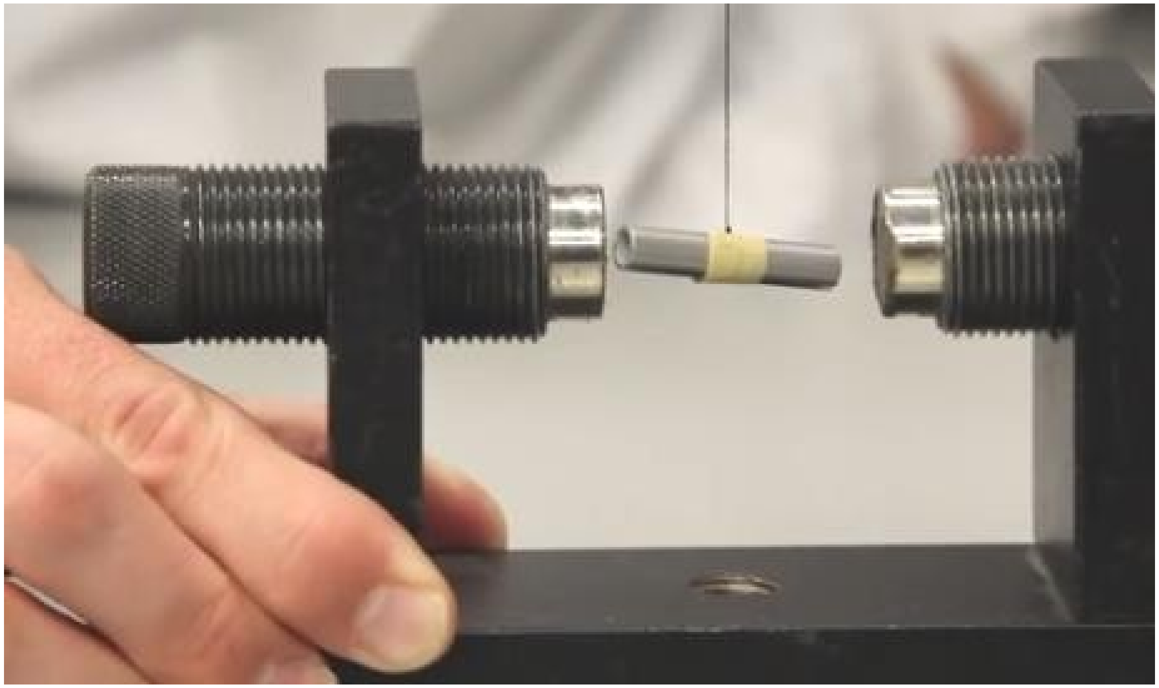
Properties of Magnetic properties of d-block elements

By Dr MAHMOUD NAJIM

All Tables and Examples from:
Shriver & Atkins
Inorganic Chemistry, 5th Ed.

Dia- and Para-Magnetism



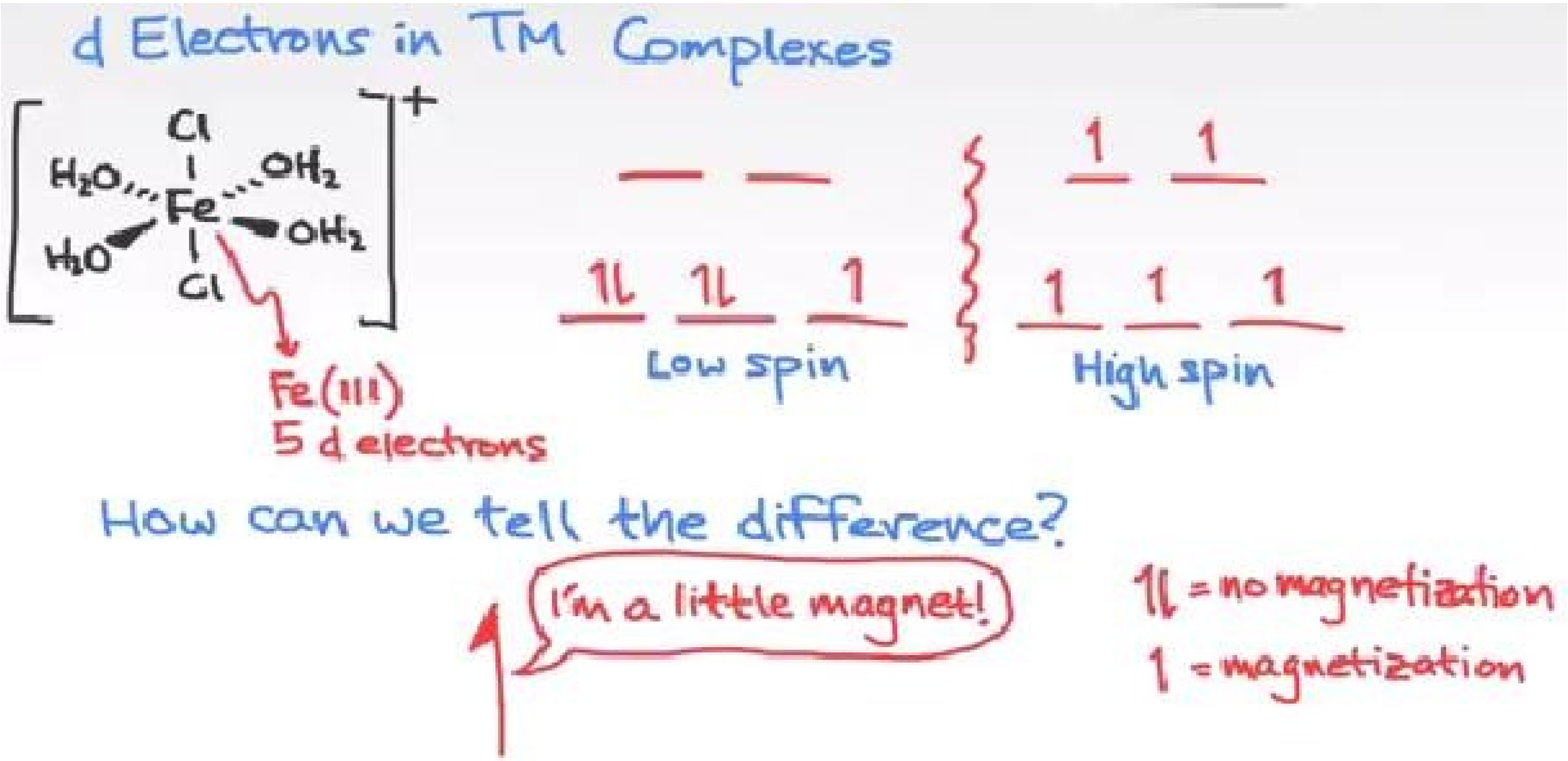
Attractive of odd es to magnetic field

Magnetic Properties

Paramagnetism arises from unpaired electrons. Each electron has a magnetic moment with one component associated with the spin angular momentum of the electron and (except when the quantum number l ¼0) a second component associated with the orbital angular momentum.

(p.579)

Where does magnetism come from ?

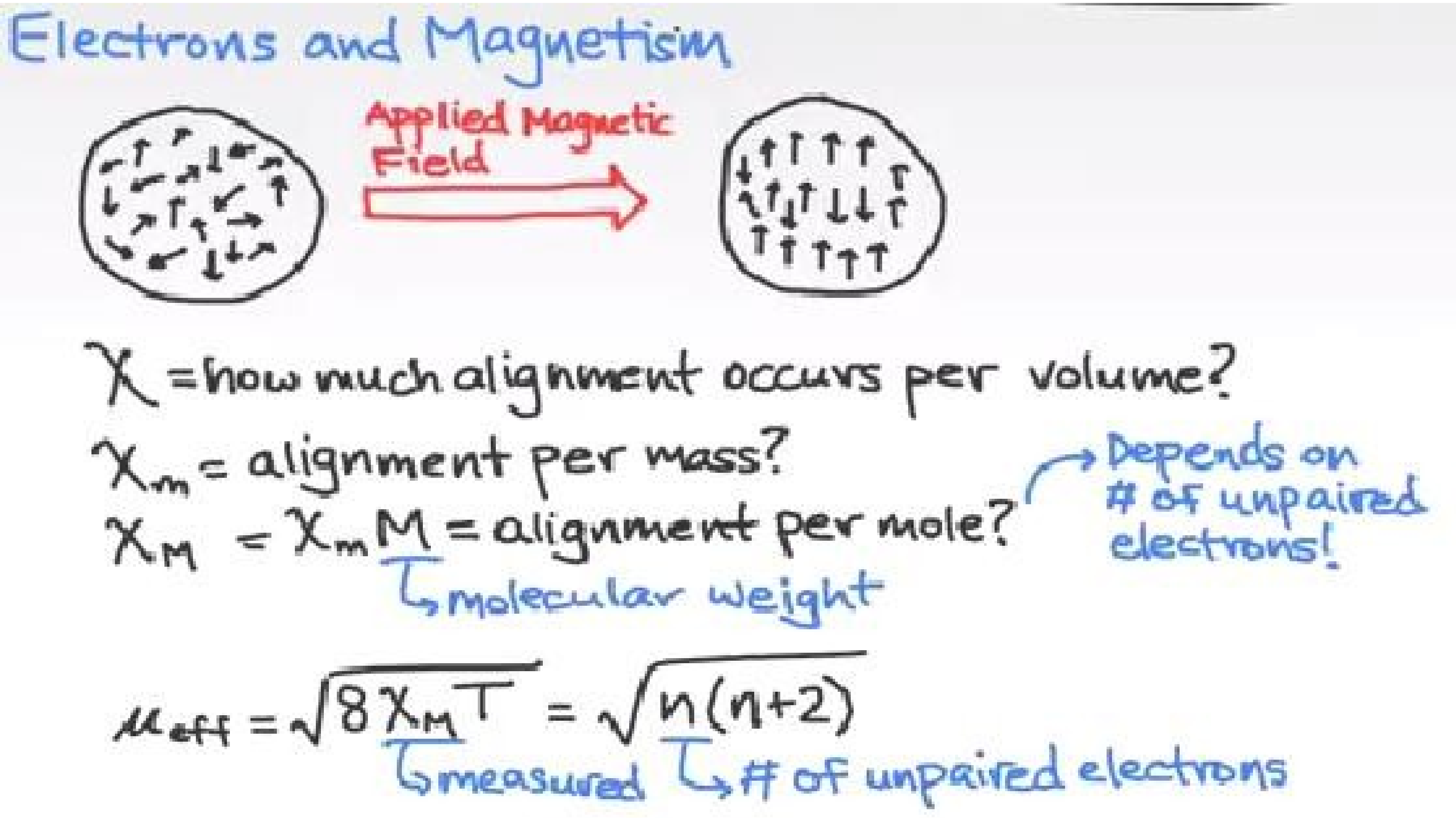


d Electrons in TM Complexes

How can we tell the difference?

↑↓ = no magnetization
↑ = magnetization

Effect of unpaired electrons



Electrons and Magnetism

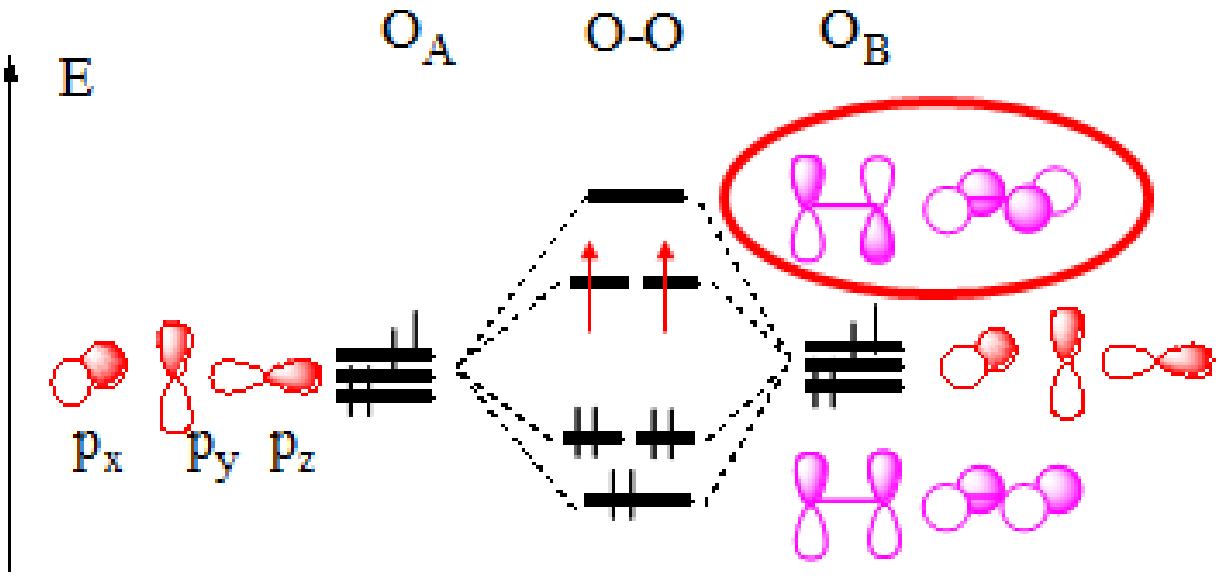
χ = how much alignment occurs per volume?

