

## Magnetic properties of transition & inner transition metal complex

### Types of magnetic behaviour:

Paramagnetic → The substance having  $\mu > 1$  are called the paramagnetic substance ( $\mu \rightarrow$  magnetic permeability) Eg:  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{Al}$ ,  $\text{Ti}$ .

Diamagnetic → The substance having  $\mu < 1$  are called the ~~para~~ diamagnetic substance. Eg:  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{Cu}$ .

Ferromagnetic → Ferromagnetic compounds have their atomic magnetic moment (spins) aligned in the same direction, resulting in a strong, permanent net magnetic moment. Eg:  $\text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$ .

Antiferromagnetic → Antiferromagnetic compounds have adjacent magnetic moments aligned oppositely, leading to a net magnetic moment of zero. Eg:  $\text{MnO}$ ,  $\text{Co}$ .

### Curie's law:

This law states that the magnetic susceptibility ( $\chi$ ) of a paramagnetic material is inversely proportional to the absolute temperature ( $T$ ):

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

Where,  $C \rightarrow$  Curie constant.

Application → It applies to ideal paramagnetic materials where magnetic dipoles are independent of each other and do not interact.

### Curie - Weiss law:

This law is an adaptation of Curie's law that accounts for the presence of interactions between magnetic dipoles in a material, which becomes significant above a certain threshold temperature, known as the Curie temp ( $T_c$ )

$$\chi = \frac{C}{T - T_c}$$

$$\text{or, } \chi = \frac{C}{(T - \theta)}$$

Where,  $\theta \rightarrow$  The Weiss const. ( $\theta = T_c$ ).

Application  $\rightarrow$  It provides a more accurate description for ferromagnetic materials above their Curie temperature, in their paramagnetic phase.

### Orbital and Spin magnetic moments:

Magnetic moments arise from two distinct electron motion: the orbital magnetic moment from an electron's revolution around the nucleus and the spin magnetic moment from an electron's intrinsic spin.

### Orbital Magnetic moment ( $\mu_L$ ):

Origin  $\rightarrow$  This arises from the electron's motion around the nucleus.

Quenching  $\rightarrow$  In transition metal complexes, the surrounding ligands create a crystal field that restricts the electron's movement. This restriction, known as orbital quenching, significantly reduces or completely eliminates the orbital contribution to the total magnetic moment.

Temperature dependence  $\rightarrow$  Because the orbital contribution is affected by the chemical environment, it can be temperature dependent, a contrast to the spin-only moment.

### Spin-Magnetic moment ( $\mu_s$ ):

Origin  $\rightarrow$  Arises from the intrinsic spin of an electron, a fundamental property of elementary particles.

The Spin-only magnetic moment can be calculated using the formula:  $\mu = \sqrt{n(n+2)} \text{ BM}$ ,  $n \rightarrow$  No. of unpaired e<sup>-</sup>.

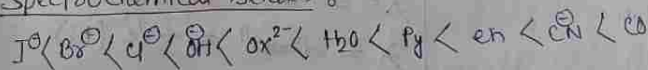
Generally spin-magnetic moment independent of the chemical environment (temperature).

— x —

$\rightarrow$  Branch of chemistry especially concerned with the magnetic properties of chemical compounds.

$\rightarrow$  With this technique we can determine the magnetic properties or magnetism of the co-ordination complexes.

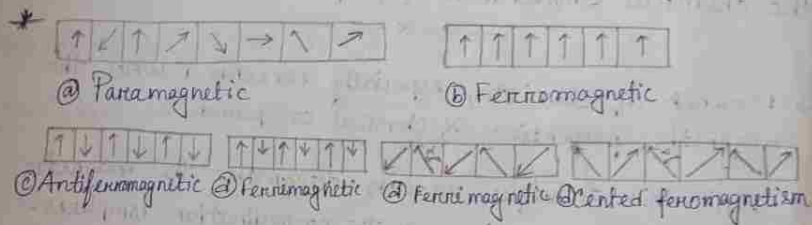
### Spectrochemical Series:



Transition metal complexes  $\rightarrow$  Low Spin  $\rightarrow$  Strong field ligand  
 $\rightarrow$  High Spin  $\rightarrow$  Weak field ligand

Temp dependence of magnetic susceptibility of different types of magnetic materials:

→ When an external magnetic field (H) is applied on a paramagnetic substances, the paramagnetic substances will try to orient in the direction of the field. But thermal excitation will try to orient the molecules randomly. Thus the effect of H and T will mutually oppose and the molecules will orient in different angles with the direction of the field.



