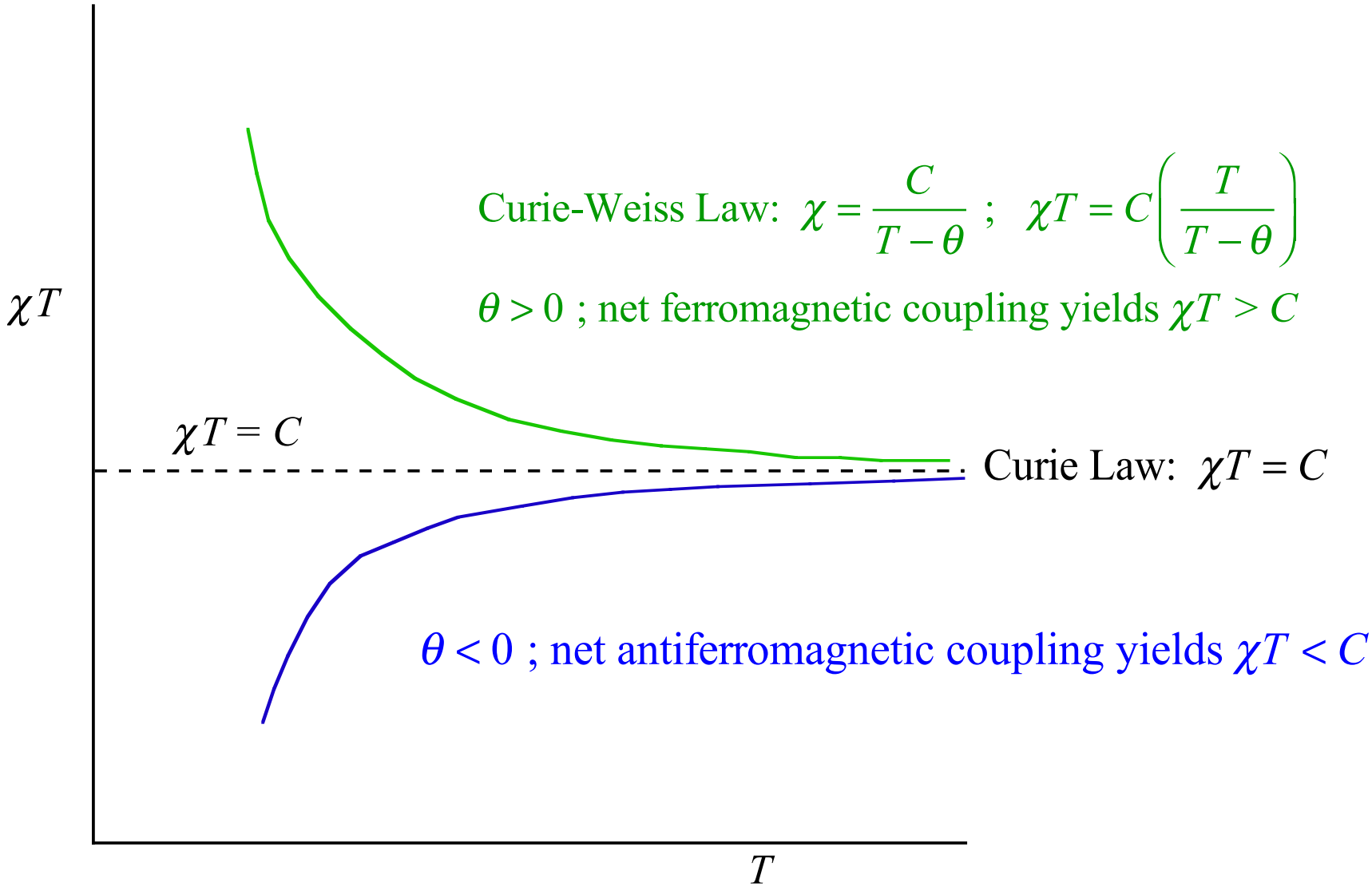
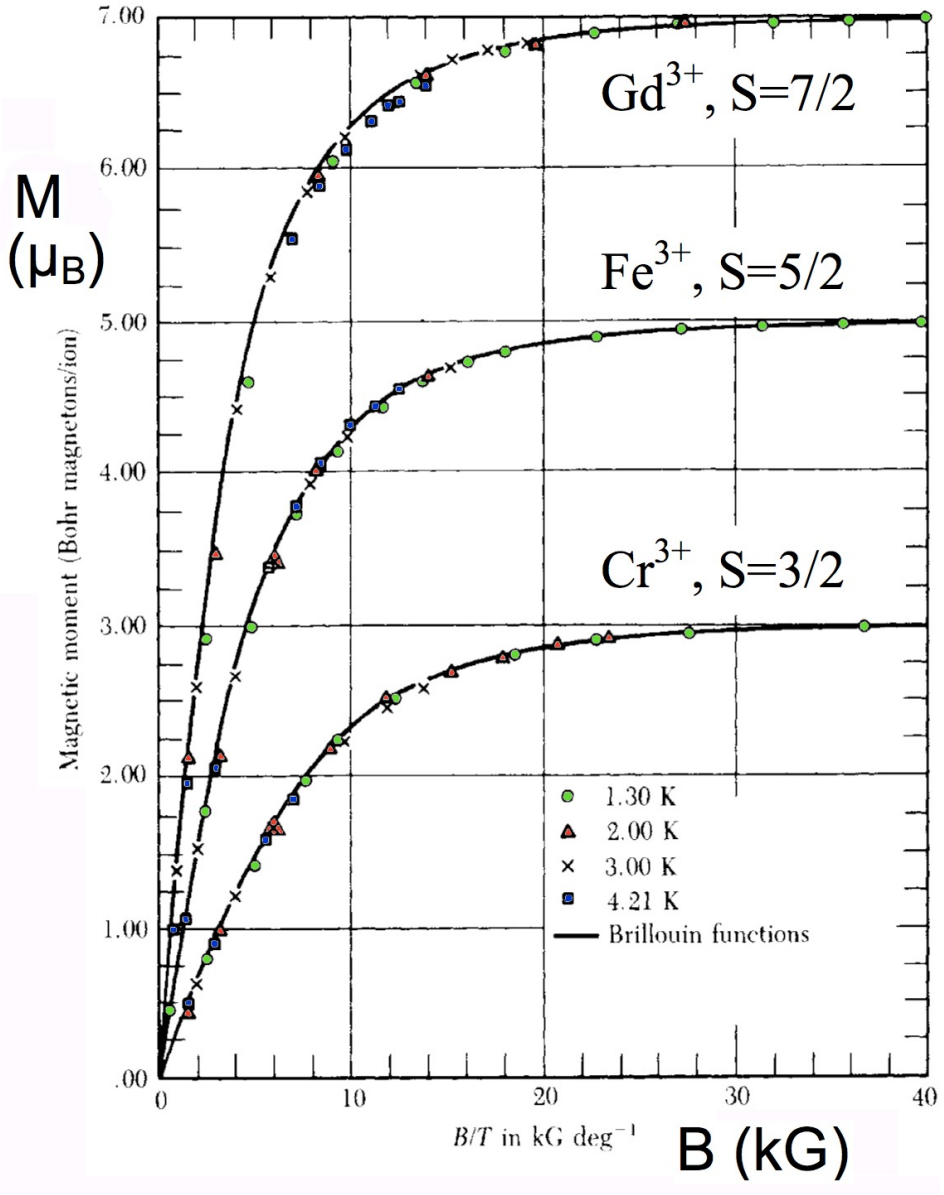
Non-ideal Paramagnets; Molecular Systems



22

Paramagnet Saturation: $\mu_B H > k_B T$

Orchard, p. 49 & section 3.10



$$\bar{\mu} = \frac{\sum_{M_J=-J}^{J} \mu_{M_J} e^{-E_{M_J}/k_B T}}{\sum_{M_J=-J}^{J} e^{-E_{M_J}/k_B T}} = \frac{\sum_{M_J=-J}^{J} M_J g_J \mu_B e^{M_J g_J \mu_B H/k_B T}}{\sum_{M_J=-J}^{J} e^{M_J g_J \mu_B H/k_B T}}$$

$$\text{Let } x = \frac{g_J \mu_B H}{k_B T} \quad ; \quad \text{then} \quad \bar{\mu} = g_J \mu_B \frac{d}{dx} \ln\left(\sum_{M_J=-J}^{J} e^{M_J x} \right)$$

$$\sum_{M_J=-J}^{J} e^{M_J x} = e^{Jx} \sum_{M_J=-2J}^{0} e^{M_J x} = e^{Jx} \sum_{M_J=0}^{2J} e^{-M_J x} = e^{Jx} \left(\sum_{M_J=0}^{\infty} \left(e^{-x}\right)^{M_J} - \sum_{M_J=2J+1}^{\infty} \left(e^{-x}\right)^{M_J} \right)$$

$$= e^{Jx} \left(\sum_{M_J=0}^{\infty} \left(e^{-x}\right)^{M_J} - \left(e^{-x}\right)^{2J+1} \sum_{M_J=0}^{\infty} \left(e^{-x}\right)^{M_J} \right) =$$

$$e^{Jx}\left(1 - e^{-(2J+1)x}\right) \sum_{M_J=0}^{\infty} \left(e^{-x}\right)^{M_J} = \left(\frac{e^{Jx} - e^{-(J+1)x}}{1 - e^{-x}} \right)$$

$$= \frac{e^{(2J+1)x/2} - e^{-(2J+1)x/2}}{e^{x/2} - e^{-x/2}} = \frac{\sinh \frac{(2J+1)x}{2}}{\sinh \frac{x}{2}} \quad \Rightarrow \bar{\mu} = g_J \mu_B \frac{d}{dx} \ln \left(\frac{\sinh \frac{(2J+1)x}{2}}{\sinh \frac{x}{2}} \right)$$

$$\bar{\mu} = g_J \mu_B J B_J(y) \quad ; \quad y = J \frac{g_J \mu_B H}{k_B T}$$

$$B_J(y) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} y - \frac{1}{2J} \coth \frac{y}{2J}$$

$$\coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}} \to 1 \text{ as } x \to \infty$$

$B_J(y) \to 1$ as $y \to \infty$ Brillouin Functions

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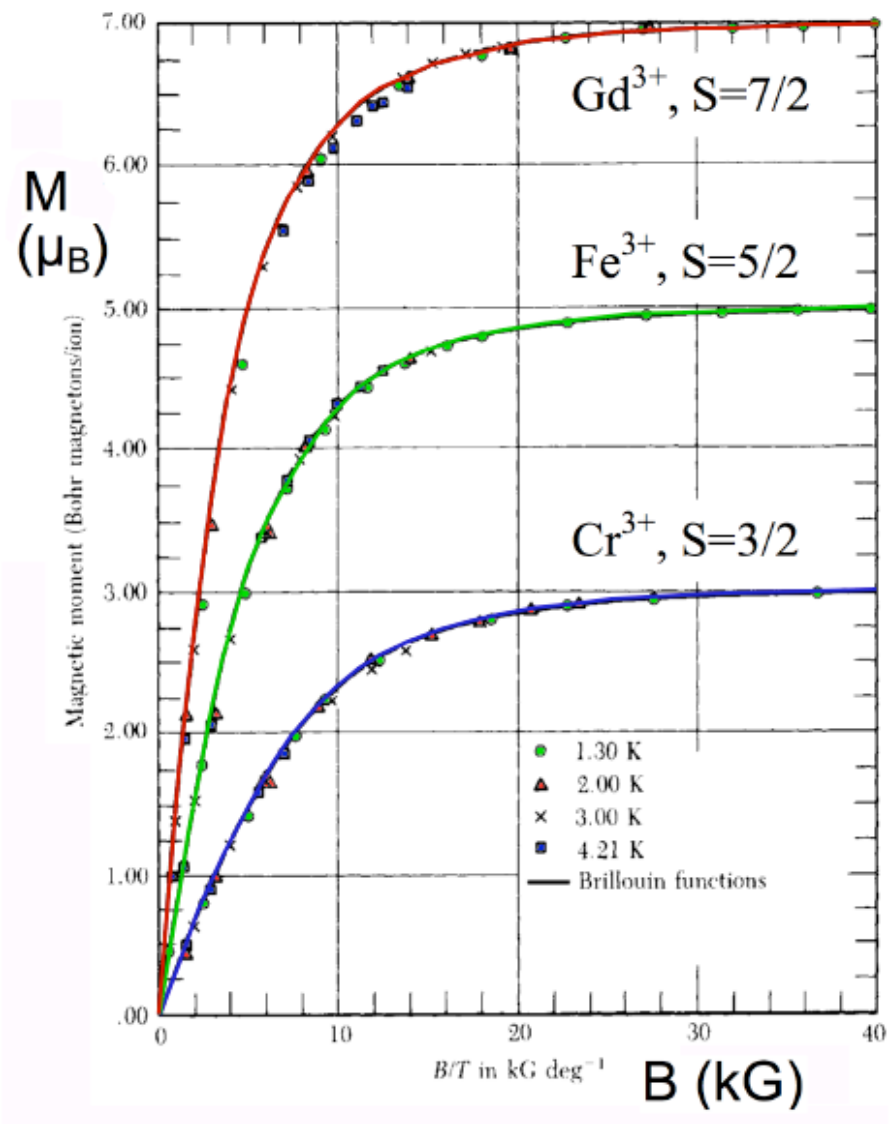
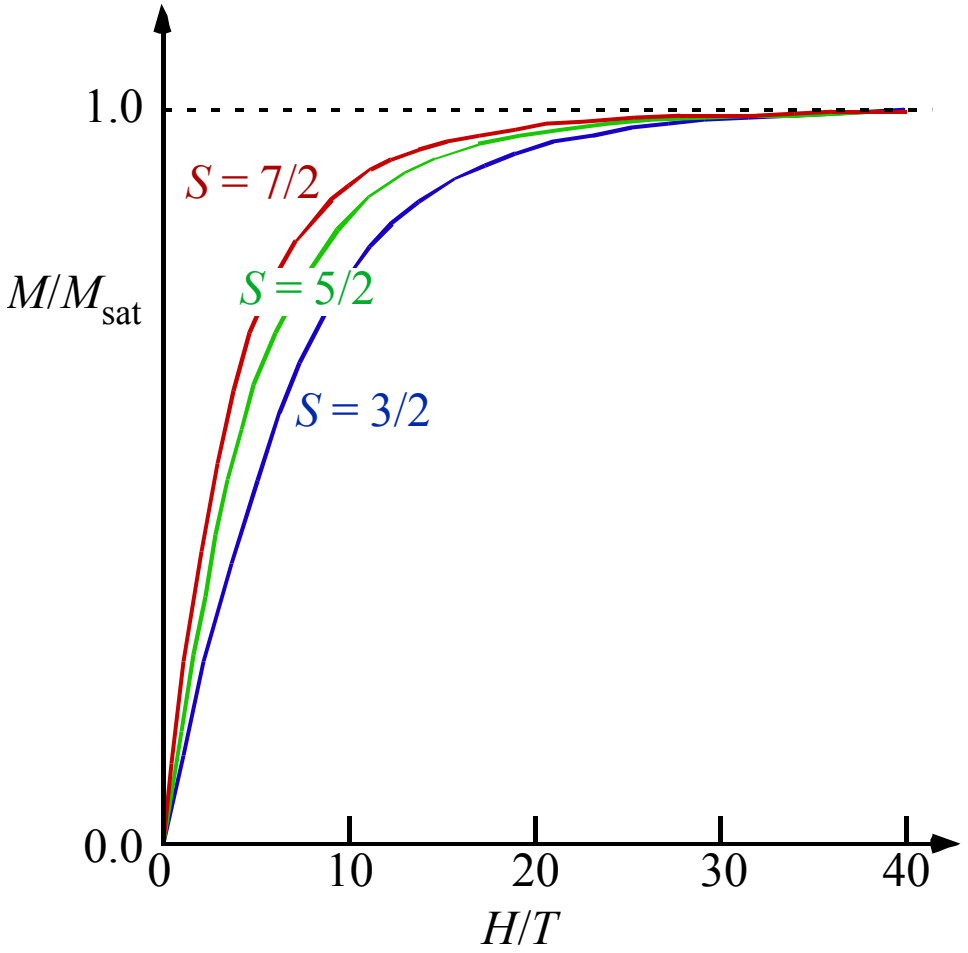
Paramagnet Saturation: $\mu_B H > k_B T$

Orchard, section 3.10



Scaled saturation curves



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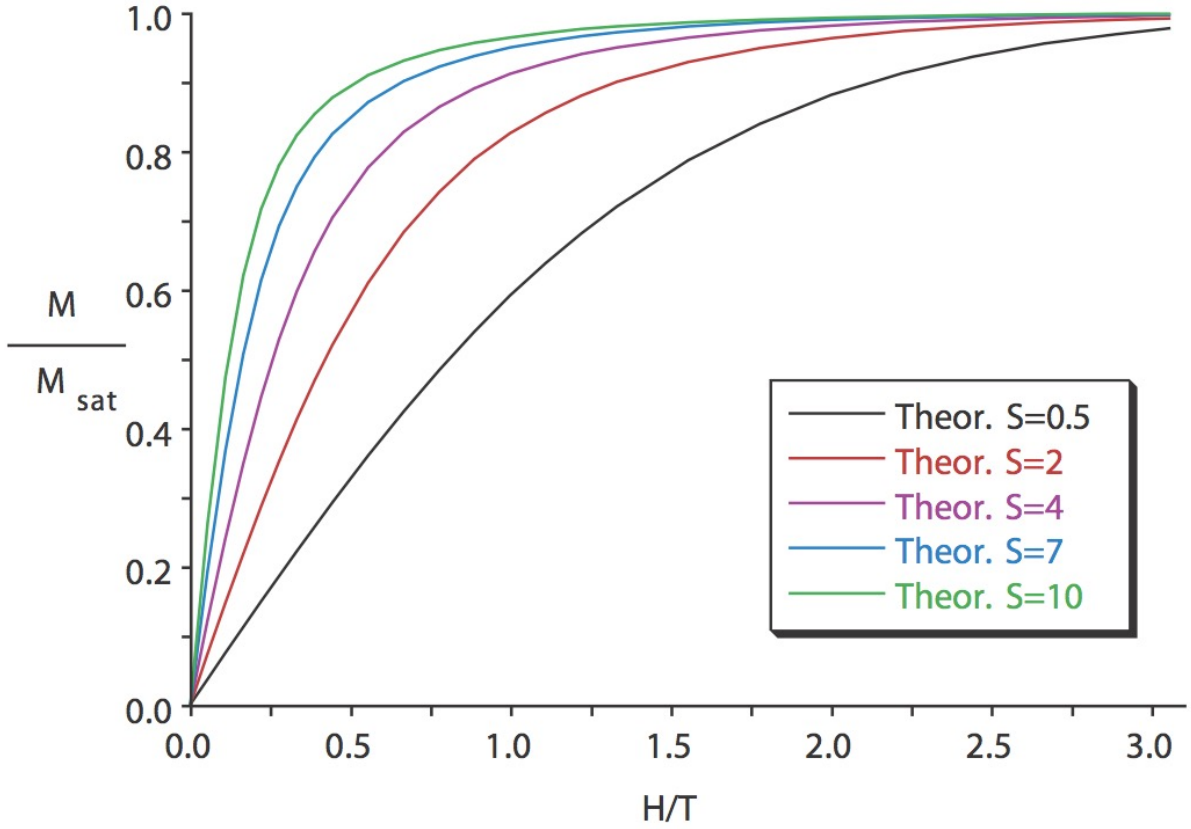
Saturation Measurements to identify Spin States

The Brillouin functions have a characteristic shape for each *J* (or *S* for spin-only cases).

