❖ Orbital Contribution: Effect of Ligand-Field

In the prewave-mechanical model of the atom, the orbital angular momentum was thought to be generated due to the circular motion of an electron in its orbit. This revolutionary motion of the negatively charged particle was supposed to contribute orbital magnetic moment to the total magnetic moment, as we have discussed in the first section of this chapter. However, as we all know that the concept of orbits is no longer valid because of its violation to the Heisenberg uncertainty principle; the physical realization of orbital angular momentum and its contribution to magnetic moment on the basis of wave mechanical model is a must. In the wave mechanical description of atom, the magnitude of orbital angular momentum along a particular axis depends upon the rotational feasibility of an atomic or molecular orbital about the same axis-line to carry itself into a degenerate and identical orbital. This can better be understood by taking the example of *d*-orbital set. A rotation of 45° about *z*-axis will transform $d_{x^2-y^2}$ into d_{xy} orbital, and rotation through 90° would give two equivalent states; resulting in a 2 units of angular momentum (unit = $h/2\pi$) about *z*-axis. The same can be said about d_{xy}, which is also having an angular momentum of 2 units about *z*-axis. Moreover, a rotation of 90° about *z*-axis will transform d_{xz} into d_{yz} orbital; and therefore, would give only one equivalent states, resulting only 1 unit of angular momentum about *z*-axis for both the orbitals. However, the rotation of d_{z^2} about *z*-axis will not be able to transform it into any other orbital; resulting in a zero-unit angular momentum about *z*-axis.

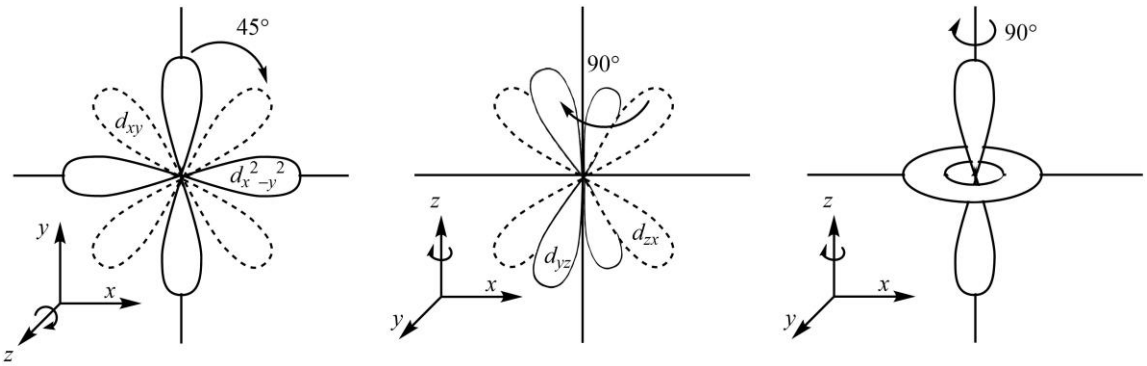

Figure 9. The circulation of electron density in a partially filled *d*-subshell about the *z*-axis.

It is also worthy to mention that the resultant orbital angular momentum would exist only if the degenerate set of interconvertible orbitals is unsymmetrically occupied. Though we already know that the generation of the orbital magnetic moment was analogs to the magnetic effect generated by the current in a solenoid; the better visualization can be made if we think of a circular wire with uniform charge density. If this circular wire is rotated by any angle about the axis perpendicular to its plane, it will be left in a physically identical state, like nothing has moved. On the other hand, if we use a solenoid, instead of a ring, the ends of the wire coil would be in a different location after the rotation. The prerequisite for a non-zero orbital motion is exactly the same. Any spherically symmetric distribution of electron density would not result in an orbital angular momentum (like a single electron in *s*-orbital or multi-electron cloud with S state).