L-S Coupling  
↑ Angular quantum number  
Spin quantum number

$$E = \frac{Ze^2 h^2}{8\pi^2 m^2 c^2 h^3} (L \cdot S)$$

$$\lambda = d^1 - d^4 = +ve (HS)$$

$$\lambda = d^6 - d^9 = -ve (HS)$$

$$\lambda = \frac{+E}{2S}$$

$$\lambda \propto Z_{eff}$$

$$\lambda \propto \frac{1}{q^3}$$

Spin-orbit coupling constant.

A → One type of orientation } Spectroscopic  
E → Two type of orientation } Ground state  
T → Three type of orientation }

Molecular and atomic terms :- Greater than half field

$$2S+1 L_J, S=1, L=3$$

For,  $d_2 = 3F_2$

$$J = |L+S| \text{ to } |L-S|$$

S	P	d	f
l = 0	1	2	3



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$$n_{C_n} = \frac{n!}{n!(n-n)!} \quad \begin{cases} n \rightarrow \text{Total the number of orbitals} \\ n \rightarrow \text{Given electrons} \end{cases}$$

$$10C_2 = \frac{10!}{2 \times 8!} = \frac{10 \times 9}{2} = 45$$

$$S = \frac{1}{2} + \frac{1}{2} = 1$$

$$2S + 1 = 2 \times 1 + 1 = 3$$

1	1			
$m_l = -2$	$-1$	$0$	$+2$	$+1$

$$L = \sum |m_l| = |-2-1| = 3$$

### SQUID magnetometer

Superconducting Quantum Interference device.

$\mu_{\text{exp}} / \mu_{\text{eff}}$  or  $\mu_T = \mu_{\text{so}} + \mu_o \leftarrow$  Orbital quantum numbers.

$$= \sqrt{4s(s+1) + L(L+1)} \quad \text{B.M.}$$

$$= \sqrt{4 \times \frac{1}{2} \times \frac{1}{2} + 1} = \sqrt{n(n+2)} \quad \text{B.M.}$$

# d-orbitals having orbital configuration, the following condition must be satisfied:-

- (i) Orbitals must be degenerate, if ground state is T-term, the system must show.
- (ii) Orbitals must be interconvertible (by angle rotation).
- (iii) Orbitals must not change spin during inter-conversion.

# Spectroscopic term:

$t_{2g}, t_2 \rightarrow$  Interconvertible.

$e \rightarrow$  Not interconvertible

	G.S	E.S	For
$d_1$	✓	✗	$d^1 = 2T$
$d_2$	✓	✓	$d^2 = 3T$
$d_3$	✗	✓	$d^3 = 4A$

# When there is term A, E in ground state, orbital contribution can generate by mixing of the ground state with excited state via spin orbital coupling.

\* Ground state having T-configuration (orbital contribution).

$$\mu_{\text{eff}} = \mu_B \left( 1 - \frac{\alpha \lambda}{10 Dq} \right)$$

$$\Rightarrow \mu_{\text{eff}} < \mu_{\text{so}} \quad (d^1 - d^4)$$

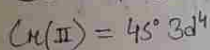
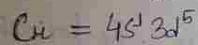
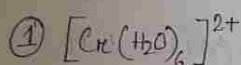
$$\mu_{\text{eff}} > \mu_{\text{so}} \quad (d^6 - d^9)$$

\* Spin multiplicity must not change after excitation.

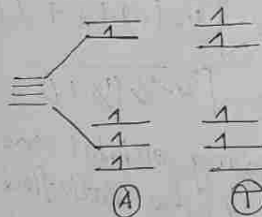
$$\alpha = E_{\text{exc}} = 2$$

$$\alpha = A_{\text{exc}} = 4$$

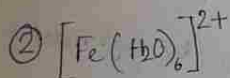
[Oct. Td. then  $\mu_{\text{eff}}$  is almost  $\mu_{\text{so}}$ .  
10Dq) 10Dq  $\mu_{\text{eff}} \approx \mu_{\text{so}}$ .



