CHAPTER 9

Magnetic Properties of Transition Metal Complexes:

❖ Elementary Theory of Magneto-Chemistry

The history of magnetism starts earlier than 600 B.C., but the initiation of conceptual understanding
dates back only in the twentieth century, after which the scientific community started developing technologies
based on this understanding. The phenomenon of magnetism was most likely first detected in a mineral
magnetite, also called “lode stone (Fe₃O₄)”, which is essentially a chemical compound of iron and oxygen with
inverse spinal structure. In the ancient times, the Greeks were the first who used this compound, and called it
a magnet due to its remarkable capability to attract iron pieces, or other blocks of the same material. Plato
(428-348 B.C.) and Aristotle have also given some description about permanent magnets in their writings. The
first record of a magnetic compass used for navigational purpose comes from a Chinese writing (1040 A.D.).
The first systematic scientific investigation of the phenomenon of magnetism was carried out by a British
physicist William Gilbert (1540-1603); who also discovered that the earth is also a weak magnet itself. A
French military engineer and physicist Charles-Augustin de Coulomb (1736-1806) initiated the quantitative
studies of magnetic phenomena in the eighteenth century. He gave the inverse square law, telling that the
attraction force between two magnetic objects is directly proportional to the multiplication of their individual
field strengths and inversely proportional to the square of their distance of separation. Danish physicist, H. C.
Oersted (1777-1851), first proposed a link between the magnetism and electricity. French physicist Andre
Marie Ampere (1775-1836) and British physicist Michael Faraday (1791-1869) carried out the experiments
involving the effects of magnetic and electric fields on one another. Finally, the legendary Scotsman, James
Clerk Maxwell (1831-1879), provided the theoretical basis to the physics of electromagnetism in the nineteenth
century by showing that the magnetism and electricity are just the two faces of the same coin.

The modern point of view of magnetism in condensed matter originates from the work of two French
physicists, Pierre Curie (1859-1906) and Pierre Weiss (1865-1940). Pierre Curie studied how the temperature
affects magnetism of different materials, and witnessed that magnetism vanished quickly above a certain
critical temperature in materials like iron. Pierre Weiss put forward a theory about magnetism which was based
upon the internal magnetic field, present at molecular scale, which is proportional to the magnetic average that
align the micro-magnets in magnetic substances. Today’s understanding of magnetic phenomena counts on the
theory of the motion and interactions of electrons in atoms, given by Ernest Ising and Werner Heisenberg. The
study of magnetic field generated by the motion of electrons and nuclei in different materials help us to
rationalize various fundamental effects and phenomenon. For example, the nuclear magnetic resonance is one
of the most important tool to characterize organic and inorganic compounds; or the study of magnetic
properties of transition metal complexes has provided a beautiful insight of stereochemistry of metal centres
and the nature of metal-ligand bonding. The branch of chemistry which is especially concerned with the
magnetic properties of chemical compounds is generally called as magneto-chemistry.
Basic Terminology

Now before we start to discuss the classical and quantum mechanical aspects of magneto-chemistry, some terms which will be used very frequently, must be defined.

1. Magnetic field strength \((H)\): The magnetic fields produced by currents are calculated using Biot-Savart Law or Ampere's Law; and are generally measured in Tesla (T). However, when the fields so created pass through the magnetic things which can have magnetic fields induced internally; uncertainties can arise about which part of the field comes from the material considered and which part of the field comes from the external currents. Therefore, it is a common practice to distinguish the two by defining another magnetic field quantity "\(H'\)" usually called as "magnetic field strength". Thus, the magnetic field strength \((H)\) is one of two ways that can be used to express the magnetic field intensity. To be precise, a distinction is made between magnetic flux density \(B\), measured in Newton per ampere-meter (N/mA), also called tesla (T) and magnetic field strength \(H\), measured in amperes per meter (A/m).

2. Magnetic induction \((B)\): The phenomenon of rise of magnetism in a specimen of magnetic material when it is placed in an external magnetic field is called as magnetic induction. The term "magnetic induction" is sometimes also referred as "magnetic flux density" which may be defined as the total number of magnetic lines of force crossing a unit area around a point positioned inside an object placed in the magnetizing field. The generally used symbol for magnetic induction or magnetic flux density is \(B\); and the relationship between total magnetic flux \((\phi)\) and magnetic flux density is \(B = \phi/a\), where \(a\) is the cross-sectional area in square meter. The SI unit for magnetic flux density is the Tesla (T) which is equal to Weber/m² or NmA.

3. Magnetic permeability \((\mu)\): The magnetic permeability, or simply the permeability, may be defined as the relative decrease or increase in the total magnetic-field inside a substance compared to the magnetizing field, the given material placed within. In other words, the permeability of a material is equal to the magnetic flux density \((B)\) created within the material by a magnetizing field divided by the intensity of magnetizing field i.e magnetic field strength \((H)\). Therefore, magnetic permeability is defined as \(\mu = B/H\). In SI units, permeability is measured in Henry per meter (H/m), or equivalently in Newton (kg m/s²) per amperes squared (NA²).

4. Intensity of magnetization \((I)\): The intensity of magnetization represents the extent up to which a material has been magnetized under the influence of magnetizing field. Intensity of magnetization of a magnetic material is thus defined as the magnetic moment per unit volume of the material i.e. \(I = M/N\), where \(M\) is the magnetic moment which is equal to the product of pole strength and the distance of separation of magnetic poles of the specimen. Like \(H\), the intensity of magnetization is also measured in amperes per meter (A/m).

5. Magnetic susceptibility \((K, \chi, \chi_m)\): The magnetic susceptibility is simply a measure of the magnetic properties of a material. The magnetic susceptibility shows whether a substance is repelled out or attracted into a magnetic field, which in turn has practical applications. Mathematically, volume susceptibility \((K)\) is the ratio of intensity of magnetization to the applied magnetizing field intensity i.e. \(K = I/H\). Now because the units of \(I\) and \(H\) are same, volume susceptibility is a dimensionless quantity. However, volume susceptibility divided by density of material is called as mass susceptibility \((\chi)\) which is measured in cm³ g⁻¹. The \(\chi\) multiplied by molar mass is called as molar susceptibility \((\chi_m)\) which is measured in cm³ mol⁻¹.
The Classical Concept of Magnetism

The classical theory of magnetism was developed long before the quantum mechanics. The Lenz's law states that when a substance is placed within a magnetic field of strength $H$, the field induced within the substance ($B$) differs from $H$ by $4\pi I$ i.e. the difference is proportional to the intensity of magnetization of the material. Mathematically, we can state this relationship as:

$$B = H + 4\pi I \tag{1}$$

Dividing equation (1) throughout by $H$, we get

$$\frac{B}{H} = 1 + 4\pi \frac{I}{H} \tag{2}$$

Now putting the value of $I/H = K$ (volume susceptibility) in equation (2), we get

$$\frac{B}{H} = 1 + 4\pi K \quad \text{or} \quad 4\pi K = \frac{B}{H} - 1 \tag{3}$$

For some materials, the ratio of $B/H$ is less than one, which means the value of $K$ is negative, these materials are labelled as diamagnetic materials. For some materials, the ratio of $B/H$ is greater than one, which means the value of $K$ is positive, these materials are labelled as paramagnetic materials. The mass susceptibility ($\chi$) in cm$^3$ g$^{-1}$ can be obtained as:

$$\chi = \frac{K}{d} \tag{4}$$

Or the molar susceptibility in cm$^3$ mol$^{-1}$ can be calculated from equation (4) as follows:

$$\chi_M = \chi \times M \tag{5}$$

Where $d$ and $M$ are the density and gram molar mass of the material, respectively. Since this value includes the underlying diamagnetism of paired electrons, it is necessary to correct for the diamagnetic portion of $\chi_M$ to get a corrected paramagnetic susceptibility i.e. measured susceptibility ($\chi_M$) = paramagnetic susceptibility ($\chi_M^p$) + diamagnetic susceptibility ($\chi_M^d$).

$$\chi_M^p = \chi_M - \chi_M^d \tag{6}$$

The values of these corrections are generally tabulated in the laboratory manuals and are available on-line too.

A French physicist, Pierre Curie, was investigating the effect of temperature on magnetic properties in the ending times of nineteenth century. He discovered that, for a large number of paramagnetic substances, molar magnetic susceptibility ($\chi_M$) varies inversely with the temperature. This observation is called as Curie law, which states that:

$$\chi_M \propto \frac{1}{T}$$
\[
\chi_M = \frac{C}{T}
\]  
(7)

Where \( C \) is the Curie constant having different magnitude for different substances. Curie also discovered that for every ferromagnetic substance, there is a temperature \( T_C \) above which, the normal paramagnetic behaviour occurs. Later work by Onnes and Perrier showed that, for many paramagnetic substances, a more precise relationship is:

\[
\chi_M = \frac{C}{T + \theta}
\]  
(8)

Where \( \theta \) is the Weiss constant, and the equation (8) is popularly known as the Curie-Weiss law. The symbol “\( \theta \)” used in equation (8) is sometimes replaced by \( T_C \) because in the case of ferromagnetic materials, the value of \( \theta \) calculated by Curie-Weiss plot, is actually equal to the negative of their Curie temperature. That’s why, there is another popular form of the Curie-Weiss law as given below.

\[
\chi_M = \frac{C}{T - \theta}
\]  
(9)

The conventions shown in equation (8) are more widely accepted by the British and American academics, while the form with negative sign is more popular in the Indian and German universities. Furthermore, Louis Neel, another French physicist, observed that for every antiferromagnetic substance, there is a temperature \( T_N \) above which, the normal paramagnetic behaviour occurs.

Figure 1. Plot of magnetic susceptibility vs temperature for normal paramagnetic, ferromagnetic and antiferromagnetic materials.

Normally, the reciprocal of magnetic susceptibility is plotted verses temperature (\( 1/\chi_M \) vs \( T \) is follows a straight line equation); which makes the use of both forms of Curie-Weiss law. The symbol “\( \theta \)” in equation (9) is replaced by \( T_C \), which gives suitable form for ferromagnetic substances (magnetic moments of atoms align to produce a strong magnetic effect); while the replacement of the symbol “\( \theta \)” by \( T_N \) in equation (8) gives the suitable form for antiferromagnetic materials (magnetic moments of atoms align anti-parallel to produce a strong magnetic effect).
Therefore, for ferromagnetic substances

\[ \chi_M = \frac{C}{T - T_C} \quad (10) \]

For antiferromagnetic substances

\[ \chi_M = \frac{C}{T + T_N} \quad (11) \]

It is also worthy to mention that the normal paramagnetic behaviour of ferromagnetic or antiferromagnetic materials is observed only when \( T > \theta \).

Figure 2. Plot of reciprocal of magnetic susceptibility vs temperature for normal paramagnetic, ferromagnetic and antiferromagnetic materials.

Thus, for ferromagnetic and antiferromagnetic materials, the value of \( \theta \) is generally labelled \( T_C \) (Curie temperature) and \( T_N \) (Neel temperature), respectively.

- **The Quantum Mechanical Concept of Magnetism**

The genesis of magnetic phenomena in all atoms lies in the orbital and spin motions of electrons and how these electrons interact with each other. The orbital motion of electron gives rise to the orbital magnetic moment (\( \mu_o \)), and the spin motion generates the spin magnetic moment (\( \mu_s \)). The total magnetic moment of an atom is actually the resultant of the two aforementioned effects. Now, though the wave mechanical model of an atom is more precise in the rationalization of different atomic properties, the prewave mechanical model of an atom is still very much of use for understanding certain quantum mechanical effects. In Bohr model, the electron is considered as a negatively charged hard sphere which spin about its own axis as well as revolves around the positively charged heavy centre of the atom. The pictorial representation of the rise of magnetic moment by these two kinds of motion is shown below.
Figure 3. The generation of orbital magnetic moment ($\mu_1$) and spin magnetic moment ($\mu_s$) from prewave mechanical quantum theory.