Hence, we can say that a free ion present in a state other than S, will have an orbital angular momentum, and thereby orbital magnetic moment too. Nevertheless, if this orbital degeneracy is removed by complexation or by trapping it in a solid host matrix, the magnitude of orbital angular momentum would be somewhat more or less quenched. If the orbital degeneracy is slightly reduced, the contribution of the orbital magnetic moment would be quenched incompletely or partially. However, as in addition to the orbital degeneracy, the unsymmetrical filling is also a necessary condition for an orbital moment, we should work out different Mulliken states satisfying these conditions. Therefore, in order to show the orbital magnetic contribution to the total magnetic moment, there should be an unsymmetrically occupied degenerate set of orbitals that can be interconverted or transformed into each other through rotational motion.

- ***Ligand Field Effect on the Orbital Contribution in Octahedral Complexes***

The octahedral coordination of a transition metal center removes the degeneracy of *d*-subshell into two main orbital-sets. The first degenerate set of d_{xy}, d_{yz}, d_{zx} is of t_{2g} symmetry; while the second degenerate set of $d_{x^2-y^2}$ and d_{z^2} is having e_g symmetry now. Thus, owing to the different energies of $d_{x^2-y^2}$ and d_{xy}, the interconversion of these orbitals through a rotation of 45° about *z*-axis is not possible anymore. This gives a zero angular momentum along *z*-axis for electron present in any of these two. Nevertheless, the interconversion of d_{xz} into d_{yz} orbital through a rotation of 90° about *z*-axis is still feasible because of their orbital degeneracy in t_{2g} symmetry. Hence, an unsymmetrical filling of t_{2g} orbital-set results in a non-zero orbital angular momentum; and consequently, non-zero orbital magnetism along *z*-axis. The unsymmetrical filling of e_g orbital-set will not result in any orbital magnetism due to lack of their interconversion.

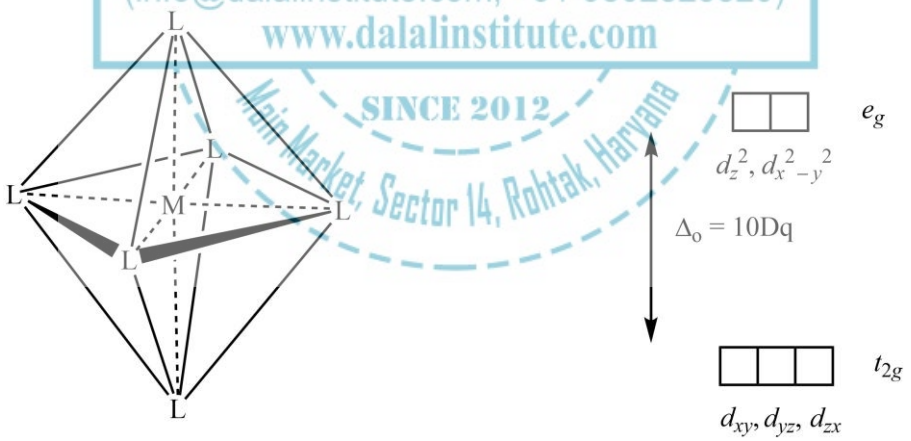

Figure 10. The octahedral coordinative environment of transition metal center and corresponding crystal field splitting pattern of *d*-subshell.

Now, we can find out which electronic configurations in high-spin (spin-free) or low spin (spin paired) octahedral complexes of transition metals will show an orbital contribution to the total magnetic moment, and which will have the same absent.

1. Electronic configurations with orbital magnet: Recalling the prerequisites of orbital magnetism; unsymmetrically occupied, degenerate set of interconvertible orbitals; the configurations suitable for the presence of orbital magnetic moment are given below.

Table 4. Octahedral transition metal complexes having orbital magnetic moments.

Weak-field		Strong-field	
Electronic configuration	Ground state	Electronic configuration	Ground state
d^1 (t_{2g}^1)	$^2T_{2g}$	d^1 (t_{2g}^1)	$^2T_{2g}$
d^2 (t_{2g}^2)	$^3T_{1g}$	d^2 (t_{2g}^2)	$^3T_{1g}$
d^6 (t_{2g}^4 e_g^2)	$^5T_{2g}$	d^4 (t_{2g}^4)	$^3T_{1g}$
d^7 (t_{2g}^5 e_g^2)	$^4T_{1g}$	d^5 (t_{2g}^5)	$^2T_{2g}$

It is worthy to note that all ground Mulliken states which show an orbital contribution to the total magnetic moment are of "T" nature.