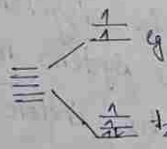
$$\therefore \mu_{\text{eff}} < \mu_{\text{so}}$$



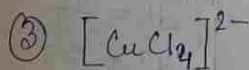
Orbital contribution on excited state but it's -ve direction because  $d^4$ 's +ve



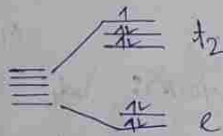
$$\therefore \mu_{\text{eff}} > \mu_{\text{so}}$$



⊕ Ground state.



tetrahedral



\*  $K_4[Fe(CN)_6] \Rightarrow$  Diamagnetic / No orbital contribution.  
 Strong field (high spin)

\*  $[CoF_6]^{3-}$   $[Co(NH_3)_6]Cl_3 \Rightarrow$  Always form low spin complex

Exceptions:  $[CoF_6]^{3-}$   
 $[CoF_6(H_2O)_3]$

\*  $M(NH_3)_4(ox)$   
 Tetrahedral distortion.  
 $ns^2(n-1)d^{1-10}np^6$   
 $[ns^2(n-2)f^{1-14}ns^{1-2}]$

$$\mu_{eff} = \mu_J = g \sqrt{J(J+1)} \text{ B.M.}$$

$g \rightarrow$  Lande's splitting factor.

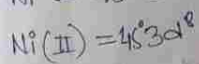
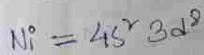
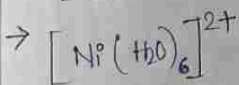
$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

\* Lanthanoids are very stable at +3 state.

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 but  
 tion  
 +ve

\*\* Lanthanoids have higher magnetic moment as compared to transition metals crystal field cannot interact with  $f$  because it is deeply sitted inside.

$$\mu_{so} = \sqrt{n(n+2)} \text{ B.M.}$$



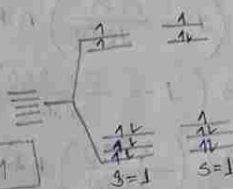
1	1	1	1	1	1
$m_l = -2$	$-1$	$0$	$+1$	$+2$	

$$L = \sum m_l = |-4 - 2 + 0 + 1 + 2| = |-3| = 3$$

$$\because S = 1, L = 3, J = L + S = 4$$

$$2S+1 L_J = 3F_4$$

S	P	d	f
0	1	2	3



$$g = 1 + \frac{4(4+1) + 1(1+1) - 3(3+1)}{2 \times 4(4+1)}$$

$$= 1 + \frac{10}{40} = \frac{5}{4}$$

$$\mu_J = \frac{5}{4} \sqrt{4(4+1)} \text{ B.M.}$$

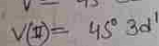
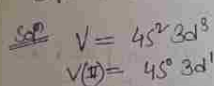
$$= \frac{5}{4} \times \sqrt{20} = \frac{5}{4} \times 2\sqrt{5} = 5.59 \text{ B.M.}$$

$$\therefore \mu_{eff} = \mu_{so} \left( 1 - \frac{\alpha \lambda}{10Dq} \right)$$

$$\therefore \mu_{eff} > \mu_{so}$$

Q. Calculate the effective magnetic moment for  $VCl_4$  complex.

Given,  $10Dq = 8000 \text{ cm}^{-1}$ ,  $\lambda = 250 \text{ nm}$



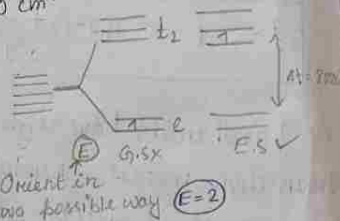
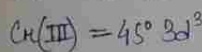
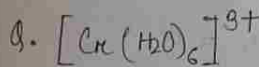
$$\mu_{so} = \sqrt{1(1+2)} = 1.732 \text{ B.M.}$$

$$\mu_{eff} = \mu_{so} \left( 1 - \frac{\alpha \lambda}{10Dq} \right) \text{ B.M.}$$