Thus, we can agree on the fact that a more conceptual comprehensive understanding of the phenomena of magnetism in different chemical compounds requires us to start from the most elementary ideas of spin and orbital magnetic moments.

1. **Orbital magnetic moment ($\mu_1$)**: The motion of a negatively charged electron in a circular path is very much analogous to the current flowing through a ring of conducting material. Consequently, a magnetic field in a direction perpendicular to the plane of the ring or orbit is generated. The strength of the magnetic field thus produced can be obtained by multiplying the magnitude of the current flowing ($i$) with the surface area of that ring ($A$). Mathematically, the magnitude of the orbital magnetic moment ($\mu_1$) can be given as:

$$\mu_1 = iA = \left(\frac{e\omega}{2\pi c}\right)\pi r^2$$

(12)

Where $e$ is the electronic charge, $\omega$ is the angular velocity of the electron, $c$ is the velocity of light and $r$ is the radius of the orbit. From the quantum theory of angular momentum, we know that the magnitude of angular momenta of an orbiting electron is given by the following relation.

$$L_{\text{quantum mechanical}} = \sqrt{l(l + 1)} \frac{\hbar}{2\pi}$$

(13)

Where $L$ is magnitude angular momentum due to orbital motion and $l$ is the quantum number for the same. Moreover, the magnitude of angular momentum from classical mechanics is given by the product of angular velocity ($\omega$) and moment of inertia ($I$).

$$L_{\text{classical}} = I\omega$$

(14)

Putting $I = mr^2$ in equation (14) we get

$$L_{\text{classical}} = mr^2\omega$$

(15)
Now, it is a well-known fact that all values of quantum domain are also present in the classical domain though the vice-versa is not true. Therefore, we can put equation (13) equal to equation (15) to find the classical analogues.

\[ mr^2 \omega = \sqrt{l(l + 1)} \frac{h}{2\pi} \]  \hspace{1cm} (16)

Or

\[ \omega r^2 = \sqrt{l(l + 1)} \frac{h}{2\pi mn} \]  \hspace{1cm} (17)

Putting value of \( \omega r^2 \) from equation (17) into equation (12), we get

\[ \mu_1 = \frac{e}{2c} \left( \sqrt{l(l + 1)} \frac{h}{2\pi mn} \right) \]  \hspace{1cm} (18)

\[ \mu_1 = \sqrt{l(l + 1)} \left( \frac{eh}{4\pi mc} \right) \]  \hspace{1cm} (19)

\[ \mu_1 = \sqrt{l(l + 1)} \text{ B.M.} \]  \hspace{1cm} (20)

Comparing equation (20) and equation (13), we can conclude that the magnitude of magnetic moment (\( \mu_1 \)) in the units of Bohr magneton (B.M.) is equal to orbital angular momentum (\( L \)) measured in the units of \( h/2\pi \). It is also worthy to note that both the vectors (\( \mu_1 \) and \( L \)) are collinear but oriented in opposite direction. In other words, if the magnetic moment is oriented upward to the orbit plane, orbital angular momentum is downward, and vice-versa.

2. Spin magnetic moment (\( \mu_s \)): In 1926, two American-Dutch physicists, named Samuel Goudsmit and George Uhlenbeck, observed that the angular momentum possessed by the moving electron is actually greater than the orbital angular momentum. This excess of angular momentum was then attributed to the spinning motion of the electron. This spinning motion of a negatively charged electron about its own axis is also analogous to the current carrying circular conductor. Accordingly, a magnetic field, in a direction along to the spinning axis, is generated. They also postulated that the ratio of the spin magnetic moment (\( \mu_s \)) measured in the units of B.M. to the spin angular momentum (\( S \)) measured in the units of \( h/2\pi \), must be equal to 2. This ratio is called as Lande splitting factor, or the “\( g \)” value.

\[ \frac{\mu_s}{S} = \frac{\mu_s}{\sqrt{s(s + 1)}} = g \]  \hspace{1cm} (21)

\[ \mu_s = g\sqrt{s(s + 1)} = 2\sqrt{s(s + 1)} \text{ B.M.} \]  \hspace{1cm} (22)

Where \( s \) is the quantum number defining spin motion of the electron and \([s(s + 1)]^{1/2} \) is the corresponding spin angular momentum in the units of \( h/2\pi \) as discussed earlier.
Both types of magnetic moment will interact with the external magnetic field, and will tend to align themselves along the direction of the field; which in turn will reinforce the magnitude of the applied field. In multi electron systems, the spin motion of the individual electrons will interact with each other to give resultant spin motion quantum number "S"; while the orbital motion of individual electrons will interact to give resultant orbital motion quantum number "L". Now, if L and S do not interact with each other, the overall magnetic moment will just be the sum of their individual magnetic moments. However, if resultant spin motion and resultant orbital motion do couple, the overall magnetic moment will be obtained from "J" i.e. total angular momentum quantum number. The phenomena like diamagnetism, paramagnetism, or ferromagnetism arises as a result of alignments and interactions of theses micro magnets.

- **Classes of Magnetic Materials**

  The most primitive way to classify different materials on the basis of their magnetic properties is how they respond to externally applied magnetic field. Thereafter, we can discuss the cause or interaction responsible for such behaviour. In some material, the atomic scale magnetic moments do not interact with each other; while in some cases the strong interaction may lead to very complex magnetic profile depending upon the structural specificity. Different magnetic materials can be classified into the following four major classes:

1. **Diamagnetic materials:** When some substances are placed in external magnetic field, the number of magnetic lines of forces passing through the substance is less than the number magnetic lines of force passing through the vacuum. This eventually means that the ratio of $B/H$ is less than one, which gives a negative value of magnetic susceptibility ($K$). Such substances are called as diamagnetic substance and are repelled by the external magnetic field.

   ![Diamagnetic body](image)

   \[ \frac{B}{H} < 1 \]

   No individual micromagnets

   Figure 4. The behaviour of a diamagnetic body in externally applied magnetic field and corresponding magnetic domain.

Diamagnetic substances do not have unpaired electrons, and therefore the magnetic moment produced by one electron is cancelled out by the other one. The phenomenon of diamagnetism is 1000 times weaker than paramagnetism, which makes it unobservable in substances with unpaired electrons. However, the measured magnetic susceptibilities must be corrected for the underlying diamagnetic effect, because most of the materials do contain paired electrons. Diamagnetic susceptibility is generally independent both of field strength and temperature.
2. Paramagnetic materials: When some substances are placed in external magnetic field, the number of magnetic lines of forces passing through the substance is more than the number magnetic lines of force passing through the vacuum. This eventually means that the ratio of $B/H$ is greater than one, which gives a positive value of magnetic susceptibility ($K$). Such substances are called as paramagnetic substance and are attracted by the external magnetic field.

![Randomly oriented micromagnets](image)

Figure 5. The behaviour of a paramagnetic body in externally applied magnetic field and corresponding magnetic domain.

Paramagnetic substances do have unpaired electrons, and therefore there is a net magnetic moment possessed by individual constituents. However, these micro-magnets are randomly oriented. The paramagnetic susceptibility of these materials decreases with the increase of temperature and follow simple Curie law. Hence, the paramagnetic susceptibility is generally independent of field strength, but markedly dependent on temperature of the system.

3. Ferromagnetic materials: When some substances are placed in external magnetic field, the number of magnetic lines of forces passing through the substance is hugely greater than the number magnetic lines of force passing through the vacuum. This eventually means that the ratio of $B/H$ is much greater than 1, which gives a positive value of magnetic susceptibility ($K$) of order as high as $10^4$. Such substances are called as ferromagnetic substance and are strongly attracted by the external magnetic field.

![Parallel alignment micromagnets](image)

Figure 6. The behaviour of a ferromagnetic body in externally applied magnetic field and corresponding magnetic domain.
Ferromagnetic substances do have unpaired electrons, and therefore there is a net magnetic moment possessed by individual constituents. However, special interaction of these micro-magnets makes them orient parallel to each other yielding very strong paramagnetism. The hysteresis and remanence and are characteristic features of ferromagnetic materials. Hence, the ferromagnetic susceptibility depends upon the field strength as well as the temperature of the system considered.

4. Antiferromagnetic materials: When some substances are placed in external magnetic field, the number of magnetic lines of forces passing through the substance is slightly greater than the number magnetic lines of force passing through the vacuum. This eventually means that the ratio of $B/H$ is slightly greater than one, which gives a very small positive value of magnetic susceptibility ($K$). Such substances are called as antiferromagnetic substance and are weakly attracted by the external magnetic field.

![Antiferromagnetic substance](image)

\[ \frac{B}{H} \geq 1 \]

Antiparallel alignment micromagnets

Figure 7. The behaviour of an antiferromagnetic body in externally applied magnetic field and corresponding magnetic domain.

Antiferromagnetic substances do have unpaired electrons, and therefore are expected to show paramagnetism due to the presence of net magnetic moment possessed by individual constituents. However, special interaction of these micro-magnets makes them orient antiparallel to each other yielding very small value of positive magnetic susceptibility. The ferromagnetic susceptibility usually depends on the temperature of the system only, though the dependence on field strength is also observed sometimes.
Guoy’s Method for Determination of Magnetic Susceptibility

The simplest method used for measuring the magnetic susceptibilities of transition metal complexes was proposed by a French physicist, named Louis Georges Gouy. In 1889, He obtained a mathematical expression revealing that the force is actually proportional to volume susceptibility ($K$) or the interaction of material in a uniform external magnetic field. From this derivation, Gouy suggested that the balance measurements taken for tubes of material suspended in a magnetic field could evaluate the expression for volume susceptibility. Though Gouy never tested his scientific proposal, this inexpensive and simple technique would become a blueprint of the Gouy balance; and therefore, for measuring magnetic susceptibilities.
The determination of a magnetic susceptibility depends on the measurement of $B/H$. From the classical description of magnetism, Lenz's law can be stated as:

$$\frac{B}{H} = 1 + 4\pi K$$  \hspace{1cm} (23)

where $B/H$ is called the magnetic permeability of the material and $K$ is the magnetic susceptibility per unit volume ($\mu H$). The Gouy's method includes the measurement of force on the sample by externally applied magnetic field and depends upon the tendency of the sample to align itself in high or low magnetic field strength. The force at any given point of the sample (say $dx$) is given by:

$$dF = \mu_0 H K dV \frac{dH}{dx}$$  \hspace{1cm} (24)

Where $\mu_0$ symbolizes the permeability of the vacuum (value is 1 when using c.g.s. system of units), $dV$ is the volume of the sample at point $dx$, $H$ is the magnitude of the magnetic field at point $dx$ and $K$ represents the magnetic susceptibility per unit volume. The Gouy tube, packed uniformly with the sample is placed in the magnetic field such that each end of the glass tube experiences a constant field strength. In order to achieve this situation, the Guoy tube must be packed to a certain height like 10 or 15 cm, and the tube is then hanged between the electromagnetic poles in such a way that the bottom of the sample lies in the centre of the magnetic field (an area where a uniform field strength can be easily achieved); while the top of the sample is out of the field ($H = 0$). Now, the total magnitude of the force acting on the sample can be calculated just by integrating the equation (24).
CHAPTER 9 Magnetic Properties of Transition Metal Complexes:

\[ F = \mu^0 AK \left[ \frac{H^2}{2} \right]_0 \]  \hspace{1cm} (25)

\[ F = \frac{\mu^0 AKH^2}{2} \]  \hspace{1cm} (26)