When magnetic ion concentrations or *g*-values are not known, the saturation measurements can yield J (or S) for near-ideal Curie-Law systems.

Saturation measurements are only useful for getting the low-T moment and only if the system if nearly ideal (i.e., molecular, *noninteracting*, moments)



$$\bar{\mu} = g_J \mu_B J B_J(y) \;\; ; \;\; y = \frac{J g_J \mu_B H}{k_B T}$$

$$B_J(y) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} y - \frac{1}{2J} \coth \frac{y}{2J}$$

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Origins of Curie Law Deviations

- The Weiss constant, θ, incorporates the effects of intermolecular/interionic magnetic coupling above the ordering temperatures of ferro-, antiferro-, and ferrimagnets.
- There are several sources of non-Curie Law behavior that have an *intramolecular* origin.

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Origins of Curie Law Deviations

- The simplest deviation: $g \neq g_e$. This doesn't alter the temperature dependence, but it does alter the computed value of *S*. The correct value of *g* to use is: $g^2 = {}^1/_3(g_x^2 + g_y^2 + g_z^2)$
- Temperature-independent (Van Vleck) paramagnetism (TIP). To more carefully discuss the origin of this kind of case, we'll need to use the Generalized Treatment of Susceptibility - see below!
- Another kind of T-independent paramagnetism arises from the conduction electrons in metals (Pauli paramagnetism).
- Zero Field Splitting and first-order orbital effects.
- Temperature variations due to coupling *within* a

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Magnetism of Ln^{3+} Complexes

○ $n_{eff} = g_J[J(J+1)]^{\frac{1}{2}}$

■ $n_{eff} = [4S(S+1) + L(L+1)]^{\frac{1}{2}}$

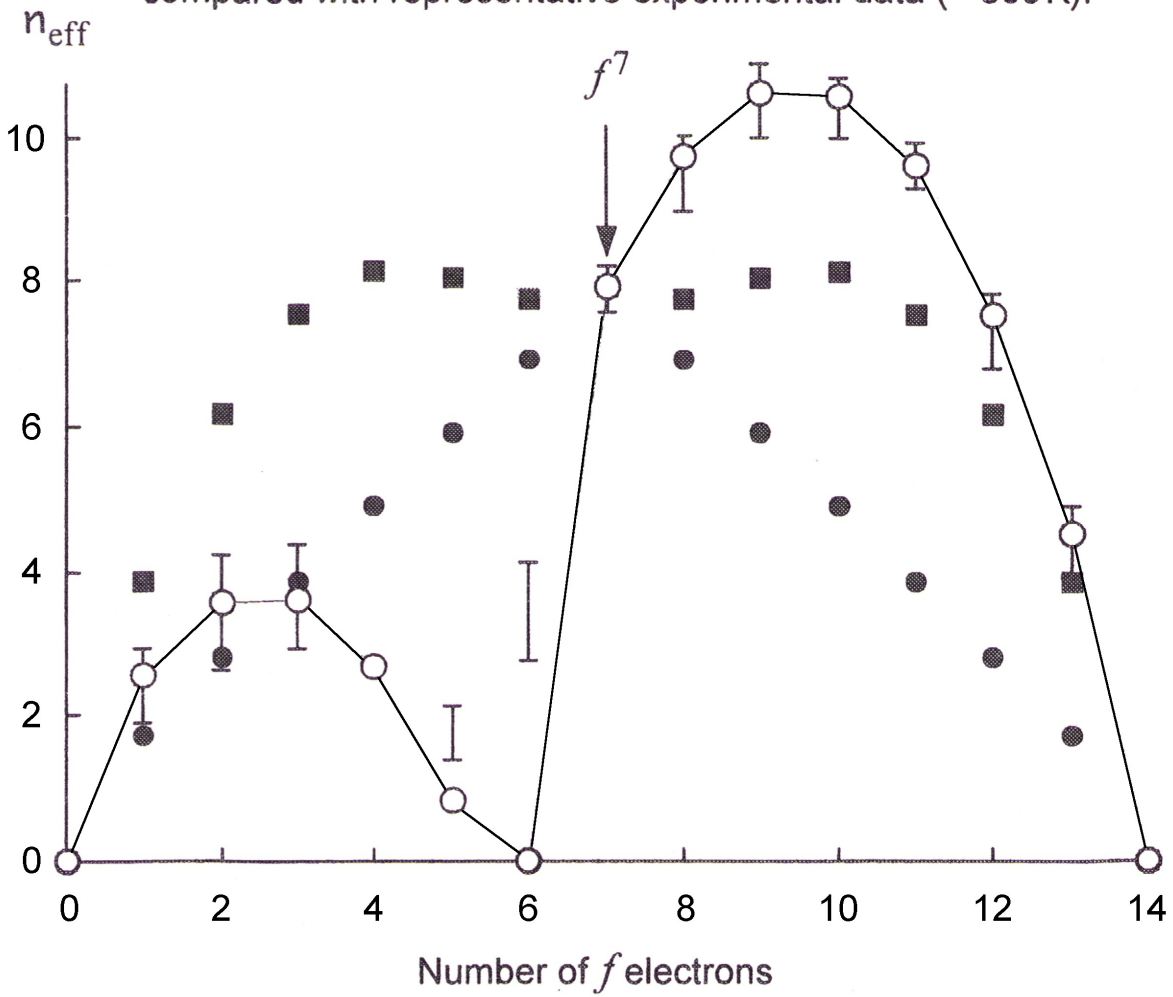
● $n_{eff} = 2[S(S+1)]^{\frac{1}{2}}$

I – the error bar defines the range of experimental values of n_{eff} at about 300 K. [Much of the variation is due to *crystal field effects*, as explained in section (5).]

The asymmetry of the ○ plot reflects *multiplet inversion.*
[See NB (J) of § 2.5(4).]

The symmetry about $N = 7$ of the other two plots is consequent upon the *hole theorem.*
[See NB (H) of § 2.4(3).]

Fig. 4.9 Simple estimates of n_{eff} for Ln^{3+} ions $4f^N$ compared with representative experimental data (~ 300 K).



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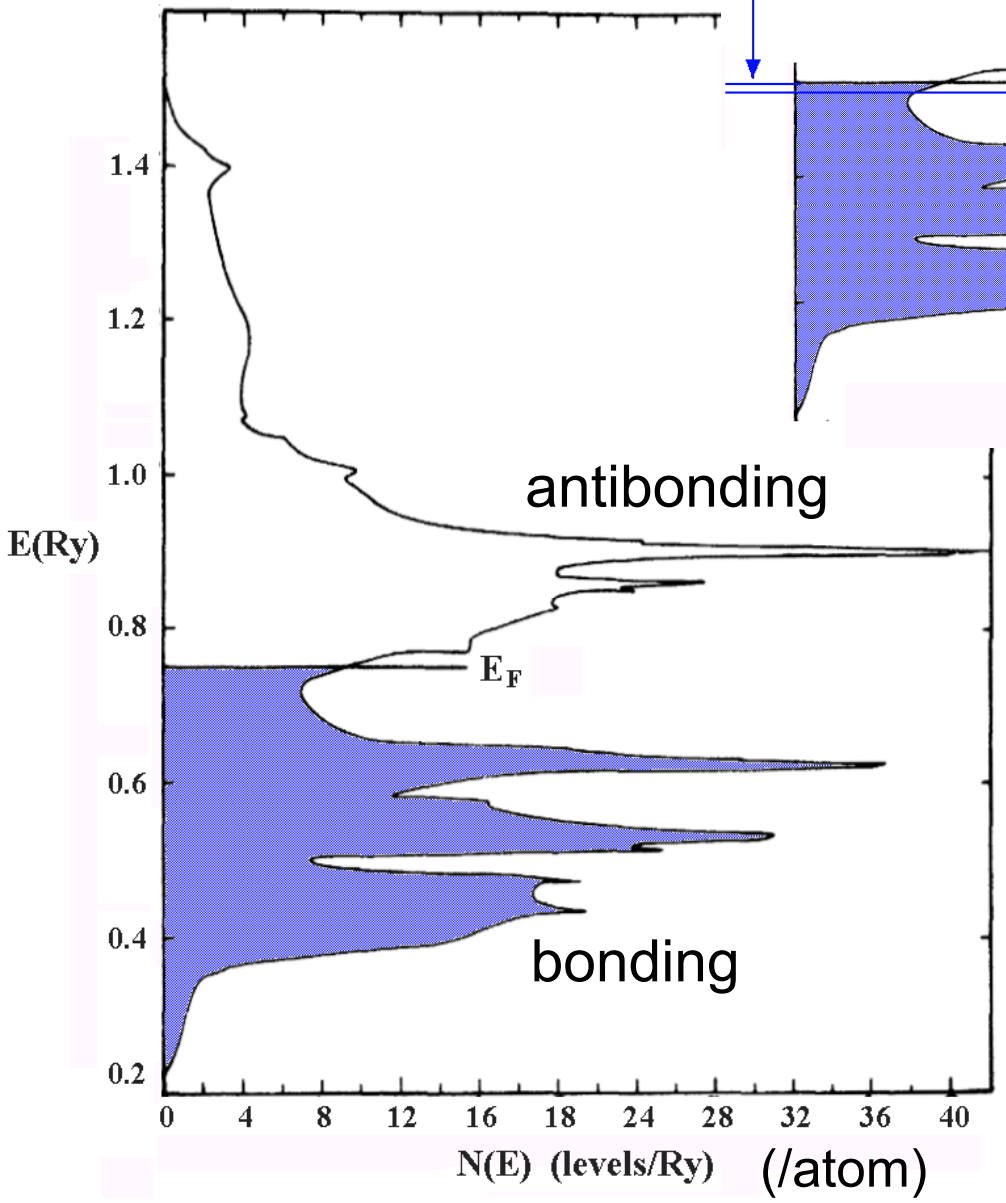
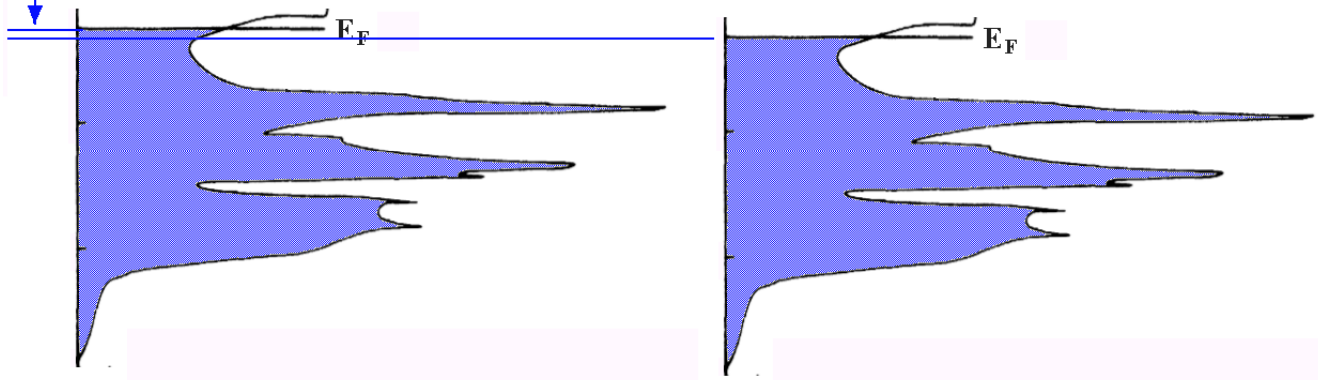
Pauli Paramagnetism

Valence electron DOS for Mo.



$\mu_B H$



$\chi = \mu_B^2 N(E_F)$

The Zeeman interaction introduces a *small* difference in up- and down-spin populations.

D. D. Koelling, F. M. Mueller, A. J. Arko, J. B. Ketterson, *Phys. Rev. B,* **1974,** *10,* 4889

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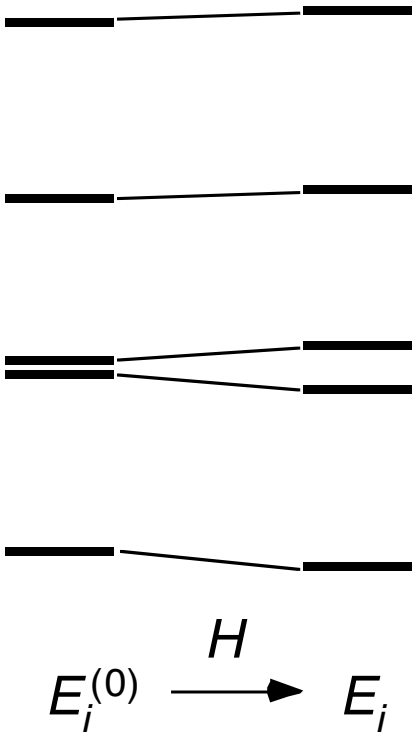

Generalized Treatment of Susceptibility (Van Vleck)

- Energy shifts are generally small compared to spacings between levels (except for degeneracies).

$$M = \frac{N\sum_i \mu_i e^{-E_i/k_BT}}{\sum_i e^{-E_i/k_BT}}$$

Perturbation expansion:

$$e^{-E_i/k_BT} = e^{-E_i^{(0)}/k_BT} e^{-(E_i^{(1)}H + E_i^{(2)}H^2 + \cdots)/k_BT} \simeq e^{-E_i^{(0)}/k_BT}\left(1 - \frac{E_i^{(1)}H}{k_BT}\right)$$

$$E_i = E_i^{(0)} + E_i^{(1)}H + E_i^{(2)}H^2 + \cdots$$

$$\left(E_i = -\boldsymbol{\mu}_i \bullet \mathbf{H}\right) \Rightarrow \mu_i = -\frac{\partial E_i}{\partial H}$$

$$\mu_i \simeq E_i^{(1)} + 2E_i^{(2)}H$$

$$M \simeq \frac{N\sum_i \left(E_i^{(1)} + 2E_i^{(2)}H\right)\left(1 - \frac{E_i^{(1)}H}{k_BT}\right)e^{-E_i^{(0)}/k_BT}}{\sum_i \left(1 - \frac{E_i^{(1)}H}{k_BT}\right)e^{-E_i^{(0)}/k_BT}} \quad (1)$$

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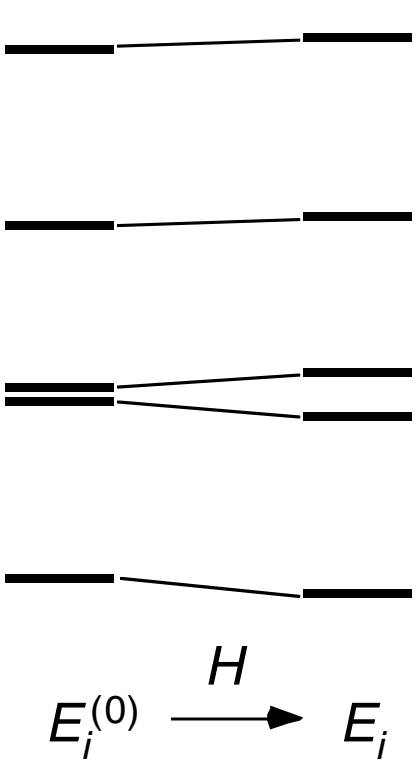

Generalized Treatment of Susceptibility (Van Vleck)

If a material is not magnetically ordered, it will have no permanent magnetization. Therefore, $M_{H=0} = 0$.

$$M_{H=0} = \frac{N\sum_i E_i^{(1)} e^{-E_i^{(0)}/k_BT}}{\sum_i e^{-E_i^{(0)}/k_BT}} = 0 \; ; \quad \therefore \text{ numerator} = 0$$

Using this and expanding equation (1) to terms linear in H: $M \simeq \dfrac{N\sum_i \left(\dfrac{\left(E_i^{(1)}\right)^2}{k_BT} - 2E_i^{(2)} \right) e^{-E_i^{(0)}/k_BT}}{\sum_i e^{-E_i^{(0)}/k_BT}} H$; and finally, since $\chi = \dfrac{\partial M}{\partial H}$,

$E_i^{(1)}$ and $E_i^{(2)}$ are obtained from perturbation theory.

$$\chi = \frac{N\sum_i \left(\dfrac{\left(E_i^{(1)}\right)^2}{k_BT} - 2E_i^{(2)} \right) e^{-E_i^{(0)}/k_BT}}{\sum_i e^{-E_i^{(0)}/k_BT}} \qquad (2)$$

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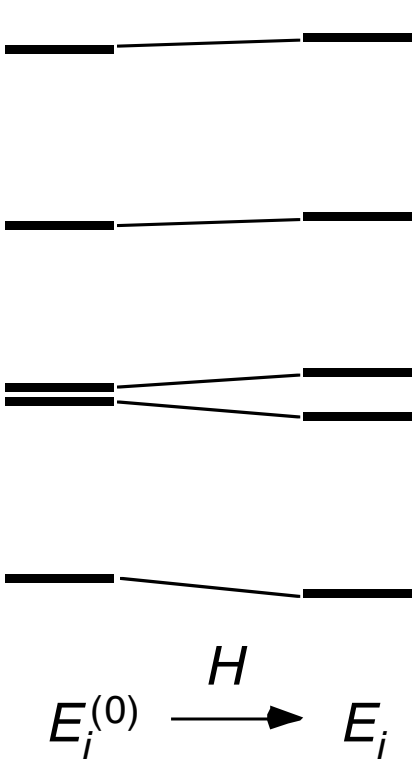
Generalized Treatment of Susceptibility (Van Vleck)



$$\chi = \frac{N\sum_i \left(\frac{\left(E_i^{(1)}\right)^2}{k_B T} - 2E_i^{(2)} \right) e^{-E_i^{(0)}/k_B T}}{\sum_i e^{-E_i^{(0)}/k_B T}} \qquad (2)$$

$E_i^{(1)}$ and $E_i^{(2)}$ are obtained from perturbation theory.

$$E_i^{(1)} = \left\langle \Psi_i^{(0)} \middle| \mathcal{H}_{\text{Zeeman}} \middle| \Psi_i^{(0)} \right\rangle = \mu_B H \left\langle \Psi_i^{(0)} \middle| L_z + 2S_z \middle| \Psi_i^{(0)} \right\rangle$$

$$E_i^{(2)} = \sum_{n \neq i} \frac{\left\langle \Psi_i^{(0)} \middle| \mathcal{H}_{\text{Zeeman}} \middle| \Psi_n^{(0)} \right\rangle \left\langle \Psi_n^{(0)} \middle| \mathcal{H}_{\text{Zeeman}} \middle| \Psi_i^{(0)} \right\rangle}{E_n^{(0)} - E_i^{(0)}} = \sum_{n \neq i} \frac{\left| \left\langle \Psi_i^{(0)} \middle| L_z + 2S_z \middle| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_i^{(0)}}$$

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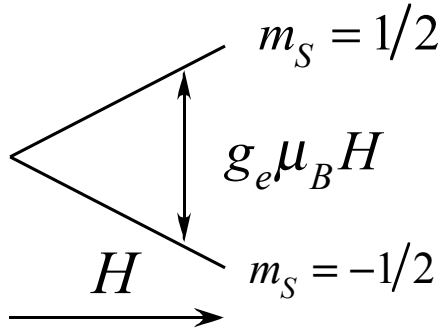
Curie's Law from the Van Vleck Formula