$$= 1.73 \left( 1 - \frac{2 \times 250}{8000} \right) \text{ B.M.}$$

$$= 1.732 \left( \frac{7500}{8000} \right) \text{ B.M.}$$

$$= 1.6265 \text{ B.M.}$$



No orbital contribution on ground state

Orbital contribution on excited state



$$\mu_{s,0} = \sqrt{3(3+2)} = 3.8 \text{ B.M.}$$

$$\therefore \mu_{\text{eff}} < \mu_{s,0}$$

$$2S+1 L_J = {}^4F_{3/2} \quad \left\{ \begin{array}{l} 2S+1 = 2 \times \frac{3}{2} + 1 \\ = 4 \end{array} \right\}$$

$$J = L - S = 3 - \frac{3}{2} = \frac{3}{2}$$

$$g = 1 + \frac{\frac{3}{2}(\frac{3}{2}+1) + \frac{3}{2}(\frac{3}{2}+1) - 3(3+1)}{2 \times \frac{3}{2}(\frac{3}{2}+1)}$$

$$= 1 + \frac{\frac{15}{4} + \frac{15}{4} - 12}{\frac{15}{2}}$$

$$= 1 - 0.6$$

$$= 0.4$$

$$Q. [\text{CoCl}_4]^{2-}$$

$$\text{Co} = 4s^2 3d^7$$

$$\text{Co(II)} = 4s^0 3d^7$$

$$\mu_{\text{eff}} > \mu_{s,0}$$

$$\therefore 2S+1 L_J = {}^4F_{9/2}$$

$$\mu_{s,0} = \sqrt{3(3+2)} = \sqrt{15} = 3.87$$

$$g = 1 + \frac{\frac{9}{2} \times \frac{11}{2} + \frac{3}{2}(\frac{9}{2}) - 12}{\frac{9}{2} \times \frac{11}{2}}$$

$$= 1 + \frac{86}{99 \times 2}$$

$$= \frac{198 + 86}{198}$$

$$= 1.83$$

1	1	1		
-2	-1	0	+1	+2

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$$L = \sum |m_l| = |-2-1+0+1+2| = 3$$

$$\mu_J = g \sqrt{J(J+1)}$$

$$= 0.4 \sqrt{\frac{3}{2}(\frac{5}{2})}$$

$$= 0.4 \sqrt{\frac{15}{4}}$$

$$= 0.4 \times 1.92$$

$$= 0.768$$

1	1	1	1	1
-2	-1	0	+1	+2

$$m_l = -2 -1 0 +1 +2$$

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$$L = |-3| = 3$$

$$J = L + S = 3 + \frac{3}{2} = \frac{9}{2}$$

$$\mu_J = g \sqrt{J(J+1)}$$

$$= 1.3 \sqrt{\frac{9}{2} \times \frac{11}{2}}$$

$$= 1.3 \times 4.97$$

$$= 6.46$$

### \* ④ Spin-orbit coupling constants : Splitting of the energy levels :

To measure the strength of interaction between the spin and orbital angular momenta, spin-orbit coupling constants are used  $\zeta$  (ZETA) and  $\lambda$ .

- No. of unpaired electrons in free ions : In the free ions all the d-orbitals are degenerate and in such cases the no. of unpaired e<sup>-</sup>s can be computed.

For,  $d^1 - d^4$ ,  $\lambda = +ve$

$d^6 - d^9$ ,  $\lambda = -ve$

[ $\because \lambda$  is redundant for  $d^5$  and  $d^{10}$ .]

- No. of unpaired electrons in complexes :

In the presence of crystal fields, degeneracy of the d-orbitals is lifted. In octahedral crystal field —

(i)  $t_{2g}$  ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ )

(ii)  $e_g$  ( $d_{x^2-y^2}$  and  $d_{z^2}$ )

### \* Effect of oxidation state : $\uparrow$

It is evident that the spin-orbit coupling constant increases with the increase of positive oxidation state, more correctly  $Z_{eff}$  and decreases with the increase of radius ( $r$ ).

### ② Factors controlling the magnitude of Spin-Orbit Coupling Constant:

#### • Effect of effective nuclear charge ( $\propto Z_{eff}$ ):

$Z_{eff}$  increases with the increase of atomic number in a period and in a group for the d- and f-block metals. For the lanthanides and actinides, because of the low shielding  $(n-2)f$  and  $(n-1)d$  electrons,  $Z_{eff}$  increases and consequently the spin-orbit coupling constant becomes relatively higher than that of the d-block metal ions.