Where \( A \) is the area of cross section of the sample. The force can easily be measured by the apparent change in mass when the external magnetic field is switched on.

\[ F = g\Delta w \]  \hspace{1cm} (27)

Where \( g \) is the acceleration due to gravity and \( \Delta w \) is the apparent deviation in mass. From equation (26) and equation (27), we get:

\[ g\Delta w = \frac{\mu^0 AKH^2}{2} \]  \hspace{1cm} (28)

It is also worthy to mention that some correction must be made for the tube, because it possesses its own magnetic properties due to air filled within the tube, and the nature of its construction materials. Therefore, the equation (28) takes the form:

\[ g\Delta w' = \frac{\mu^0 A (K - K') H^2}{2} \]  \hspace{1cm} (29)

Where \( \Delta w' = \Delta w + \delta \), \( \delta \) is a constant allowing for the magnetic properties of the empty tube, \( K' \) is the volume susceptibility of the replaced air. This gives:

\[ K = \frac{2g\Delta w'}{\mu^0 A H^2} + K' \]  \hspace{1cm} (30)

Converting from volume susceptibility \( (K) \) to mass susceptibility \( (\chi) \) leads to:

\[ \chi = \frac{K}{\rho} = \frac{KV}{W} = \frac{2g\Delta w'V}{\mu^0 A H^2W} + \frac{K'V}{W} \]  \hspace{1cm} (31)

\[ \chi = \frac{\beta\Delta w'}{W} + \frac{K'V}{W} \]  \hspace{1cm} (32)

\[ \chi = \frac{(\alpha + \beta\Delta w')}{W} \]  \hspace{1cm} (33)

Where \( \alpha = K'V \) is a correction constant incorporated for the air replaced by the sample, \( \beta = (2gV)/(\mu^0 A H^2) \) is also a constant which depends upon the strength of the magnetic field and \( W \) is the weight of the sample under consideration. In order to measure the mass susceptibility a sample more accurately, the predetermine of \( \alpha \), \( \beta \) and \( \delta \) is necessary. Therefore, the dependence of these constants on the magnetic field strength, the amount of
sample put in the tube and the tube itself emphasizes on the fact that each analyst must find their value for every new configuration.

Determination of the constants can be carried out by selecting a tube and a small nichrome-wire to make an assembly which will allow the tube to be hanged from the analytical balance so that the bottom of the tube is aligned halfway between the mutually-facing poles of the electromagnets used, and sample’s top is above the magnet and thus subject to a zero field strength.

i) Calculation of δ: Adjust the zero on the Guoy’s balance, then suspend the empty tube from the balance and measure its weight (W1). Now turn on the electromagnets to desired magnetic field strength and reweigh the tube (W2). The force on the Guoy’s tube, δ, is thus δ = W2 − W1. The value will would be negative because the tubes are generally diamagnetic and are pushed out of the magnetic field.

ii) Calculation of a: Fill the water in Guoy’s tube to the required marking and weigh it, this will give the value of W3. Now considering the density of water at this temperature as 1.00 g cm⁻³, this volume of water would be equal to the volume of the sample. Hence, V = (W3 − W1)/1.00, where the changes in weight should be expressed in grams. Now, a = K'V or a = 0.029 × (W3 − W1) in 10⁻⁶ c.g.s. units, where 0.029 is the volume susceptibility of the air.

ii) Calculation of β: The measurement of β requires a standard compound whose magnetic properties are already known. Most commonly used calibrants are [Ni(en)3]S₂O₃ and Hg[Co(SCN)₄]. Now because of fact that the magnetic properties are usually temperature dependent, the susceptibility of the calibrant must be determined at a temperature exactly similar to what is required for the sample. Record the temperature, T₁, and then fill the tube to the required height with the calibrant and weigh it with magnetic field off (W₄) and on (W₅). For [Ni(en)3]S₂O₃, use χ = 3172/T in 10⁻⁶ c.g.s units; while for HgCo(SCN)₄ the χ = 4985/(T+10) in 10⁻⁶ in c.g.s unit can be used at temperature T. Using this χ then β = (χW − a)/Δw', where Δw' = (W₅ − W₄) − δ in mg and W = (W₄ − W₁) in grams.


**Calculation of Magnetic Moments**

The resultant magnetic moment of any magnetic material (including free transition metal ions or their complexes) arises due to the orbital and spin motions of electrons and how these electrons interact with one another. The validation and applicability of any magnetic theory depends upon the precision of its theoretical results with the experimental one. The theoretical as well as experimental approach to magnetic moments are given below.

📍 *Experimental Calculation of Magnetic Moments*

It is pretty funny to say but the magnetic moment of a substance cannot be calculated from experiment directly. The experimental determination of magnetic moment ($\mu$) requires the measurement of magnetic susceptibility ($\chi$) first. This experimental value of paramagnetic susceptibility is then used to find the value of magnetic moment by using certain quantum mechanical correlation. Now as we know that the experimentally measured molar paramagnetic susceptibility ($\chi_M^p$) is actually the sum of paramagnetic ($\chi_M^p$) and diamagnetic
(\(\chi_M\)) susceptibilities. Hence, actually value of paramagnetic susceptibility is obtained by subtracting the diamagnetic susceptibility from the experimentally measured susceptibility.

\[
\chi_M = \chi_M^p + \chi_M^D \\
\chi_M^D = \chi_M - \chi_M^p
\]

(34)

(35)

The diamagnetic susceptibility is possessed by almost every material due to the presence of paired electrons in the valence or deeper shells. The root cause of diamagnetism is the motion of negatively charged particles in the applied magnetic field. This motion creates an orbital electric current and the applied magnetic field makes thoses orbits to precess about its direction of application. This precession is called as Larmor precession (depends upon the strength of the applied field) that generates its own internal magnetic field in a direction opposite to the external one. Consequently, the magnetic lines of force try to bypass the material which in turn imparts a negative value to magnetic susceptibility. The atomic diamagnetic susceptibility per mole of atom (\(\chi_M^{D,\text{atomic}}\)) can be calculated using equation (36).

\[
\chi_M^{D,\text{atomic}} = \frac{N e^2}{6mc^2} \sum_{i=1}^{n} <r_i^2>
\]

(36)

Where \(n\) is the number of electrons in the atom under consideration, \(N\) is the Avogadro number, \(m\) is the mass of the electron, \(c\) is the velocity of the light and \(<r_i^2>\) is the mean square radius of the \(i\)th electron. Therefore, larger the number of electron in an atom, greater will be the magnitude of diamagnetic susceptibility. The total molar magnetic susceptibility of a chemical compound is the sum of contributions from diamagnetic susceptibility per mole of atom (\(\chi_M^{D,\text{atomic}}\)) and diamagnetic susceptibility per mole of bond (\(\chi_M^{D,\text{bond}}\)). The \(\chi_M^{D,\text{atomic}}\) and \(\chi_M^{D,\text{bond}}\) are generally labelled as Pascal’s constants.

Table 1. The value of Pascal’s constants for different atoms and bonds.

<table>
<thead>
<tr>
<th></th>
<th>(\chi_M^{D,\text{atomic}}) (cm(^3) mol(^{-1}))</th>
<th>(\chi_M^{D,\text{bond}}) (cm(^3) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-2.9</td>
<td>-12.8</td>
</tr>
<tr>
<td>C</td>
<td>-6.0</td>
<td>-12.8</td>
</tr>
<tr>
<td>C (aromatic)</td>
<td>-6.2</td>
<td>-12.8</td>
</tr>
<tr>
<td>N</td>
<td>-5.6</td>
<td>-12.8</td>
</tr>
<tr>
<td>N (aromatic)</td>
<td>-4.6</td>
<td>-5.0</td>
</tr>
<tr>
<td>O</td>
<td>-4.6</td>
<td>-15.0</td>
</tr>
<tr>
<td>Cl</td>
<td>-20.1</td>
<td>-10.4</td>
</tr>
</tbody>
</table>

\(\text{H, C, N, O, Cl}\)
The calculation of $\chi_M^{D}$ using Pascal’s constants can be exemplified by taking the case of pyridine and acetone.

**i) Molar diamagnetic susceptibility ($\chi_M^{D}$) for pyridine:** The contributions from diamagnetic susceptibility per mole of atom ($\chi_M^{D, \text{atomic}}$) and diamagnetic susceptibility per mole of bond ($\chi_M^{D, \text{bond}}$) is given below. It should also be noted that the contribution from bonds will be included in the ring values of N and C.

5 carbons of aromatic ring = $-31.0 \times 10^{-6}$ cm$^3$ mol$^{-1}$

5 hydrogens = $-14.5 \times 10^{-6}$ cm$^3$ mol$^{-1}$

1 nitrogen of aromatic ring = $-4.6 \times 10^{-6}$ cm$^3$ mol$^{-1}$

Total = $-50.1 \times 10^{-6}$ cm$^3$ mol$^{-1}$

**ii) Molar diamagnetic susceptibility ($\chi_M^{D}$) for acetone:** The contributions from diamagnetic susceptibility per mole of atom ($\chi_M^{D, \text{atomic}}$) and diamagnetic susceptibility per mole of bond ($\chi_M^{D, \text{bond}}$) is given below. It should also be noted that the contribution from C–C and C–H bonds is zero.

3 carbons = $-18.0 \times 10^{-6}$ cm$^3$ mol$^{-1}$

6 hydrogens = $-17.4 \times 10^{-6}$ cm$^3$ mol$^{-1}$

1 oxygen = $-4.6 \times 10^{-6}$ cm$^3$ mol$^{-1}$

1 CO double bond = $-6.3 \times 10^{-6}$ cm$^3$ mol$^{-1}$

Total = $-33.7 \times 10^{-6}$ cm$^3$ mol$^{-1}$

It is also worthy to remember that the molar diamagnetic susceptibility is independent of temperature and is always negative.

Now once the molar diamagnetic susceptibility is known, the corrected paramagnetic susceptibility ($\chi_M^{P}$) can be obtained from equation (35). Nevertheless, $\chi_M^{P}$ should further be corrected for temperature independent paramagnetism (TIP) for more precise and accurate results. The temperature independent paramagnetism arises due to the mixing of ground state and excited state under the effect of externally applied magnetic field. From quantum mechanical description of magnetism, the magnitude of paramagnetic susceptibility can be given as follows:

$$\chi_M^{P} = -\frac{N\mu_{\text{eff}}}{3kT}$$  \hspace{1cm} (36)

Where $\mu_{\text{eff}}$ is the magnetic moment per mole of the material (in the units of B.M.), $N$ is the Avogadro number, $T$ is the absolute temperature and $k$ is the Boltzmann constant. Putting the values of different constants in equation (36), we get

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{P} T} \text{ B.M.}$$  \hspace{1cm} (37)
Theoretical Calculation of Magnetic Moments

The valence bond model is the most basic theoretical approach to calculate the effective magnetic moment of transition metal atoms or ions (complexed or free). Now owing to the fact that the valence bond theory does not consider the splitting of free ion term arising from inter-electronic repulsion, there are three possible scenarios for the calculation of effective magnetic moment as given below.