2. Electronic configurations without orbital magnet: Recalling the prerequisites of orbital magnetism; unsymmetrically occupied, degenerate set of interconvertible orbitals; the configurations suitable for the absence of orbital magnetic moment are given below.

Table 5. Octahedral transition metal complexes having no orbital magnetic moments.

Weak-field		Strong-field	
Electronic configuration	Ground state	Electronic configuration	Ground state
d^3 (t_{2g}^3)	$^4A_{2g}$	d^3 (t_{2g}^3)	$^4A_{2g}$
d^4 (t_{2g}^3 e_g^1)	^5E_g	d^6 (t_{2g}^6)	$^1A_{1g}$
d^5 (t_{2g}^3 e_g^2)	$^6A_{1g}$	d^7 (t_{2g}^6 e_g^1)	^2E_g
d^8 (t_{2g}^6 e_g^2)	$^3A_{2g}$	d^8 (t_{2g}^6 e_g^2)	$^3A_{2g}$
d^9 (t_{2g}^6 e_g^3)	^2E_g	d^9 (t_{2g}^6 e_g^3)	^2E_g
d^{10} (t_{2g}^6 e_g^4)	$^1A_{1g}$	d^{10} (t_{2g}^6 e_g^4)	$^1A_{1g}$

It can be clearly seen that all ground Mulliken states which do not show orbital contribution are of either "A" or of "E" nature.

➢ *Ligand Field Effect on the Orbital Contribution in Tetrahedral Complexes*

The tetrahedral coordination of a transition metal center removes the degeneracy of *d*-subshell into two main orbital-sets. The first degenerate set of d_{xy}, d_{yz}, d_{zx} is of t_2 symmetry; while the second degenerate set of $d_{x^2-y^2}$ and d_{z^2} is having *e* symmetry now. Thus, owing to the different energies of $d_{x^2-y^2}$ and d_{xy}, the interconversion of these orbitals through a rotation of 45° about *z*-axis is not possible anymore. This gives a zero angular momentum along *z*-axis for electron present in any of these two. Nevertheless, the interconversion of d_{xz} into d_{yz} orbital through a rotation of 90° about *z*-axis is still feasible because of their orbital degeneracy in t_2 symmetry. Hence, an unsymmetrical filling of t_2 orbital-set results in a non-zero orbital angular momentum; and consequently, non-zero orbital magnetism along *z*-axis. The unsymmetrical filling of *e* orbital-set will not result in any orbital magnetism due to the lack of their interconversion.

Figure 11. The tetrahedral coordinative environment of transition metal center and corresponding crystal field splitting pattern of *d*-subshell.

Now at this point, it is worthy to recall the electron-hole inverse relationship again, which states that the number of microstates and hence all free ion terms for d^n and d^{10-n} configuration are same. However, as the magnitude of the crystal field experienced positive electrons is same as what experienced by the negative electrons, but is of opposite sign; the splitting pattern for d^n and d^{10-n} configuration are also opposite of each other. Furthermore, owing to the hole formalism in quantum mechanics, strong field configuration of t_{2g}^4, t_{2g}^5, e_g^3 give rise to the same terms as given by the strong field configuration of t_{2g}^2, t_{2g}^1, e_g^1. However, weaker inter-electronic repulsion is considered as the perturbation over stronger V_o. Similarly, the splitting pattern of d^n tetrahedral is just the opposite of what is for d^n octahedral. However, no *g* or *u* are used in the tetrahedral case because there is no center of symmetry in a tetrahedral geometry. Hence, we can conclude that the hole-formalism and octahedral-tetrahedral inverse relationship is all term symbols including the ground state. Now, we can find out which electronic configurations in high-spin (spin-free) tetrahedral complexes of transition metals will show an orbital contribution to the total magnetic moment, and which will have the same absent. It is also important to note that here we don't need to consider the low spin cases because the smaller magnitude of crystal field splitting in tetrahedral complexes always avoids pairing of electrons.