#### • Effect of orbit radius ( $\propto \frac{1}{r^n}$ ):

For a particular metal ion, with the increase of oxidation state, the size of the metal ion decreases (i.e.  $r$  decreases) and  $Z_{eff}$  increases (due to less screening). Consequently,  $\lambda$  increases with the increase of oxidation state for a particular metal ion. Thus  $\lambda(Fe^{3+}) > \lambda(Fe^{2+})$ ,  $\lambda(Co^{3+}) > \lambda(Co^{2+})$ .

#### • Periodic position of the metal ions:

For the heavier congeners among the d-block metal ions the size does not practically increase but  $Z_{eff}$  increases so that  $\lambda$  increases for the heavier congeners. i.e.  $\lambda(Hf^{2+}) > \lambda(Zr^{2+}) > \lambda(Ni^{2+})$ ;  $\lambda(Os^{3+}) > \lambda(Ru^{3+}) > \lambda(Fe^{3+})$ .

$$\lambda = \frac{1}{2} \left( \frac{1}{r} + \frac{1}{r'} \right) \propto \frac{1}{r^2}$$

• Nephelauxetic effect:- In a complex, electron cloud expansion leads to an effective increase in orbital radius, thus in a complex,  $\lambda$  decreases compared to that of the free ion. This increase occurs by 20-25%.

• Quenching of Orbital Contribution to magnetic moment by crystal field.

In the free atoms or ions in the gaseous phase, orbital contribution arises but in a chemical environment, the behaviour is completely different.

For a free electron ( $s = \frac{1}{2}, l = 0, j = \frac{1}{2}$ )  $g = 2$ .  
For the halogen atoms ( $ns^2 np^5$ ) in the gaseous phase in the ground state ( $2p_3/2, l = 1, s = \frac{1}{2}, j = \frac{3}{2}$ )  $g = \frac{4}{3}$ .

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

If the orbital motion make its full contribution to the magnetic moment, then it will lead to the following relation in the cases where  $\vec{L}$  and  $\vec{S}$  don't couple effectively i.e. they contribute independently.

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.}$$

### A. Possibility of Quenching of Orbital Contribution :-

An electron will produce an orbital moment around a particular axis if it is possible axis, if it is possible to transform the orbital into an equivalent degenerate around the axis. The  $dx^2 - y^2$  orbital can be converted into any orbital by  $45^\circ$  rotation around the  $z$ -axis. By  $90^\circ$  rotation the  $dx^2$  into  $dy^2$  or  $dz^2$ .

\* To have the orbital contribution to the magnetic moment, the following condition must be satisfied

(i) Condition of degeneracy :- The concerned orbitals which are mutually transformable through the symmetry operation must be degenerate.

(ii) Condition of mutual transformability through the symmetry rotation :- The orbital must be mutually transformable by rotation about some axis.

$dx^2 - y^2 \longleftrightarrow dx^2 - y^2$   
(Rotation by  $45^\circ$  around the  $z$  axis)

$dx^2 \longleftrightarrow dx^2$   
(Rotation by  $90^\circ$  around the  $z$  axis)

$dx^2 \longleftrightarrow dx^2$   
(Rotation by  $90^\circ$  around the  $x$  axis)

$dx^2 \longleftrightarrow dy^2$   
(Rotation by  $90^\circ$  degree around  $y$  axis).



Thus, the mutually transformable  $d$ -orbitals are present in the  $t_2(g)$  set of  $d$  orbitals and octahedral crystal field. The  $dx^2-y^2$  and  $dz^2$  orbitals do constitute the  $e(g)$  set are not mutually transformable because of their different shapes. Thus, the  $t_2(g)$  set can make an orbital contribution but the  $e(g)$  set fails to make any contribution.

(iii) Condition of Spin:- The orbitals must not contain the electrons of similar spin.