The Van Vleck formalism can be used to derive Curie's Law; just retain the leading term in the numerator of eqn. (2):

$$\chi = \frac{N\sum_i \left(\frac{\left(E_i^{(1)}\right)^2}{k_B T} - 2E_i^{(2)} \right) e^{-E_i^{(0)}/k_B T}}{\sum_i e^{-E_i^{(0)}/k_B T}} \simeq \frac{N\sum_i \left(\frac{\left(E_i^{(1)}\right)^2}{k_B T} \right) e^{-E_i^{(0)}/k_B T}}{\sum_i e^{-E_i^{(0)}/k_B T}}$$



Now, $E_i = E_i^{(0)} + E_i^{(1)} H$, where $E_i^{(1)} = g M_S \mu_B$

$$\left(\begin{array}{c} \sum_{-S}^{S}(1) = 2S+1 \\ \sum_{-S}^{S} x^2 = \frac{1}{3}S(S+1)(2S+1) \end{array} \right)$$

$$\chi = \frac{N\sum_i \left(\frac{\left(E_i^{(1)}\right)^2}{k_B T} \right) e^{-E_i^{(0)}/k_B T}}{\sum_i e^{-E_i^{(0)}/k_B T}} = \frac{Ng^2\mu_B^2 \sum_i \left(\sum_{M_S=-S}^{S} \frac{\left(M_S\right)^2}{k_B T} \right) e^{-E_i^{(0)}/k_B T}}{\sum_i \left(\sum_{M_S=-S}^{S} (1) \right) e^{-E_i^{(0)}/k_B T}} = \frac{Ng^2\mu_B^2 S(S+1)}{3k_B T}$$

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Temperature Independent (Van Vleck) Paramagnetism (TIP)

- TIP is significant when the ground state is diamagnetic ($E_i^{(0)} = 0$), but there are many paramagnetic excited states with energies substantially greater than $k_B T$ ($E_n^{(0)} - E_0^{(0)} >> k_B T$), but still not *too* high in energy.
- Only the second-order Zeeman mixing of excited states into the ground state (by the field) makes an appreciable contribution. Use of eqn. (2) shows the *T*-independence:

diamagnetic ground state: $\mu_B H \left\langle \Psi_i^{(0)} \middle| L_z + 2S_z \middle| \Psi_i^{(0)} \right\rangle = 0$

$$\chi = \frac{N \sum_i \left(\frac{\left(E_i^{(1)}\right)^2}{k_B T} - 2E_i^{(2)} \right) e^{-E_i^{(0)}/k_B T}}{\sum_i e^{-E_i^{(0)}/k_B T}} \sim \frac{N E_0^{(2)}}{\sum_i e^{-E_i^{(0)}/k_B T}} \quad ; \quad E_0^{(2)} = \sum_{n \neq i} \frac{\left| \left\langle \Psi_0^{(0)} \middle| \mathcal{H}_{\text{Zeeman}} \middle| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_0^{(0)}}$$

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Examples: T-independent effects

Diamagnetic susceptibilities

ion	χ_m * (10^{-6} cm^3 mol^{-1})
Li^+	– 0.6
Na^+	– 5
K^+	– 13
Cs^+	– 31

compound	χ_m † (10^{-6} cm^3 mol^{-1})
$Li_2[CrO_4]$	+20.7
$Na_2[CrO_4]$	+15.4
$K_2[CrO_4]$	–3.6
$Cs_2[CrO_4]$	–51.7
$K[MnO_4]$	+27.8
$Cs[MnO_4]$	+3.5

Notes:

†The values given in the table at right are from *Orchard* (p. 81), divided by $4\pi \times 10^{-6}$ to convert them to cgs units. See p. 6 for more. *From Selwood.

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Empirical Corrections

Curie-Weiss plus T-independent corrections: $\chi = \chi_0 + \frac{C}{T - \theta}$

- In practice, a fit of the χ data including a *T*-independent term, χ_0, is often included to account for diamagnetism and TIP empirically ($\chi_0 = \chi_{dia} + \chi_{TIP}$).

WARNING: empirical corrections like this can be dangerous when used indiscriminately! The magnitude of the correction has to be sensible (and small!). Furthermore, since neither χ_{dia} nor χ_{TIP} is dependent on field, the *H*-dependence of the data should be checked!

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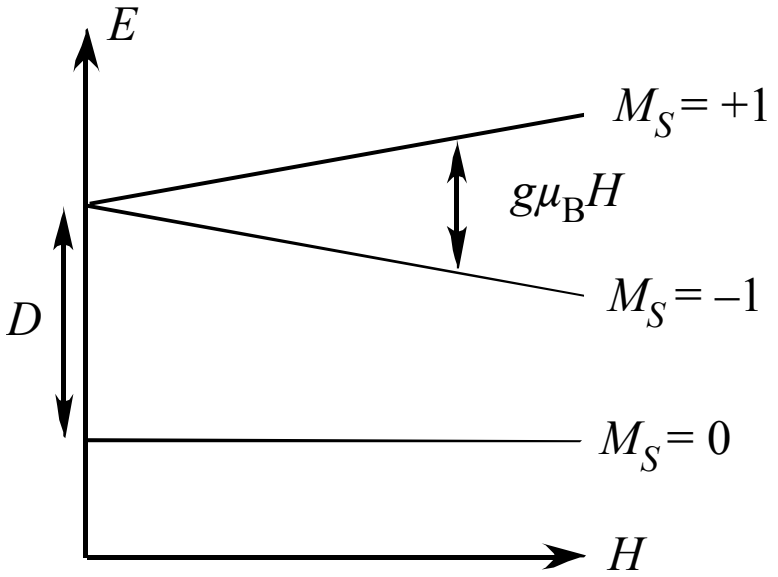
ZFS: Effect on Susceptibility



$$\mathcal{H}_{eff} = \mu_B \mathbf{H} \bullet \mathbf{g} \bullet \hat{\mathbf{S}} + D\left(\hat{S}_z^2 - \frac{S(S+1)}{3}\right)$$

$$E_i = E_i^{(0)} + E_i^{(1)} H + E_i^{(2)} H^2 + \cdots$$

Bearing in mind the definitions of the terms that go into Van Vleck's formula ($E_i^{(2)} = 0$) :

$E_0^{(0)} = 0$; $E_0^{(1)} = 0$

$E_{\pm 1}^{(0)} = D$

$E_{\pm 1}^{(1)} = \pm g M_S \mu_B$

$$\chi = \frac{N\sum_i \frac{\left(E_i^{(1)}\right)^2}{k_B T} e^{-E_i^{(0)}/k_B T}}{\sum_i e^{-E_i^{(0)}/k_B T}} = N\frac{0 + \frac{\left(g\mu_B\right)^2}{k_B T} e^{-D/k_B T} + \frac{\left(-g\mu_B\right)^2}{k_B T} e^{-D/k_B T}}{1 + 2e^{-D/k_B T}} = N\frac{8\mu_B{}^2}{k_B T}\frac{e^{-D/k_B T}}{\left(1 + 2e^{-D/k_B T}\right)}$$

CAUTION: $e^{-(E_i^{(1)}H + E_i^{(2)}H^2 + \cdots)/k_B T} \simeq 1 - \frac{E_i^{(1)} H}{k_B T}$ actually only applies when $k_B T \gg E_i^{(1)} H$

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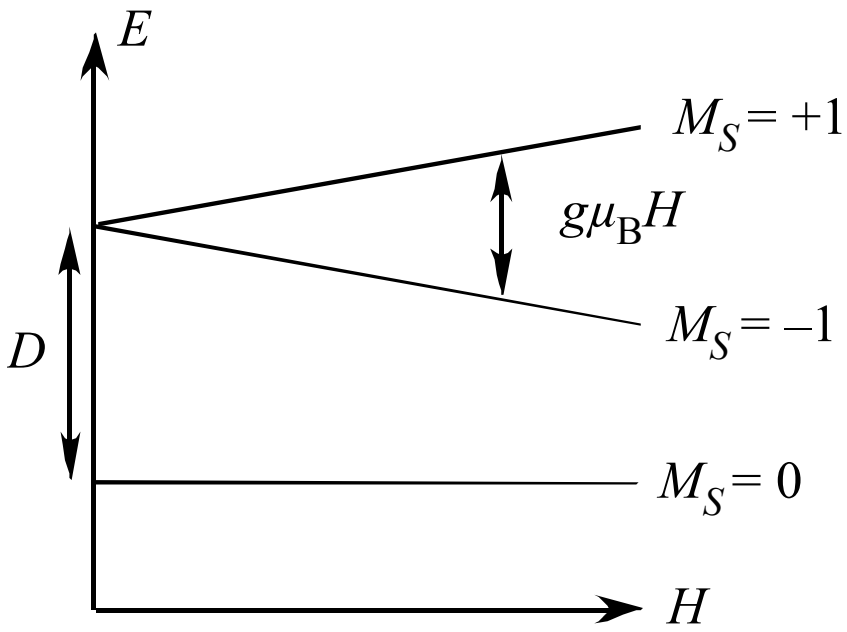
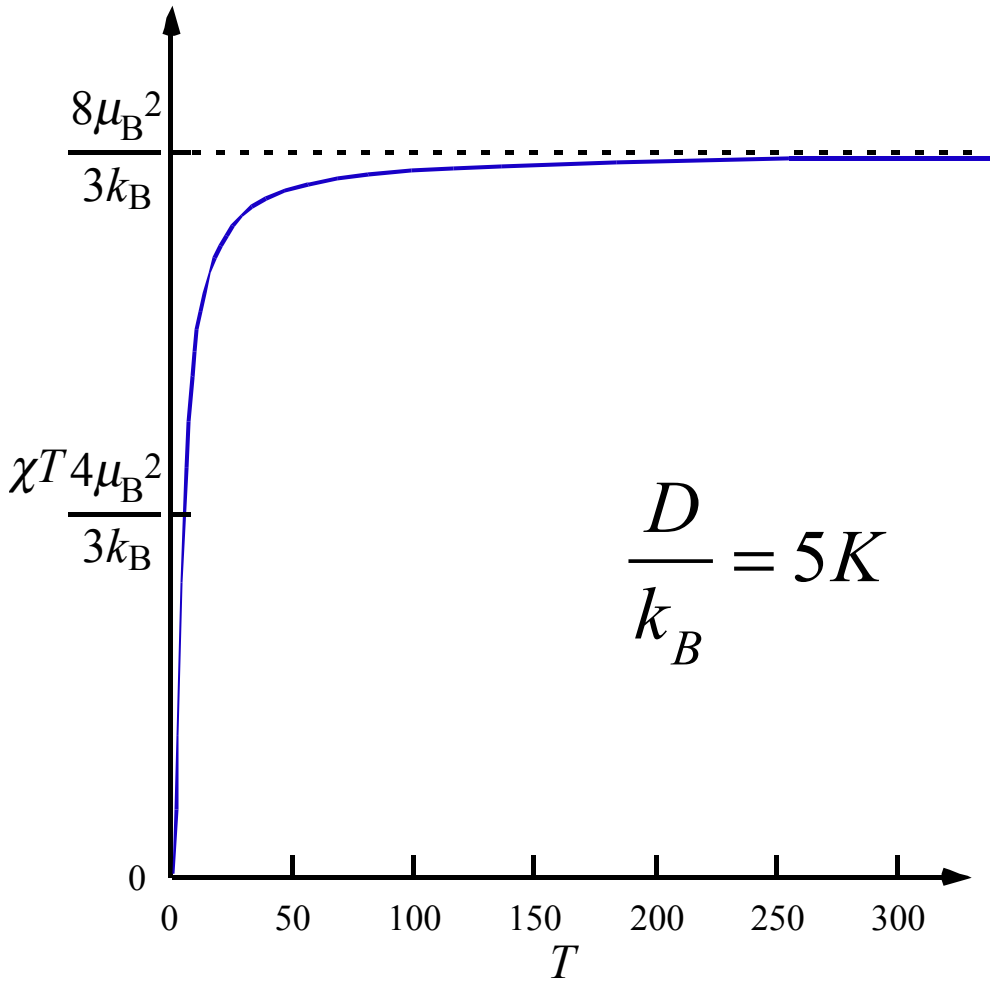
ZFS: Effect on Susceptibility





$$\chi = N\frac{8\mu_B^{\ 2}}{k_B T}\frac{e^{-D/k_B T}}{\left(1+2e^{-D/k_B T}\right)}$$

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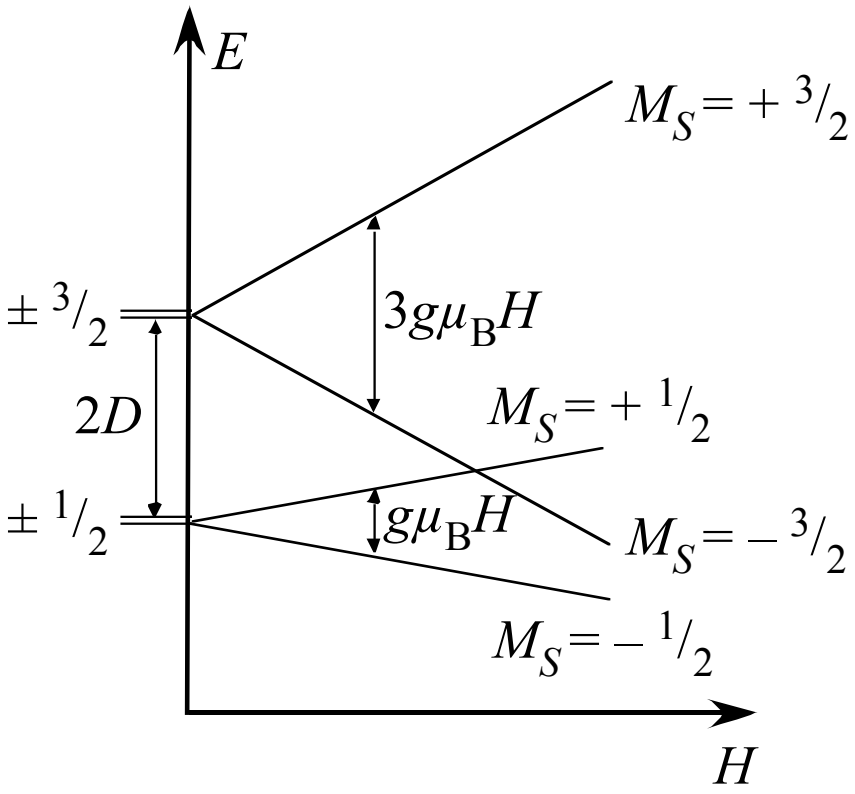
Cr^{3+} ZFS: S = 3/2



$$E_i = E_i^{(0)} + E_i^{(1)} H + E_i^{(2)} H^2 + \cdots$$

Bearing in mind the definitions of the terms that go into Van Vleck's formula ($E_i^{(2)} = 0$) :

$E^{(0)}_{\pm 1/2} = 0$; $E^{(1)}_{\pm 1/2} = \pm\,^1/_2 g M_S \mu_B$

$E^{(0)}_{\pm 3/2} = 2D$

$E^{(1)}_{\pm 3/2} = \pm\,^3/_2 g M_S \mu_B$

$$\chi = \frac{N\sum_i \left(E_i^{(1)}\right)^2 e^{-E_i^{(0)}/k_B T}}{k_B T \sum_i e^{-E_i^{(0)}/k_B T}}$$

$$\chi = N\frac{\left(\frac{1}{2}g\mu_B\right)^2 + \left(-\frac{1}{2}g\mu_B\right)^2 + \left[\left(\frac{3}{2}g\mu_B\right)^2 + \left(-\frac{3}{2}g\mu_B\right)^2\right]e^{-2D/k_B T}}{k_B T\left(2 + 2e^{-2D/k_B T}\right)} = N\frac{\mu_B{}^2}{k_B T}\frac{1 + 9e^{-2D/k_B T}}{\left(1 + e^{-2D/k_B T}\right)}$$

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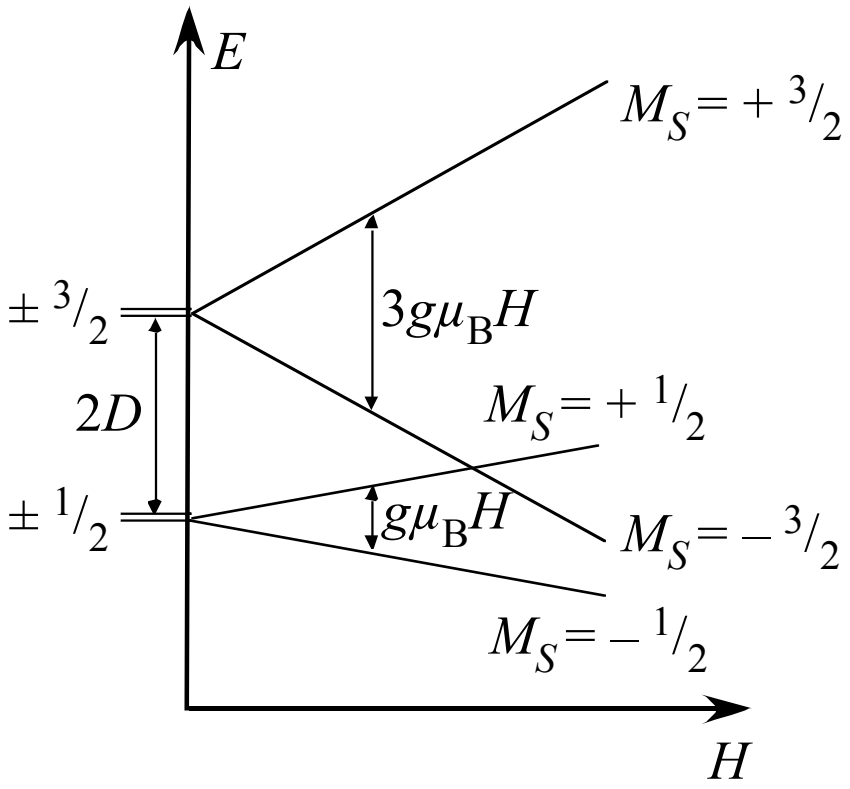
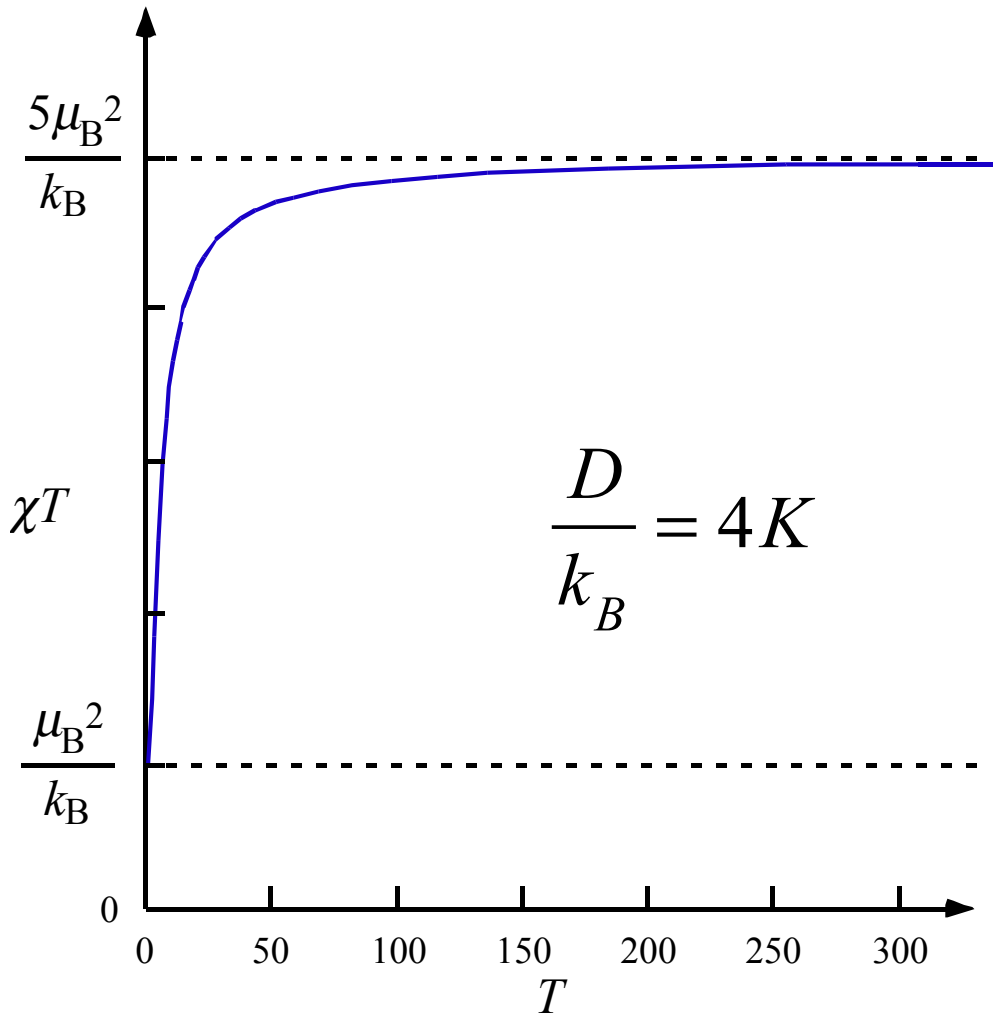
ZFS: S = 3/2





$$\chi = N\frac{\mu_B^{\,2}}{k_B T}\frac{1+9e^{-2D/k_B T}}{\left(1+e^{-2D/k_B T}\right)}$$