1. Resultant orbital motion \( (L) \) and resultant spin motion \( (S) \) contribute independently: When the \( J \) states after \( L-S \) coupling are very close to each other energetically, the thermal energy would be sufficient to populate all \( J \)-levels of \( ^{2S+1}L \) state. This situation is pretty much analogues to the case when spin and orbital motion are completely decoupled from each other. In other words, \( L-S \) would not be effective in distinguishing transition metal atoms or ions on the basis of total motion. Therefore, the effective magnetic moment will be given by the following relation:

\[
\mu_{\text{eff}} = \sqrt{4S(S+1) + L(L+1)} \text{ B. M.} \tag{38}
\]

Hence, the relationship shown in the equation (38) does not consider the any quenching of orbital magnetic moment at all.

2. Resultant orbital motion \( (L) \) and resultant spin motion \( (S) \) couple with each other: When the \( J \) states after \( L-S \) coupling are very far to each other energetically, the thermal energy would not be sufficient to populate all \( J \)-levels of \( ^{2S+1}L \) state. This in turn would result in an almost hundred percent population density in the ground \( ^{2S+1}L \) state. This situation is pretty much analogues to the case when spin and orbital motion are coupled each to other. Therefore, the effective magnetic moment will be given by the following relation:

\[
\mu_{\text{eff}} = g\sqrt{J(J+1)} \text{ B. M.} \tag{39}
\]

Where \( g \) is the gyromagnetic ratio or Landé splitting factor whose value can be found as follows:

\[
g = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)} \tag{40}
\]

It must be noted that resultant spin motion \( (S) \), resultant orbital motion \( (L) \) and total motion \( (J) \) quantum number used in equation (40) belong to ground state term symbol.

3. Resultant spin motion \( (S) \) contribute but resultant orbital motion quenched: In this case the orbital motion contribution to the effective magnetic moment is completely quenched and \( \mu_{\text{eff}} \) is calculated using spin only formula. Therefore, the effective magnetic moment should be calculated as:

\[
\mu_{\text{eff}} = \sqrt{4S(S+1)} \text{ B. M.} \tag{41}
\]

Equation (41) can also be written the form given below.

\[
\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B. M.} \tag{42}
\]

Where \( n \) is the number of unpaired electrons.
A comparison of theoretically calculated magnetic moments (using different expressions) of various transition metal complexes along with their experimental values are listed in the following table.

Table 2. The comparison of theoretically calculated and experimental magnetic moments (B.M.).

<table>
<thead>
<tr>
<th>Metal centre</th>
<th>Ground state</th>
<th>$\mu_{\text{eff}} = [4S(S+1)+L(L+1)]^{1/2}$</th>
<th>$\mu_{\text{eff}} = g[J(J+1)]^{1/2}$</th>
<th>$\mu_{\text{eff}} = [4S(S+1)]^{1/2}$</th>
<th>$\mu_{\text{eff}}$ (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{3+}$</td>
<td>$^2$D$\gamma$</td>
<td>3.00</td>
<td>1.55</td>
<td>1.73</td>
<td>1.7 – 1.8</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>$^3$F$_2$</td>
<td>4.47</td>
<td>1.65</td>
<td>2.85</td>
<td>2.7 – 2.9</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>$^4$F$_{3/2}$</td>
<td>5.20</td>
<td>0.70</td>
<td>3.87</td>
<td>3.7 – 3.9</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>$^1$D$_0$</td>
<td>5.48</td>
<td>0</td>
<td>4.90</td>
<td>4.8 – 4.9</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>$^6$S$_{5/2}$</td>
<td>5.92</td>
<td>5.92</td>
<td>5.92</td>
<td>5.7 – 6.0</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>$^4$D$_4$</td>
<td>5.48</td>
<td>6.71</td>
<td>4.90</td>
<td>5.0 – 5.6</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>$^4$F$_{9/2}$</td>
<td>5.20</td>
<td>6.63</td>
<td>3.87</td>
<td>4.3 – 5.2</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>$^3$F$_4$</td>
<td>4.47</td>
<td>5.59</td>
<td>2.87</td>
<td>2.9 – 3.5</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>$^2$D$_{5/2}$</td>
<td>3.00</td>
<td>3.55</td>
<td>1.73</td>
<td>1.8 – 2.1</td>
</tr>
</tbody>
</table>

The results clearly indicate that the experimental value of $\mu_{\text{eff}}$ is significantly different than those calculated theoretically. Nevertheless, the spin only formula seems to be the best bet out of three different approaches; which in turn implies that the orbital contribution is probably very much quenched in case metal complexes of first transition series. The plausible reason for this kind of behaviour on the basis of valence bond theory is the hindrance faced by the orbital motion of metal electrons due to ligand cloud; and the extent to which orbital motion is hindered controls the contribution of orbital magnetic moment. However, valence bond theory does not provide any sophisticated explanation for qualitative and quantitative nature of the quenching of orbital magnetic moment. The orbital contribution to magnetic moment and its behaviour under different kinds of ligand field will be rationalized on the basis on crystal field theory in the forthcoming sections of this chapter.

By comparing theoretically calculated magnetic moment the experimental values, one can also comment on the outer or inner orbital nature of the complex. For example, the experimental magnetic moment for [Fe(H$_2$O)$_6$]$^{2+}$ is about 5.0 B.M.; which suggests an outer orbital configuration with four unpaired electron (4.9 B.M.), as theoretically calculated magnetic moment for inner orbital complex would be zero. Similarly, the zero value of experimental magnetic moment for [Fe(CN)$_6$]$^{4-}$ complex suggests an inner orbital configuration with zero unpaired electron (0.0 B.M.), as theoretically calculated spin only magnetic moment for outer orbital complex would be 4.9 B.M.
Magnetic Properties of Free Ions

The resultant magnetic behaviour of free ions; whether we talk about transition metals or lanthanides; arises as a result of spin-spin, orbital-orbital and spin-orbital interactions. Now stating more precisely, after considering the effect of spin-spin coupling and orbital-orbital coupling, the further degeneracy removal of the free ion terms is carried out by spin-orbital interaction (L-S coupling) that mainly leads to three different cases depending upon its relative magnitude with thermal energy. The determination of magnetic moment or magnetic susceptibility in these three situations is discussed below.

Magnitude of L-S Coupling in Ground State is Much Greater Than Thermal Energy

If the J states after spin-orbital interaction are very far to each other energetically, the thermal energy (kT) would not be adequate to populate all J-levels of \( ^{2S+1}L \) state. This in turn would result in a Boltzmann distribution in which almost all of the population density is lying in the ground state \( ^{2S+1}L_0 \). Consequently, the effective magnetic moment will be given by the equation (43) as:

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

(43)

Where \( g \) is the Lande splitting factor or gyromagnetic ratio whose value can be found as follows:

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

(44)

In case the resultant orbital angular momentum quantum number is zero i.e. \( L = 0 \), The value of \( J = S \) and equation (43) will become:

\[
\mu_{\text{eff}} = g \sqrt{S(S+1)} \text{ B. M.}
\]  

(45)

Now because the value of gyromagnetic ratio or Lande splitting factor for free electron is 2, equation (45) takes the following form.

\[
\mu_{\text{eff}} = 2 \sqrt{S(S+1)} \text{ B. M.}
\]  

(46)

Owing to the relationship between resultant spin quantum number and number of unpaired electrons \( S = n/2 \), equation (46) can also be written the form given below.

\[
\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B. M.}
\]  

(47)

Where \( S \) is the resultant spin quantum number and \( n \) is the number of unpaired electrons. The equation (45 – 47) are also called as spin only formula as they do not include any contribution from the orbital motion.

This type of magnetic behaviour is generally shown by lanthanide ions. A comparison of theoretically calculated magnetic moments of various lanthanide ions with their experimental observed values is presented in the following table.
Table 3. The comparison of theoretically calculated and experimental magnetic moments (B.M.) of trivalent lanthanide ions.

<table>
<thead>
<tr>
<th>metal ion</th>
<th>electronic configuration</th>
<th>ground state term symbol</th>
<th>gyromagnetic ratio</th>
<th>$\mu_{\text{eff}} = g[J(J+1)]^{1/2}$</th>
<th>$\mu_{\text{eff}}$ (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$</td>
<td>$f^0$</td>
<td>$^1S_0$</td>
<td>–</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>$f^1$</td>
<td>$^2F_{5/2}$</td>
<td>6/7</td>
<td>2.54</td>
<td>2.3 – 2.5</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>$f^2$</td>
<td>$^3H_4$</td>
<td>4/5</td>
<td>3.58</td>
<td>3.4 – 3.6</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>$f^3$</td>
<td>$^4I_{9/2}$</td>
<td>8/11</td>
<td>3.62</td>
<td>3.5 – 3.6</td>
</tr>
<tr>
<td>Pm$^{3+}$</td>
<td>$f^4$</td>
<td>$^5I_4$</td>
<td>3/5</td>
<td>2.68</td>
<td>2.7 – 2.8</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>$f^5$</td>
<td>$^6H_{5/2}$</td>
<td>2/7</td>
<td>0.84</td>
<td>1.5 – 1.6</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>$f^6$</td>
<td>$^7F_0$</td>
<td>–</td>
<td>0</td>
<td>3.4 – 3.6</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>$f^7$</td>
<td>$^8S_{7/2}$</td>
<td>2</td>
<td>7.94</td>
<td>7.8 – 8.0</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>$f^8$</td>
<td>$^7F_6$</td>
<td>3/2</td>
<td>9.72</td>
<td>9.4 – 9.6</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>$f^9$</td>
<td>$^6H_{15/2}$</td>
<td>4/3</td>
<td>10.63</td>
<td>10.4 – 10.5</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>$f^{10}$</td>
<td>$^5I_8$</td>
<td>5/4</td>
<td>10.60</td>
<td>10.3 – 10.5</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>$f^{11}$</td>
<td>$^4I_{15/2}$</td>
<td>6/5</td>
<td>9.57</td>
<td>9.4 – 9.6</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>$f^{12}$</td>
<td>$^3H_6$</td>
<td>7/6</td>
<td>7.63</td>
<td>7.1 – 7.4</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>$f^{13}$</td>
<td>$^2F_{7/2}$</td>
<td>8/7</td>
<td>4.50</td>
<td>4.4 – 4.9</td>
</tr>
<tr>
<td>Lu$^{3+}$</td>
<td>$f^{14}$</td>
<td>$^1S_0$</td>
<td>–</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The results clearly indicate that the experimental values of $\mu_{\text{eff}}$ for most of the lanthanide ions are pretty much comparable to their experimental counterparts. However, the magnetic moment for Eu$^{3+}$ and Sm$^{3+}$ calculated using equation (43) are zero, suggesting them as diamagnetic which is quite strange as they are actually having considerable amount of paramagnetism. This is obviously due to the fact that the energy difference between their ground state term and first excited state is comparable to thermal energy i.e. $\Delta E = kT$. Therefore, even at the room temperature, a part of total population of Sm$^{3+}$ and Eu$^{3+}$ ions would be present in their excited states, which in turn are obviously having a different value of total angular momentum quantum number (J-value) and gyromagnetic ratio (g-value).
CHAPTER 9 Magnetic Properties of Transition Metal Complexes:

- **Magnitude of L-S Coupling Ground State is Comparable to Thermal Energy**

  If the separation between $J$ states after spin-orbital interaction is comparable to the thermal energy ($kT$) available, the resultant value of magnetic moment is governed by a complex function of temperature. In this scenario, the total magnetic susceptibility will be having contributions from first order Zeeman effects of involved states according to their Boltzmann weights, as well as from second order Zeeman effects from neighbouring levels. Mathematically, the magnetic susceptibility will be given as follows:

  $$\chi_M = \frac{N}{3kT} \sum g^2 \beta^2 j(j+1)(2j+1)e^{-\Delta E/kT} \sum (2j+1)e^{-\Delta E/kT}$$  \hspace{1cm} (48)

  It can clearly be seen from equation (48) that the magnitude of magnetic susceptibility does not depend directly on the reciprocal of temperature, and thus does not follow Curie-Wei ss law. The theoretically calculation for Sm$^{3+}$ ion, according to equation (48), yielded a magnetic moment of 1.38 B.M.; which pretty much comparable to the experimental one. Similarly, satisfactory results are also obtained for trivalent europium ions.