B. Quenching of orbital moment in the octahedral and tetrahedral geometries:

$t_2g$  ( $dxy, dyz, dzx$ ) and  $eg$  ( $dx^2-y^2, dz^2$ )

This is an octahedral crystal field, the mutually transformable  $dxy$  and  $dx^2-y^2$  orbitals are non degenerate (i.e. are of different energies) orbital contribution from this orbital is quenched. The mutually transformable  $dyz$  &  $dzx$ ,  $dxy$  and  $dyz$  and  $dxy$  &  $dzx$  orbitals are degenerate.

Thus for the octahedral and tetrahedral crystal field, there is no orbital contribution from the  $eg$  and  $e$  set but  $t_2g$  and  $t_2$  set can make the orbital contribution if the

Third condition of spin is satisfied.

In the octahedral field, the  $t_{2g}^3$  configuration fails to make any orbital contribution from the  $e_g$  and  $e$  set but the  $t_{2g}$  and  $t_2$  set can make the orbital contribution if the third condition of spin is satisfied.

In the octahedral field, the  $t_{2g}^3$  configuration fails to make any orbital contribution. Here the two conditions i.e. degeneracy and transformability but on rotation the orbital  $d_{xy}$  and  $d_{yz}$  convert into  $d_{yz}$ ,  $d_{zx}$  and  $d_{xy}$  orbital respectively which is already occupied by an electron of the same spin, because of the same ground, the  $t_{2g}^6$  configuration cannot make orbital contribution.

eg:  $t_{2g}^1, t_{2g}^2, t_{2g}^3, t_{2g}^4, t_{2g}^5$  i.e.  $t_{2g}^x$  ( $x=1, 2, 4, 5$ ) } Ground state + term making orbital contribution  
 t<sub>2g</sub>:  $t_{2g}^1, t_{2g}^2, t_{2g}^3, t_{2g}^4, t_{2g}^5$  i.e.  $t_{2g}^x$  ( $x=1, 2, 4, 5$ ) } making orbital contribution

The above configuration (which can make orbital contribution) experience the J-T distortion which can lift the degeneracy. Thus even after Jahn-Teller splitting, the mutually transformable  $d_{xy}$ ,  $d_{yz}$  or  $d_{zx}$  remain degenerate.

$$\mu_{\text{eff}} = g \sqrt{J(J+1)} \text{ BM}$$

$$L = 6$$

$$S = 3/2$$

1	1	1							
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$$J = |L - S|$$

$$= 6 - 3/2$$

$$= 9/2$$

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

$$= J + \frac{\frac{9}{2}(\frac{9}{2}+1) + \frac{3}{2}(\frac{3}{2}+1) - 6(6+1)}{2 \times \frac{9}{2}(\frac{9}{2}+1)}$$

$$= J + \frac{\frac{9}{2} \times \frac{11}{2} + \frac{3}{2} \times \frac{5}{2} - 42}{9 \times \frac{11}{2}}$$

$$= J + \frac{\frac{99}{2} + \frac{15}{2} - 42}{99 \times \frac{11}{2}} = J + \frac{\frac{99+15-84}{2}}{99 \times \frac{11}{2}}$$

$$= \frac{8}{11} J$$

$$= J - \frac{59}{198} = \frac{191}{198}$$

$$\mu_J = \frac{8}{11} \sqrt{\frac{9}{2} \times \frac{3}{2}}$$

$$= \frac{8}{11} \sqrt{\frac{99}{4}} = \frac{8}{11} \times 5 = \frac{40}{11} = 3.62 \text{ B.M.}$$

\* By  $3+$

11	11	1	1	1	1	1
-3	-2	-1	0	+1	+2	+3

$$L = \sum |m_l|, J = L + S$$

$$= 5 + \frac{5}{2}$$

$$= \frac{15}{2}$$

$$g = \frac{4}{3}$$

$$\mu_J = \frac{4}{3} \sqrt{\frac{15}{2} \times \frac{17}{2}} = 10.62 \text{ B.M.}$$

$$g = J + \frac{\frac{15}{2}(\frac{15}{2}+1) + \frac{5}{2}(\frac{5}{2}+1) - 5(5+1)}{2 \times \frac{15}{2}(\frac{15}{2}+1)}$$

$$= J + \frac{\frac{15}{2}(\frac{17}{2}) + \frac{5}{2} \times \frac{7}{2} - 30}{15 \times \frac{17}{2}} = J + \frac{\frac{255}{4} + \frac{35}{4} - 30}{\frac{255}{2}}$$