χ_m = alignment per mass?

$\chi_M = \chi_m \underbrace{M}_{\text{molecular weight}}$ = alignment per mole? → Depends on # of unpaired electrons!

$$\mu_{eff} = \sqrt{8\,\underbrace{\chi_M}_{\text{measured}}\,T} = \sqrt{\underbrace{n}_{\text{\# of unpaired electrons}}(n+2)}$$

Example of paramagnetism: Oxygen



orthogonal π molecular orbitals

paramagnetic, spin S =1

Gouy Balance

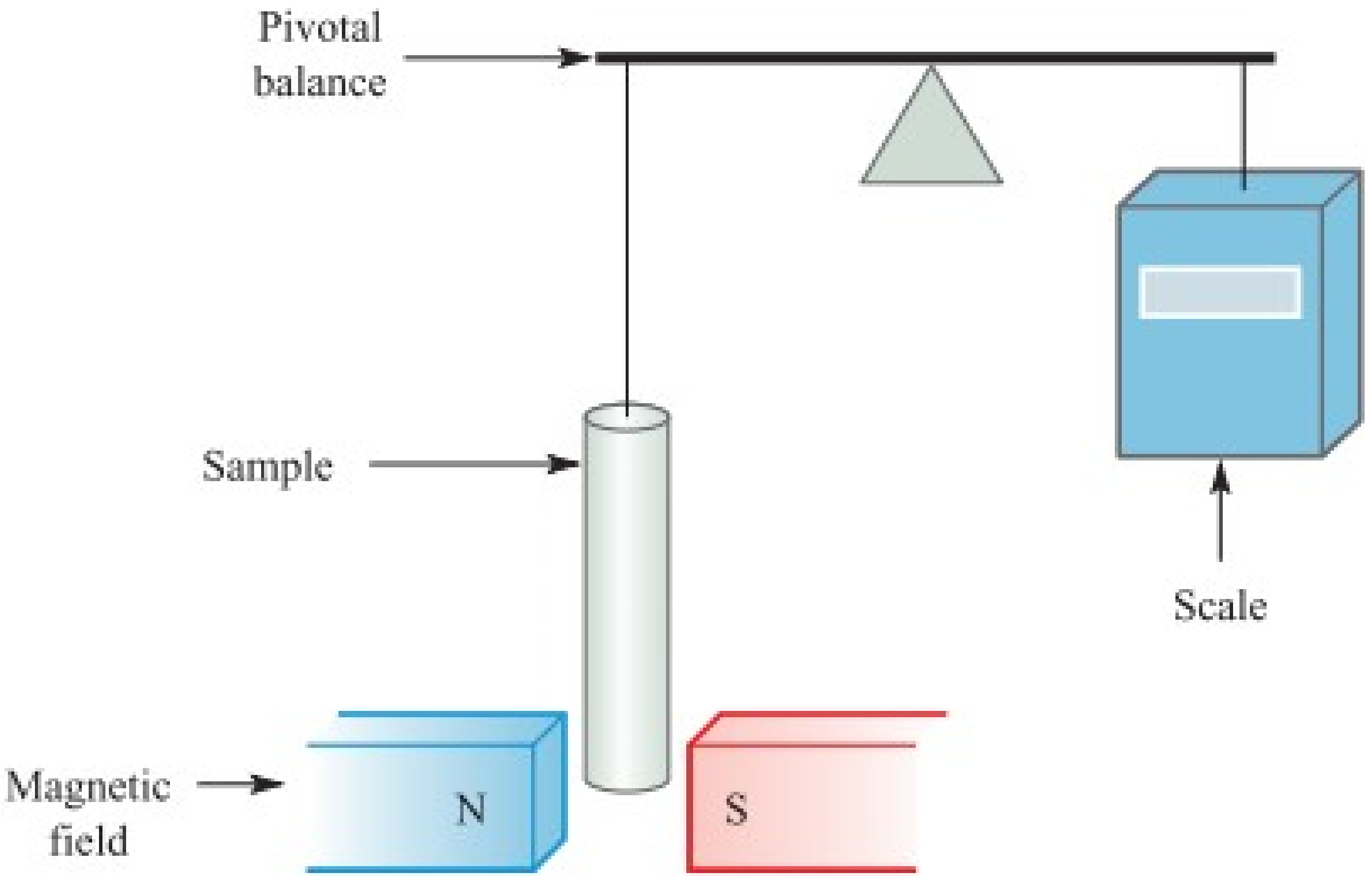
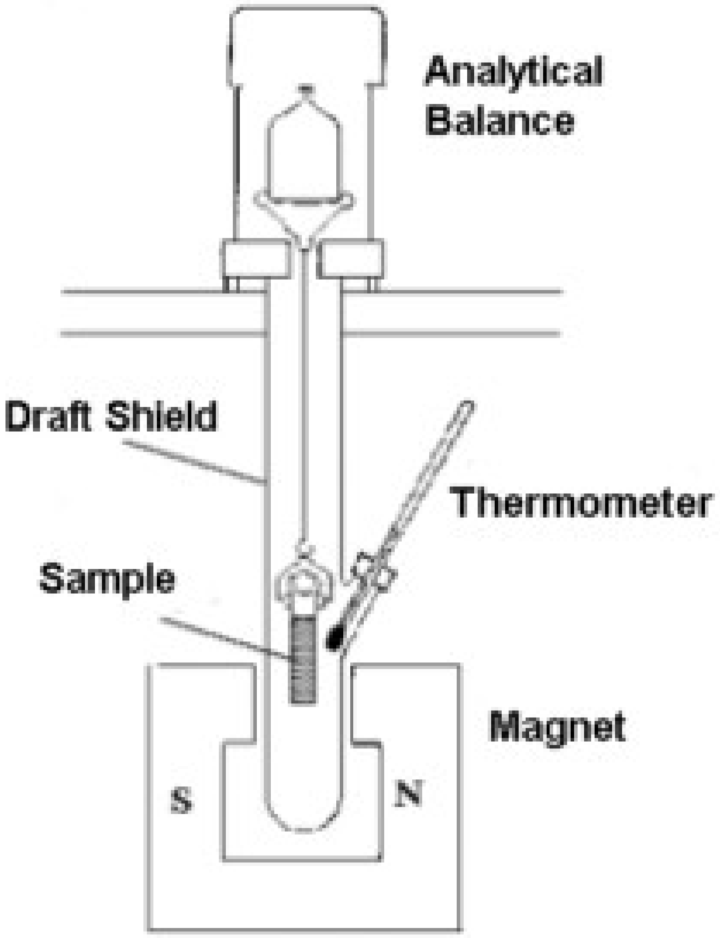
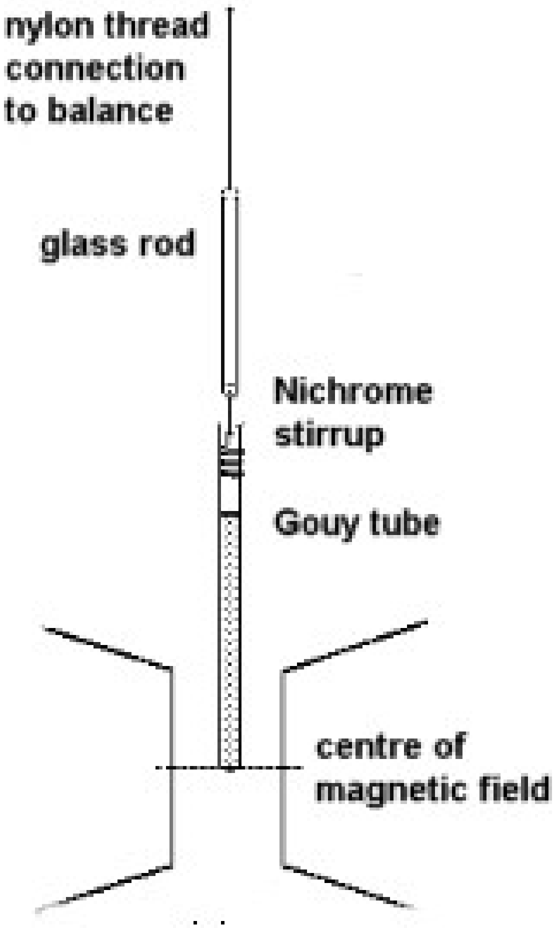


Fig. 20.21 Schematic representation of a Gouy balance.


Analytical
Balance
Draft Shield
Thermometer
Sample
Magnet
S
N

1

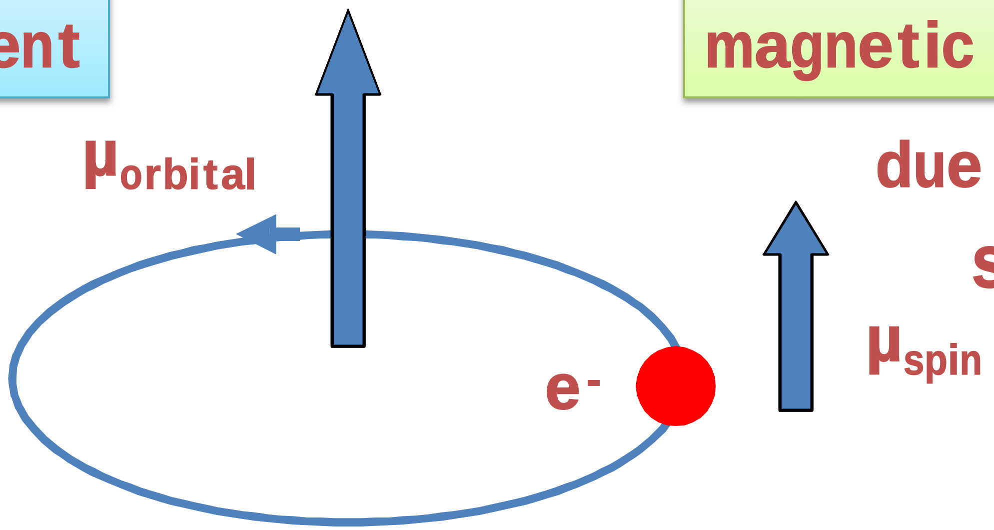

nylon thread
connection
to balance
glass rod
Nichrome
stirrup
Gouy tube
centre of
magnetic field