- **Magnitude of L-S Coupling Ground State is Much Less Than Thermal Energy**

  If the energy separation between $J$ states (generated after L-S coupling) is much less than the thermal energy ($kT$) available, all of the $J$-levels of $2S+1L$ ground state. This situation is pretty much analogous to the case when spin and orbital motion are completely decoupled from each other. In other words, L-S interaction would not be effective in distinguishing different metal ions on the basis of total motion. Therefore, the effective magnetic moment will be given by the following relation:

  $$\mu_{\text{eff}} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.}$$  \hspace{1cm} (49)

  Hence, the relationship shown in the equation (49) does not consider the any quenching of orbital magnetic moment at all. In this case the resultant orbital angular momentum quantum number is zero i.e. $L = 0$, the L will be completely eliminated from equation (49) and we will get:

  $$\mu_{\text{eff}} = \sqrt{4S(S+1)} \text{ B.M.}$$  \hspace{1cm} (50)

  Owing to the relationship between spin multiplicity and number of unpaired electrons ($S = n/2$), equation (50) can also be written the form given below.

  $$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B.M.}$$  \hspace{1cm} (51)

  Where $S$ is the spin multiplicity and $n$ is the number of unpaired electrons. The equation (50, 51) are also called as spin only formula as they do not include any contribution from orbital motion. Now it is worthy to note that no free transition metal exists with very small $J$-separation relative to thermal energy; however, had they shown such behaviour, we would have used the equation (49) to calculate their magnetic moment. In that case, a comparative analysis of the results from equation (49) and equation (51) could be used to estimate the contribution exclusively from the orbital motion.
• Orbitual Contribution: Effect of Ligand-Field

In the prewave-mechanical model of 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 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 $45^\circ$ about $z$-axis will transform $d_{xy}$ into $d_{xy}$ orbital, and rotation through $90^\circ$ would give two equivalent states; resulting a 2 units of angular momentum (unit = $h/2\pi$) about $z$-axis. The same can be said about $d_{yz}$, which is also having an angular momentum of 2 units about $z$-axis. Moreover, a rotation of $90^\circ$ about $z$-axis will transform $d_{xz}$ into $d_{xz}$ 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 a zero-unit angular momentum about $z$-axis.

![Figure 9](image)

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 orbital magnetic moment was analogous 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 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 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 orbital magnetic moment would be quenched incompletely or partially. However, as in addition to the orbital degeneracy, 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 orbital magnetic contribution to the total magnetic moment, there should be an unsymmetrically occupied degenerate set of orbitals which can be interconverted or transformed into each other through a rotational motion.

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

The octahedral coordination of a transition metal centre removes the degeneracy of d-subshell into two main orbital-sets. The first degenerate set of \( d_{xy}, d_{yz}, d_{xz} \) is of \( t_{2g} \) symmetry; while 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 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 any orbital magnetism due to lack of their interconversion.

![Image](image.png)

Figure 10. The octahedral coordinative environment of transition metal centre 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 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.

<table>
<thead>
<tr>
<th>Electronic configuration / Ground state</th>
<th>Weak-field</th>
<th>Strong-field</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^1 (t_{2g}^{-1})$</td>
<td>$^{2}T_{2g}$</td>
<td>$d^1 (t_{2g}^{-1})$</td>
</tr>
<tr>
<td>$d^2 (t_{2g}^{-2})$</td>
<td>$^{3}T_{1g}$</td>
<td>$d^2 (t_{2g}^{-2})$</td>
</tr>
<tr>
<td>$d^5 (t_{2g}^{-4} e_g)$</td>
<td>$^{5}T_{2g}$</td>
<td>$d^4 (t_{2g}^{-4})$</td>
</tr>
<tr>
<td>$d^7 (t_{2g}^{-5} e_g)$</td>
<td>$^{4}T_{1g}$</td>
<td>$d^6 (t_{2g}^{-5})$</td>
</tr>
</tbody>
</table>

It is worthy to note that all ground Mulliken states which show 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.

<table>
<thead>
<tr>
<th>Electronic configuration / Ground state</th>
<th>Weak-field</th>
<th>Strong-field</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^3 (t_{2g}^{-3})$</td>
<td>$^{4}A_{2g}$</td>
<td>$d^3 (t_{2g}^{-3})$</td>
</tr>
<tr>
<td>$d^6 (t_{2g}^{-3} e_g^{-1})$</td>
<td>$^{5}E_g$</td>
<td>$d^6 (t_{2g}^{-3} e_g^{-1})$</td>
</tr>
<tr>
<td>$d^9 (t_{2g}^{-3} e_g^{-2})$</td>
<td>$^{6}A_{1g}$</td>
<td>$d^7 (t_{2g}^{-3} e_g^{-2})$</td>
</tr>
<tr>
<td>$d^9 (t_{2g}^{-6} e_g^{-2})$</td>
<td>$^{3}A_{2g}$</td>
<td>$d^8 (t_{2g}^{-6} e_g^{-2})$</td>
</tr>
<tr>
<td>$d^{10} (t_{2g}^{-6} e_g^{-3})$</td>
<td>$^{2}E_g$</td>
<td>$d^{10} (t_{2g}^{-6} e_g^{-3})$</td>
</tr>
<tr>
<td>$d^{10} (t_{2g}^{-6} e_g^{-4})$</td>
<td>$^{1}A_{1g}$</td>
<td>$d^{10} (t_{2g}^{-6} e_g^{-4})$</td>
</tr>
</tbody>
</table>

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 centre removes the degeneracy of $d$-subshell into two main orbital-sets. The first degenerate set of $d_{xy}, d_{xz}, d_{yz}$ is of $t_2$ symmetry; while 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 $45^\circ$ 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 $d_{x^2}$ into $d_{yz}$ orbital through a rotation of $90^\circ$ 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 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 any orbital magnetism due to lack of their interconversion.

![Figure 11. The tetrahedral coordinative environment of transition metal centre and corresponding crystal field splitting pattern of $d$-subshell.](image)

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 $t_{2g}^7, t_{2g}^1, e_g^1$. However, weaker inter-electronic repulsion is considered as the perturbation over stronger $V_o$. Similarly, the splitting pattern of $d^0$ tetrahedral is just opposite of what is for $d^6$ octahedral. However, no $g$ or $u$ are used in the tetrahedral case because there is no centre of symmetry in a tetrahedral geometry. Hence, we can conclude that the hole-formalism and octahedral-tetrahedral inverse relationship is all term symbols including ground state. Now, we can find out which electronic configurations in high-spin (spin free) tetrahedral complexes of transition metals will show 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 avoid 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.

<table>
<thead>
<tr>
<th>Electronic configuration</th>
<th>Ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^3 (e^2 t_z^1)$</td>
<td>$^4T_1$</td>
</tr>
<tr>
<td>$d^4 (e^2 t_z^2)$</td>
<td>$^5T_2$</td>
</tr>
<tr>
<td>$d^5 (e^4 t_z^3)$</td>
<td>$^3T_1$</td>
</tr>
<tr>
<td>$d^6 (e^4 t_z^5)$</td>
<td>$^2T_2$</td>
</tr>
</tbody>
</table>

It can be clearly seen that all ground Mulliken states which show 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.

<table>
<thead>
<tr>
<th>Electronic configuration</th>
<th>Ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^1 (e^2)$</td>
<td>$^2E$</td>
</tr>
<tr>
<td>$d^2 (e^2)$</td>
<td>$^3A_2$</td>
</tr>
<tr>
<td>$d^6 (e^6 t_z^3)$</td>
<td>$^6A_1$</td>
</tr>
<tr>
<td>$d^8 (e^8 t_z^5)$</td>
<td>$^5E$</td>
</tr>
<tr>
<td>$d^7 (e^8 t_z^3)$</td>
<td>$^4A_2$</td>
</tr>
<tr>
<td>$d^{10} (e^4 t_z^6)$</td>
<td>$^1A_1$</td>
</tr>
</tbody>
</table>

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 orbital contribution to the total magnetic moment.
CHAPTER 9 Magnetic Properties of Transition Metal Complexes:

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 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 same multiplicity lies above the “A” or “E” state, the spin-orbital coupling may mix the excited state into ground one such that 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 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 spin-orbital coupling parameter ($\lambda$) and is inversely proportional to the energy difference of the states to be mixed ($\Delta$). Mathematically, the relationship between spin-orbital interaction and total effective magnetic moment can be stated as:

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

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

1. Calculation of $\mu_{\text{eff}}$ 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 ($2g^{3}e_g^{2}$): Keeping in mind that there are no high energy terms of same multiplicity in $d^5$ high-spin complexes; and putting value of $\Delta = 10Dq$ and $\alpha$ as zero in equation (52), we get

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

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

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 \(d^5\) low-spin complexes; and putting \(\mu_{s.o.} = 0\), value of \(\Delta = 10Dq\) and \(\alpha\) as zero in equation (52), we get

\[
\mu_{\text{eff}} = 0 \left( 1 - 0 \times \frac{\lambda}{\Delta} \right)
\]  

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

2. Calculation of \(\mu_{\text{eff}}\) for E terms: The ground Mulliken state of E symmetry exists for the weak field octahedral complex with \(d^4\) and \(d^8\) configurations; and strong field octahedral complexes with \(d^6\).

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

\[
\mu_{\text{eff}} = \mu_{\text{s.o.}} \left( 1 - 2 \times \frac{\lambda}{10Dq} \right)
\]

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.

\[
\mu_{\text{eff}} = \mu_{\text{s.o.}} \left( 1 - 2 \times \frac{|\lambda|}{10Dq} \right)
\]

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) \(d^6\) strong-field weak-field (\(t_{2g}^5\) \(e_g^1\)): Putting value of \(\Delta = 10Dq\) (the energy gap between ground \(^2E_g\) and \(^2T_{2g}\)) and \(\alpha\) as 2 in equation (52), we get

\[
\mu_{\text{eff}} = \mu_{\text{s.o.}} \left( 1 - 2 \times \frac{\lambda}{10Dq} \right)
\]

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.

\[
\mu_{\text{eff}} = \mu_{\text{s.o.}} \left( 1 + 2 \times \frac{|\lambda|}{10Dq} \right)
\]

Hence, for \(d^6\) 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 \(\mu_{\text{eff}}\) for \(A_2\) terms: The ground Mulliken state of \(A_2\) symmetry exists for the weak field as well as octahedral complex with \(d^3\) and \(d^8\) configurations.

i) \(d^3\) weak-field strong-field (\(t_{2g}^3\) \(e_g^1\)): Putting value of \(\Delta = 10Dq\) (the energy gap between ground \(^4A_{2g}\) and \(^4T_{2g}\)) and \(\alpha\) as 4 in equation (52), we get:
\( \mu_{\text{eff}} = \mu_{\text{s.o.}} \left( 1 - 4 \times \frac{\lambda}{10Dq} \right) \)  

(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.