Q. Except fairly c  
Explains

Ans: For

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experim

$\Delta E$  is v

So tha

the

$$= J + \frac{2(255 + 35 - 120)}{24 \times 255} = J + \frac{170}{510} = \frac{680}{510} = \frac{4}{3} \neq$$

\*  $\text{Sm}^{+3}$ ,  $\text{Eu}^{+3}$

$$g = \frac{7}{4} \quad J = 3$$

$$\mu_{\text{eff}} = 0$$

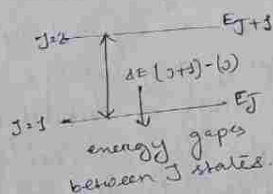
$$\mu_{\text{obs}} = 3.4 - 3.6 \text{ B.M.}$$

$$\mu_{\text{eff}} = 0.89 \text{ B.M.}$$

$$\mu_{\text{obs}} = 3.5 - 3.6$$

\*  $\Delta E \approx k_B T$  → Thermal energy.  
only for two lanthanoids  
( $\text{Sm}^{+3}$ ,  $\text{Eu}^{+3}$ )

$$\Delta E J(J+1) \gg k_B T$$



Q. Except  $\text{Sm}^{+3}$  and  $\text{Eu}^{+3}$  all other lanthanoids fairly agree with the calculated magnetic moment,  $\mu_J$ . Explain the statement?

Ans: For  $\text{Sm}^{+3}$  and  $\text{Eu}^{+3}$ , the energy gap betn the ground state and excited state ( $\Delta E$ ) is small and equivalent to thermal energy ( $k_B T$ ). It is observed that there is a drastic change betn the calculated and experimental magnetic moment,  $\mu_J$ . For all other lanthanoids  $\Delta E$  is very much greater than thermal energy ( $k_B T$ ). So that all other lanthanoids fairly agree with the calculated  $\mu_J$ .

Orbital Contribution to the magnetic moment :-

- From the ground T-state
- From the excited T-state through mixing with the ground state via spin orbit coupling. It may be +ve or -ve depending on the sign of spin orbit coupling constant.

\* Octahedral vs square planar :-

The triply degenerate group ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ) can make an orbital contribution better than the doubly degenerate ( $d_{yz}$ ,  $d_{zx}$ ) group. Thus the possibility of orbital contribution in the square planar complex is reduced more compared to octahedral complex. In the low symmetry complexes (a crystal field effect) the orbital contribution is quenched more.

\* Orbital contribution from the excited state through spin orbit coupling :-

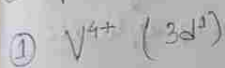
Where the electronic configuration of the ground state (i.e. A and E terms) cannot satisfy the required condition for an orbital contribution. The T-term can make an orbital contribution. Thus, if there is an excited T-state having the same multiplicity as with the ground state and if it can mix with the ground state through the spin orbit coupling, then an orbital contribution from the excited state can occur.



$$\mu = \mu_{\text{spin only}} \left( 1 - \frac{\alpha \lambda}{10 Dq} \right) \text{ B.M.}$$

- $\mu_{\text{eff}} > \mu_{\text{spin}}$  for the high spin  $d^6$  to  $d^9$  configuration.
- $\mu_{\text{eff}} < \mu_{\text{spin}}$  for the high spin  $d^1$  to  $d^4$  configuration.

\* The spin-orbit coupling contribution is more important for weak field ligands as compared to strong field ligand. Thus the spin-orbit coupling contribution is more important in tetrahedral complexes compared to that in octahedral complexes.