2

Origin of *Magnetism*

« Orbital » magnetic moment

« Intrinsic » magnetic moment



due to the spin

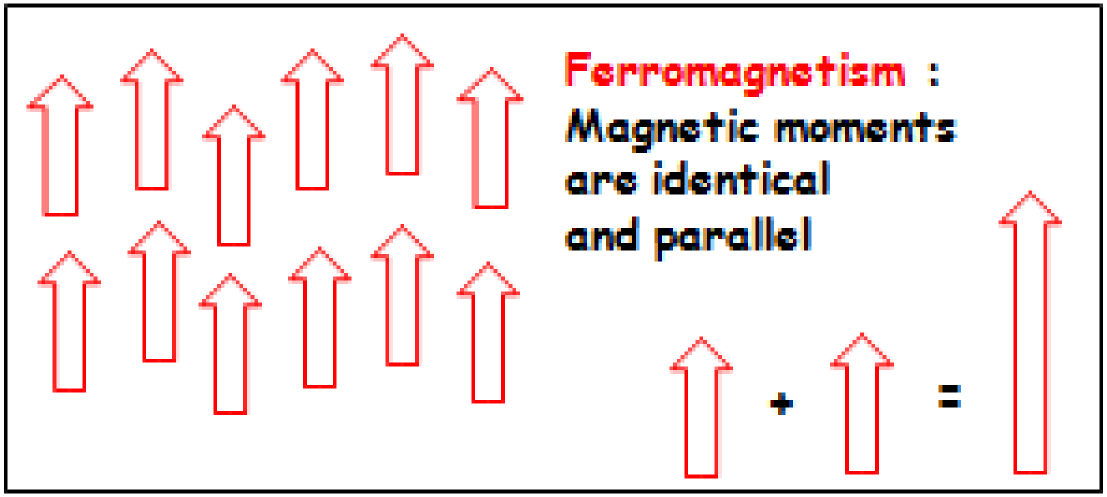
$s = \pm 1/2$

$\mu_{orbital} = g_l \times \mu_B \times \ell$

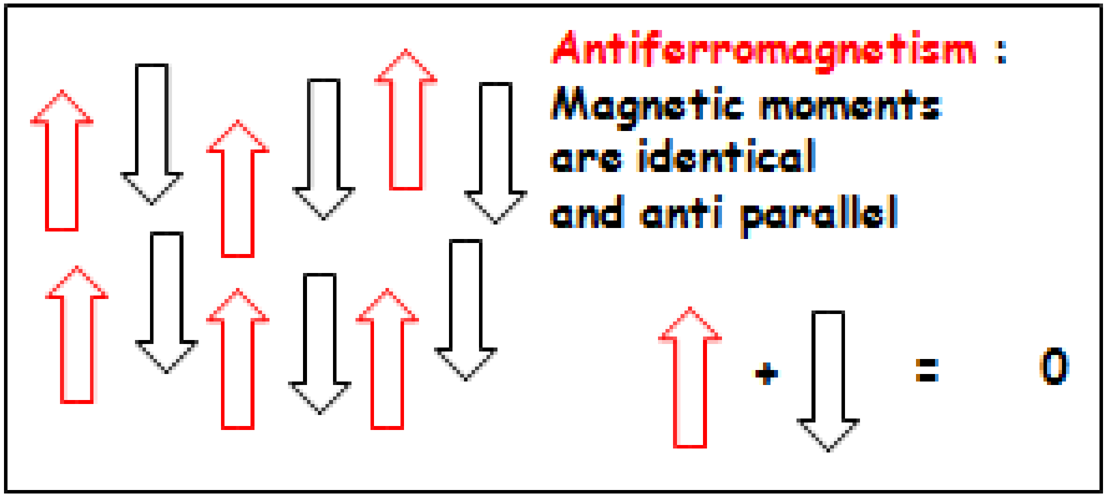
$\mu_{spin} = g_s \times \mu_B \times s \approx \mu_B$

$$\boxed{\mu_{total} = \mu_{orbital} + \mu_{spin}}$$

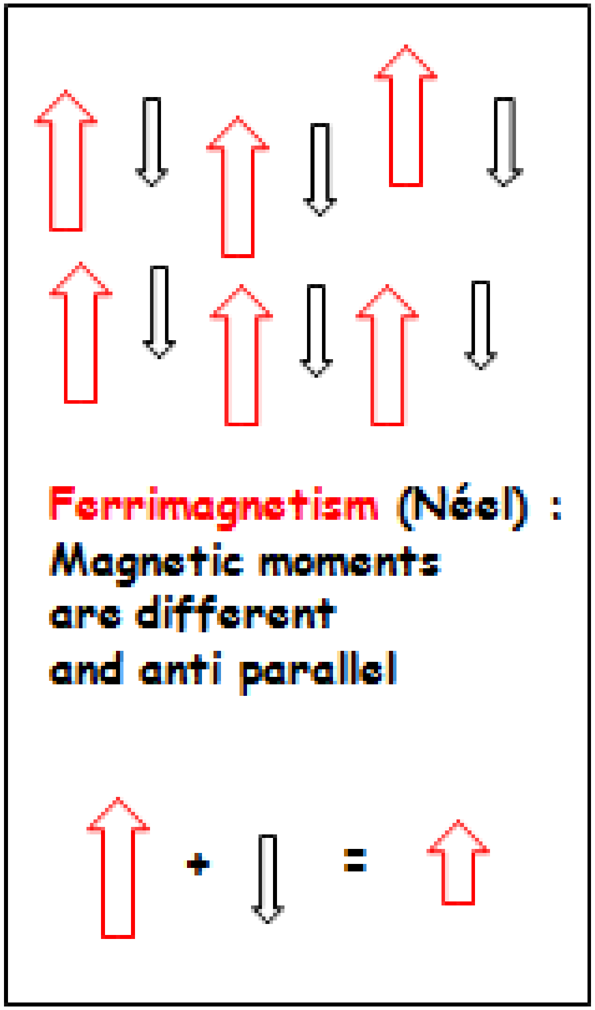
Magnetic Order :
ferro- , antiferro- and ferri-magnetism



Ferromagnetism :
Magnetic moments
are identical
and parallel



Antiferromagnetism :
Magnetic moments
are identical
and anti parallel



Ferrimagnetism (Néel) :
Magnetic moments
are different
and anti parallel

Para-magnetism

Atoms that have unpaired electrons (also metals) and therefore a total electron-spin S.
These individual magnetic moments can be oriented by an outer magnetic field to line up.

Paramagnetic substances are not magnetic by themselves but can become magnetic when an outer field is applied.

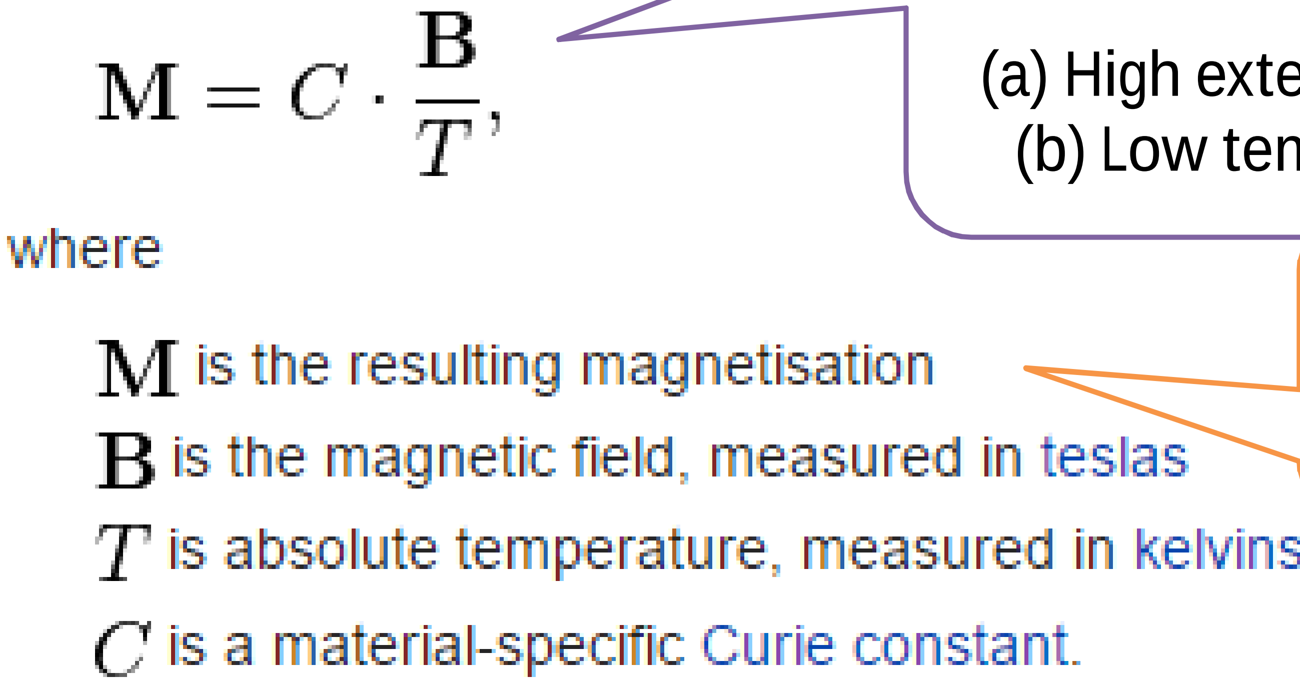
Every ferromagnetic material has a Curie-Temperature Tc where it loses its permanent magnets and becomes para-magnetic.

Curies Law

Describes the “magnetic susceptibility” of a material dependent on the outer field B and Temperature T

=> <u>High magnetization M</u>:

(a) High external field B
(b) Low temperature



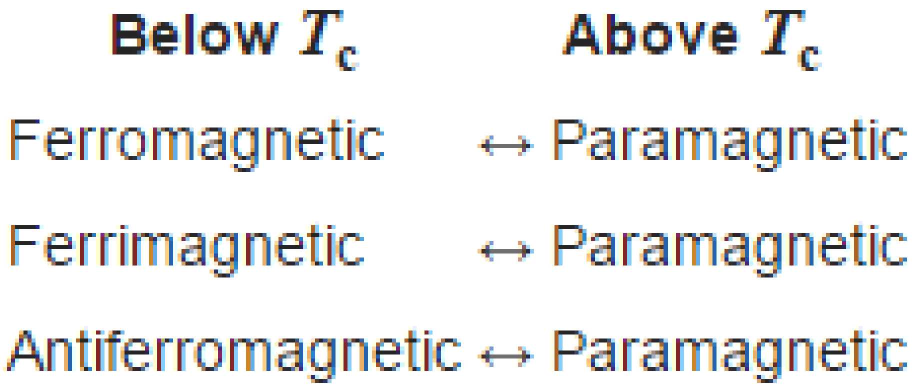
$$\mathbf{M} = C \cdot \frac{\mathbf{B}}{T},$$

where

$\mathbf{M}$ is the resulting magnetisation
$\mathbf{B}$ is the magnetic field, measured in teslas
T is absolute temperature, measured in kelvins
C is a material-specific Curie constant.

Or: ‘chi”
= magn. susceptibility

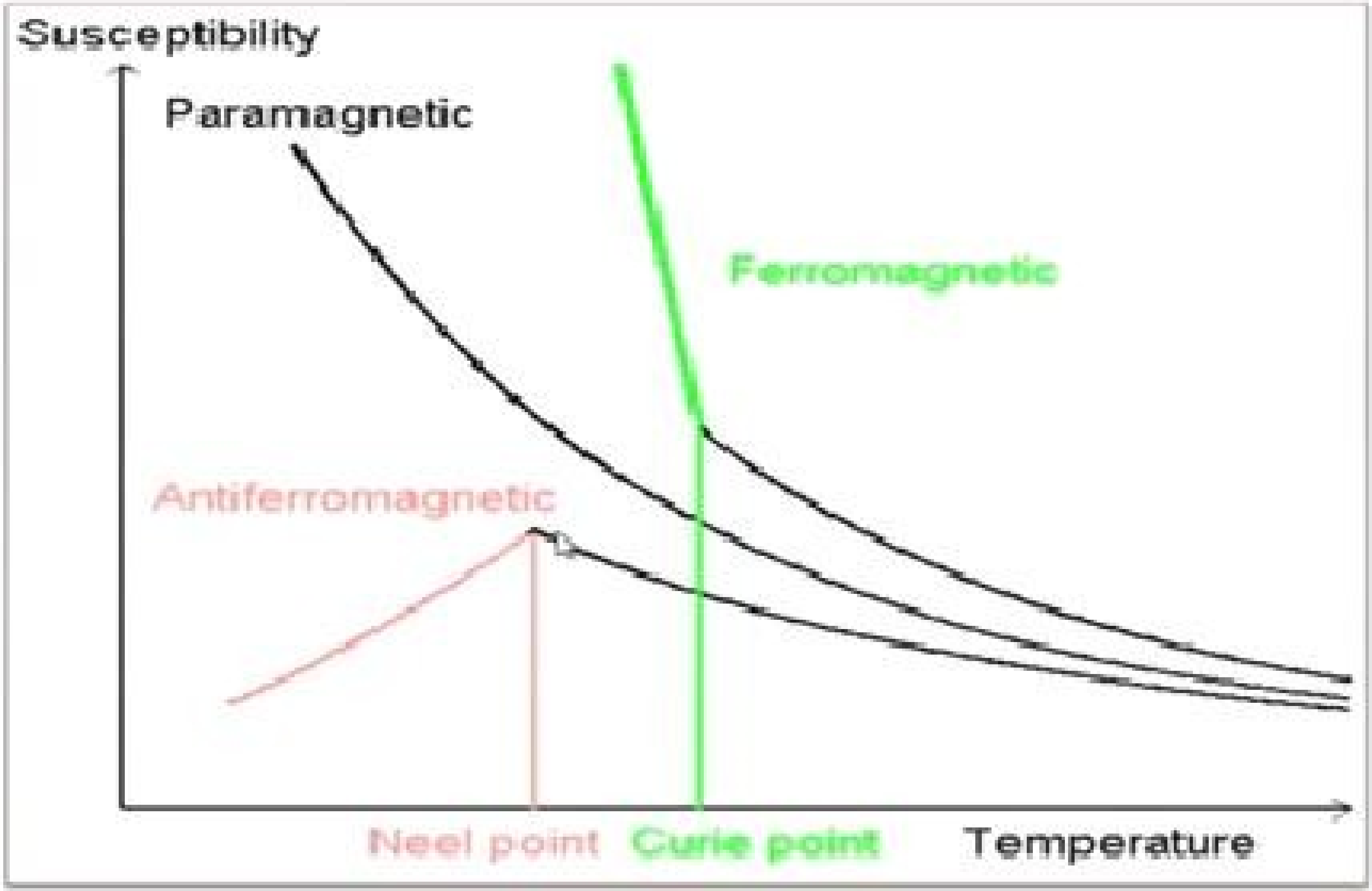
Curies Temperature Tc



Below T_c		Above T_c
Ferromagnetic	↔	Paramagnetic
Ferrimagnetic	↔	Paramagnetic
Antiferromagnetic	↔	Paramagnetic