\( \mu_{\text{eff}} = \mu_{\text{s.o.}} \left( 1 - 4 \times \frac{|\lambda|}{10Dq} \right) \)  

(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 value of \( \Delta = 10Dq \) (the energy gap between ground \( ^3E_g \) and \( ^3T_{2g} \)) and \( \alpha \) as 4 in equation (52), we get

\( \mu_{\text{eff}} = \mu_{\text{s.o.}} \left( 1 - 4 \times \frac{\lambda}{10Dq} \right) \)  

(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.

\( \mu_{\text{eff}} = \mu_{\text{s.o.}} \left( 1 + 4 \times \frac{|\lambda|}{10Dq} \right) \)  

(62)

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

\( \Rightarrow \) \textit{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 which have neither the spin nor the orbital degeneracy, yet show weak paramagnetism. Consider the case of \( \text{MnO}_4^- \) or \( [\text{Co(NH}_3)_6]^{3+} \), 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 behaviour 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 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.
Application of Magneto-Chemistry in Structure Determination

The paramagnetic susceptibility of transition metal complexes can be used to obtain the information about electronic structure, stereochemistry and the nature of metal–ligand bond. The primary applications of magneto-chemistry in the structure determination of coordination compounds are given below.

Determination of the Oxidation State of Transition Metal Centre

The most widely used application of paramagnetic susceptibility measurement is the determination formal oxidation number of the transition metal centre. The aforementioned use relies on the finding of number of unpaired electrons present on the central metal atom or ion. The diamagnetic allowance due to ligands attached is usually ignored; however, corrections must be made for the large orbital contribution to the magnetic moment. For instance, some of the low-spin Co\(^{2+}\) complexes have a \(\mu_{\text{eff}}\) around 2.9 B.M., though they have only one unpaired electron \(t_{2g}^5 e_g^1\). Likewise, some of the high-spin Co\(^{3+}\) complexes have a \(\mu_{\text{eff}}\) around 4.9 B.M.; suggesting four unpaired electrons, though they have only three unpaired electrons \(t_{2g}^5 e_g^2\). Therefore, in order find the spin only magnetic moment; and thus the correct number of unpaired electrons; the temperature dependent study of magnetic susceptibility is pretty much essential. Furthermore, the larger magnitude of spin-orbital interaction can also affect the spin-only magnetic moment to a significant extent in some cases like the low spin complexes of Os\(^{4+}\) ion. For example, the effective magnetic moments of low-spin complexes Fe\(^{3+}\) and Ru\(^{4+}\) complexes are about 2.83 B.M.; which is pretty much close to their spin-only value, suggesting two unpaired electrons, which is obviously correct. However, the \(\mu_{\text{eff}}\) for [OsCl\(_6\)]\(^{2-}\) complex is only 1.4 B.M.; suggesting only one unpaired electron, which is pretty far from reality. Therefore, spin-orbital coupling corrections are also necessary in some cases.

In addition to the orbital magnetism, or the spin-orbital coupling effect; there are two more difficulties in the precise measurement of formal oxidation state of the transition metal centres. The first one is the electron delocalization and use of non-innocent ligands; for instance, the neutral [Be(bipyridyl)\(_2\)] complex is expected to be diamagnetic with neutral Be as the central atom. However, the compound is actually paramagnetic due to the delocalization of two electrons from metal to two bipyridyl chelate ligands. Therefore, if the ligand attached can accommodate one or more unpaired electrons in appropriate molecular orbitals, then a paramagnetic complex with bivalent beryllium can also be obtained. In such cases, the assignment of formal oxidation state is carried out only after X-ray and EPR (electronic paramagnetic resonance) studies. The second anomaly can arise from metal-metal interactions leading to unexpected electron pairing that depends upon the nature of the ligand used. For example, vanadium hexa-carbonyl, [V(CO)\(_6\)], is paramagnetic with one unpaired electron. However, one of the neutral dinuclear cluster of vanadium, [(Diarsine)(CO)\(_4\)V–V(CO)\(_4\)(Diarsine)], is diamagnetic in nature; even though the oxidation number of the vanadium is same in both. Therefore, a correct molecular weight measurement is pretty much necessary in such cases for fruitful interpretation of experimental results. Moreover, in magnetically concentrated materials, the ferromagnetic or antiferromagnetic interaction must be resolved by magnetic susceptibility measurements as a function of temperature or the field-strength.
Determination of the Electronic Configuration of Transition Metal Centre

The energy difference between high-spin and low-spin configurations of a transition metal centre in most of the complexes is pretty larger than the available thermal energy. Therefore, most of the complexes are either high-spin like [FeF₆]³⁻, or low-spin like [Fe(CN)₆]³⁻, over a wide range temperature; which makes it quite easy to distinguish and designate their electronic configurations. Nevertheless, there are complexes in which energy gap between high-spin and low-spin configurations is quite comparable to thermal energy, leading to a rearrangement of electron filling as function of temperature or slight variation of coordinative environment. The magnetic susceptibility measurements can be used to detect such phenomena as the number of unpaired electrons varies during the course of spin-equilibria under consideration. For instance, some square-planar complexes of Ni²⁺ (d⁸) are diamagnetic but can be converted into paramagnetic tetrahedral or octahedral complexes with two unpaired electrons. Similarly, penta-coordinated Schiff's-base complexes of bivalent cobalt (d⁷) also show high-low spin equilibria with three and one unpaired electrons, respectively.

Moreover, the magnetic susceptibility measurements can also be used to identify the exact orbital occupied by the unpaired electron, which depends upon the formal charge and the ligand field strength. For example, the orbital occupied by the unpaired electron in potassium (K) is 4s, while the isoelectronic Ti³⁺ ion bears the unpaired electron in its 3d orbital; which is obviously due to the difference in Zₚ arising from changes in formal charge. The surprisingly large magnetic moment of magnetically dilute [FeCl₄]²⁻ complex may also be explained in terms of mixing of 3d⁶ configuration (4 unpaired electrons) with 3d⁵ 4s¹ configuration due to change of Zₚ. The theoretical calculations suggest that the spin-orbital coupling can only increase the μₚ of [FeCl₄]²⁻ from 4.9 B.M. (μₚ₀) to 5.1 B.M. at maximum, which is not even close to the experimentally observed magnetic moment (5.5 B.M.). The only rational explanation for such an exceptionally high magnetic moment relies on the overlap covalency between Fe²⁺ and Cl⁻ ligand which decreases the charge on the metal centre to an extent where a considerable contribution from the 3d⁵ 4s¹ configuration (6.92 B.M.) to the 3d⁶ configuration is possible. Furthermore, spin pairing due to covalent bonding, [(Diarsine)(CO)₄ V−V(CO)₄ (Diarsine)], can also cause μₚ to deviate significantly. Finally, magnetic exchange coupling (ferromagnetism and antiferromagnetism) in magnetically concentrated systems have the capacity to make everything a mess in the analysis; and therefore requires special treatment in such cases.

Determination of the Stereochemistry of Various Transition Metal Complexes

One of the most valuable application of paramagnetic susceptibility measurements is to find the stereo-chemical arrangements of different ligands attached to the transition metal centre. The paramagnetic susceptibility measurements can be exploited in two ways to do so; the first one relies upon the determination of unpaired electrons, while the second one depends upon the determination of exact magnitude of orbital magnetism. Both of the approaches with suitable examples are given below.

1. Stereochemistry from unpaired electrons: The possibility of stereochemistry-prediction of transition metal complexes from unpaired electrons arises from the fact the ligand coordination prefers to adapt the most symmetrical geometry unless the metals d-electron cloud is not spherically symmetrical. For instance, d⁸ and d¹⁰ configurations are spherically symmetrical; and therefore, results in linear, triangular, perfect tetrahedral,
trigonal bipyramidal, octahedral and pentagonal bipyramidal geometries for 2, 3, 4, 5, 6 and 7 coordination number, respectively. Furthermore, if the cloud is not spherically symmetric, slightly distorted octahedral, tetragonal, or square-planar geometries can be obtained. The slightly distorted octahedron refers to an octahedron with two of the bond lengths differing by less than 0.05 Å from the other four. On the other hand, the tetragonal geometry here refers to an octahedral structure with two coaxial bonds considerably longer in comparison to other four.

Table 8. Expected stereochemistry of transition metal complexes using number of unpaired $d$-electrons from crystal field theory.

<table>
<thead>
<tr>
<th>Unpaired electrons / Stereochemistry</th>
<th>Weak-field</th>
<th>Strong-field</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ($d^0$)</td>
<td>Symmetrical</td>
<td>0 ($d^0$)</td>
</tr>
<tr>
<td>1 ($d^1$, $t_{2g}^1$)</td>
<td>Slightly distorted octahedron</td>
<td>1 ($d^1$, $t_{2g}^1$)</td>
</tr>
<tr>
<td>2 ($d^2$, $e^2$ or $t_{2g}^2$)</td>
<td>Tetrahedron or slightly distorted octahedron</td>
<td>2 ($d^2$, $e^2$ or $t_{2g}^2$)</td>
</tr>
<tr>
<td>3 ($d^3$, $t_{2g}^3$)</td>
<td>Perfect octahedron</td>
<td>3 ($d^3$, $t_{2g}^3$)</td>
</tr>
<tr>
<td>4 ($d^4$, $t_{2g}^3$ $e^1$)</td>
<td>Square-planar or tetragonal</td>
<td>2 or 0 ($d^4$, $t_{2g}^4$ or $e^4$)</td>
</tr>
<tr>
<td>5 ($d^5$, $e^2$ $t_{2g}^3$ or $t_{2g}^3$ $e^2$)</td>
<td>Tetrahedron or perfect octahedron</td>
<td>1 ($d^5$, $t_{2g}^5$)</td>
</tr>
<tr>
<td>4 ($d^6$, $t_{2g}^4$ $e^2$)</td>
<td>Slightly distorted octahedron</td>
<td>0 ($d^6$, $t_{2g}^6$)</td>
</tr>
<tr>
<td>3 ($d^7$, $e^4$ $t_{2g}^3$ or $t_{2g}^3$ $e^2$)</td>
<td>Tetrahedron or slightly distorted octahedron</td>
<td>1 ($d^7$, $t_{2g}^6$ $e^1$)</td>
</tr>
<tr>
<td>2 ($d^8$, $t_{2g}^6$ $e^2$)</td>
<td>Perfect octahedron</td>
<td>0 ($d^8$, $t_{2g}^6$ $e^2$)</td>
</tr>
<tr>
<td>1 ($d^9$, $t_{2g}^6$ $e^3$)</td>
<td>Square planar or tetragonal</td>
<td>1 ($d^9$, $t_{2g}^6$ $e^3$)</td>
</tr>
<tr>
<td>0 ($d^{10}$)</td>
<td>Symmetrical</td>
<td>0 ($d^{10}$)</td>
</tr>
</tbody>
</table>
Electronic configuration from $d^1$ to $d^9$ may or may not have spherically symmetrical cloud after complexation; therefore, a distortion is expected if any asymmetry is present. The distortion of an octahedron can occur in one of three ways; the first one involves an unsymmetrical filling of $t_{2g}$ level ($t_{2g}^1$, $t_{2g}^2$, $t_{2g}^4$ and $t_{2g}^5$) which will have little effect on the octahedron is because the indirect encounter metal between orbitals and the ligands, leading slightly distorted perfect octahedral geometry. On the other hand, if the asymmetry occurs in $e_g$ level, then a tetragonal or square planar geometry may be produced depending upon whether the two ligands are repelled or lost along the $z$-axis, respectively. However, it is also worthy to mention that the diamagnetism in $d^9$ complexes does not confirm a square-planar geometry as is also possible in compatible tetragonal geometry. Metal complexes with $d^9$ configuration can have zero, two, or four unpaired electrons yielding tetrahedral, tetragonal or square-planar geometries. Hence, we can say that the stereochemistry-chemistry prediction on the basis of number of unpaired electrons is not very much reliable. Furthermore, consider the example of $[\text{Co(NO}_2\text{)}_6]^{2-}$ complex in which cobalt is present in $+2$ oxidation state. The experimental magnetic moment for this complex is about 1.9 B.M., which unexpectedly low for an octahedral complex; because the octahedral geometries of Co(II) usually have three unpaired electrons ($\mu_{\text{eff}} = 4.85-5.2$ B.M.), while the presence of one unpaired electron in Co(II) is generally related to a square pyramidal or square planar structure ($\mu_{\text{eff}} = 2.2-2.9$ B.M.). The low magnetic moment and octahedral geometry in such cases are generally ascribed to the $\pi$-backbonding from the metal to the attached ligand.