1. Electronic configurations with orbital magnet: Recalling the prerequisites of orbital magnetism; unsymmetrically occupied, degenerate set of interconvertible orbitals; the configurations suitable for the presence of orbital magnetic moment are given below.

Table 6. Tetrahedral transition metal complexes having orbital magnetic moments.

Electronic configuration	Ground state
d^3 (e^2 t_2^1)	$^4T_1$
d^4 (e^2 t_2^2)	$^5T_2$
d^8 (e^4 t_2^4)	$^3T_1$
d^9 (e^4 t_2^5)	$^2T_2$

It can be clearly seen that all ground Mulliken states which show an orbital contribution to the total magnetic moment are of "T" nature.

2. Electronic configurations without orbital magnet: Recalling the prerequisites of orbital magnetism; unsymmetrically occupied, degenerate set of interconvertible orbitals; the configurations suitable for the absence of orbital magnetic moment are given below.

Table 7. Tetrahedral transition metal complexes with no orbital magnetic moments.

Electronic configuration	Ground state
d^1 (e^2)	^2E
d^2 (e^2)	$^3A_2$
d^5 (e^2 t_2^3)	$^6A_1$
d^6 (e^3 t_2^3)	^5E
d^7 (e^4 t_2^3)	$^4A_2$
d^{10} (e^4 t_2^6)	$^1A_1$

It can be clearly seen that all ground Mulliken states which do not show orbital contribution are of either "A" or of "E" nature.

Summarizing both the case, we can conclude that the ground Mulliken states of "T" symmetry do have an orbital magnetism; while any configuration leading to "A" or "E" state will not be able to show an orbital contribution to the total magnetic moment.

➢ *Effect of Spin-Orbital Coupling on the Orbital Contribution*

The conclusive remark after the general observation of the orbital contribution discussed so far includes that "A" and "E" terms as the ground state do not yield any orbital magnetism, while the ground state "T" terms do possess an orbital contribution to the total magnetic moment. In other words, the orbital magnetic moment is partially quenched in transition metal complexes with A or E ground Mulliken states, and the complete quenching occurs in metal complexes with ground Mulliken states of T nature. However, if a higher energy T-symmetry state with the same multiplicity lies above the "A" or "E" state, the spin-orbital coupling may mix the excited state into ground one such that a certain amount of orbital magnetic moment is introduced into the ground state also. This is because the ligand field has the ability to quench orbital angular momentum, but not spin angular momentum. Therefore, if both types of momentum are coupled by *L-S* interaction, the ligand field would not be able to separate the same multiplicity terms on the basis of their orbital angular momentum quantum number. Consequently, the ground state term is not a pure A or E anymore but does have some T character, giving significant deviation from the spin-only value of the magnetic moment.

The magnitude of orbital magnetism contribution to the total effective magnetic moment directly depends upon the value of the spin-orbital coupling parameter (λ) and is inversely proportional to the energy difference of the states to be mixed (Δ). Mathematically, the relationship between spin-orbital interaction and total effective magnetic moment can be stated as:

$$\mu_{eff} = \mu_{S.O.}\left(1 - \alpha\frac{\lambda}{\Delta}\right) \tag{52}$$

Where $\mu_{S.O.}$ is the spin-only magnetic moment, λ is the spin-orbital coupling parameter, and Δ is the energy between ground (A or E) and the excited state (T). It is also worthy to remember that the sign of the spin-orbital coupling parameter is negative for more than half field configurations while positive for less than half-filled electronic configurations. The α is a constant whose value depends upon the spectroscopic ground state term; value is 0 for ^{6}S ($^6A_1$), 2 for ^{2}D (^{2}E) and ^{5}D (^{5}E), and 4 for ^{3}F ($^3A_2$) and ^{4}F ($^4A_2$) ground state terms. The calculation of the effective magnetic moment for all these three cases is given below.