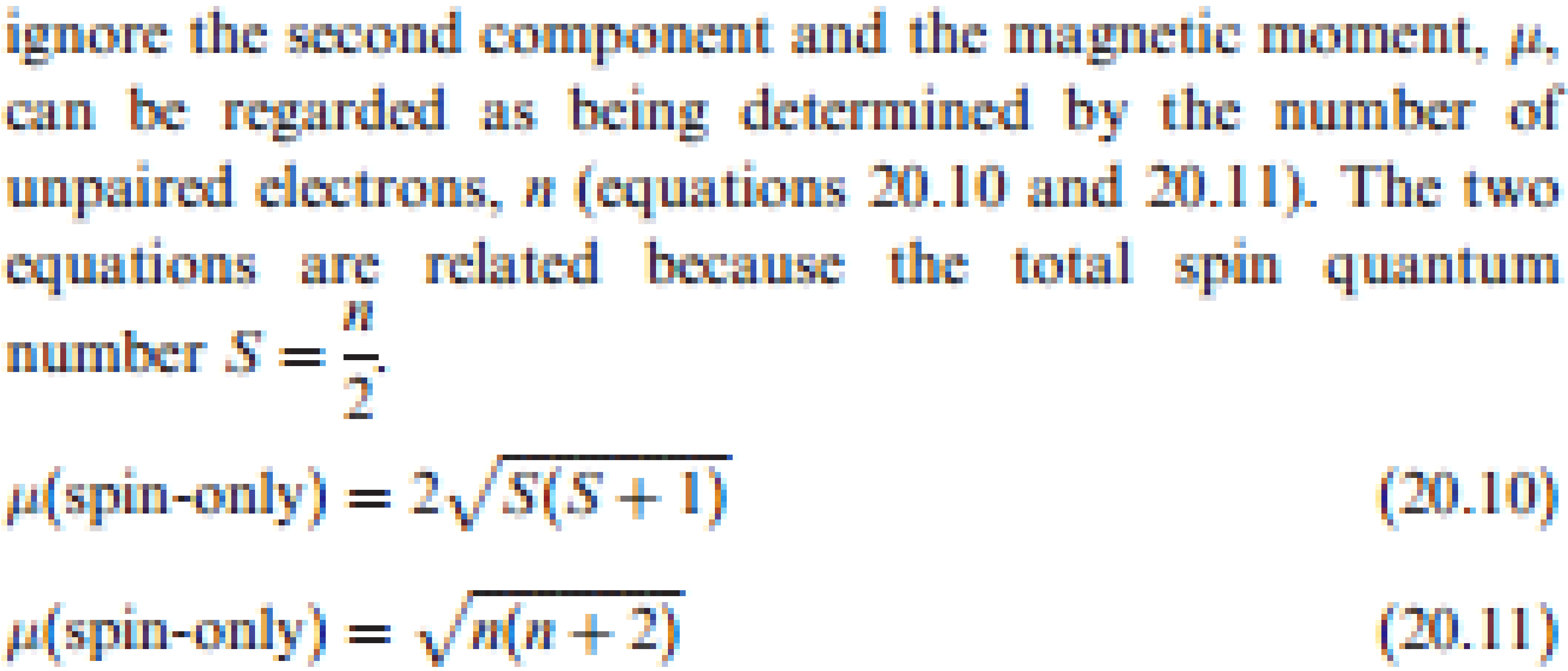
Heating up a permanent magnet brings the spins to become randomly oriented (at temperature Tc)

-> the material loses its magnetism but can still become magnetic again in an external field



Curie law, Tc and Tneel vs Ferro, Antiferro, Para

Spin-only formula

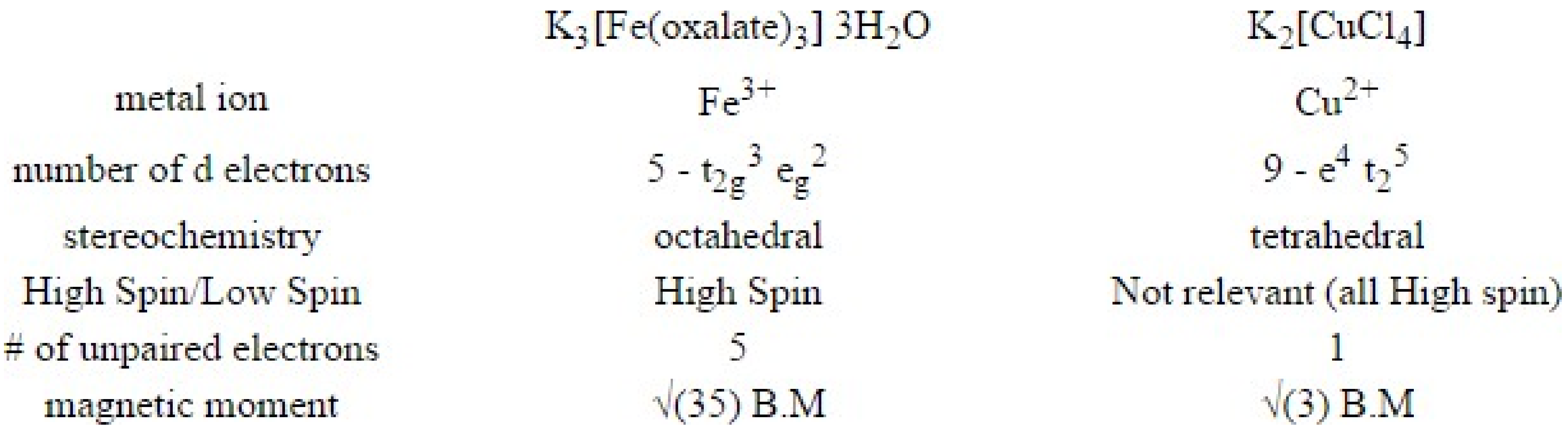


ignore the second component and the magnetic moment, μ, can be regarded as being determined by the number of unpaired electrons, n (equations 20.10 and 20.11). The two equations are related because the total spin quantum number $S = \frac{n}{2}$.

$$\mu(\text{spin-only}) = 2\sqrt{S(S+1)} \tag{20.10}$$

$$\mu(\text{spin-only}) = \sqrt{n(n+2)} \tag{20.11}$$

Examples



	$K_3[Fe(oxalate)_3]\ 3H_2O$	$K_2[CuCl_4]$
metal ion	Fe^{3+}	Cu^{2+}
number of d electrons	5 - $t_{2g}{}^3\ e_g{}^2$	9 - $e^4\ t_2{}^5$
stereochemistry	octahedral	tetrahedral
High Spin/Low Spin	High Spin	Not relevant (all High spin)
# of unpaired electrons	5	1
magnetic moment	$\sqrt{(35)}$ B.M	$\sqrt{(3)}$ B.M

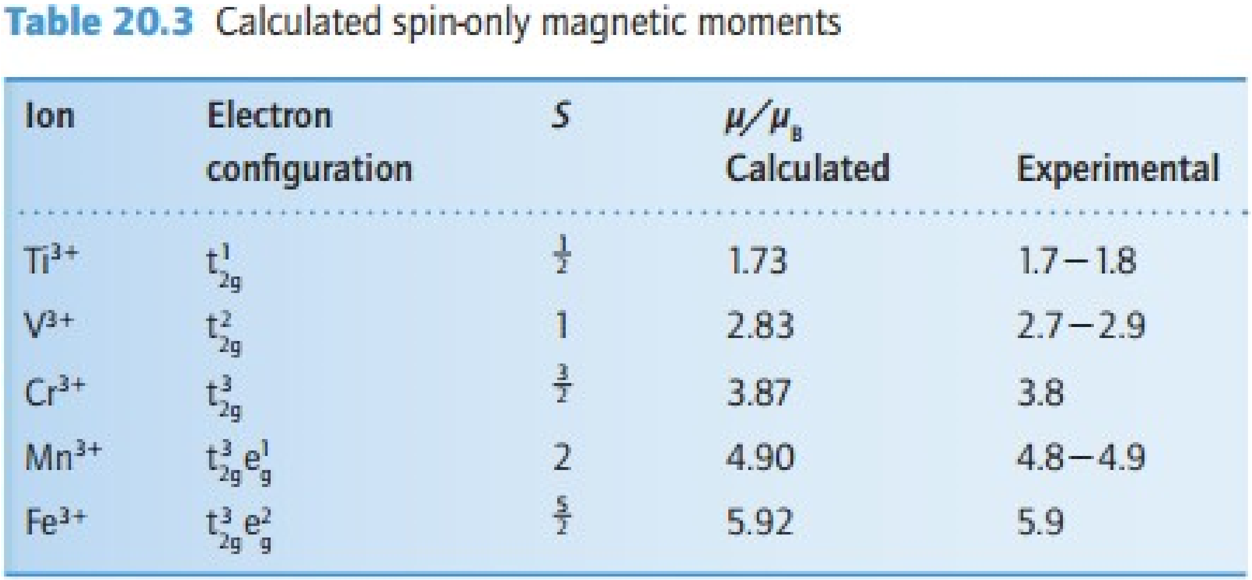
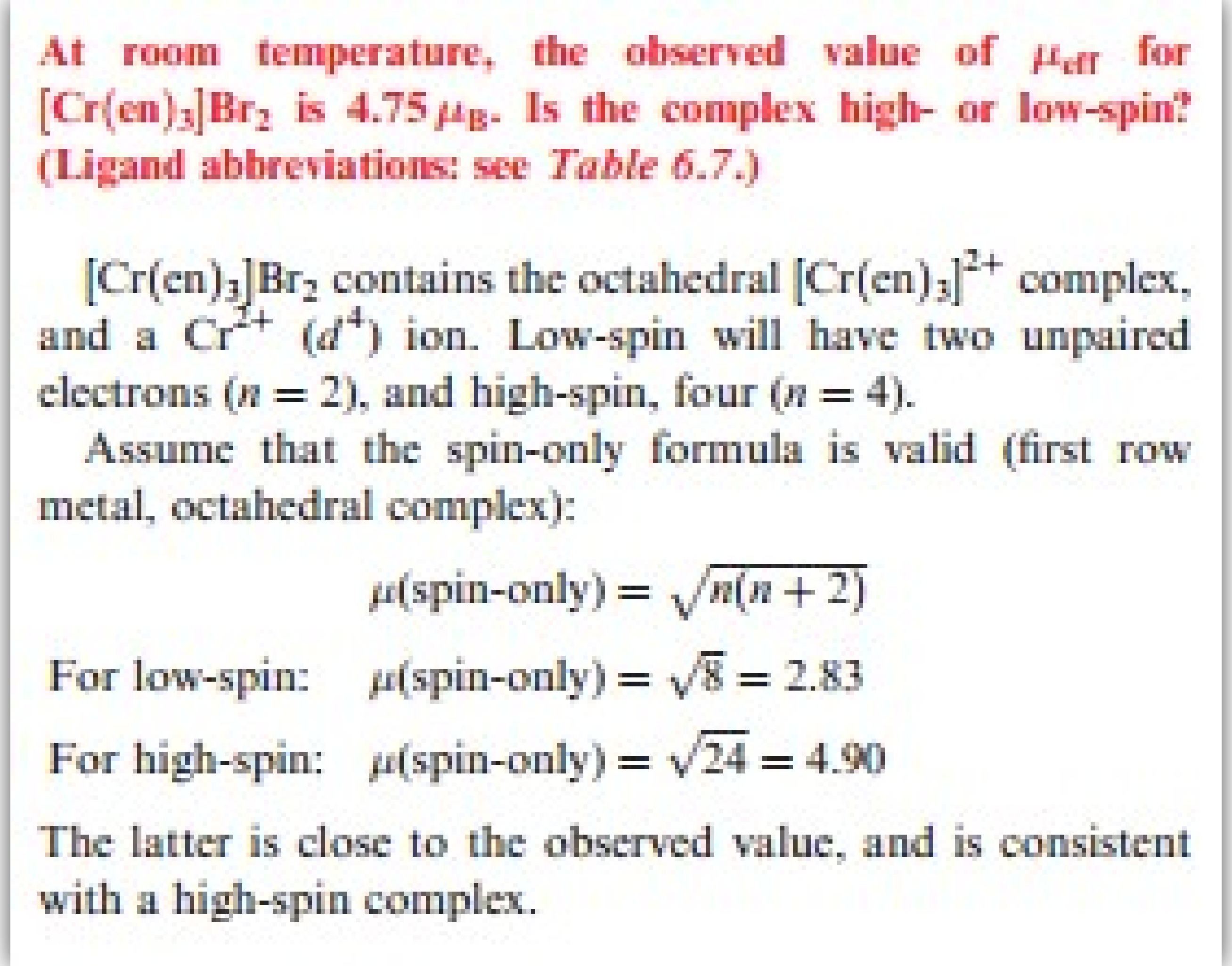