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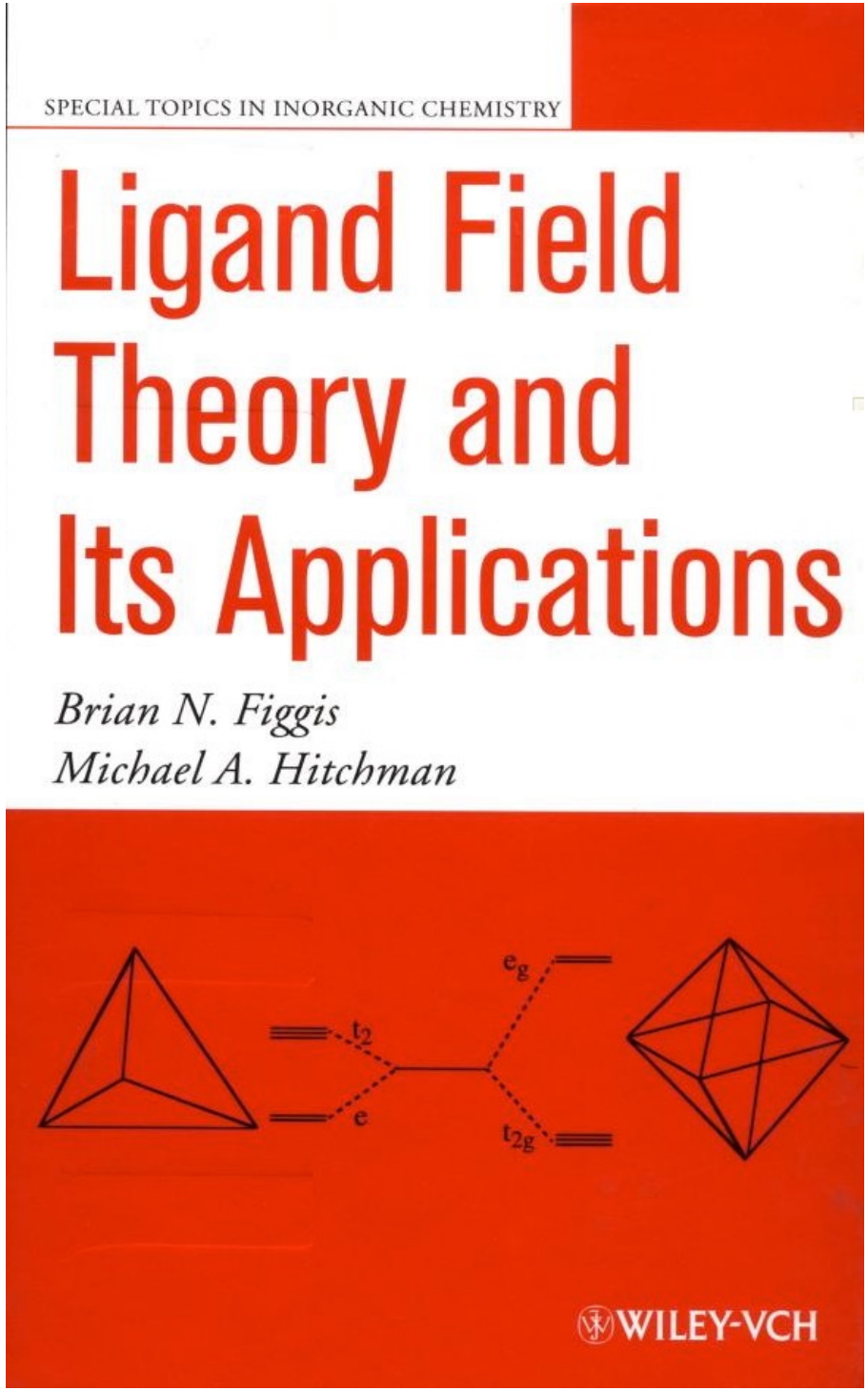
Some Room-temperature Effects

Table 5.20 m_{eff} values (/μ_B) at *ca.* 300 K for some tetrahedral complexes of Co(II) d^7 – ground state $^4A_2$ $(e)^4(t_2)^3$ – compared with the orbital splitting Δ_t (in cm^{-1}). $

	m_{eff}	Δ_t		m_{eff}	Δ_t
$[Co(NCS)_4]^{2-}$	4.36 – 4.53	4550	$[CoCl_4]^{2-}$	4.66 – 4.80	3130
$[Co(NCO)_4]^{2-}$	4.38	4150	$[CoBr_4]^{2-}$	4.80 – 4.87	2850
$[Co(N_3)_4]^{2-}$	4.47	3920	$[CoI_4]^{2-}$	4.87 – 5.01	2650
$[Co(SPh)_4]^{2-}$	4.50	3870			

The spin-only value of m_{eff} is 3.88 μ_B.
m_{eff} varies considerably with counter-cation.

- In tetrahedral complexes with some tetragonal distortion (due to an asymmetric environment) ZFS can significant affect the susceptibility.
- For Co(II), ζ is significant (ca. 530 cm^{-1}) and Δ_t isn't very large; mixing of the excited states ~ ζ^2/Δ_t, so anisotropy gives *relatively* large ZFS



Orbital Angular momentum

- In some cases, orbital contributions to magnetism can be quite large.
- This occurs orbitally degenerate states so competition with J-T distortions makes the actual observations variable.
- Well-known plots including orbital contributions to magnetism are found in

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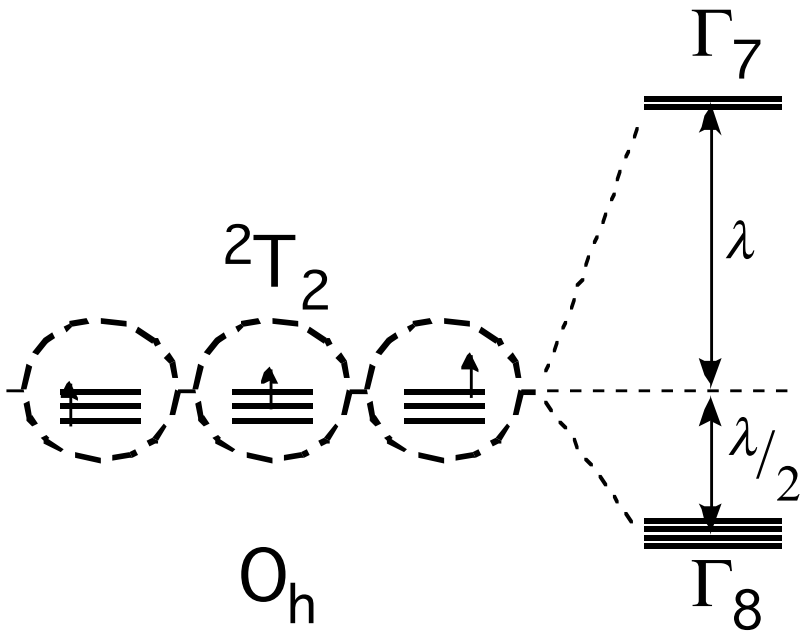
First-Order Spin-Orbit Coupling in T-states, Ti^{III} example; symmetry aspects



No JT-Distortion assumed

$$\chi(C_\alpha) = \frac{\sin(J+1/2)\alpha}{\sin\alpha/2}$$

O'	E	R	$8C_3$	$8RC_3$	$6(3C_2+3RC_2)$ $(=C_4^2+RC_4^2)$	$6C_4$	$6RC_4$	$12(6C_2'+6RC_2')$		
A_1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	1	1	−1	−1	−1		
E	2	2	−1	−1	2	0	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	3	0	0	−1	1	1	−1	(R_x, R_y, R_z); (x, y, z)	
T_2	3	3	0	0	−1	−1	−1	1		(xy, xz, yz)
Γ_6	2	−2	1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	0	$=\Gamma_{1/2}$	
Γ_7	2	−2	1	−1	0	$-\sqrt{2}$	$\sqrt{2}$	0		
Γ_8	4	−4	−1	1	0	0	0	0	$=\Gamma_{3/2}$	

$$T_2 \otimes \Gamma_{1/2} = \Gamma_7 \oplus \Gamma_8$$

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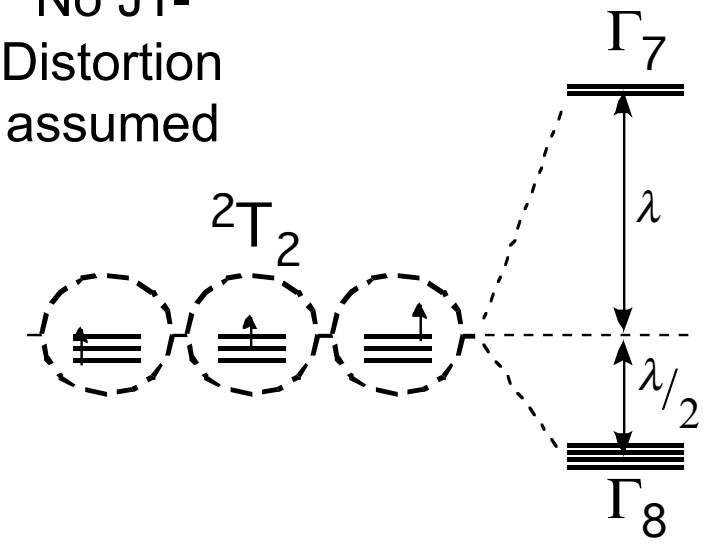
First-Order Spin-Orbit Coupling in T-states, Ti^{III} example; set up

No JT-Distortion assumed



For the $\left(t_{2g}\right)^1$ configuration, there are 6 spin-orbitals:

$$\begin{aligned}
\Psi_1 &\quad \left|d_{xy}\alpha\right\rangle \quad \tfrac{1}{\sqrt{2}}\left[\left|2\alpha\right\rangle - \left|-2\alpha\right\rangle\right] \\
\Psi_2 &\quad \left|-1\beta\right\rangle \\
\Psi_3 &\quad \left|d_{xy}\beta\right\rangle \quad \tfrac{1}{\sqrt{2}}\left[\left|2\beta\right\rangle - \left|-2\beta\right\rangle\right] \\
\Psi_4 &\quad \left|1\alpha\right\rangle \\
\Psi_5 &\quad \left|1\beta\right\rangle \\
\Psi_6 &\quad \left|-1\alpha\right\rangle
\end{aligned}$$

To evaluate the matrix elements involving these basis functions, we need:

$$\begin{aligned}
\lambda\mathbf{L}\cdot\mathbf{S}\Psi_1 &= -\tfrac{\lambda}{\sqrt{2}}\Psi_2 + \left|d_{x^2-y^2}\alpha\right\rangle \\
\lambda\mathbf{L}\cdot\mathbf{S}\Psi_2 &= \lambda\left[\left|-2\alpha\right\rangle + \tfrac{1}{2}\Psi_2\right] \\
\lambda\mathbf{L}\cdot\mathbf{S}\Psi_3 &= \tfrac{\lambda}{\sqrt{2}}\Psi_4 + \left|d_{x^2-y^2}\alpha\right\rangle \\
\lambda\mathbf{L}\cdot\mathbf{S}\Psi_4 &= \lambda\left[\left|2\beta\right\rangle + \tfrac{1}{2}\Psi_4\right] \\
\lambda\mathbf{L}\cdot\mathbf{S}\Psi_5 &= -\tfrac{\lambda}{2}\Psi_5 \\
\lambda\mathbf{L}\cdot\mathbf{S}\Psi_6 &= -\tfrac{\lambda}{2}\Psi_6
\end{aligned}$$

The spin-orbit perturbation is evaluated in the basis of these six functions

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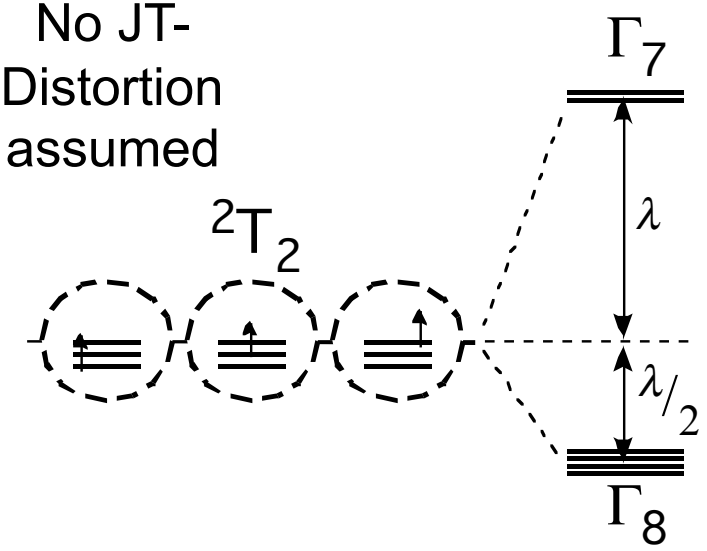
First-Order Spin-Orbit Coupling in T-states, Ti^{III} example; secular equation

No JT-Distortion assumed



For the $\left(t_{2g}\right)^1$ configuration, there are 6 spin-orbitals:

Ψ_1	$\left\|d_{xy}\alpha\right\rangle$	$\frac{1}{\sqrt{2}}\left[\left\|2\alpha\right\rangle-\left\|-2\alpha\right\rangle\right]$
Ψ_2		$\left\|-1\beta\right\rangle$
Ψ_3	$\left\|d_{xy}\beta\right\rangle$	$\frac{1}{\sqrt{2}}\left[\left\|2\beta\right\rangle-\left\|-2\beta\right\rangle\right]$
Ψ_4		$\left\|1\alpha\right\rangle$
Ψ_5		$\left\|1\beta\right\rangle$
Ψ_6		$\left\|-1\alpha\right\rangle$

Secular Equation:

$$\begin{array}{c|cccccc} & \Psi_1 & \Psi_2 & \Psi_3 & \Psi_4 & \Psi_5 & \Psi_6 \\ \Psi_1 & 0-E & -\lambda/\sqrt{2} & & & & \\ \Psi_2 & -\lambda/\sqrt{2} & \lambda/2-E & & & & \\ \Psi_3 & & & 0-E & \lambda/\sqrt{2} & & \\ \Psi_4 & & & \lambda/\sqrt{2} & \lambda/2-E & & \\ \Psi_5 & & & & & -\lambda/2-E & 0 \\ \Psi_6 & & 0 & & & 0 & -\lambda/2-E \end{array} = 0$$

The spin-orbit perturbation is evaluated in the basis of these six functions

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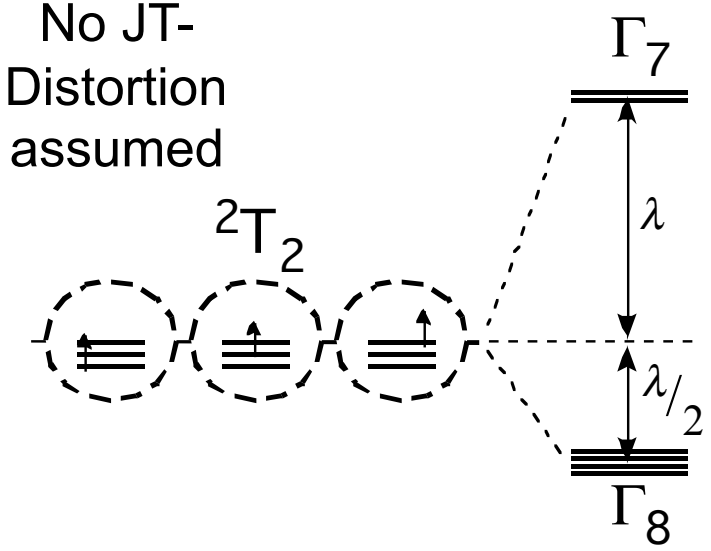
1st-Order S-O Coupling in T-states, Ti^{III} example; solutions, magnetic moments



Eigenvalues and eigenfunctions, magnetic moments

$E=+\lambda$	$\Phi_1=$	$\frac{1}{\sqrt{3}}\left[\Psi_1-\sqrt{2}\Psi_2\right]$	$-\mu_B$
2-fold degenerate	$\Phi_2=$	$\frac{1}{\sqrt{3}}\left[\Psi_3+\sqrt{2}\Psi_4\right]$	μ_B
	$\Phi_3=$	$\frac{1}{\sqrt{3}}\left[\sqrt{2}\Psi_1+\Psi_2\right]$	0
$E=-\lambda/2$	$\Phi_4=$	$\frac{1}{\sqrt{3}}\left[\sqrt{2}\Psi_3-\Psi_4\right]$	0
4-fold degenerate	$\Phi_5=$	$\Psi_5=\lvert 1\beta\rangle$	0
	$\Phi_6=$	$\Psi_6=\lvert -1\alpha\rangle$	0