1. Calculation of μ_{eff} for A_1 terms: The ground Mulliken state of A_1 symmetry exists for the weak field octahedral complex with d^5 and the strong field octahedral complexes with d^6 configurations.

i) d^5 weak field ($t_{2g}^3\ e_g^2$): Keeping in mind that there are no high energy terms of the same multiplicity in d^5 high-spin complexes, and putting the value of Δ = 10Dq and α as zero in equation (52), we get

$$\mu_{eff} = \mu_{S.O.}\left(1 - 0 \times \frac{\lambda}{\Delta}\right) \tag{53}$$

$$\mu_{eff} = \mu_{S.O.}$$

Hence, d^5 high-spin complexes are expected to give a spin-only moment of 5.92 B.M.; which is independent of temperature.

ii) d^6 strong field (t_{2g}^6): Keeping in mind that there are no unpaired electrons in d^6 low-spin complexes and putting $\mu_{S.O.} = 0$, value of $\Delta = 10Dq$ and α as zero in equation (52), we get

$$\mu_{eff} = 0\left(1 - 0 \times \frac{\lambda}{\Delta}\right) \tag{54}$$

$$\mu_{eff} = 0$$

Hence, d^6 low-spin complexes are expected to be diamagnetic in nature.

2. Calculation of μ_{eff} for E terms: The ground Mulliken state of E symmetry exists for the weak field octahedral complex with d^4 and d^9 configurations; and strong field octahedral complexes with d^7.

i) d^4 weak field ($t_{2g}^3\ e_g^1$): Putting the value of $\Delta = 10Dq$ (the energy gap between ground ^5E_g and $^5T_{2g}$) and α as 2 in equation (52), we get

$$\mu_{eff} = \mu_{S.O.}\left(1 - 2 \times \frac{\lambda}{10Dq}\right) \tag{55}$$

Now because the sign of spin-orbital coupling parameter is positive for less than half-filled configurations, the equation (55) can also be written in the following form.

$$\mu_{eff} = \mu_{S.O.}\left(1 - 2 \times \frac{|\lambda|}{10Dq}\right) \tag{56}$$

Hence, for d^4 high-spin complexes, the effective magnetic moment is less than the spin-only magnetic moment; which is also independent of temperature.

ii) d^9 strong-field weak-field ($t_{2g}^6\ e_g^3$): Putting the value of $\Delta = 10Dq$ (the energy gap between ground ^2E_g and $^2T_{2g}$) and α as 2 in equation (52), we get

$$\mu_{eff} = \mu_{S.O.}\left(1 - 2 \times \frac{\lambda}{10Dq}\right) \tag{57}$$

Now because the sign of spin-orbital coupling parameter is negative for more than half-filled configurations, the equation (57) can also be written in the following form.

$$\mu_{eff} = \mu_{S.O.}\left(1 + 2 \times \frac{|\lambda|}{10Dq}\right) \tag{58}$$

Hence, for d^9 strong-field weak-field, the effective magnetic moment is greater than the spin-only magnetic moment; which is also independent of temperature.

3. Calculation of μ_{eff} for A_2 terms: The ground Mulliken state of A_2 symmetry exists for the weak field as well as strong field octahedral complex with d^3 and d^8 configurations.

i) d^3 weak-field strong-field (t_{2g}^3): Putting the value of $\Delta = 10Dq$ (the energy gap between ground $^4A_{2g}$ and $^4T_{2g}$) and α as 4 in equation (52), we get:

$$\mu_{eff} = \mu_{S.O.}\left(1 - 4 \times \frac{\lambda}{10Dq}\right) \tag{59}$$

Now because the sign of spin-orbital coupling parameter is positive for less than half-filled configurations, the equation (59) can also be written in the following form.

$$\mu_{eff} = \mu_{S.O.}\left(1 - 4 \times \frac{|\lambda|}{10Dq}\right) \tag{60}$$

Hence, for d^3 complexes, the effective magnetic moment is less than the spin-only magnetic moment; which is also independent of temperature.

ii) d^8 strong-field weak-field ($t_{2g}^6\ e_g^2$): Putting the value of $\Delta = 10Dq$ (the energy gap between ground ^3E_g and $^3T_{2g}$) and α as 4 in equation (52), we get

$$\mu_{eff} = \mu_{S.O.}\left(1 - 4 \times \frac{\lambda}{10Dq}\right) \tag{61}$$

Now because the sign of spin-orbital coupling parameter is negative for more than half-filled configurations, the equation (61) can also be written in the following form.

$$\mu_{eff} = \mu_{S.O.}\left(1 + 4 \times \frac{|\lambda|}{10Dq}\right) \tag{62}$$

Hence, for d^8 complexes, the effective magnetic moment is greater than the spin-only magnetic moment; which is also independent of temperature.