Table 20.3 Calculated spin-only magnetic moments

Ion	Electron configuration	S	μ/μ_B	
			Calculated	Experimental
Ti^{3+}	t_{2g}^1	$\frac{1}{2}$	1.73	1.7−1.8
V^{3+}	t_{2g}^2	1	2.83	2.7−2.9
Cr^{3+}	t_{2g}^3	$\frac{3}{2}$	3.87	3.8
Mn^{3+}	$t_{2g}^3e_g^1$	2	4.90	4.8−4.9
Fe^{3+}	$t_{2g}^3e_g^2$	$\frac{5}{2}$	5.92	5.9

Conclusions from magn. susceptibility



At room temperature, the observed value of μ_{eff} for $[Cr(en)_3]Br_2$ is 4.75 μ_B. Is the complex high- or low-spin? (Ligand abbreviations: see *Table 6.7*.)

$[Cr(en)_3]Br_2$ contains the octahedral $[Cr(en)_3]^{2+}$ complex, and a Cr^{2+} (d^4) ion. Low-spin will have two unpaired electrons ($n = 2$), and high-spin, four ($n = 4$).

Assume that the spin-only formula is valid (first row metal, octahedral complex):

$$\mu(\text{spin-only}) = \sqrt{n(n+2)}$$

For low-spin: $\mu(\text{spin-only}) = \sqrt{8} = 2.83$

For high-spin: $\mu(\text{spin-only}) = \sqrt{24} = 4.90$

The latter is close to the observed value, and is consistent with a high-spin complex.

Find the electron configuration from the following observations:

(a) μeff for $[Cr(NH_3)_6]Cl_2$ is 4.85 μB.

(b) μeff for $[V(NH_3)_6]Cl_2$ is 3.9 μB.

(c) μeff for a Co(II) complex is 4.0 μB.

(d) μeff for $[Mn(NCS)_6]_4$(-) is 6.06 μB.

EXAMPLE 20.2 Inferring an electron configuration from a magnetic moment

The magnetic moment of a certain octahedral Co(II) complex is $4.0\mu_B$. What is its d-electron configuration?

Answer We need to match the possible electron configurations of the complex with the observed magnetic dipole moment. A Co(II) complex is d^7. The two possible configurations are $t_{2g}^5e_g^2$ (high spin, $N = 3$, $S = \frac{3}{2}$) with three unpaired electrons or $t_{2g}^6e_g^1$ (low spin, $N = 1$, $S = \frac{1}{2}$) with one unpaired electron. The spin-only magnetic moments are $3.87\mu_B$ and $1.73\mu_B$, respectively (see Table 20.3). Therefore, the only consistent assignment is the high-spin configuration $t_{2g}^5e_g^2$.

Self-test 20.2 The magnetic moment of the complex $[Mn(NCS)_6]^{4-}$ is $6.06\mu_B$. What is its electron configuration?

Spin Cross Over SCO

Some complexes can change from low-spin to high-spin at higher temperatures:

=> low magnetic moment -> high m.m.
=> M-L bonds short -> longer

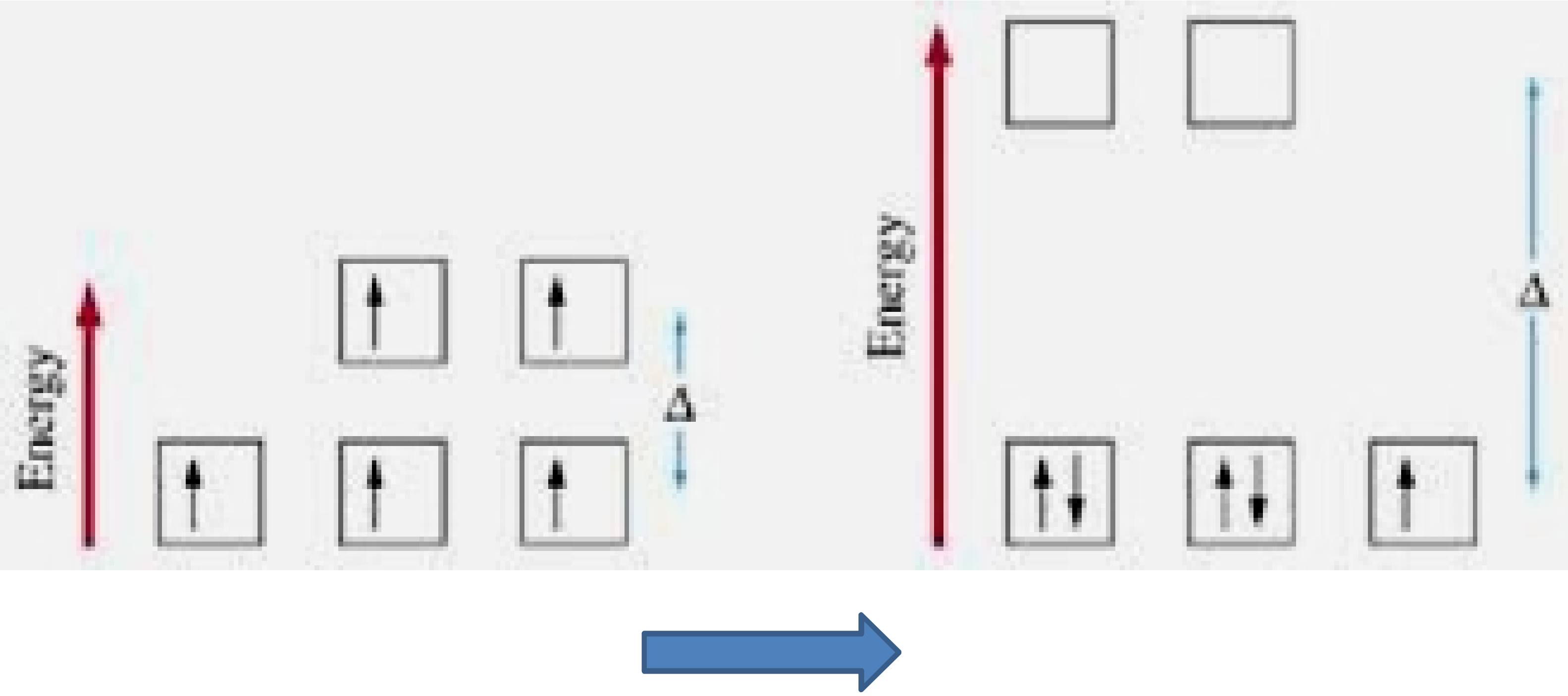
(why ?)

This can happen quickly in a small T-range

Low and high changing in Xg via temperature

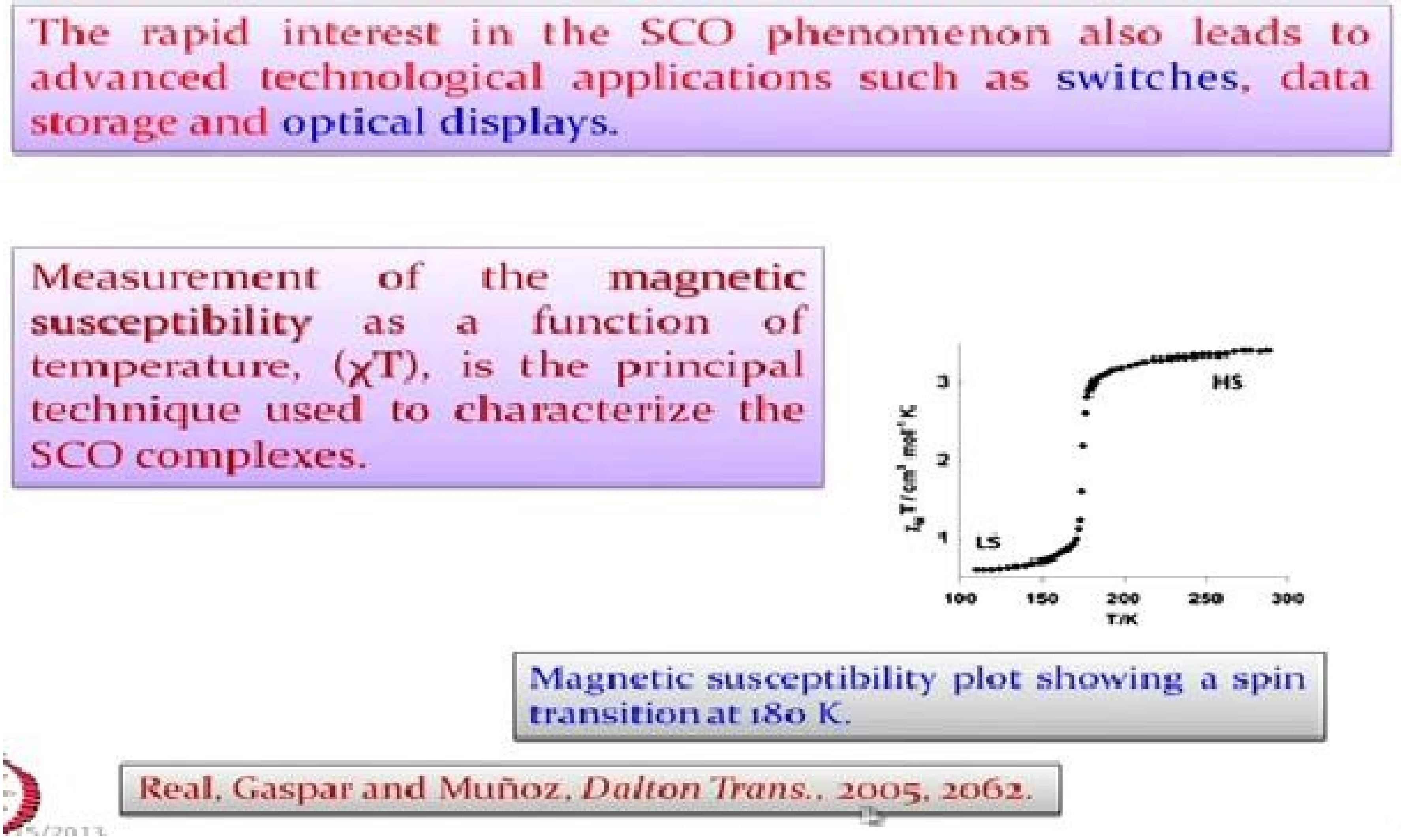
“Spin Cross Over” SCO

Increase in temperature can change a high-spin to a low-spin complex, changing the magnetic moments:



T increase

SCO applications

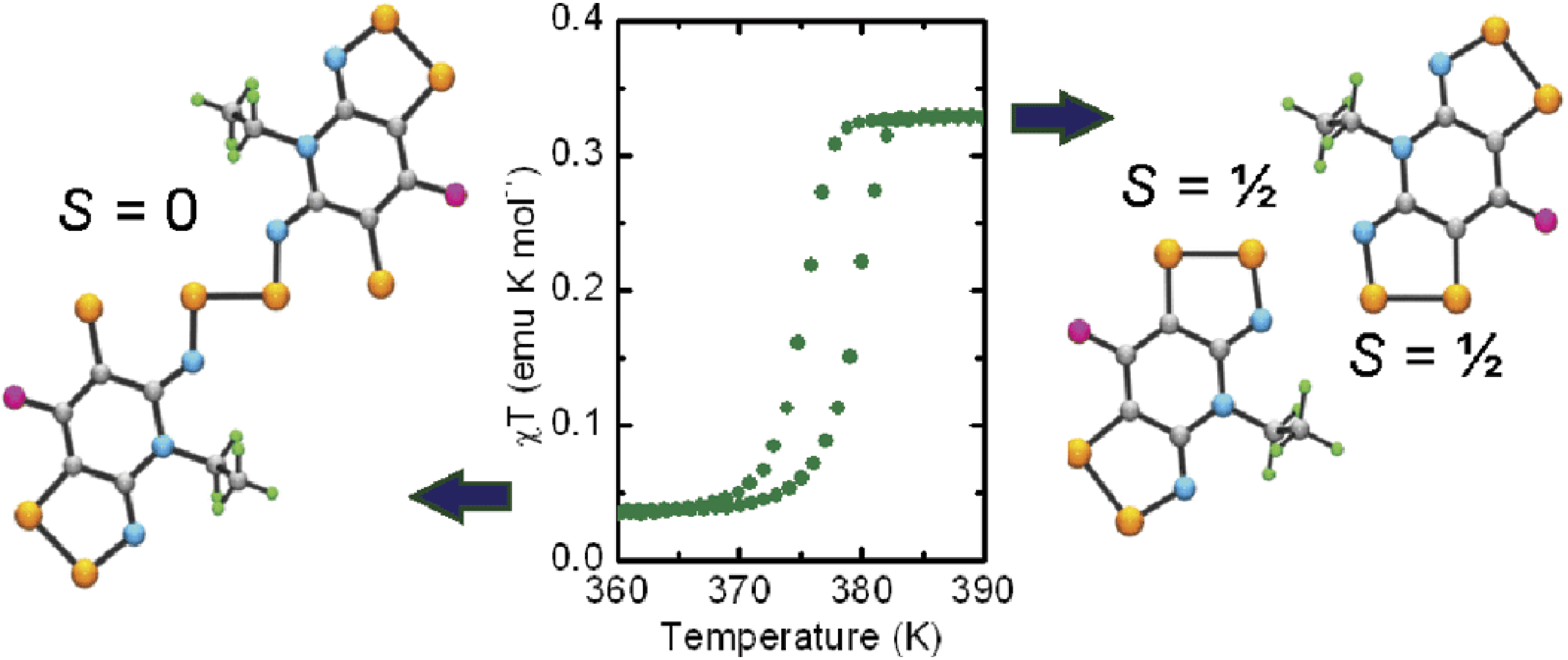


The rapid interest in the SCO phenomenon also leads to advanced technological applications such as switches, data storage and optical displays.

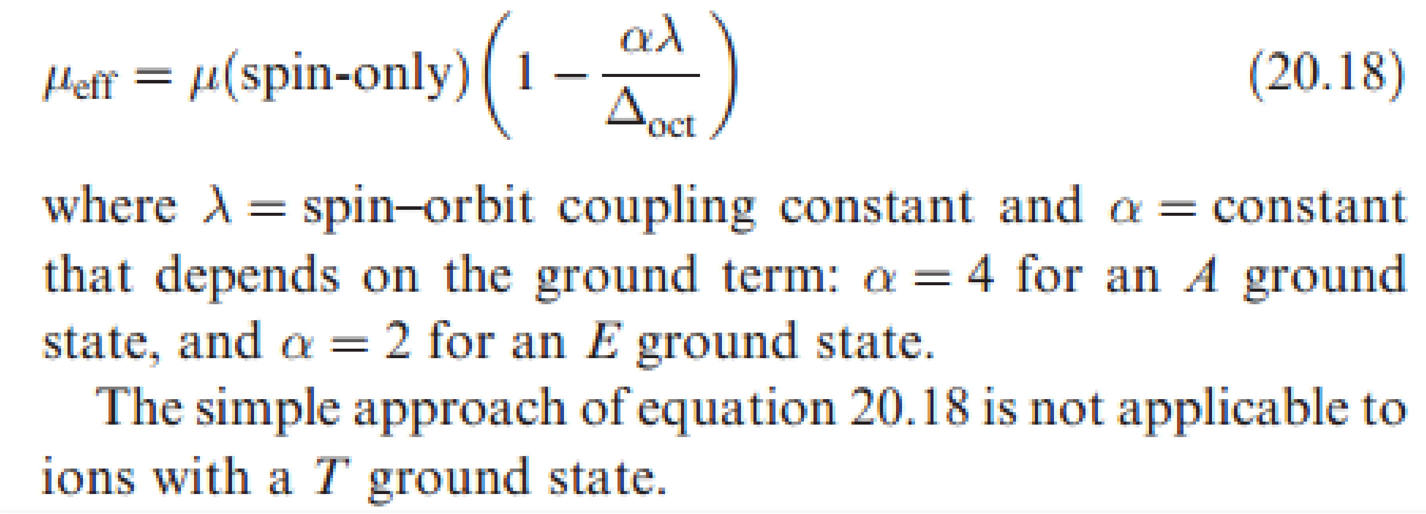
Measurement of the **magnetic susceptibility** as a function of temperature, (χT), is the principal technique used to characterize the SCO complexes.

Magnetic susceptibility plot showing a spin transition at 180 K.

Real, Gaspar and Muñoz, *Dalton Trans.*, 2005, 2062.


S = 0
S = ½
S = ½
0.4
0.3
0.2
0.1
0.0
χT (emu K mol^{-1})
360
370
380
390
Temperature (K)

Spin and orbital contributions to the magnetic moment

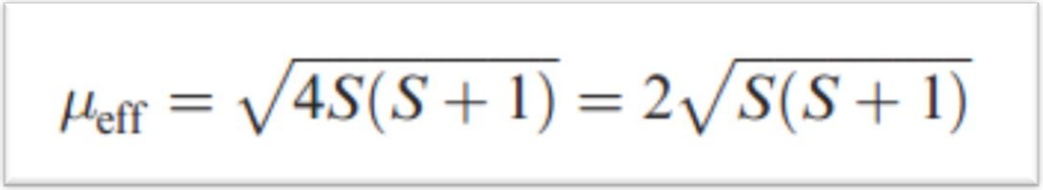


$$\mu_{\text{eff}} = \mu(\text{spin-only})\left(1 - \frac{\alpha\lambda}{\Delta_{\text{oct}}}\right) \qquad (20.18)$$

where λ = spin–orbit coupling constant and α = constant that depends on the ground term: $\alpha = 4$ for an A ground state, and $\alpha = 2$ for an E ground state.

The simple approach of equation 20.18 is not applicable to ions with a T ground state.

If S-L coupling is weak



$$\mu_{\text{eff}} = \sqrt{4S(S+1)} = 2\sqrt{S(S+1)}$$

Deviations from spin-only formula

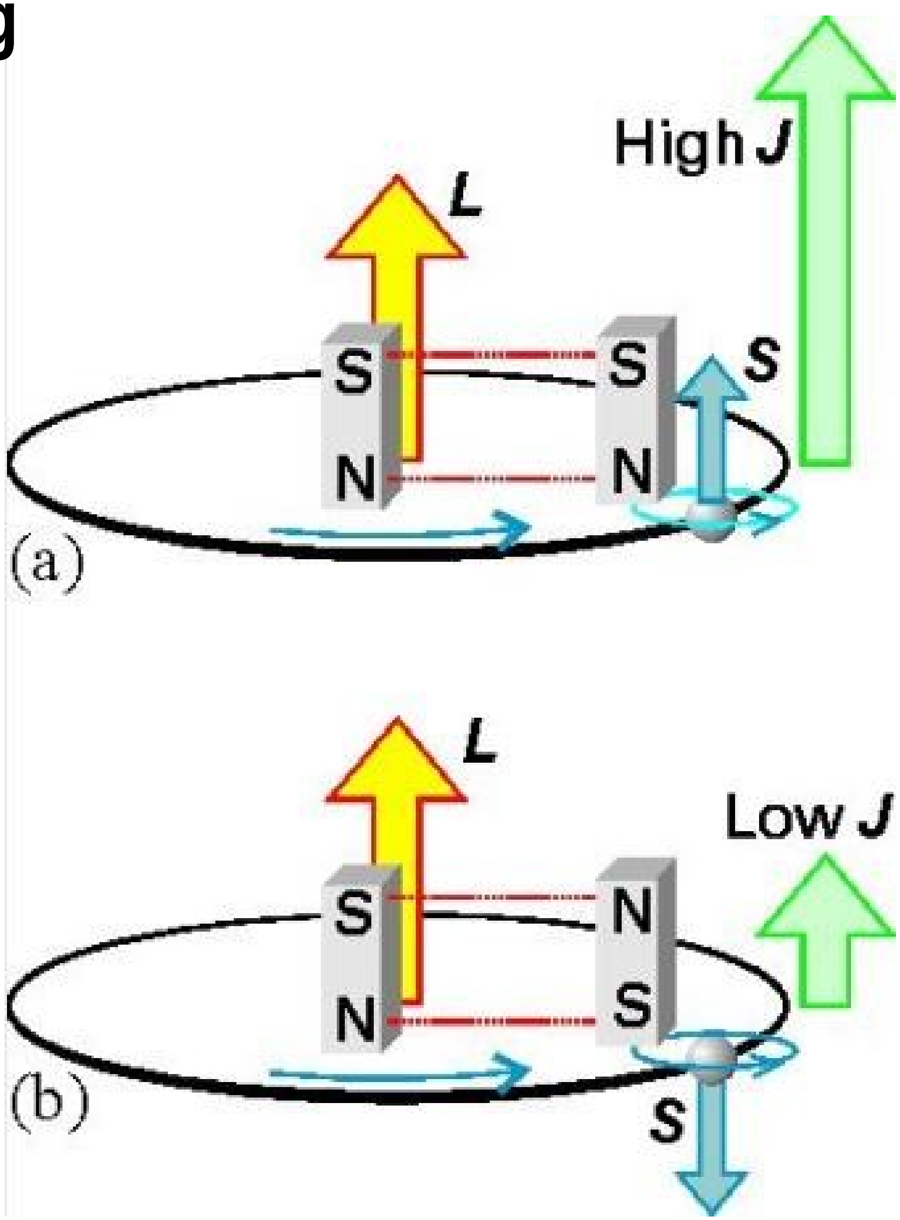
Example:

$[Fe(CN)_6]^{3-}$ has μ = 2.3μB
which is between low- and high-spin calculated
(check this out)

Russell-Saunders Coupling (L-S Coupling)

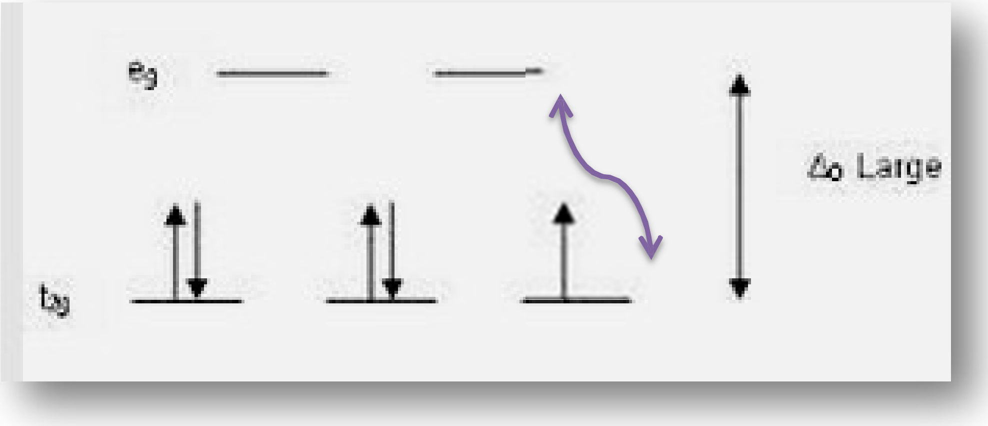
Important esp. for second and third row metal compounds
and for LS d^5, HS d^6 +d^7

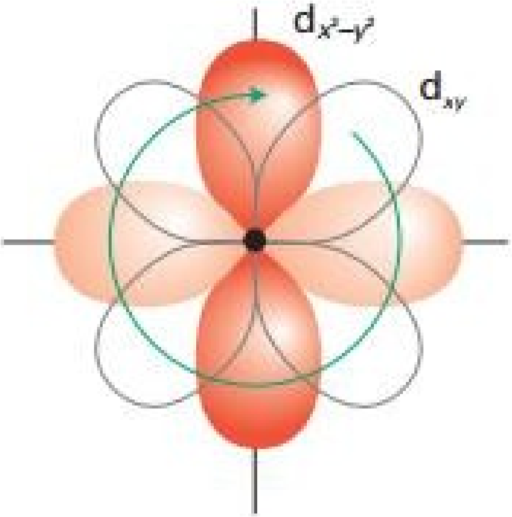
There we cannot use the simple spin-only formula anymore ☹

