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Spin Magnetic Moment
&
Orbital Magnetic Moment

Let us consider a transition metal complex of 3d elements whose central metal ion contains only unpair electrons in its 3d orbitals. The magnetic moment (μ) of one unpair electron is equal to the sum of its magnetic moment due to its orbital motion, called orbital magnetic moment (μ_L) and that due to its spin motion called spin magnetic moment (μ_S).

Thus $\mu_{L+S} = \mu_L + \mu_S$

The orbital magnetic moment (μ_L) is given by $\mu_L = g\sqrt{L(L+1)}$ B.M. $[g=1]$

The spin magnetic moment (μ_S) is given by

$\mu_S = g\sqrt{S(S+1)}$ BM $[g=2]$

Where BM = [Bohr Magneton which is equal to $\frac{eh}{4\pi mc}$] i.e. $\boxed{1\,BM = \frac{eh}{4\pi mc}}$

Here e = charge on the electron
h = Plank's constant
m = mass of the electrons
c = velocity of light.

$1\,BM = 9.27\times10^{-21}$ erg/gauss (in cgs unit)
$= 9.27\times10^{-24}$ J/Tesla (in S.I unit)

L = Resultant orbital angular momentum quantum no.

S = Resultant spin angular momentum quantum no.

'g' represents the gyromagnetic ratio i.e; the ratio of the spin magnetic moment (μ_S) to the spin angular momentum corresponding to it.

It has values 1 and 2 for μ_L and μ_S respectively.

Therefore the total magnetic moment (μ_{L+S}) is given by,

$$\mu_{L+S} = \sqrt{L(L+1)+4S(S+1)} \text{ BM}$$

In case of transition metal ions 3d series, the crystal field (i.e; the ligands surrounding the metal ions) restrict the movement of the electron round the nucleus in orbitals and hence the magnetic moment due to the orbital motion of the electron (μ_L) is quenched and hence $\sqrt{L(L+1)} = 0$. Thus the magnetic moment of an unpair electron residing in a 3d orbital of the ions of 3d series elements is given by $\mu_{L+S} = \mu_S = \sqrt{4S(S+1)}$ B.M.

If 'n' is the no. of unpaired electrons, then $S = \sum s = \frac{n}{2}$. Therefore in this case..

$$\mu_S = \sqrt{4 \cdot \frac{n}{2}\left(\frac{n}{2}+1\right)} = \sqrt{n(n+2)} \text{ B.M.}$$

For $n = 0$, $\mu_s = 0$

$n = 1$, $\mu_s = 1.73$ BM

$n = 2$, $\mu_s = 2.83$ BM

Orbital contribution in magnetic moment:

The unpaired electrons in a first transition series metal ion are located in the 3d orbitals. A transition metal ion has five 3d orbitals all of which are degenerate. In order for these electrons to generate the orbital magnetic moment, the electrons should go around the nucleus via these orbitals. For this to be possible, the three conditions must be satisfied. These are—

1) The orbitals should be degenerate.
2) The orbitals should be of similar shape & size. i.e, they should be transformable into one another by rotation about some axis and
3) The orbitals must not contain electrons of

identical spin.

- **Explanation:**

In a crystal field, the degenerate 'd' orbitals split. For example in an octahedral stereochemistry the five 'd' orbitals split into two groups of different energy — 't_{2g}' set (d_{xy}, d_{yz} & d_{zx}) and 'e_g' set ($d_{x^2-y^2}$, d_{z^2}). Although the d_{z^2} and $d_{x^2-y^2}$ orbitals are degenerate in the octahedral crystal field the shapes of these two orbitals are such that one is not transformable into the other by rotation. Thus we find that due to condition ②, the 'e_g' orbital set in the octahedral geometry ('e' orbital set in tetrahedral geometry) can not generate any orbital magnetic moment. Hence the d_{z^2} and $d_{x^2-y^2}$ orbitals are known as a non-magnetic doublet. The d_{xy}, d_{yz} and d_{zx} orbitals (t_{2g} set) obey conditions ① and ②. So it is now condition ③ that will dictated wheather or not the t_{2g} set will generate an orbital magnetic moment. Thus an octahedral complex with the d^1 ~~and~~ or d^2 configuration fullfills all the three conditions but with the d^3 configuration will not satisfy condition ③. Hence, the d^1 and d^2 configuration will carry the orbital magnetic moment but the d^3 configuration will not.

When an electron distribution admits of one arrangement, the corresponding term is a singlet(A); When two arrangements are possible, the terms is a doublet (E); with three arrangements the term is a triplet (T). We note that we can not expect the orbital contribution in the 'A' and 'E' g.s. terms, but this is not true of a 'T' g.s term. This explains why in the tetrahedral Ni(II), octahedral Co(II) (H.S) and octahedral Fe(II) (H.S) complexes the magnetic moment is higher than the spin only magnetic moment.

- Orbital contibution in 'oh' and 'td' complexes:

d^n ion	High spin 'oh' complex		Tetral contribution	
	Ground state	Orbital contribution	Ground state	Orbital contribution
d^1	$t_{2g}^1(^2T_{2g})$	Expected	$e^1(^2E)$	Not expected.
d^2	$t_{2g}^2(^3T_{1g})$	Expected.	$e^2(^3A_2)$	,,
d^3	$t_{2g}^3(^4A_{2g})$	Not expected.	$e^2t_2^1(^4T_1)$	Expected
d^4	$t_{2g}^3e_g^1(^5E_g)$	,,	$e^2t_2^2(^5T_2)$	,,
d^5	$t_{2g}^3e_g^2(^6A_{1g})$	,,	$e^2t_2^3(^6A_1)$	Not expected
d^6	$t_{2g}^4e_g^2(^5T_{2g})$	Expected	$e^3t_2^3(^5E)$	,,
d^7	$t_{2g}^5e_g^2(^4T_{1g})$	,,	$e^4t_2^3(^4A_2)$	,,
d^8	$t_{2g}^6e_g^2(^3A_{2g})$	Not expected	$e^4t_2^4(^3T_1)$	Expected
d^9	$t_{2g}^6e_g^3(^2E_g)$	,,	$e^4t_2^5(^2T_2)$	,,

some cases there is 'A' and 'E' g.s. term exhibiting (μ. effective) μ_{eff} is sufficiently higher or lower than μ_{SO}. Because there is 'T' term above on 'A' & 'E' g.s. terms with the same spin multiplicity as g.s. term, the g.s. term aquires some orbital angular momentum from the exited 'T' term through spin orbit coupling.

eg; we expect that an octahedral Ni(II) complex or a tetrahedral co(II) complex will have the spin only magnetic moment. But such a complex in reality exhibits a magnetic moment higher than μ_{SO}. This is because the excited state - $^3T_{2g}$ (Ni^{2+}, $t_{2g}^5 e_g^3$) and $^4T_2$ (Co^{2+}, $e^3 t_2^4$) carry the orbital magnetic moment. In a system having such an exited state, the spin orbit coupling brings about some mixing of the g.s. with the exited state, thus forcing some orbital contribution. The quantitative relation between μ_{eff} and $\mu_{S.O}$ is given below:

$$\mu_{eff.} = \mu_{S.O}\left[1 - \frac{\alpha\lambda}{10Dq}\right]$$

Where, $\alpha = 0$. for A_1 g.s. term

and $\alpha = 2$ for E " "

$\alpha = 4$ " A_2 " "

λ = Spin orbit coupling constant. It is negatie for greater than half filled case and positive for less than half-filled case.

That is why an octahedral Ni(II) complex or a tetrahedral Co(II) complex exhibit magnetic moment higher than μ_{SO}.