Example calculations of Magnetic Moments: $M_z=\mu_B\left(L_z+2S_z\right)$

$$\left\langle\Phi_5\middle|M_z\middle|\Phi_5\right\rangle=\mu_B\left\langle 1\beta\middle|L_z+2S_z\middle|1\beta\right\rangle=\mu_B\left[1+2\bullet\tfrac{-1}{2}\right]=0$$

$$\left\langle\Phi_1\middle|M_z\middle|\Phi_1\right\rangle=2\mu_B\left\langle\Phi_1\middle|L_z+2S_z\middle|\Phi_1\right\rangle=\frac{2\mu_B}{3}\left\langle\Psi_1-\sqrt{2}\Psi_2\middle|L_z+2S_z\middle|\Psi_1-\sqrt{2}\Psi_2\right\rangle$$

$$=\frac{\mu_B}{3}\left\langle\Psi_1\middle|L_z+2S_z\middle|\Psi_1\right\rangle+\frac{2\mu_B}{3}\left\langle\Psi_2\middle|L_z+2S_z\middle|\Psi_2\right\rangle=$$

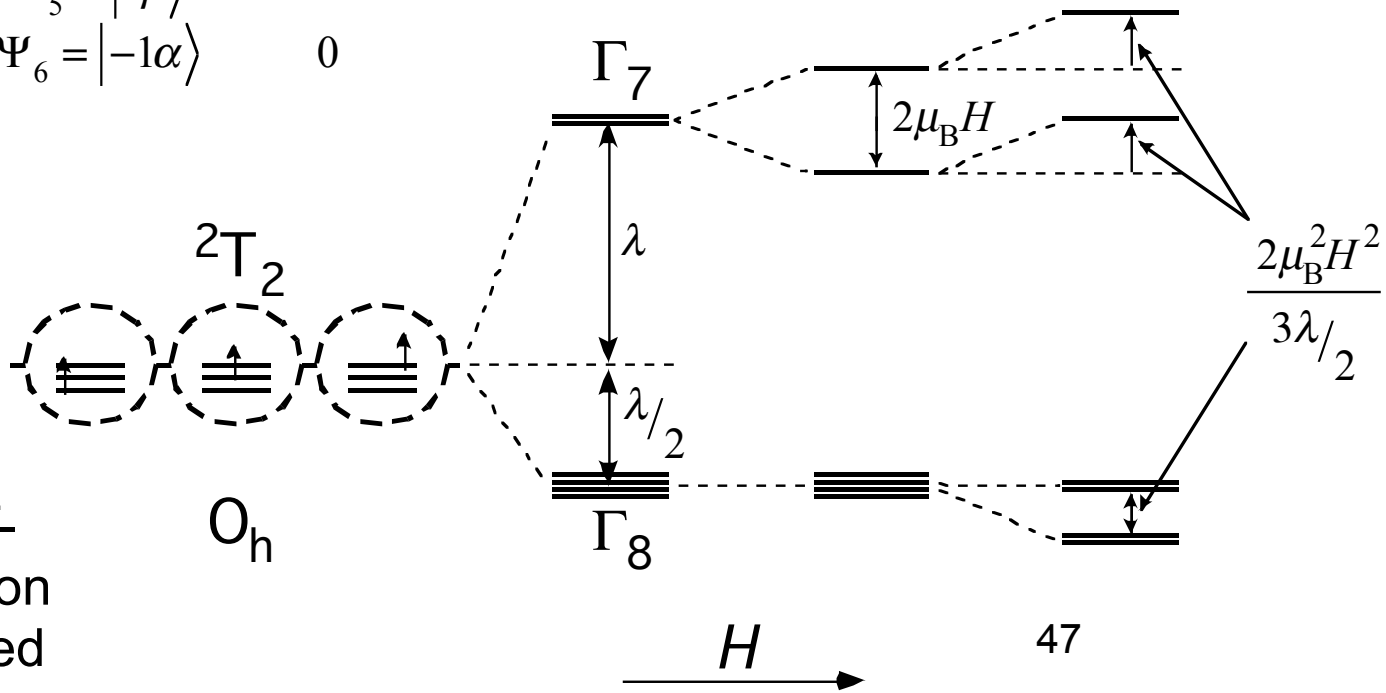
$$=\frac{\mu_B}{6}\left\langle 2\alpha\middle|L_z+2S_z\middle|2\alpha\right\rangle+\frac{\mu_B}{6}\left\langle -2\alpha\middle|L_z+2S_z\middle|-2\alpha\right\rangle+\frac{2\mu_B}{3}\left\langle -1\beta\middle|L_z+2S_z\middle|-1\beta\right\rangle=$$

$$\frac{\mu_B}{6}\left[2+2\bullet\tfrac{1}{2}-2+2\bullet\tfrac{1}{2}\right]+\frac{2\mu_B}{3}\left[-1+2\bullet\tfrac{-1}{2}\right]=\frac{2\mu_B}{6}+\frac{2\mu_B}{3}(-2)=-\mu_B$$

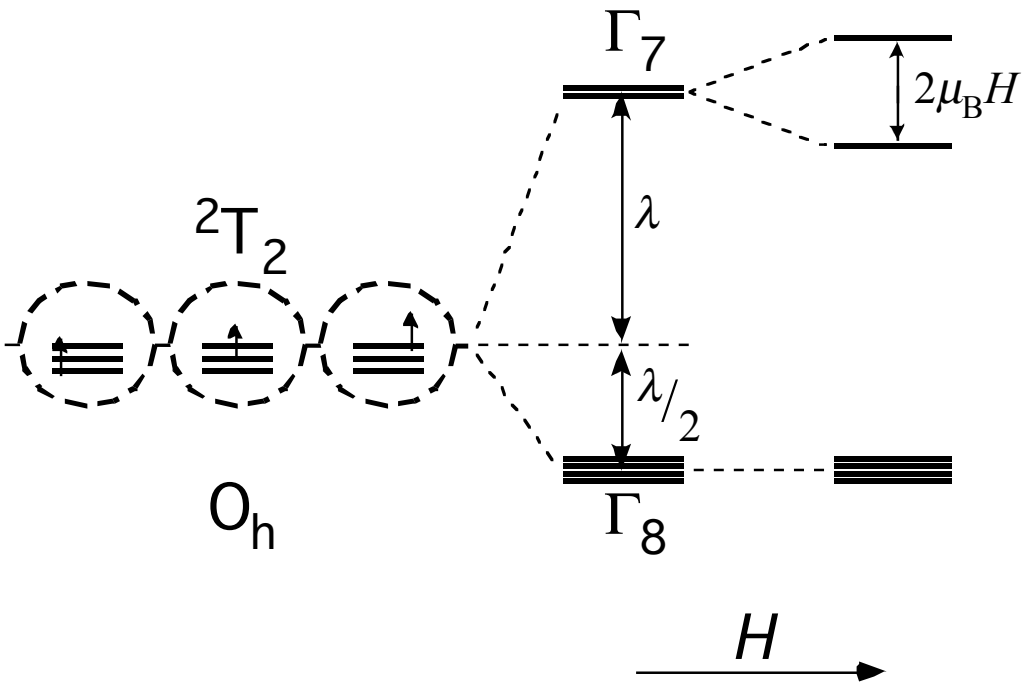
1st-Order S-O Coupling in T-states, Ti^{III} example; the big picture

Eigenvalues and eigenfunctions, magnetic moments

$E = +\lambda$	$\Phi_1 =$	$\frac{1}{\sqrt{3}}\left[\Psi_1 - \sqrt{2}\Psi_2\right]$	$-\mu_B$
2-fold degenerate	$\Phi_2 =$	$\frac{1}{\sqrt{3}}\left[\Psi_3 + \sqrt{2}\Psi_4\right]$	μ_B
	$\Phi_3 =$	$\frac{1}{\sqrt{3}}\left[\sqrt{2}\Psi_1 + \Psi_2\right]$	0
$E = -\lambda/2$	$\Phi_4 =$	$\frac{1}{\sqrt{3}}\left[\sqrt{2}\Psi_3 - \Psi_4\right]$	0
4-fold degenerate	$\Phi_5 =$	$\Psi_5 = \lvert 1\beta\rangle$	0
	$\Phi_6 =$	$\Psi_6 = \lvert -1\alpha\rangle$	0



Ti^{3+}: S.O. coupling



$$E_i = E_i^{(0)} + E_i^{(1)} H + E_i^{(2)} H^2 + \cdots$$

Bearing in mind the definitions of the terms that go into Van Vleck's formula (assume $E_i^{(2)} = 0$) :

$E_{-\lambda/2}^{(0)} = 0$; $E_{-\lambda/2}^{(1)} = 0$

$E_{\lambda}^{(0)} = 3\lambda/2$; $E_{\lambda}^{(1)} = \pm \mu_B$

$$\chi = \frac{N \sum_i \left(E_i^{(1)} \right)^2 e^{-E_i^{(0)}/k_B T}}{k_B T \sum_i e^{-E_i^{(0)}/k_B T}}$$

$$\chi = N \frac{4(0)^2 + \left[(\mu_B)^2 + (-\mu_B)^2 \right] e^{-3\lambda/2k_B T}}{k_B T \left(4 + 2e^{-3\lambda/2k_B T} \right)} = N \frac{{\mu_B}^2}{k_B T} \frac{e^{-3\lambda/2k_B T}}{\left(2 + e^{-3\lambda/2k_B T} \right)}$$

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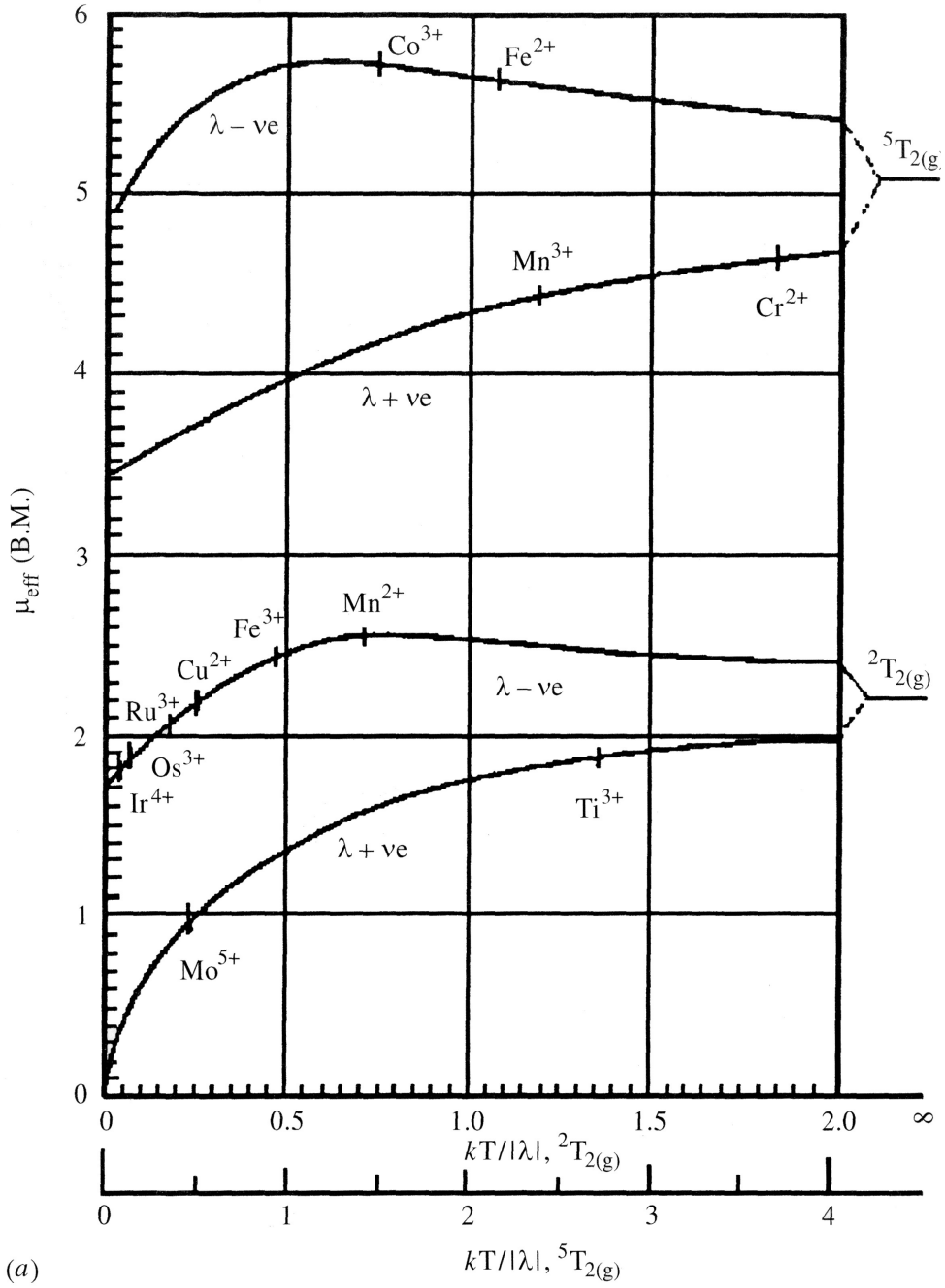
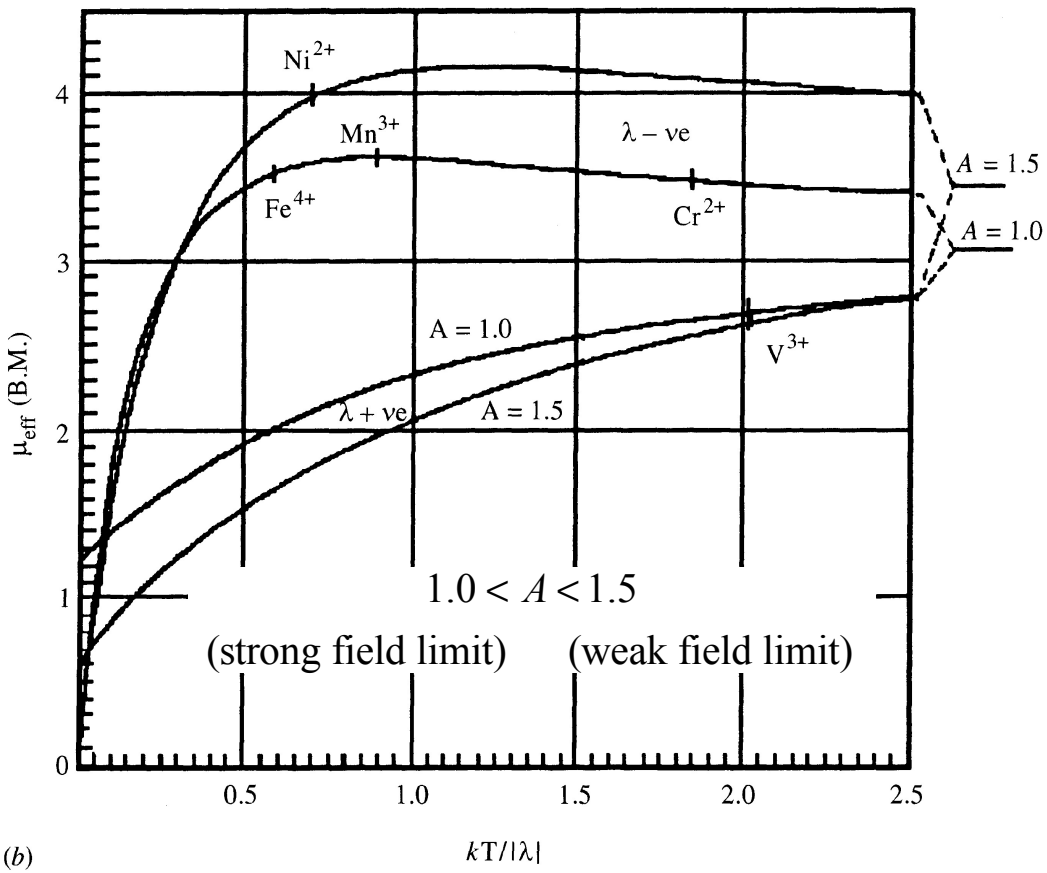
T-terms: Orbital Effects (Max.)





B. N. Figgis, M. A. Hitchman, "Ligand Field Theory and its Applications", Chapter 9.

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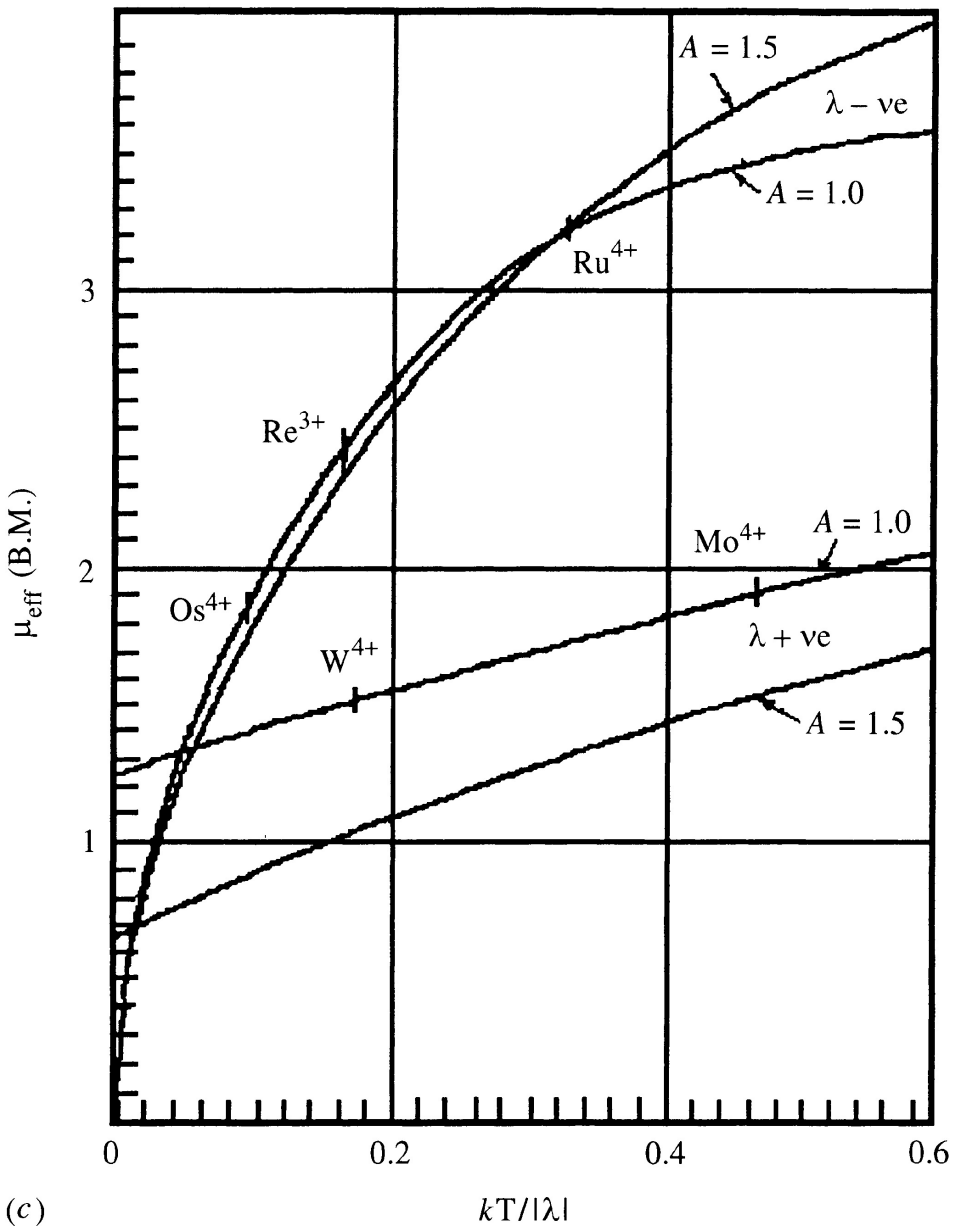
T-terms: Orbital Effects (Max.)