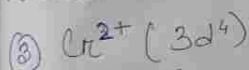
1				
-2	-1	0	+1	+2

$$2S+1 = 2 \times \frac{1}{2} + 1 = 2$$

$$L = \sum |m_l| = |-2| = 2$$

$$J = L - S = 2 - \frac{1}{2} = \frac{3}{2}$$

$$\therefore \text{Free ion term} = {}^2D_{3/2}$$



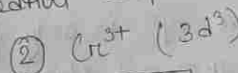
1	1	1	1	
-2	-1	0	+1	+2

$$2S+1 = 2 \times 2 + 1 = 5$$

$$L = |-2| = 2$$

$$J = L - S = 2 - 2 = 0$$

$$\therefore \text{Free ion term} = {}^5D_0$$



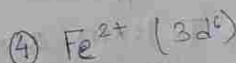
1	1	1		
-2	-1	0	+1	+2

$$2S+1 = 2 \times \frac{3}{2} + 1 = 4$$

$$L = |-3| = 3$$

$$J = L - S = 3 - \frac{3}{2} = \frac{3}{2}$$

$$\therefore \text{Free ion term} = {}^4F_{3/2}$$



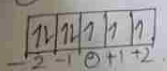
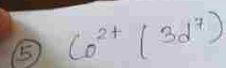
1	1	1	1	1
-2	-1	0	+1	+2

$$2S+1 = 2 \times 2 + 1 = 5$$

$$L = \sum |m_l| = 2$$

$$J = L + S = 2 + 2 = 4$$

$$\therefore \text{Free ion term} = {}^5D_4$$

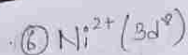


$$2S+1 = 2 \times \frac{3}{2} + 1 = 4$$

$$L = |3| = 3$$

$$J = L + S = 3 + \frac{3}{2} = \frac{9}{2}$$

$$\therefore \text{free ion term} = {}^4F_{9/2}$$

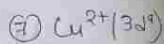


$$2S+1 = 2 \times 1 + 1 = 3$$

$$L = \sum |m_l| = 3$$

$$J = L + S = 4$$

$$\therefore \text{free ion term} = {}^3F_4$$



$$\therefore \text{free ion term} = {}^2D_{9/2}$$

\* Limitation of the eq<sup>n</sup>  $\mu_{\text{eff}} = \left(1 - \frac{\alpha \lambda}{10Dq}\right) \mu_{\text{spin only}}$

• The above eq<sup>n</sup> is only for the systems having the A and E ground states. Thus it is only applicable for the following systems:

Oct. complexes:  $d^3$ ,  $d^4$  (h.s.),  $d^7$  (l.s.),  $d^8$ ,  $d^9$

Td. complexes:  $d^1$ ,  $d^2$ ,  $d^6$ ,  $d^7$

• For the systems having  $T_1$  and  $T_2$  ground state, the above eq<sup>n</sup> is not applicable. Spin orbit coupling splitting of the T-term and the separat<sup>n</sup> energy comparable to  $k_B T$ .

• The magnetic properties of T-term are temp<sup>r</sup> dependent but A and E term are less or more insensitive to temp<sup>r</sup>.

## Super exchange phenomenon (Antiferromagnetic coupling)

(a)  $90^\circ \rightarrow$  Ferromagnetic material give.

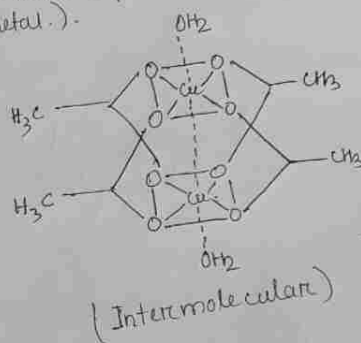
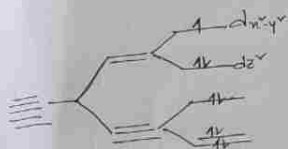
(b)  $180^\circ \rightarrow$  Anti ferromagnetic material.

\* Mixed filled ligand  $\Rightarrow$  distortion.

\* Unsymmetrical filling  $\Rightarrow$  J-T distortion.

Q. ①  $\text{Ca}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ .

Last  $e^-$  of  $d_{x^2-y^2}$  (unpaired  $e^-$  make super exchange with another metal.).



②  $[\text{Cu}_2(\text{CH}_3\text{COO})_4] \cdot 2\text{H}_2\text{O}$ .

$(\text{CH}_3\text{COO})_4$  1.4 B.M

$(\text{CH}_3\text{CH}_2\text{COOH})$  1.42 B.M

$(\text{CH}_3\text{COOH})$  1.65 B.M

$(\text{F}_3\text{COOH})$  1.90.

When super exchange phenomenon decrease due to electronegative group. magnetic moment increase.

# Electronegativity  $\uparrow$  Super exchange  $\downarrow$

Metal +ve charge  $\uparrow$  Super exchange  $\downarrow$