2. Stereochemistry from orbital magnet: The unpaired electron approach is somewhat more or less capable of shortlisting a metal complex into one of four classes. classify not sufficient to predict the exact stereochemistry of transition metal complexes. for instance, Ni(II) complexes which contain two unpaired electrons may be perfect octahedron, square bipyramidal, or tetrahedral; while the diamagnetic ones may be square-planar, square pyramidal, trigonal bipyramidal, or six-coordinate tetragonal. Nevertheless, this information can be used in conjugation with orbital magnetism approach for more precise and accurate results. For instance, consider the spin-free complexes of Co(II), in which the magnitude of $\mu_{\text{s.o.}}$ is expected to be 3.88 B.M. Now because there is no orbital degeneracy present in Co(II) tetrahedral complexes; and of course ignoring any spin-orbital coupling; its $\mu_{\text{eff}}$ is expected to be comparable to $\mu_{\text{s.o.}}$ value. However, even after considering spin-orbital coupling, the effective magnetic moment would still be lower than 4.5 B.M. On the other hand, the presence of orbital degeneracy in spin-free octahedral complexes of Co$^{2+}$ ($t_{2g}^3$ (e$^2_g$) guarantees a huge orbital magnetic component, making $\mu_{\text{eff}}$ to touch a mark of 5.1 B.M. Therefore, the contribution of orbital magnetic moment can be used as a criterion for distinguishing between tetrahedral and octahedral complexes of bivalent cobalt. It should also be noted that other analytical methods must be used for final conclusion if magnetic moment is on the borderline (4.5–4.7 B.M.), or there is large distortion of the octahedron leading to splitting of the $t_{2g}$ orbital set, or the value of crystal field splitting in tetrahedral complex is very small as it would lead to a large orbital magnetism due to spin-orbit coupling.

It must be clear again that the structure prediction discussed in this section is totally based upon the simple ligand field theory, which only consider the metals $d$-electron cloud only and ignores the lattice effects or effect of ions surrounding the complex ion. The stereo-chemical arrangements in both spin-free and spin-paired complexes with various electron configurations are given below.
Table 9. The correlation between orbital magnetism and the stereochemistry of weak field transition metal complexes.

<table>
<thead>
<tr>
<th>Stereochemistry</th>
<th>Supporting configuration</th>
<th>Unpaired electron</th>
<th>Examples</th>
<th>Expected magnetic profile considering orbital magnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect octahedral</td>
<td>$t_{2g}^3$</td>
<td>3</td>
<td>[Cr(H$_2$O)$_6$]$^{3+}$</td>
<td>Spin only moment of 3.88 B.M due to absence of orbital magnet.</td>
</tr>
<tr>
<td></td>
<td>$t_{2g}^3 e_g^2$</td>
<td>5</td>
<td>[FeF$_6$]$^{3-}$</td>
<td>Spin only moment of 5.9 B.M due to absence of orbital magnet.</td>
</tr>
<tr>
<td></td>
<td>$t_{2g}^5 e_g^2$</td>
<td>2</td>
<td>[Ni(H$_2$O)$_6$]$^{2+}$</td>
<td>Spin only moment of 2.83 B.M is expected but the orbital contribution from $t_{2g}^5 e_g^3$ increases $\mu_{eff}$ due to spin-orbital coupling.</td>
</tr>
<tr>
<td>Slightly distorted octahedron</td>
<td>$t_{2g}^1$</td>
<td>1</td>
<td>[Ti(H$_2$O)$_6$]$^{3+}$</td>
<td>Orbital contribution is expected yielding an effective magnetic moment exceeding 1.73 B.M.</td>
</tr>
<tr>
<td></td>
<td>$t_{2g}^2$</td>
<td>2</td>
<td>[V(H$_2$O)$_6$]$^{3+}$</td>
<td>Orbital contribution is expected yielding an effective magnetic moment exceeding 2.83 B.M.</td>
</tr>
<tr>
<td></td>
<td>$t_{2g}^5 e_g^2$</td>
<td>3</td>
<td>[Co(H$_2$O)$_6$]$^{2+}$</td>
<td>The orbital contribution is expected yielding an effective magnetic moment exceeding 3.88 B.M.</td>
</tr>
<tr>
<td>Square-planar or tetragonal</td>
<td>$t_{2g}^3 e_g^1$</td>
<td>4</td>
<td>MnF$_3$</td>
<td>Spin only magnetic moment of 4.9 B.M., and significant orbital magnetism is expected from $t_{2g}^2 e_g^2$ states.</td>
</tr>
<tr>
<td></td>
<td>$t_{2g}^6 e_g^3$</td>
<td>1</td>
<td>[Cu(H$_2$O)$_6$]$^{2+}$</td>
<td>Spin only magnetic moment of 1.73 B.M., and significant orbital contribution expected from $t_{2g}^5 e_g^4$.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Cu(NH$_3$)$_6$]$^{2+}$</td>
<td>Spin only magnetic moment of 1.73 B.M., and less orbital contribution expected from $t_{2g}^5 e_g^4$ states.</td>
</tr>
</tbody>
</table>

Table 9. continued on next page...
Regular tetrahedral geometry

<table>
<thead>
<tr>
<th>$e^2$</th>
<th>2</th>
<th>$[\text{FeO}_4]^{2-}$</th>
<th>Spin only magnetic moment of 2.83 B.M. is expected with no orbital contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e^2 t_2^3$</td>
<td>5</td>
<td>$[\text{FeCl}_4]^-$</td>
<td>Spin only magnetic moment of 5.9 B.M. with no orbital magnet.</td>
</tr>
<tr>
<td>$e^4 t_2^3$</td>
<td>3</td>
<td>$[\text{CoCl}_4]^{2-}$</td>
<td>Spin only magnetic moment of 3.88 B.M. with considerable orbital magnetism possibility from $e^3 t_2^4$</td>
</tr>
</tbody>
</table>

Though the orbital magnetism profiling is pretty useful in the determination of stereochemistry of various transition metal complexes, the conclusive remarks with full confidence are put after using magnetic susceptibility measurement in conjunction with other physical data like electronic absorption spectra or X-ray diffraction profile.
Magnetic Exchange Coupling and Spin State Cross Over

There are two most remarkable phenomena in the magnetoc hemistry of transition metal complexes which are pretty much unusual too. The first one is the magnetic exchange interactions, responsible for ferromagnetism and antiferromagnetism; and the other one is the high-spin low-spin equilibria, responsible for the oxygen carrying capacity of blood. In this section, we will discuss the fundamental concepts and underlying mechanism of both the phenomenon.

Magnetic Exchange Coupling

The magnetic materials can be broadly classified into two categories; magnetically dilute and magnetically concentrated. Magnetically dilute substances simply refer to the magnetic materials in which individual paramagnetic centres cannot interact with each other due to large distance of separation. On the other hand, the total-electron-spin of paramagnetic centres do interact through direct-exchange or superexchange interactions in magnetically concentrated substances, which is obviously due to the small intermicromagnetic separation. In the direct-exchange, there is a coupling between nearest neighbouring cations without involving any intermediary anion; while the superexchange is generally a strong magnetic exchange interaction between two nearest neighbouring cations through a non-magnetic anion. Now although the orbital contribution to the magnetic moment can be of considerable magnitude, it can be neglected in magnetically concentrated materials for a simplified approach to the rationalization of overall magnetic profile. Therefore, we will consider the spin-only magnetic moment (µSO) as the effective magnetic moment (µeff) in these cases. The energy of total-spin interactions of paramagnetic centres (∆E) in magnetically concentrated material can be given by the following relation.
\[ \Delta E = 2J(S)_i(S)_k \]  

Where \( J \) is the exchange-coupling constant and is a measure of the magnitude of total electron spin interaction between various paramagnetic centres. The symbols \((S)_i\) and \((S)_k\) simply represent the total-electron-spin of \( i^{th} \) and \( k^{th} \) metal centres, respectively. For ferromagnetic substances, the value of \( J \) is positive which simply implies that the total electronic spins of all paramagnetic centres are aligned parallel to each other. For antiferromagnetic substances, the value of \( J \) is negative which simply indicates that the total electronic spins of all paramagnetic centres are aligned antiparallel to each other. The important features of both of the behaviours are discussed in detail.

1. **Ferromagnetic interactions:** The magnetic susceptibility in ferromagnetic materials increases very rapidly with the decrease of temperature if measurements are carried out below a certain value of temperature. Moreover, the magnetic susceptibility in ferromagnetic materials also depends upon the strength of the magnetic field applied. The comparison of variation of magnetic susceptibility with temperature for ferromagnetic and paramagnetic substances is given below.

![Graph showing the comparison of magnetic susceptibility with temperature](image)

**Figure 12.** Plots of \( \chi \) vs \( T \) for ferromagnetic and paramagnetic materials.

It can be clearly seen that the magnetic susceptibility of paramagnetic materials follows the Curie law over the complete range of temperature. On the other hand, the ferromagnetic materials obey the Curie law only up to the \( T_C \); but if the temperature is further lowered down, we see an abrupt gain in the magnetic susceptibility. Now although the ferromagnetism generally arises from direct-exchange but the superexchange can also results in the same if the paramagnetic centres connected to diamagnetic bridge are at \( 90^\circ \) to each other. Moreover, the ferromagnetism may also arise if the tow metal ions are not identical; one having electron in \( e_g \) and other one in \( t_{2g} \). The corresponding modes of orbital interactions are shown below.
Now it’s the time to discuss one of the most interesting property of ferromagnetic materials, “the hysteresis”; which is actually responsible for the making of permanent magnets. In ferromagnetic substances, total-electron-spins of paramagnetic centres tend to align themselves parallel to each other; however, if the temperature of the system is above the Curie temperature \((T_C)\), the thermal energy \((kT)\) is enough to randomize the individual micro-magnets, and thus forbid them to do so. Consequently, all ferromagnetic substances behave in a paramagnetic fashion above the Curie temperature. However, if the temperature is lowered than \(T_C\), the thermal energy would not be sufficient to decouple the individual total-electron-spins. This, in turn, would result in the creation of small magnetic domains, each of which will be having parallel alignment of individual paramagnetic centres. Now although the magnetic moments of individual paramagnetic centres in a single “magnetic domain” are parallel to each other, the resultant magnetic moments of these “magnetic domain” are still randomly oriented; which, therefore, would not give any net magnetic moment in the absence of external magnetic field. However, when the external magnetic field is applied, the resultant magnetic moments of all magnetic domains start aligning themselves along the direction of applied magnetic field.