B. N. Figgis, M. A. Hitchman, "Ligand Field Theory and its Applications", Chapter 9.

$$1.0 < A < 1.5$$

(strong field limit) (weak field limit)

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Interactions between Magnetic Ions

- We've been mostly concerned with the way magnetic moments can be altered by the electronic structure within the ion.
- We begin to consider interactions between ions by considering dinuclear systems and the *phenomenological* Heisenberg Dirac-Van Vleck (HDVV) Hamiltonian for coupling:

$$\mathcal{H}_{\mathrm{HDVV}} = -2J\hat{\mathbf{S}}_A \bullet \hat{\mathbf{S}}_B$$

$J > 0$ ferromagnetic *coupling*
$J < 0$ antiferromagnetic *coupling*

- While this reminds us of a form expected for dipole-dipole coupling, remember that a *phenomenological* Hamiltonian is just another name for an *effective* Hamiltonian - we'll worry about where *J* comes from

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Energy Levels from $\mathcal{H}_{\mathrm{HDVV}}$

- Using manipulations similar to those used to treat spin-orbit coupling, we can rewrite $\mathcal{H}_{\mathrm{HDVV}}$:

$$\mathcal{H}_{\mathrm{HDVV}} = -2J\hat{\mathbf{S}}_A \bullet \hat{\mathbf{S}}_B$$

$$\hat{\mathbf{S}}_T = \hat{\mathbf{S}}_A + \hat{\mathbf{S}}_B \;\; ; \;\; \hat{S}_T^2 = \hat{\mathbf{S}}_T \bullet \hat{\mathbf{S}}_T = \hat{S}_A^2 + \hat{S}_B^2 + 2\hat{\mathbf{S}}_A \bullet \hat{\mathbf{S}}_B$$

$$2\hat{\mathbf{S}}_A \bullet \hat{\mathbf{S}}_B = \hat{S}_T^2 - \hat{S}_A^2 - \hat{S}_B^2$$

These are operators!

- The eigenvalues (energies) of $\mathcal{H}_{\mathrm{HDVV}}$ are then:

$$E_n = -J\left[S_T(S_T+1) - S_A(S_A+1) - S_B(S_B+1)\right]$$

These are scalars!

- In general, the coupling strength ($\sim J$) is much smaller than the splittings between the spin-states of the individual ions - which are in turn much greater than $k_B T$. ∴ We can view S_A and S_B as constants and absorb the two last terms into the zero of energy:

$$E_n = -JS_T(S_T+1) \;; \quad \text{energy spacing: } E_n(S_T) - E_n(S_T-1) = -2JS_T$$

Example: Cr^{3+} coupled to Ni^{2+}

- Possible spin states of the coupled system are determined as a vector sum (*formally* like we saw for L-S coupling and S.O. coupling)
- Van Vleck expression can be used to calculate expected susceptibility.

$$S_{Cr^{3+}} = \tfrac{3}{2}\ ;\ S_{Ni^{2+}} = 1$$

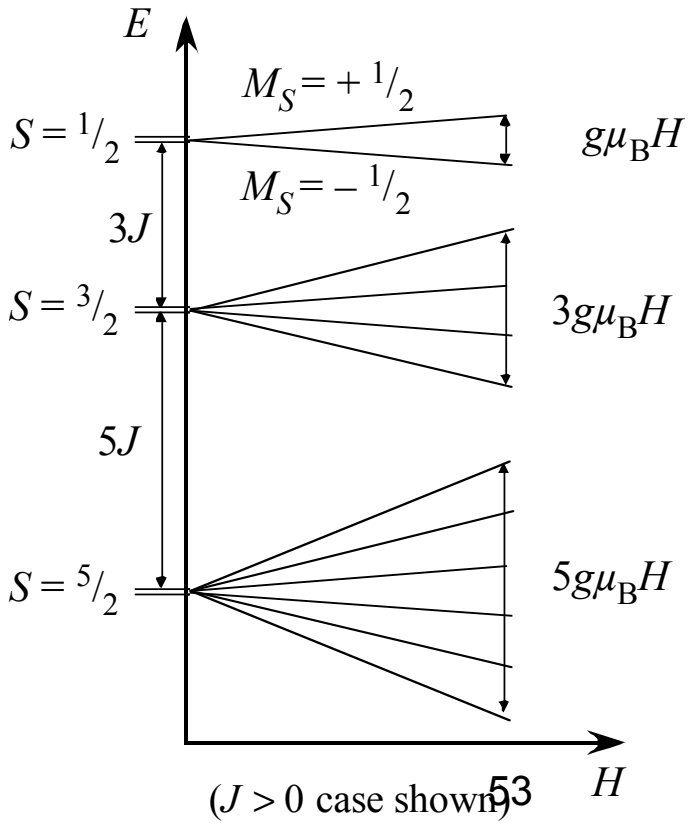
$$\mathbf{S}_T = \mathbf{S}_{Cr^{3+}} + \mathbf{S}_{Ni^{2+}}$$

possible values of S_T : $\tfrac{5}{2},\ \tfrac{3}{2},\ \tfrac{1}{2}$

$$E_n = -JS_T(S_T+1)$$

$$E_{5/2} = -J\tfrac{5}{2}(\tfrac{5}{2}+1) = \frac{-35J}{4}$$

$$E_{3/2} = \frac{-15J}{4};\ E_{1/2} = \frac{-3J}{4}$$



($J > 0$ case shown)

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$$E_i = E_i^{(0)} + E_i^{(1)} H + E_i^{(2)} H^2 + \cdots$$

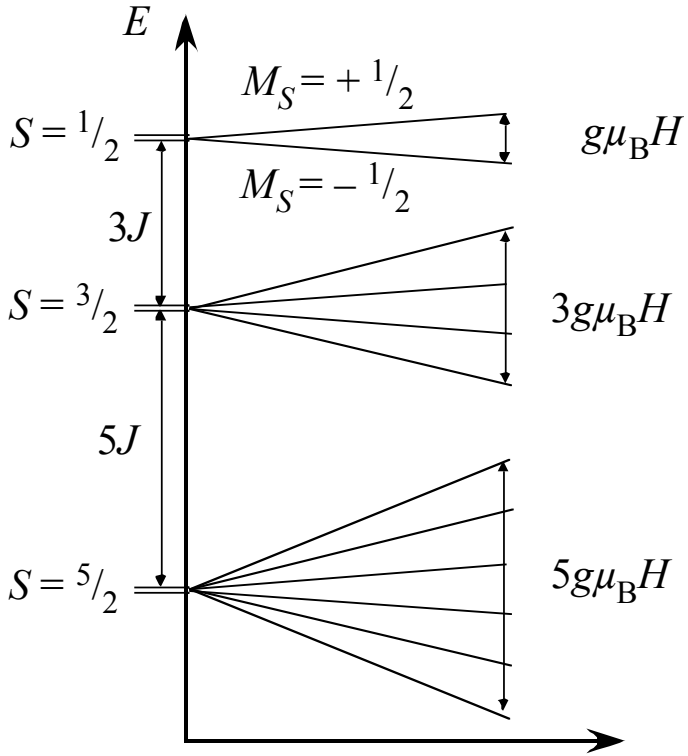
Example: Cr^{3+} coupled to Ni^{2+}

Bearing in mind the definitions of the terms that go into Van Vleck's formula ($E_i^{(2)} = 0$) :

$E_{5/2}^{(0)} = 0$; $E_{5/2}^{(1)} = \pm 1/2 g\mu_B, \pm 3/2 g\mu_B, \pm 5/2 g\mu_B$

$E_{3/2}^{(0)} = 5J$; $E_{3/2}^{(1)} = \pm 1/2 g\mu_B, \pm 3/2 g\mu_B$

$E_{1/2}^{(0)} = 8J$; $E_{1/2}^{(1)} = \pm 1/2 g\mu_B$



$$\chi = \frac{N\sum_i \left(E_i^{(1)}\right)^2 e^{-E_i^{(0)}/k_B T}}{k_B T \sum_i e^{-E_i^{(0)}/k_B T}}$$

$$\chi = N \frac{2\left(\frac{1}{2}g\mu_B\right)^2 + 2\left(\frac{3}{2}g\mu_B\right)^2 + 2\left(\frac{5}{2}g\mu_B\right)^2 + \left[2\left(\frac{1}{2}g\mu_B\right)^2 + 2\left(\frac{3}{2}g\mu_B\right)^2\right]e^{-5J/k_B T} + \left[2\left(\frac{1}{2}g\mu_B\right)^2\right]e^{-8J/k_B T}}{k_B T\left(6 + 4e^{-5J/k_B T} + 2e^{-5J/k_B T}\right)}$$

$$\chi = N \frac{\mu_B{}^2}{k_B T} g^2 \frac{\frac{35}{2} + 5e^{-5J/k_B T} + \frac{1}{2}e^{-8J/k_B T}}{\left(6 + 4e^{-5J/k_B T} + 2e^{-5J/k_B T}\right)}$$

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A General Formula for Two Coupled Ions

Using Van Vleck's formula and the previous example as guidance, it isn't hard to write a general formula for any two coupled centers:

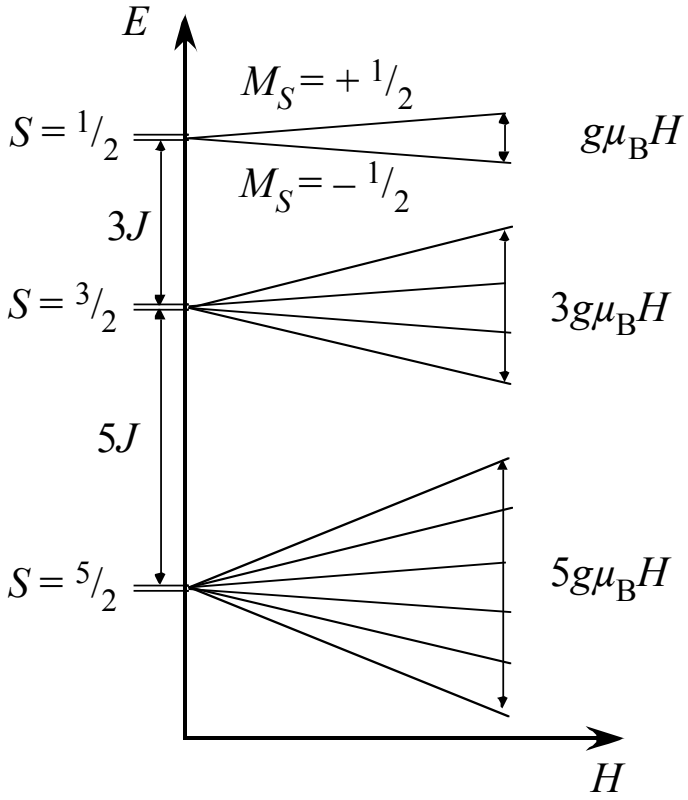
$$\chi_m = \frac{Ng^2\mu_B^2 \sum_n a_n e^{-E_n^{(0)}/k_BT}}{k_BT \sum_n b_n e^{-E_n^{(0)}/k_BT}} \simeq \frac{3}{8} \frac{g^2 \sum_n a_n e^{-E_n^{(0)}/k_BT}}{T \sum_n b_n e^{-E_n^{(0)}/k_BT}}$$

Where we've used the fact that $\frac{N\mu_B^2}{k_B} \simeq 0.375 = \frac{3}{8}$.

Also, $a_n = \frac{1}{3} S_T(S_T+1)(2S_T+1)$; $b_n = (2S_T+1)$

Note that the sum over n refers to all the values that S_T takes, from $S_A + S_B$ down to $|S_A - S_B|$

We'll express the coupling constant J in kelvin: $J(K) = J/k_B$



($J > 0$ case shown)

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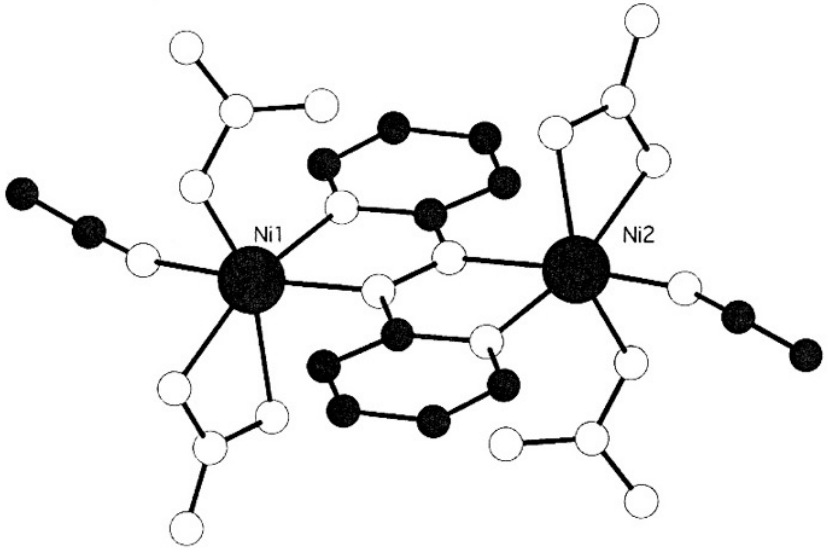
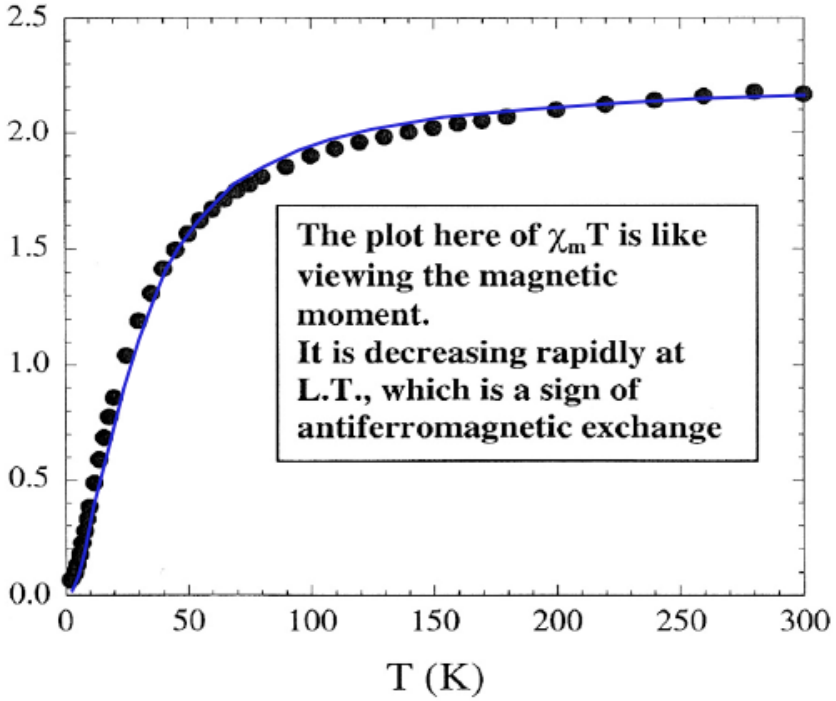
$Ni_2(abpy)(CH_3CN)_2(NO_3)_2]$



$\{[Ni_2(abpy)(CH_3CN)_2(NO_3)_2\}$



$$\chi_m = \frac{3}{8}\frac{g^2\sum_n a_n e^{-E_n^{(0)}/k_B T}}{T\sum_n b_n e^{-E_n^{(0)}/k_B T}} = \frac{3}{8}\frac{g^2\left(0+2e^{2J/T}+10e^{8J/T}\right)}{T\left(1+3e^{2J/T}+5e^{8J/T}\right)}$$

$$(J<0)$$

Fitted line has added term (C/T) with C = 0.08, J = –11K, g = 2.03

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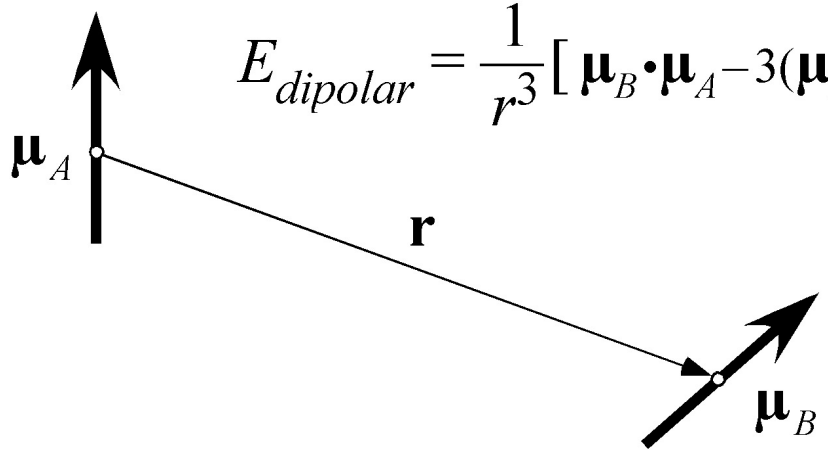
Dipolar Interaction: Weak!

- The energy of the magnetic dipole-dipole interaction falls off as the cube of the distance between dipoles and is too weak to explain magnetic coupling.



$$E_{dipolar} = \frac{1}{r^3}[\,\boldsymbol{\mu}_B \cdot \boldsymbol{\mu}_A - 3(\boldsymbol{\mu}_A \cdot \hat{\mathbf{r}})(\boldsymbol{\mu}_B \cdot \hat{\mathbf{r}})]$$

$$\hat{\mathbf{r}} = \frac{\mathbf{r}}{|\mathbf{r}|}$$

$$E_{dipolar} \approx \frac{(g\mu_B)^2}{r^3} \approx \left(\frac{e\hbar}{mc}\right)^2 \left(\frac{1}{r}\right)^3 = \left(\frac{e\hbar}{mc}\right)^2 \left(\frac{me^2}{\hbar^2}\right)^2 \frac{1}{a_0}\left(\frac{a_0}{r}\right)^3 \approx \left(\frac{e\hbar}{mc}\right)^2 \left(\frac{me}{\hbar^2}\right)^2 \left(\frac{a_0}{r}\right)^3 \left(\frac{e^2}{a_0}\right)$$

$$= \left(\frac{e^2}{\hbar c}\right)^2 \left(\frac{a_0}{r}\right)^3 (27.2\text{ eV}) = \alpha^2 \left(\frac{a_0}{r}\right)^3 (27.2\text{ eV}) \simeq \left(\frac{a_0}{r}\right)^3 \left(\frac{27.2}{137^2}\text{ eV}\right)$$

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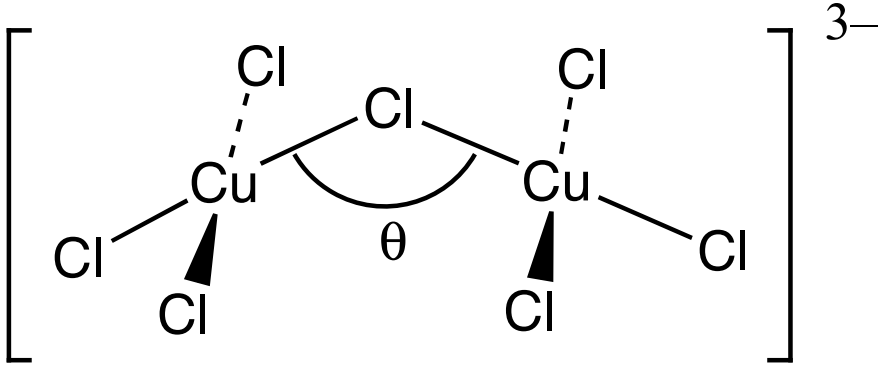
What controls coupling?