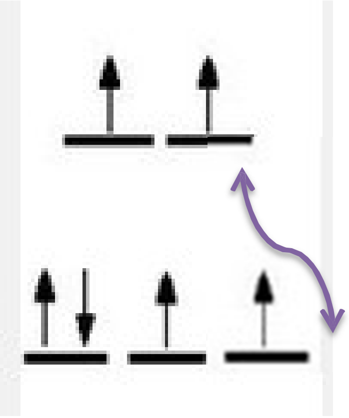


Russe-Saunders J=S+L coupling in TS

Strong Spin-Orbit coupling for:
LS d^5, HS d^6 +d^7

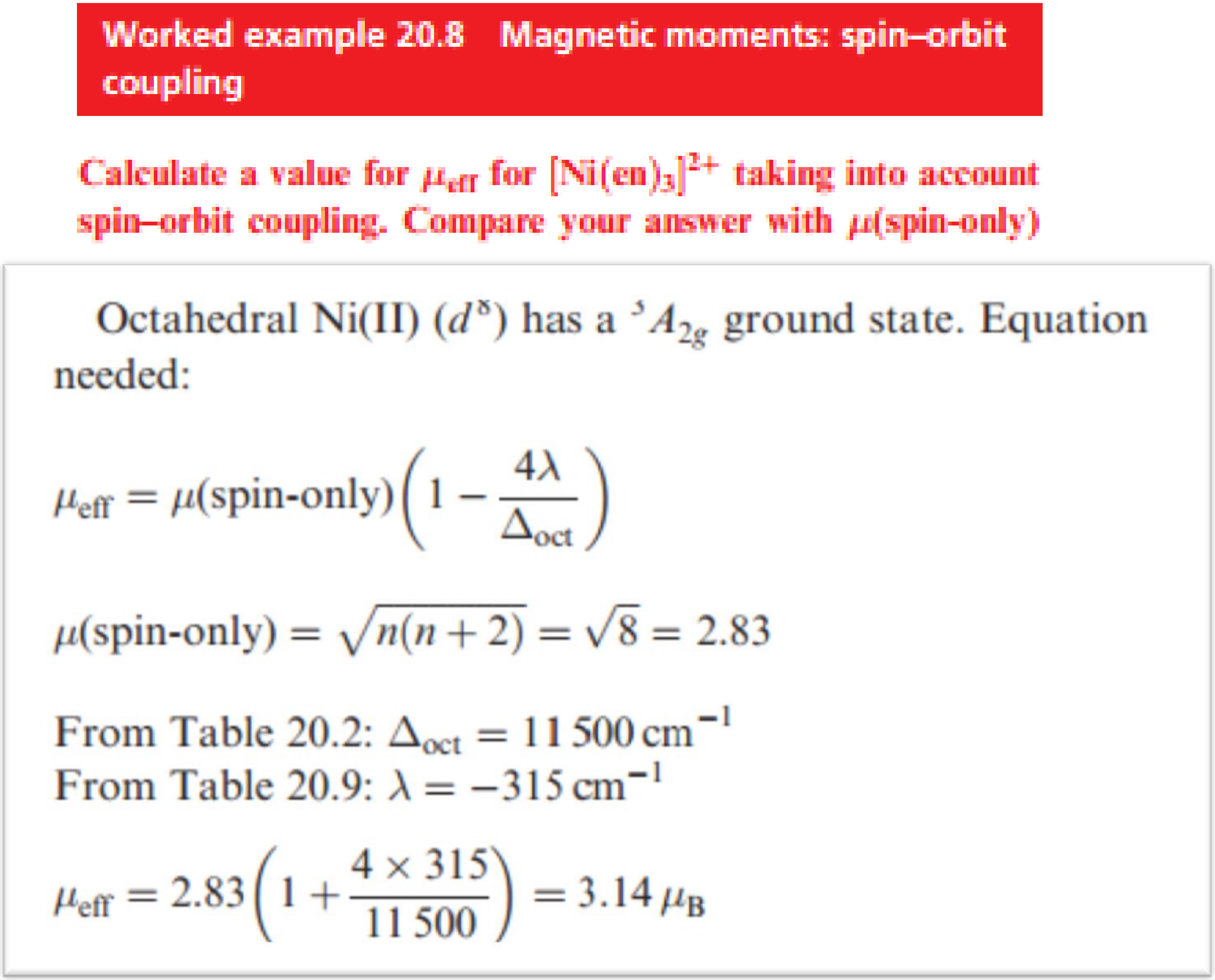






The unpaired electron in dxy can use the empty or half-filled dx2-y2 orbital to cause a rotation about the nucleus (Atkins p.479)

Spin-orbit coupling



Worked example 20.8 Magnetic moments: spin–orbit coupling

Calculate a value for μ_{eff} for $[Ni(en)_3]^{2+}$ taking into account spin–orbit coupling. Compare your answer with μ(spin-only)

Octahedral Ni(II) (d^8) has a $^3A_{2g}$ ground state. Equation needed:

$$\mu_{eff} = \mu(\text{spin-only})\left(1 - \frac{4\lambda}{\Delta_{oct}}\right)$$

$$\mu(\text{spin-only}) = \sqrt{n(n+2)} = \sqrt{8} = 2.83$$

From Table 20.2: $\Delta_{oct} = 11\,500\ \text{cm}^{-1}$

From Table 20.9: $\lambda = -315\ \text{cm}^{-1}$

$$\mu_{eff} = 2.83\left(1 + \frac{4 \times 315}{11\,500}\right) = 3.14\ \mu_B$$

Is higher than spin-only – typical for d-complexes with more than half-filled d-shell

Info to solve problems:

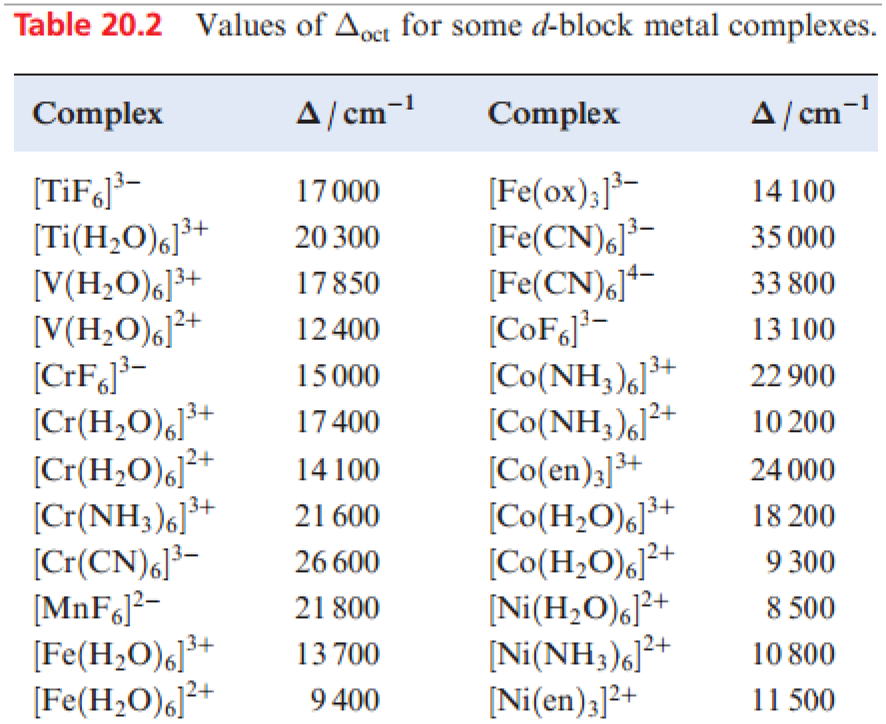


Table 20.2 Values of Δ_{oct} for some *d*-block metal complexes.

Complex	Δ / cm^{-1}	Complex	Δ / cm^{-1}
$[TiF_6]^{3-}$	17 000	$[Fe(ox)_3]^{3-}$	14 100
$[Ti(H_2O)_6]^{3+}$	20 300	$[Fe(CN)_6]^{3-}$	35 000
$[V(H_2O)_6]^{3+}$	17 850	$[Fe(CN)_6]^{4-}$	33 800
$[V(H_2O)_6]^{2+}$	12 400	$[CoF_6]^{3-}$	13 100
$[CrF_6]^{3-}$	15 000	$[Co(NH_3)_6]^{3+}$	22 900
$[Cr(H_2O)_6]^{3+}$	17 400	$[Co(NH_3)_6]^{2+}$	10 200
$[Cr(H_2O)_6]^{2+}$	14 100	$[Co(en)_3]^{3+}$	24 000
$[Cr(NH_3)_6]^{3+}$	21 600	$[Co(H_2O)_6]^{3+}$	18 200
$[Cr(CN)_6]^{3-}$	26 600	$[Co(H_2O)_6]^{2+}$	9 300
$[MnF_6]^{2-}$	21 800	$[Ni(H_2O)_6]^{2+}$	8 500
$[Fe(H_2O)_6]^{3+}$	13 700	$[Ni(NH_3)_6]^{2+}$	10 800
$[Fe(H_2O)_6]^{2+}$	9 400	$[Ni(en)_3]^{2+}$	11 500

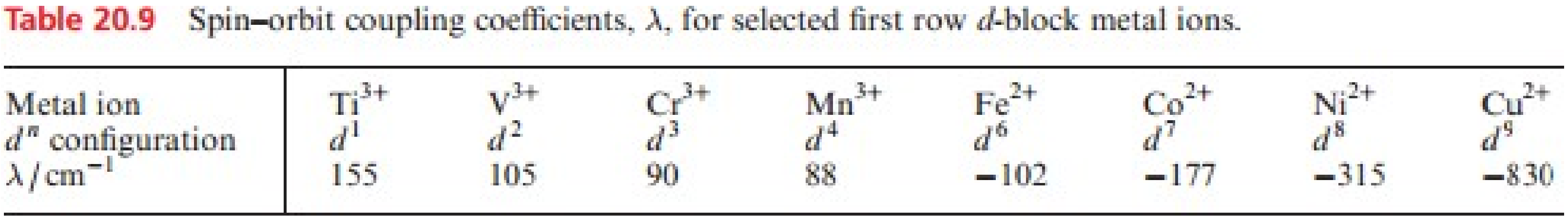
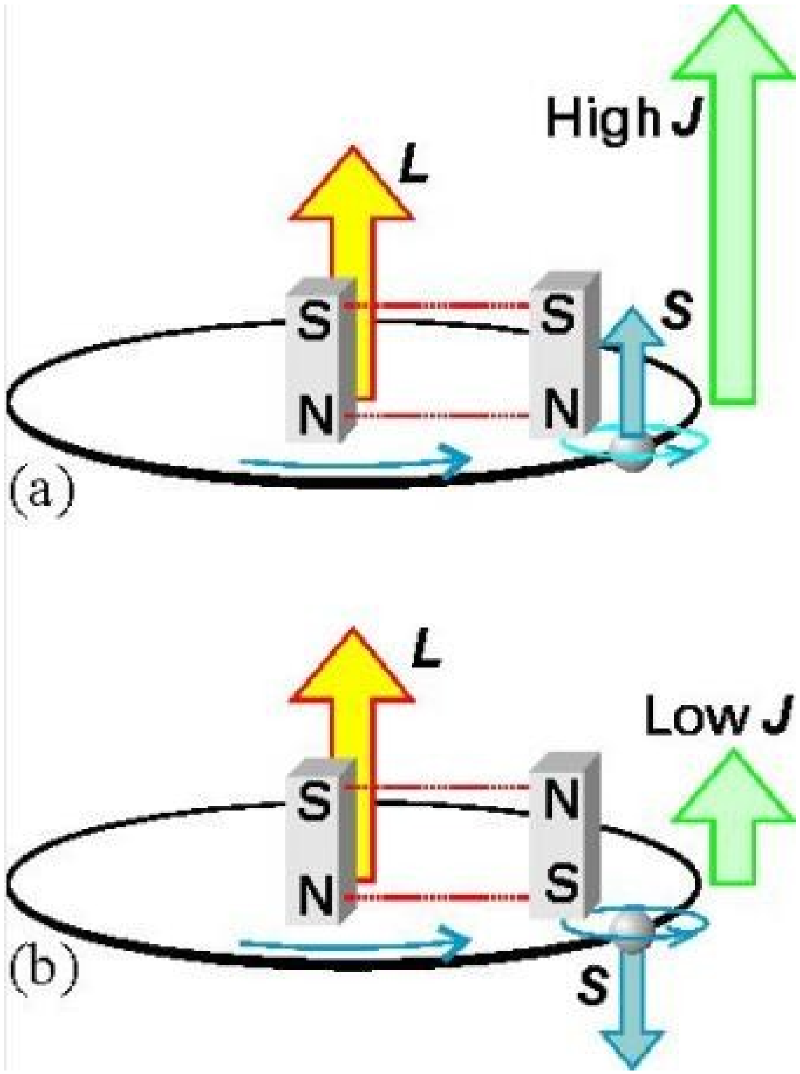


Table 20.9 Spin–orbit coupling coefficients, λ, for selected first row *d*-block metal ions.