Figure 14. The alignment of magnetic domains in ferromagnetic materials when the external magnetic field is applied.
The magnitude of this domain alignment rises with the increase in the strength of the applied magnetic field; and this will continuously happen till all magnetic domains are aligned. The further increase in the magnetic field strength will not be able to enhance the magnetic susceptibility. Now though the thermal energy is continuously trying to randomize this alignment of “magnetic domains”, it would not always be able to do so completely even if the external magnetic field is turned off.

![Diagram of magnetization process](image)

Figure 15. The magnetization of ferromagnetic material from zero field and the hysteresis loop responsible for the retention of magnetism.

The magnetization of ferromagnetic material is governed by a non-linear curve along OA, attaining a saturation state. However, when the applied field strength decreased back to zero, the demagnetization does not follow AO but the path AB, resulting in a non-zero magnetic moment even if the applied field strength is lowered down to zero. For a complete randomization of magnetic domains, the magnetic field should be applied and then increased in opposite direction; which, consequently, would result in a decrease of magnetization along path BC. The further increase in the magnetic field strength in opposite direction will actually induce the magnetization of the ferromagnetic material in reversed manner with again a saturation state, represented by the path CD. Now if the reversed magnetic field is lowered down to zero, material would again be left with non-zero magnetization (DE). For a complete randomization of “magnetic domains” along EF, an increasing applied field strength in forward direction is needed. Finally, the further increase in magnetic field will again magnetize the material along FA, completing the hysteresis loop. This retention of “magnetic domain” alignments imparts the permanent magnetism to the ferromagnetic material and called as hysteresis; and has applications in memory storage devices like computer hard disk drives.
2. Antiferromagnetic interactions: The magnetic susceptibility in antiferromagnetic materials decreases very rapidly with the decrease of temperature if measurements are carried below a certain value of temperature. Moreover, the magnetic susceptibility in antiferromagnetic materials also sometimes depends upon the strength of the magnetic field applied. The comparison of variation of magnetic susceptibility with temperature for antiferromagnetic and paramagnetic substances is given below.

![Graph showing the variation of magnetic susceptibility with temperature for antiferromagnetic and paramagnetic substances.](image)

Figure 16. Plots of $\chi$ vs $T$ for antiferromagnetic and paramagnetic materials.

It can be clearly seen that the magnetic susceptibility of paramagnetic materials follows the Curie law over the complete range of temperature. On the other hand, the antiferromagnetic materials obey the Curie law only up to the $T_N$; but if the temperature is further lowered down, we see an abrupt decline the magnetic susceptibility.

Now if the antiparallel alignment of total-electronic-spins of individual paramagnetic centres wants to occur without any interference of a diamagnetic centre, it would be possible only via the formation of normal covalent bond in which half-filled orbitals of the participating paramagnetic centres overlap with each other. Sometimes, the pairing of electrons occurs without the formation of any covalent bond. For instance, recent studies have shown that there is no direct metal–metal bond in Fe$_2$(CO)$_9$, and the individual iron centres have one unpaired electrons but the pairing results in a net zero total-electron-spin. However, in most of the cases, the pairing of total-electron spins of paramagnetic centres in antiferromagnetic materials occurs via a mediation of a diamagnetic atom or ion. The second mechanism is so profound that even if distance of separation between paramagnetic centres is very small, the pairing of total-electron-spin takes place via the diamagnetic bridge. The diamagnetic mediation is usually done by $O^{2-}$ or halide ions. The classic example of this kind of antiferromagnetism is MnO; in which oxide ions serve in bridging.
Therefore, the pairing of total-electron-spins in MnO can be understood in terms of the overlap of five half-filled $d$-orbitals of one Mn$^{2+}$ ion with five half-filled (opposite spin) $d$-orbitals from five neighbouring Mn$^{2+}$ ions via oxide ion bridging.

Now if we omit the oxide ion bridges for simplicity, each paramagnetic centre would be surrounded by the similar paramagnetic centres but with opposite total-electron-spin. This, in turn, will form an interpenetrating antiferromagnetic lattice.

![Diagram of interpenetrating antiferromagnetic lattice]
Hence, in antiferromagnetic substances, total-electron-spins of paramagnetic centres tend to align themselves antiparallel to each other; however, if the temperature of the system is above the Neel temperature ($T_N$), the thermal energy ($kT$) is enough to randomize the individual micro-magnets, and thus forbid them to do so. Consequently, all antiferromagnetic substances behave in a paramagnetic fashion above the Neel temperature. However, if the temperature is lowered than $T_N$, the thermal energy would not be sufficient to decouple the individual total-electron-spins. This, in turn, would result in the creation of antiferromagnetic lattice, in which total-electron-spins of individual paramagnetic centres are aligned antiparallel to each other. The antiferromagnetic coupling is temperature dependent and sometimes field-dependent too. Furthermore, the phenomena of antiferromagnetism can also occur within the same molecule, and that what we call intramolecular antiferromagnetism. This kind of antiferromagnetism is generally arise through a direct metal–metal bond like $[\text{Cu}_2(\text{OAc})_4](\text{H}_2\text{O})_2$ and $K_4[\text{Cl}_3\text{Ru}–\text{RuCl}_3]$; however, in some compounds like $K_4[\text{Cl}_3\text{Ru}–\text{O}–\text{RuCl}_3]$, the mediation via diamagnetic centre does exist.

The antiparallel alignment of total-electron-spins may also lead to a different type of material “ferrimagnetic”, which have the have the magnetic profile just like ferromagnets. The magnetic susceptibility in ferrimagnetic materials increases rapidly (but at slightly lower rate than ferromagnetic) with the decrease of temperature if measurements are carried below a certain value of temperature ($T_C$). Moreover, like ferromagnetic materials, the magnetic susceptibility in ferrimagnetic materials also depends upon the strength of the magnetic field applied. Now though the magnetic behaviour of ferrimagnetic material resemble ferromagnetic materials, the ferrimagnetic materials do have antiparallel alignment of total-electron-spins like in antiferromagnetic materials. However, these paramagnetic ions are present in two different sets of lattice sites. In other words, the ferrimagnetic materials also have antiparallel alignment of total-electronic-spins, but unlike antiferromagnetism, they do not cancel each other completely, resulting in a permanent magnetism.

![Figure 20. The ordering of total-electron-spins in Ferrimagnetic materials.](image)

Owing to the resemblance in overall magnetic profile ferromagnetism, the oldest known magnetic substance, “loadstone” was originally classified as a ferromagnetic in nature. However, only after the Neel’s discovery of ferrimagnetism and antiferromagnetism in 1948, we came to know that $\text{Fe}_3\text{O}_4$ is actually a ferrimagnet substance.
In transition metal chemistry, most of the compounds for a given stereochemistry are either high-spin or low-spin for a wide range of conditions like temperature, pressure, or the replacement of ligands etc. However, there are complexes which show a transformation from high-spin to low-spin state with keeping its stereochemistry somewhat more or less the same. Now it is quite well-known fact that metal complexes from $d^6$ to $d^7$ electronic configurations in octahedral crystal fields may result in high or low-spin system depending on the strength of the surrounding crystal field. Most of the complexes with aforementioned configurations are either high-spin or low-spin over a wide range of temperature, pressure or other conditions like slight variation in ligand field. However, in some of the complexes the strength of the ligand field is such that the separation of high-multiplicity term and low-multiplicity terms is very small and quite comparable to the thermal energy available. Now though the high-spin–low-spin crossover can occur, and does occur, in $d^6–d^7$ complexes, ninety percent of the reported cases belong to Fe$^{2+}$ ($d^6$) complexes. This can be better understood from the partial correlation diagram of $d^6$ octahedral complexes.

![Diagram of partial correlation diagram of $d^6$ octahedral complexes showing the transformation of ground state from $^5T_{2g}$ to $^1A_{1g}$ as the ligand-field increases.](image)

It can be clearly seen that the energy gap between high-spin and low-spin states near the crossover point is quite small and comparable to the thermal energy; therefore, the temperature does have a great effect on the position of the high-spin–low-spin equilibria.
The study of these spin crossover phenomena is pretty easy to do as the number of unpaired electron in the two states are different. For instance, the $d^6$ complexes of Fe$^{2+}$ are diamagnetic in low-spin state while have four unpaired electrons in the high-spin state. Thus, a variation in the magnitude of magnetic moment is expected as we after spin crossover. Consider the example of [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$]; in which the high-spin state transforms into to low-spin with decrease of temperature. Both of these complexes exist in the high-spin $^5T_{2g}$ ground state with effective magnetic moments slightly greater than the spin-only value for four unpaired electrons. However, the moment of [Fe(phen)$_2$(NCS)$_2$] at 174 K suddenly drops to below 1 B.M. Similarly, the same thing does happen in [Fe(phen)$_2$(NCSe)$_2$] but at 232 K. As the temperature is lowered than these specific temperatures, the complexes start to exist in the $^1A_{1g}$ ground state.

![Diagram of $d^6$ octahedral complexes](image)

Figure 21. The partial correlation diagram of $d^6$ octahedral complexes.

Other examples of this includes Fe$^{3+}$ surrounded by six sulphur ligands in [Fe(S$_2$CNR$_2$)$_3$] complex. The preference of low-spin state at lower temperature and higher pressure can be explained terms of the volume factor. High-spin octahedral complexes have larger volume due to the presence of electron in $e_g$ orbitals; while low-spin octahedral complexes have electron density concentrated in $t_{2g}$ orbitals. Now because the lowering of temperature and increment of pressure support the lower volume, low-spin state is also favoured at lower value of temperature. In haemoglobin, the replacement of water molecule by dioxygen also induces a spin-crossover, which in turn results in the phenomenon of cooperativity, which is essential for our life.
Problems

Q 1. Discuss the classical theory of magnetochemistry in detail.

Q 2. What is Curie-Weiss law? Does it fit the phenomenon of ferromagnetism and antiferromagnetism?

Q 3. What are the different classes of magnetic materials? Give a brief comparison of their magnetic susceptibility with special emphasis upon the field strength and temperature.

Q 4. Discuss the Guoy’s method for the determination of magnetic susceptibility in detail.

Q 5. How would you calculate the magnetic moment of transition metal complexes experimentally?

Q 6. Discuss the relationship between spin-orbital coupling and magnetic moment.

Q 7. The experimental magnetic moment of Sm$^{3+}$ and Eu$^{3+}$ are different from their spin only value as well as from calculated using total angular momentum quantum number, why?

Q 8. What are the prerequisites for the orbital contribution to the magnetic moment?

Q 9. Discuss the ligand field effect on the orbital contribution in octahedral complexes.

Q 10. What is temperature independent paramagnetism?

Q 11. Discuss the effect of spin-orbital coupling upon the orbital contribution to the total magnetic moment.

Q 12. What are the applications of magnetochemistry in the structure determination of inorganic compounds?

Q 13. Define Curie temperature ($T_C$) and Neel temperature ($T_N$).

Q 14. What is magnetic exchange coupling? Explain in detail with special emphasis on ferrimagnetism.

Q 15. Explain the phenomenon of spin-state cross-over using suitable examples.
Bibliography


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