- How does the sign and magnitude of J change with angle (θ)?
- delocalized and localized picture (Hay, Thiebault, and Hoffmann, *J. Am. Chem. Soc.* **1975,** *97*, 4884).



$$E_T - E_S \equiv -2J = J_{12} - \tfrac{1}{2}\left(J_{aa} + J_{ab}\right) + \frac{\left(\varepsilon_2 - \varepsilon_1\right)^2}{2K_{12}} = -2K_{ab} + \frac{\left(\varepsilon_2 - \varepsilon_1\right)^2}{J_{aa} - J_{ab}}$$

$(E_T \equiv E_{S=1}\ ;\ E_S \equiv E_{S=0})\quad \phi_1, \phi_2, \varepsilon_1, \varepsilon_2 :$ *delocalized* orbitals & energies ;

$\phi_a = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)\ ,\ \phi_b = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$: localized orbitals

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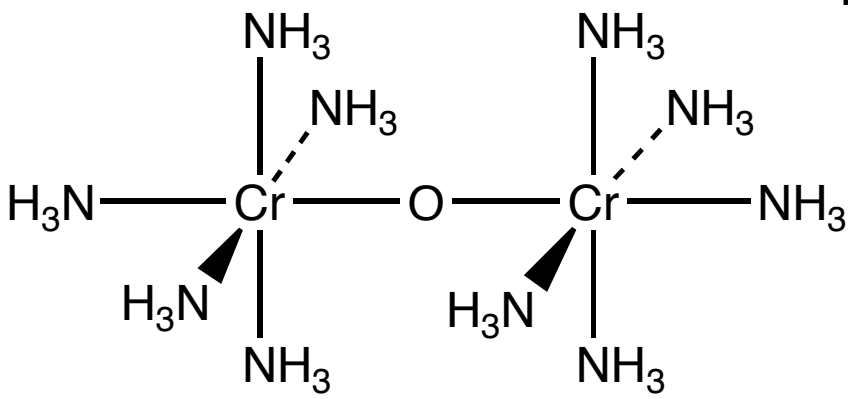
180˚ π orbital superexchange



$J \sim -200\ \text{cm}^{-1}$

$$E_T - E_S = -2J = J_{12} - \tfrac{1}{2}\left(J_{aa} + J_{ab}\right) + \frac{\left(\varepsilon_1 - \varepsilon_2\right)^2}{2K_{12}}$$

$$E_T - E_S = -2J = -2K_{ab} + \frac{\left(\varepsilon_1 - \varepsilon_2\right)^2}{J_{aa} - J_{ab}}$$

$$\left(E_T \equiv E_{S=1} \;\; ; \;\; E_T \equiv E_{S=0}\right)$$

Compare $[Ru_2(\mu\text{-}O)Cl_{10}]^{4-}$

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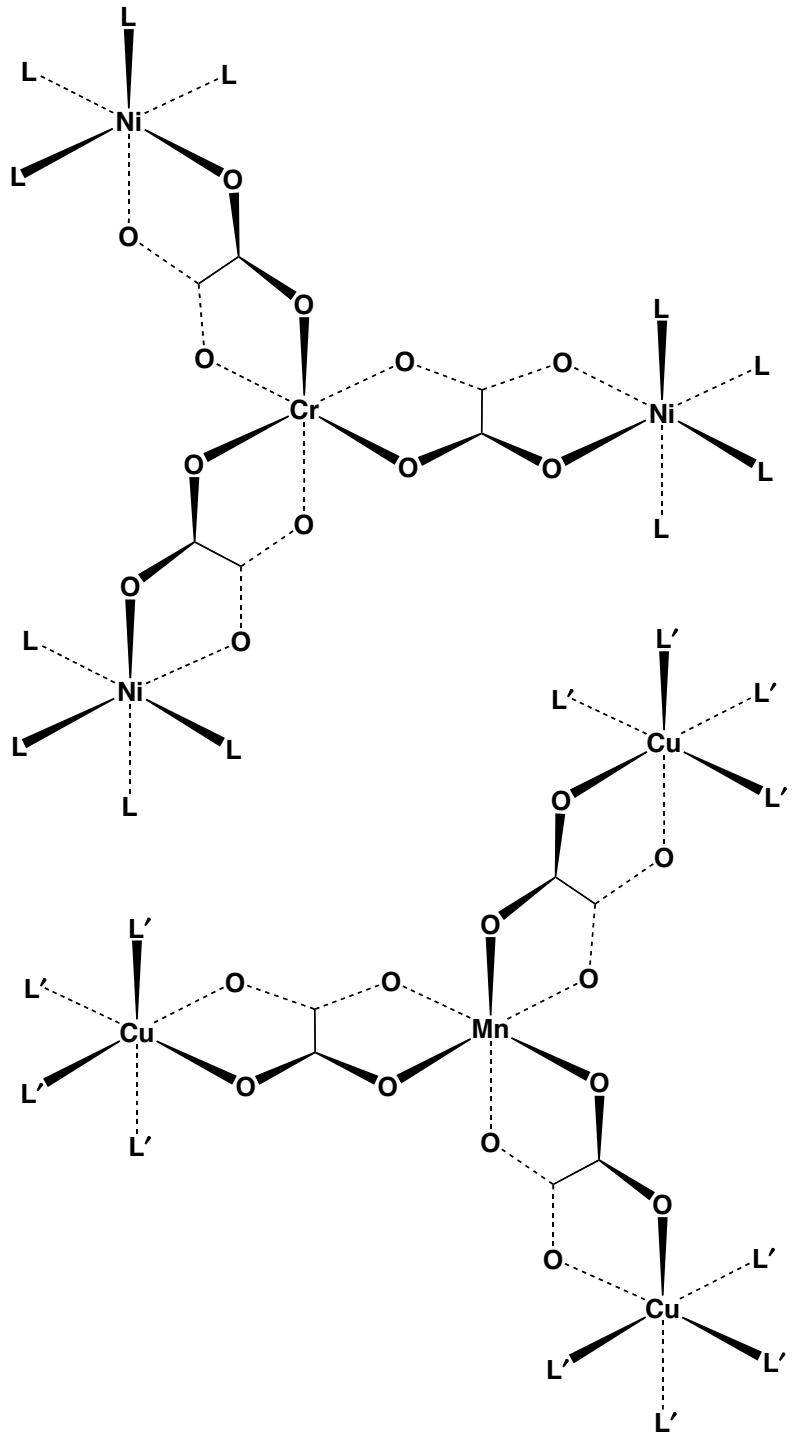

Orthogonal Orbitals or Not

$[(L_4Ni)_3Cr]^{3+}$: $(d^8)_3d^3$

$[(L_4Cu)_3Mn]^{3+}$: $(d^9)_3d^5$

L, L´ = Schiff base (imine) ligands

Pei, Journoux, & Kahn, *Inorg. Chem.* **1989,** *28*, 100.

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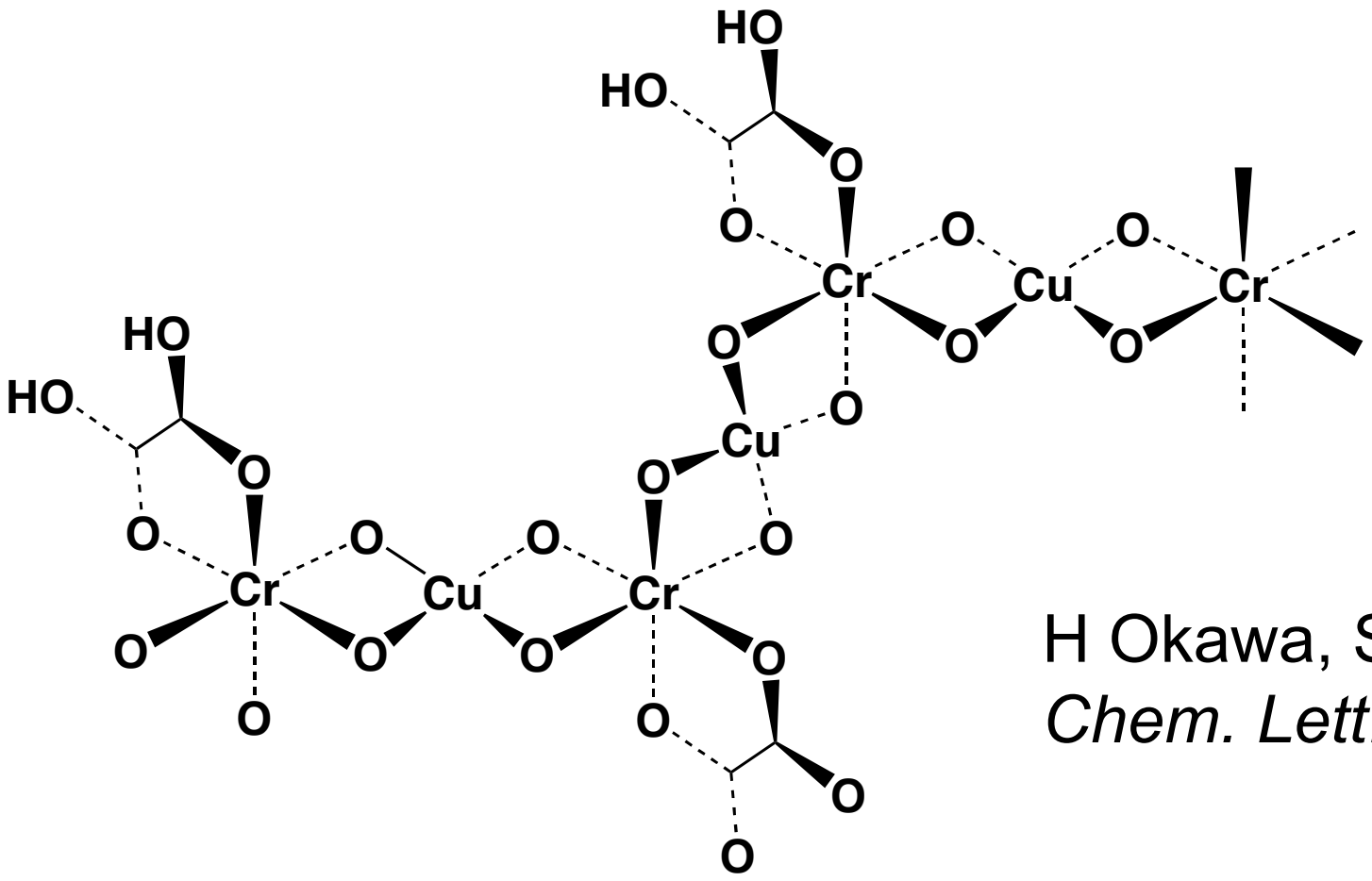
A Polymeric Analog

$NBu_4^+[Cu^{II}Cr^{III}(ox)_3^-]$:
d^8d^3



H Okawa, S Kida,et al.,
Chem. Lett. **1990**, 87

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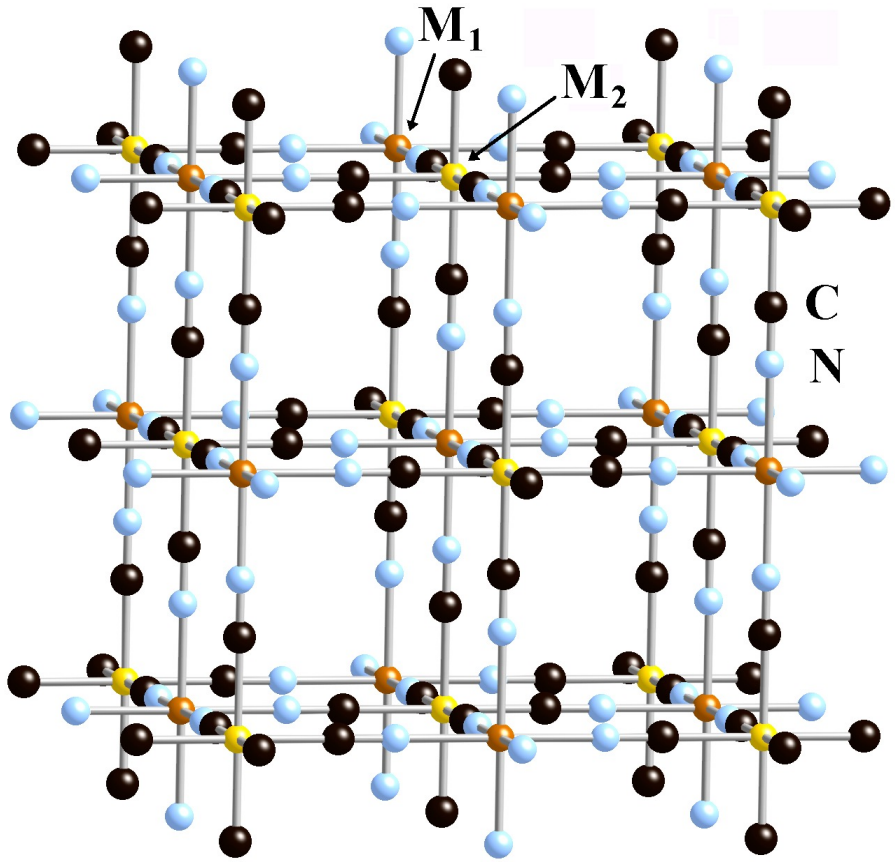
Magnetic Prussian Blues

Table 1. Experimental T_C [K] values for some Prussian blue analogues.

MM′	Compound	Configuration	T_c	Ref.
$Cr^{III}V^{II}$[a]	$KV[Cr(CN)_6]\cdot 2H_2O$	$t_{2g}^3–t_{2g}^3/t_{2g}^2$	376	[6]
$Cr^{III}V^{II}$/ V^{III}	$K_{0.058}V[Cr(CN)_6]_{0.79}(SO_4)_{0.058}$	$t_{2g}^3–t_{2g}^3/t_{2g}^2$	372	[5]
	$K_{0.50}V[Cr(CN)_6]_{0.95}\cdot 1.7H_2O$	$t_{2g}^3–t_{2g}^3/t_{2g}^2$	350	[5]
	$V[Cr(CN)_6]_{0.86}\cdot 2.8H_2O$	$t_{2g}^3–t_{2g}^3/t_{2g}^2$	315	[4]
	$V[Cr(CN)_6]_{0.69}(SO_4)_{0.23}\cdot 3.0H_2O$	$t_{2g}^3–t_{2g}^3/t_{2g}^2$	315	[8]
$Cr^{III}Cr^{II}$	$[Cr_5(CN)_{12}]\cdot 10H_2O$	$t_{2g}^3–t_{2g}^3e_g^1$	240	[50]
$Mn^{II}V^{II}$	$(Et_4N)_{0.5}Mn_{1.25}[V(CN)_5]\cdot 2H_2O$	$t_{2g}^3e_g^2–t_{2g}^3$	230	[51]
$Cr^{III}Cr^{II}$	$Cs_{2/3}Cr[Cr(CN)_6]_{8/9}\cdot 4.4H_2O$[b]	$t_{2g}^3–t_{2g}^3e_g^1$	190	[50]
$V^{II}Mn^{II}$	$Cs^2Mn[V(CN)_6]$	$t_{2g}^3–t_{2g}^3e_g^2$	125	[51]
$Cr^{III}V^{IV}$	$(VO)[Cr(CN)_6]_{2/3}\cdot 3.3H_2O$	$t_{2g}^3–t_{2g}^1$	115	[52]
$Cr^{III}Mn^{II}$	$CsMn[Cr(CN)_6]$	$t_{2g}^3–t_{2g}^3e_g^2$	90	[53]
	$(NMe_4)Mn[Cr(CN)_6]$	$t_{2g}^3–t_{2g}^3e_g^2$	59	[54]
$Mn^{IV}Mn^{II}$	$Mn[Mn(CN)_6]\cdot 1.14H_2O$	$t_{2g}^3–t_{2g}^3e_g^2$	49	[55,56]
$Co^{II}Co^{II}$	$Co_3[Co(CN)_5]_2\cdot 8H_2O$	$t_{2g}^6e_g^1–t_{2g}^5e_g^2$	38	[57]
$Mn^{II}Mn^{II}$	$K_2Mn[Mn(CN)_6]$	$t_{2g}^5–t_{2g}^3e_g^2$	41	[58]
$Mn^{III}Mn^{II}$	$CsMn[Mn(CN)_6]\cdot 0.5H_2O$	$t_{2g}^4–t_{2g}^3e_g^2$	41	[58]
	$(NMe_4)[Mn_2(CN)_6]$	$t_{2g}^4–t_{2g}^3e_g^2$	28	[54]
$Mn^{II}Mn^{III}$	$Mn_3[Mn(CN)_6]_2\cdot 12H_2O$	$t_{2g}^5–t_{2g}^3e_g^1$	37	[58]
	$Mn_3[Mn(CN)_6]_2\cdot 12H_2O\cdot 1.7CH_3OH$	$t_{2g}^3e_g^2–t_{2g}^4$	29	[59]
$Mn^{III}Mn^{III}$	$Mn[Mn(CN)_6]$	$t_{2g}^4–t_{2g}^3e_g^1$	31	[56]
$Mn^{III}V^{III}$	$V[Mn(CN)_6]$	$t_{2g}^4–t_{2g}^2$	28	[56]
$Mn^{III}Cr^{III}$	$Cr[Mn(CN)_6]$	$t_{2g}^4–t_{2g}^3$	22	[56]
$Fe^{III}Co^{II}$	$Co_3[Fe(CN)_6]_2$	$t_{2g}^5–t_{2g}^5e_g^2$	14	[60]
$Fe^{III}Mn^{II}$	$Mn_3[Fe(CN)_6]_2$	$t_{2g}^5–t_{2g}^3e_g^2$	9	[61]
$Fe^{III}Fe^{II}$	$Fe_4[Fe(CN)_6]_3\cdot xH_2O$	$t_{2g}^5–t_{2g}^4e_g^2$	6[c]	[62]
$Fe^{III}Ni^{II}$	$Ni_3[Fe(CN)_6]_2$	$t_{2g}^5–t_{2g}^6e_g^2$	24[c]	[60]
$Mn^{III}Ni^{II}$	$Ni_3[Mn(CN)_6]_2\cdot 12H_2O$	$t_{2g}^4–t_{2g}^6e_g^2$	30[c]	[63]
	$CsNi[Mn(CN)_6]\cdot H_2O$	$t_{2g}^4–t_{2g}^6e_g^2$	42[c]	[63]
$Cr^{III}Ni^{II}$	$Ni_3[Cr(CN)_6]_2\cdot 9H_2O$	$t_{2g}^3–t_{2g}^6e_g^2$	60[c]	[63,64]
	$CsNi[Cr(CN)_6]\cdot 2H_2O$	$t_{2g}^3–t_{2g}^6e_g^2$	90[c]	[64]

[a] Although this compound is formulated as stoichiometric, a certain amount of V^{III} is present that is responsible for its ferrimagnetic behavior. [b] Or $Cs_6Cr_9[Cr(CN)_6]_8\cdot 40H_2O$. [c] The critical temperature in those cases corresponds to a ferromagnetic state, at difference with other compounds in which it corresponds to ferrimagnetic ordering.