- ***Temperature Independent Paramagnetism (TIP)***

In the previous section, we concluded that owing to the A_1 symmetry of the ground state and zero unpaired electron, the strong field complexes of d^6 configuration should be diamagnetic in nature. In other words, there should be no spin-only or the orbital magnetism in spin paired complexes d^6 metal ions. However, that is not hundred-percent true because there are some complexes that have neither the spin nor the orbital degeneracy, yet show weak paramagnetism. Consider the case of MnO_4^- or $[Co(NH_3)_6]^{3+}$, which do not have unpaired electron (no spin degeneracy) and are lacking ground Mulliken state of T-symmetry (no orbital degeneracy); suggesting zero spin-only and zero orbital magnetism. Nevertheless, both of these compounds are weakly paramagnetic in nature. This exceptional behavior can be attributed to the existence of a low-lying excited state which does have the necessary orbital degeneracy and is still a singlet. When the external magnetic field is applied, some of the excited state mixes itself into the ground state resulting in a perturbed ground state that possesses some of the properties of the excited one. The experiments have shown that these complexes have small orbital paramagnetism, which at times, is enough to cancel out the inherent diamagnetism. This kind of paramagnetism is also called temperature-independent paramagnetism due to its non-reliance on the thermal population of Boltzmann levels.

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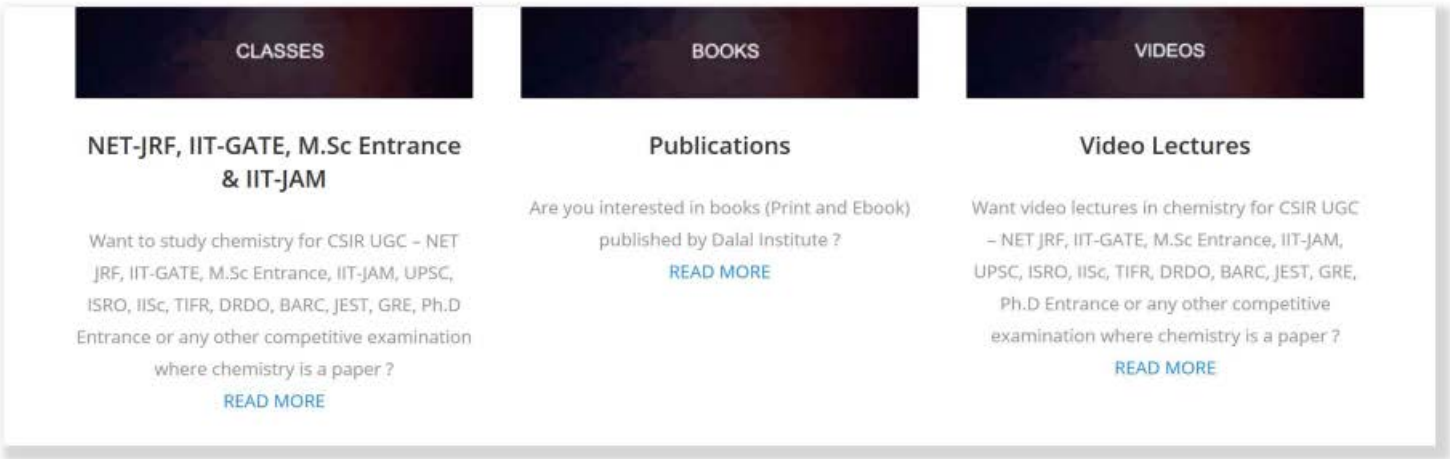

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