Metal ion	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
d^n configuration	d^1	d^2	d^3	d^4	d^6	d^7	d^8	d^9
λ / cm^{-1}	155	105	90	88	−102	−177	−315	−830

Spin-Orbit coupling

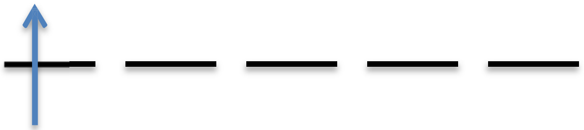
Russell-Saunders Coupling


L
High J
S
S
S
N
N
(a)
L
Low J
S
N
N
S
S
(b)

Electronic states review

Alternative to state the electron configuration of an ion as 4s2 3d6, we can express this configuration as “microstates”:

Ti(3+):
4s0 3d1



Microstates:

S = ½

L = 2 (“d”)

=> J = 5/2, 3/2 (L+S),(L+S-1),…(L-S)

Ground State with lowest J: $\mathbf{{}^{2}D_{3/2}}$

Term symbols (Sec 13.16/P, Box 20.5/I)

$$^{(2S+1)}L_J$$

- L = total orbital angular momentum quantum number

L	0	1	2	3	...
	S	P	D	F	...

  Two electrons with l_1, l_2 give

  $$L = l_1 + l_2,\ l_1 + l_2 - 1,\ \cdots, |l_1 - l_2|$$

- S = total spin angular momentum quantum number

  $$S = s_1 + s_2,\ s_1 + s_2 - 1,\ \cdots, |s_1 - s_2|$$

  (But it's easier to count the number of up and down spins)

  $2S + 1$ = spin multiplicity (singlet, double, triplet, ...)

- J = total angular momentum quantum number

  $$J = L + S,\ L + S - 1,\ \cdots, |L - S|$$

Hund's Rule for the Lowest Energy Term of a given configuration

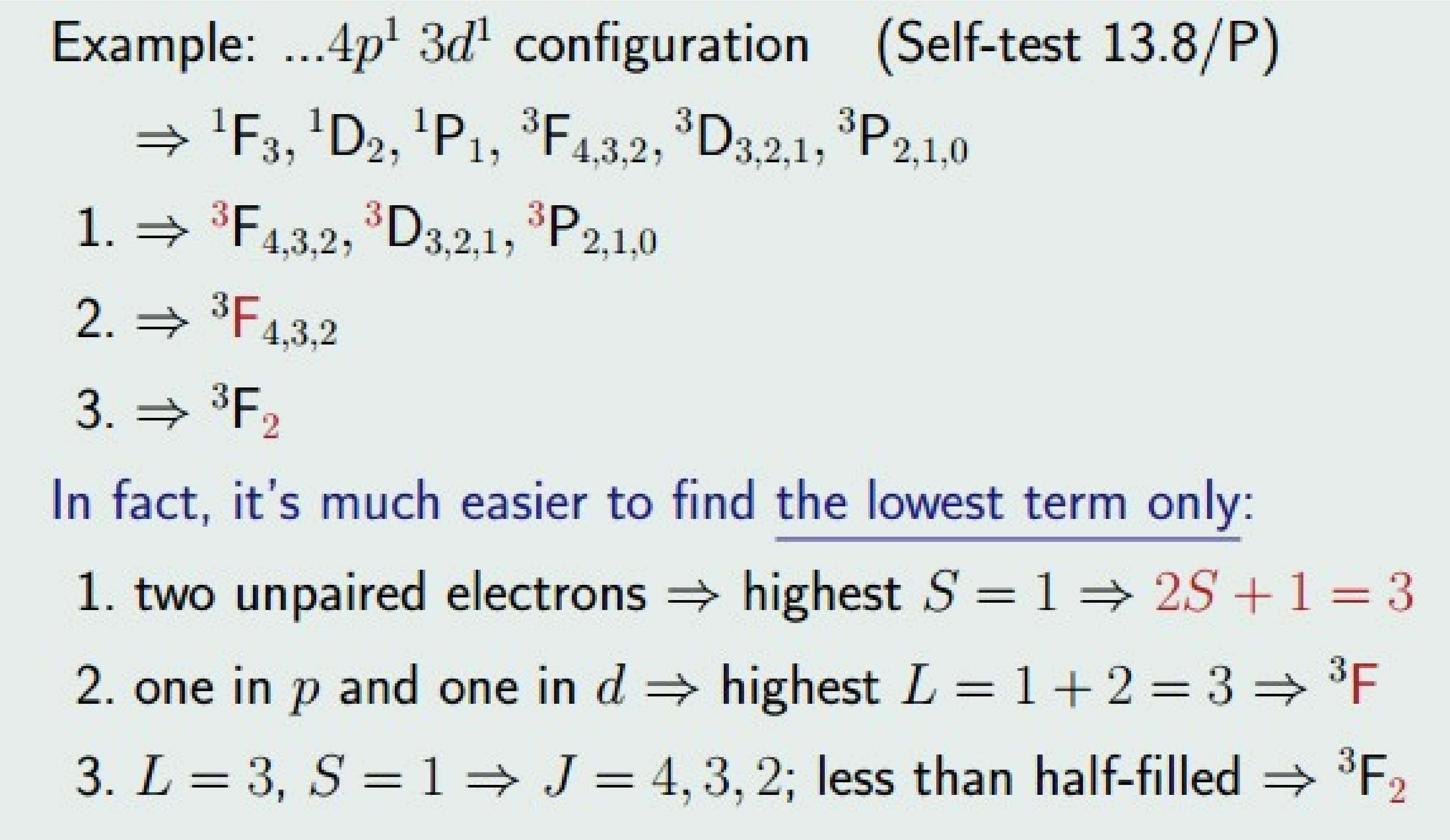
1. Highest Multiplicity $2S+1$
2. Highest value of L
3. $\begin{cases} \text{Lowest value of } J \text{ when less than half-filled} \\ \text{or} \\ \text{Highest value of } J \text{ when more than half-filled} \end{cases}$

Selection Rules for Many-electron Atoms

- $\Delta S = 0$
- $\Delta L = 0,\ \pm 1,$
- $\Delta l = \pm 1$ for the electron excited in the transition
- $\Delta J = 0,\ \pm 1$ but $J = 0 \rightarrow J = 0$ is forbidden

The rules on J are exact. Those on l, L, S presume that these quantum numbers are well-defined.

Examples



Example: ...$4p^1\ 3d^1$ configuration (Self-test 13.8/P)

$\Rightarrow {}^1\mathrm{F}_3,\ {}^1\mathrm{D}_2,\ {}^1\mathrm{P}_1,\ {}^3\mathrm{F}_{4,3,2},\ {}^3\mathrm{D}_{3,2,1},\ {}^3\mathrm{P}_{2,1,0}$

1. $\Rightarrow {}^3\mathrm{F}_{4,3,2},\ {}^3\mathrm{D}_{3,2,1},\ {}^3\mathrm{P}_{2,1,0}$
2. $\Rightarrow {}^3\mathrm{F}_{4,3,2}$
3. $\Rightarrow {}^3\mathrm{F}_2$

In fact, it's much easier to find the lowest term only:

1. two unpaired electrons $\Rightarrow$ highest $S = 1 \Rightarrow 2S + 1 = 3$
2. one in p and one in d $\Rightarrow$ highest $L = 1 + 2 = 3 \Rightarrow {}^3\mathrm{F}$
3. $L = 3,\ S = 1 \Rightarrow J = 4, 3, 2$; less than half-filled $\Rightarrow {}^3\mathrm{F}_2$

The ground configuration of a Ti^{2+} ion is [Ar]$3d^2$.

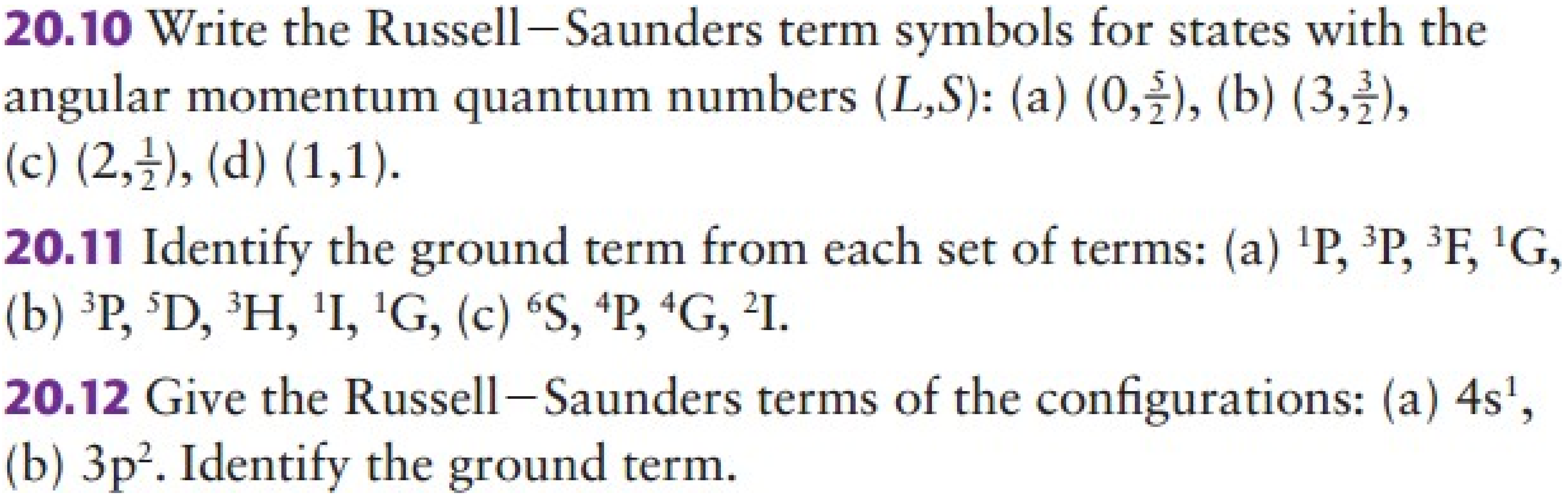
What is the term of lowest energy and which level of that term lies lowest?

1. two unpaired electrons $\Rightarrow$ highest $S = 1 \Rightarrow 2S + 1 = 3$
2. two in d in parallel spin $\Rightarrow$ highest $L = 1 + 2 = 3 \Rightarrow {}^3\mathrm{F}$
3. $L = 3,\ S = 1 \Rightarrow J = 4, 3, 2$; less than half-filled $\Rightarrow {}^3\mathrm{F}_2$

Now, try:

C	[He]$2s^2\ 2p^2$	${}^3\mathrm{P}_0$
N	[He]$2s^2\ 2p^3$	${}^4\mathrm{S}_{3/2}$
O	[He]$2s^2\ 2p^4$	${}^3\mathrm{P}_2$
Cr^{3+}	[Ar]$3d^3$	${}^4\mathrm{F}_{3/2}$
Mn^{3+}	[Ar]$3d^4$	${}^5\mathrm{D}_0$
Fe^{3+}	[Ar]$3d^5$	${}^6\mathrm{S}_{5/2}$

Atkins p.505



20.10 Write the Russell–Saunders term symbols for states with the angular momentum quantum numbers (L,S): (a) $(0,\frac{5}{2})$, (b) $(3,\frac{3}{2})$, (c) $(2,\frac{1}{2})$, (d) $(1,1)$.

20.11 Identify the ground term from each set of terms: (a) ^{1}P, ^{3}P, ^{3}F, ^{1}G, (b) ^{3}P, ^{5}D, ^{3}H, ^{1}I, ^{1}G, (c) ^{6}S, ^{4}P, ^{4}G, ^{2}I.

20.12 Give the Russell–Saunders terms of the configurations: (a) $4s^1$, (b) $3p^2$. Identify the ground term.