E Ruiz, A Rodrguez-Fortea,S Alvarez, M Verdaguer, Chem. Eur. J. **2005,** *11*, 2135.

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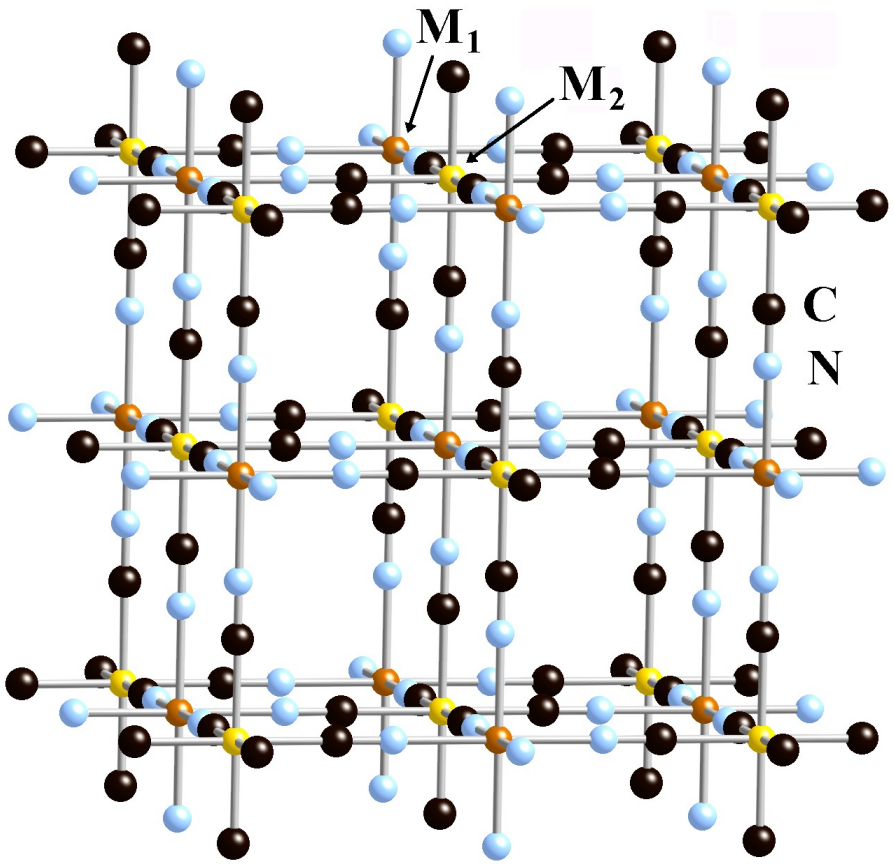
Magnetic Prussian Blues

Table 3. Exchange-coupling constants J for the molecular models $[(HNC)_5M\text{-}CN\text{-}M'(NCH)_5]^{n+}$, and some examples with the $[(NC)_5M\text{-}CN\text{-}M'(NC)_5]^{n-}$ model (J' values), calculated with the B3LYP functional.

M, M′	Configuration	J [cm^{-1}]	J' [cm^{-1}]
$Mn^{III}V^{II}$	t_{2g}^4–t_{2g}^3	−503	−283
$Mo^{III}V^{II}$	t_{2g}^3–t_{2g}^3	−422	−358
$Cr^{III}Mo^{II}$	t_{2g}^3–t_{2g}^4	−372	−194
$V^{III}V^{II}$	t_{2g}^2–t_{2g}^3	−360	−270
$Cr^{III}V^{II}$	t_{2g}^3–t_{2g}^3	−241	−150
$Mo^{III}Cr^{II}$	t_{2g}^3–$t_{2g}^3e_g^1$	−186	
$Mn^{III}Cr^{II}$	t_{2g}^4–$t_{2g}^3e_g^1$	−122	
$Cr^{III}V^{IV}O$	t_{2g}^3–t_{2g}^1	−101	
$V^{III}V^{III}$	t_{2g}^2–t_{2g}^2	−99	
$V^{II}V^{II}$	t_{2g}^3–t_{2g}^3	−86	
$Cr^{III}Cr^{II}$	t_{2g}^3–$t_{2g}^3e_g^1$	−70	
$Mo^{III}Cr^{III}$	t_{2g}^3–t_{2g}^3	−63	
$Cr^{III}V^{III}$	t_{2g}^3–t_{2g}^2	−56	
$Mo^{III}V^{III}$	t_{2g}^3–t_{2g}^2	−52	
$Mn^{IV}Cr^{III}$	t_{2g}^3–t_{2g}^3	−33	
$Mn^{\bar{I}\bar{I}\bar{I}}V^{\bar{I}\bar{I}\bar{I}}$	t_{2g}^4–t_{2g}^2	−31	
$Cr^{III}Cr^{III}$	t_{2g}^3–t_{2g}^3	−29	
$V^{II}Mn^{II}$	t_{2g}^3–$t_{2g}^3e_g^2$	−23	
$Cr^{III}Mn^{II}$	t_{2g}^3–$t_{2g}^3e_g^2$	−18	
$V^{III}Ni^{II}$	t_{2g}^2–$t_{2g}^6e_g^2$	+24	
$Cr^{III}Ni^{II}$	t_{2g}^3–$t_{2g}^6e_g^2$	+28	
$Ti^{III}Cr^{III}$	t_{2g}^1–t_{2g}^3	+37	
$Mn^{IV}Ni^{II}$	t_{2g}^3–$t_{2g}^6e_g^2$	+121	
$Ti^{III}V^{II}$	t_{2g}^1–t_{2g}^3	+161	



E Ruiz, A Rodrguez-Fortea,S Alvarez, M Verdaguer, Chem. Eur. J. **2005,** *11*, 2135.

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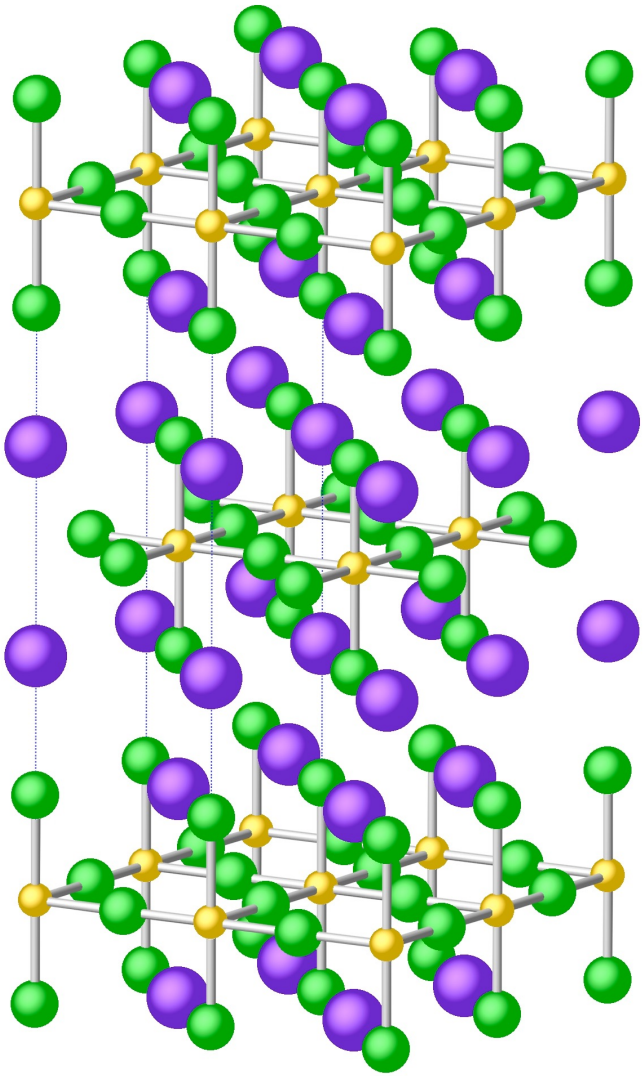
Careful Study of Structure Can Be Revealing

Ferromagnets		S	(μ/μ_B)	T_C(K)
Rb_2CrCl_4 *	Cr^{2+} (d^4 - HS)	2	5.8	57
K_2CuF_4 *	Cu^{2+} (d^4 - HS)	1/2	1.8	6
$La_{0.7}Sr_{0.3}MnO_3$ †	Mn^{3+} (d^4 HS), Mn^{4+} (d^3 HS)	2 & 3/2	3.7	350
† perovskite ; * K_2NiF_4-type				

P A Cox, "The Electronic Structure and Chemistry of Solids" Oxford, **1987.**



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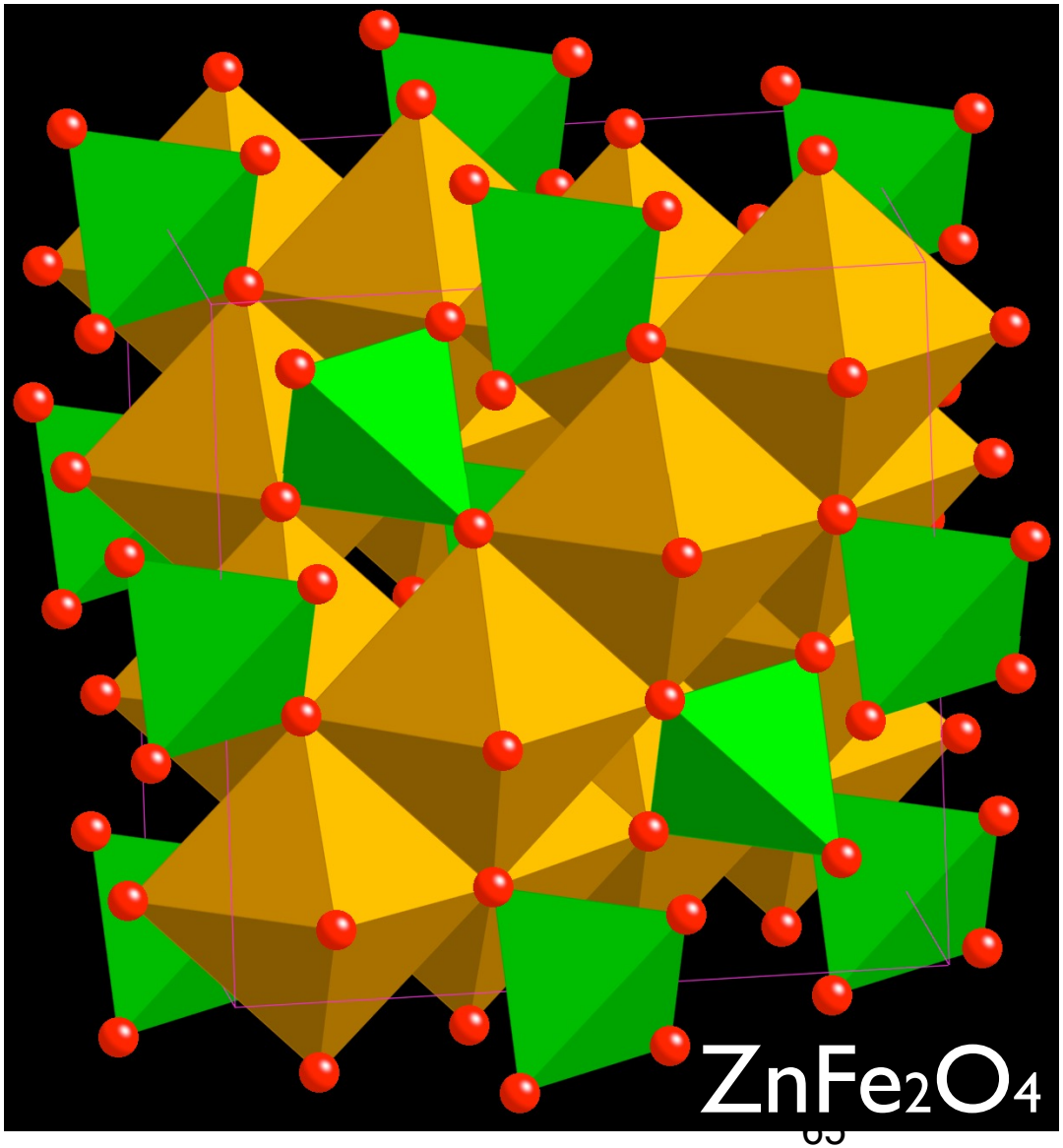
Spinels and Inverse Spinels

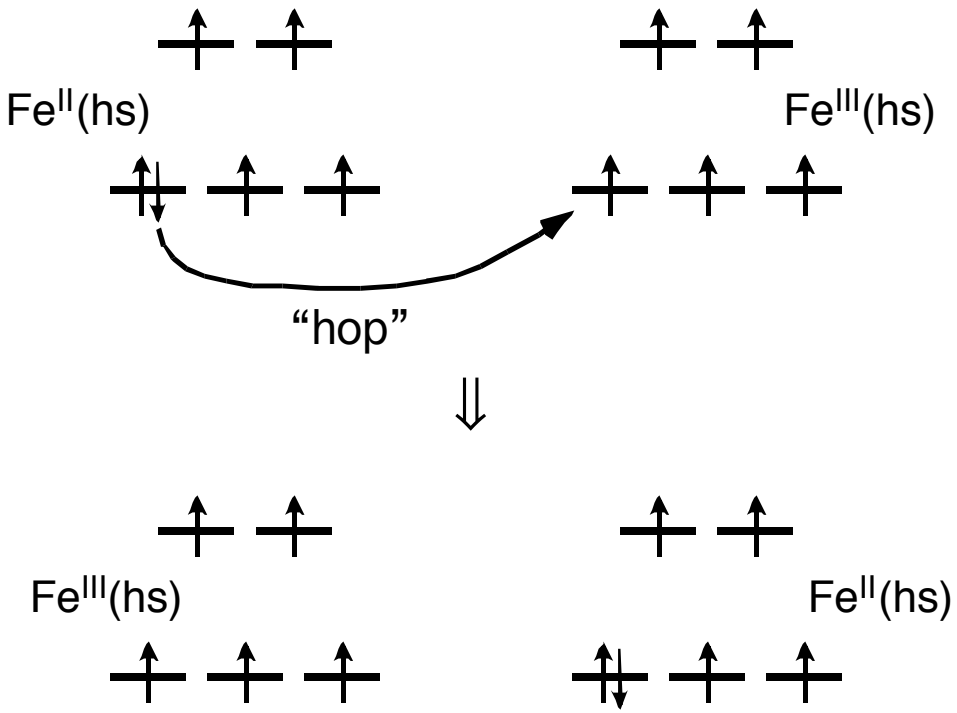
Spinel: $MgAl_2O_4$
~ $A^{tet}B^{oct}{}_2O_4$

Normal:
$(A^{II})^{tet}(B^{III})^{oct}{}_2O_4$
Inverse:
$(B^{III})^{tet}(A^{II}B^{III})^{oct}O_4$

Normal:
$(Mn^{II})^{tet}(Mn^{III})^{oct}{}_2O_4$
Inverse:
$(Fe^{III})^{tet}(Fe^{II}Fe^{III})^{oct}O_4$



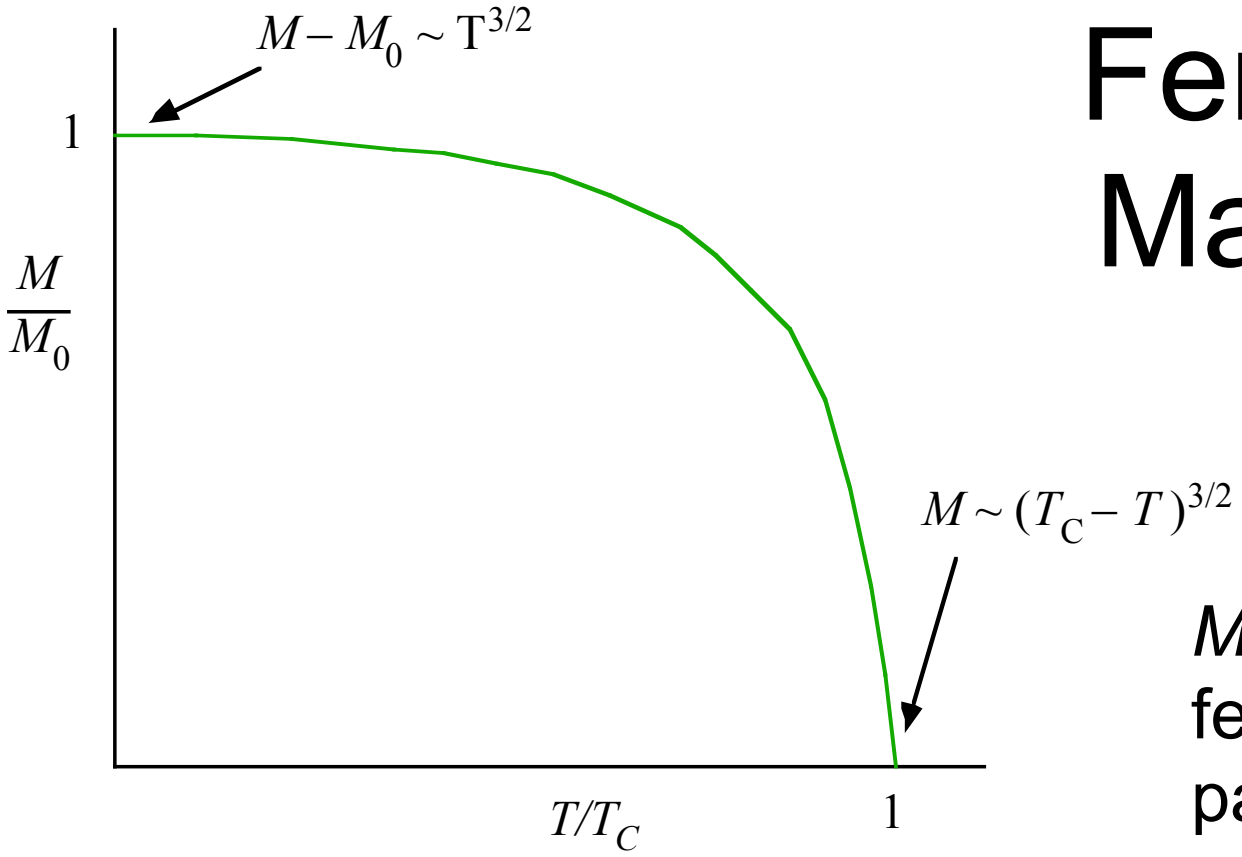
Double-Exchange in Magnetite (Fe_3O_4)



- The 'transfer' of an up-spin electron would leave the ion from which the electron is transferred (the left-hand ion) in a higher energy state.
- e^- transferred must have opposite spin to those of the 'receiving' ion. (Pauli principle.)

$\therefore$ double-exchange gives ferromagnetic coupling.

Ferromagnetic Magnetization



M is much larger for a ferromagnet than a paramagnet.

In reduced coordinates, T/T_C and M/M_0, the behavior of ferromagnets is fairly universal, as long as the dimensionality of the coupled spins is the same (i.e., the coupling between moments extends in 3-dimensions).

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