TDC Part III
Paper VI
Inorganic Chemistry

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TOPIC:-UNIT II, MAGNETIC PROPERTIES, SPIN AND ORBITAL CONTRIBUTION TO MAGNETIC MOMENTS

SPI N AND ORBITAL CONTRIBUTION TO MAGNETIC MOMENTS

Various complexes of transition metals (mostly first transition series elements) give a magnetic moment much higher than μ_s. This is due to the orbital contributions to magnetic moment. The spin angular momentum of an electron is independent of its surroundings and therefore, the spin moment of unpaired electron remains, unaffected by changes in chemical bonding of the compound provided that there is no spin pairing because of bonding. On the conflicting, the orbital angular momentum of the electron depends upon the chemical environment. The orbital contribution of magnetic moment may get compensated or quenched. Thus, as a result, the observed magnetic moments are very close to spin only magnetic moment value.

The quenching of orbital angular momentum can be easily explained on the basis of Crystal Field Theory of bonding in transition metal complexes.

The unpaired electrons in a first transition series are present in the 3d orbitals. A transition metal ion has five 3d orbitals which are degenerate. An electron possesses as angular momentum along a given axis if it is possible to transform its orbital by rotation around this axis into another orbital which is equivalent to it in shape, axis and energy.

Thus, for orbital contribution to the magnetic moment, there must be two or more degenerate orbitals which can be inter converted by rotation about a suitable axis and these orbitals must be unequally occupied.

The orbital angular momentum along the given axis possessed by the electron in such an orbital is equal to the number of times the orbital gets transformed in to the equivalent orbital during a rotation of 90° around that axis. If the orbital degeneracy is lost by chemical bonding or crystal field effects, the orbital contribution to the total magnetic moment is partially or completely quenched.

Let us consider a free metal ion in which all the d orbitals are degenerate. An electron in d_{x2-y2} orbital will contribute to orbital angular momentum equal to 2 units of $h/2\pi$ along z- axis because a rotation of d_{x2-y2} orbital by 45^0 around the z- axis takes it to equivalent d_{xy} orbital **(**Figure 3.2**).**

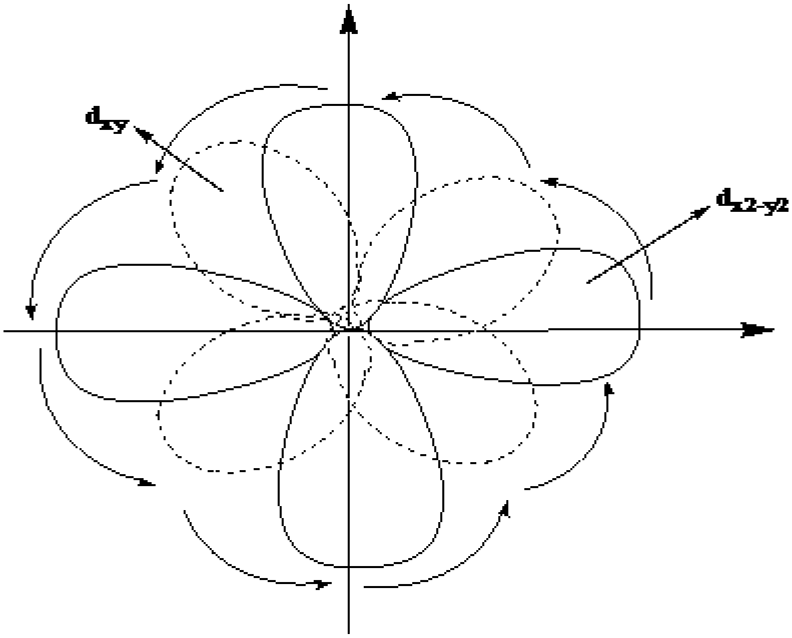

Figure 3.2. *Circulation of electron density about z axis in* d_{xy} *and* d_{x2-y2} *orbitals*

In the above discussion, it is clear that a rotation of d_{x2-y2} orbital by 90° around z- axis will carry this orbital in to d_{xy} orbital 2 times. Similarly, we can also say that an electron in d_{xy} orbital will contribute to orbital angular momentum of two in the units of h/2π along z- axis. Similarly, an electron in d_{xz}orbital will have an orbital angular momentum equal to 1 unit of h/2π along z- axis because d_{xz} orbital gets transformed into an equivalent d_{yz} orbital by rotating the d_{xz} orbital around x- axis by an angle of 90°.

When the metal ion is surrounded octahedrally by six ligands, the degeneracy of d-obritals gets disturbed. The d_{xy} and d_{x2-y2} orbitlas acquire different energies and therefore, are non-equivalent. As a result, an electron in d_{x2-y2} orbtial cannot be equated with an electron in d_{xy} orbital. In other words, the d_{x2-y2} orbital cannot be transformed into d_{xy} orbital and vice versa by rotation of the orbital along z-axis. Thus, the electron in d_{x2-y2} orbital will not cause to have orbital contribution along the z-axis.