

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 the mineral magnetite, also called “lodestone (Fe_3O_4)”, which is essentially a chemical compound of iron and oxygen with inverse spinel structure. In 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 of 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 the molecular scale, which is proportional to the magnetic average that aligns 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 the magnetic field generated by the motion of electrons and nuclei in different materials help us to rationalize various fundamental effects and phenomenon. For example, nuclear magnetic resonance is one of the most important tools 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 centers 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 the 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 (ϕ) 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 N/mA.

3. Magnetic permeability (μ): 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 ampere squared (NA⁻²).

4. Intensity of magnetization (I): The intensity of magnetization represents the extent up to which a material has been magnetized under the influence of the magnetizing field. The intensity of magnetization of a magnetic material is thus defined as the magnetic moment per unit volume of the material i.e. $I = M/V$, 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 , χ , χ_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 the 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 the density of the material is called as mass susceptibility (χ) which is measured in cm³ g⁻¹. The χ multiplied by molar mass is called as molar susceptibility (χ_M) which is measured in cm³ mol⁻¹.

➤ **The Classical Concept of Magnetism**

The classical theory of magnetism was developed long before 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:

$$B = H + 4\pi I \quad (1)$$

Dividing equation (1) throughout by H , we get

$$\frac{B}{H} = 1 + 4\pi \frac{I}{H} \quad (2)$$

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

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

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

$$\chi = \frac{K}{d} \quad (4)$$

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

$$\chi_M = \chi \times M \quad (5)$$

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 χ_M to get a corrected paramagnetic susceptibility i.e. measured susceptibility (χ_M) = paramagnetic susceptibility (χ_M^P) + diamagnetic susceptibility (χ_M^D).

$$\chi_M^P = \chi_M - \chi_M^D \quad (6)$$

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 the nineteenth century. He discovered that, for a large number of paramagnetic substances, molar magnetic susceptibility (χ_M) varies inversely with the temperature. This observation is called as Curie law, which states that:

$$\chi_M \propto \frac{1}{T}$$

$$\chi_M = \frac{C}{T} \quad (7)$$

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 behavior occurs. Later work by Onnes and Perrier showed that, for many paramagnetic substances, a more precise relationship is:

$$\chi_M = \frac{C}{T + \theta} \quad (8)$$

Where θ is the Weiss constant and the equation (8) is popularly known as the Curie-Weiss law. The symbol “ θ ” used in equation (8) is sometimes replaced by T_C because in the case of ferromagnetic materials, the value of θ 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.

$$\chi_M = \frac{C}{T - \theta} \quad (9)$$

The conventions shown in equation (8) are more widely accepted by the British and American academics, while the form with a negative sign is more popular in 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 behavior occurs.

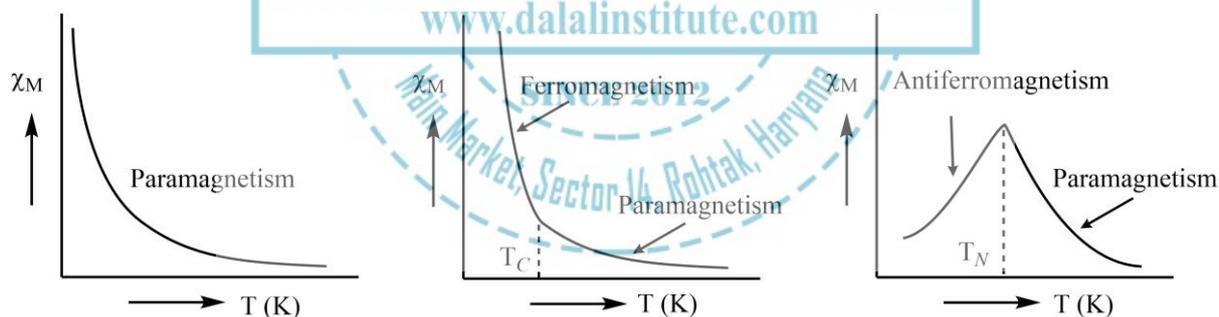


Figure 1. Plot of magnetic susceptibility vs temperature for normal paramagnetic, ferromagnetic and antiferromagnetic materials.

Normally, the reciprocal of magnetic susceptibility is plotted versus temperature ($1/\chi_M$ vs T follows a straight line equation); which makes the use of both forms of Curie-Weiss law. The symbol “ θ ” 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 “ θ ” 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 behavior of ferromagnetic or antiferromagnetic materials is observed only when $T > \theta$.

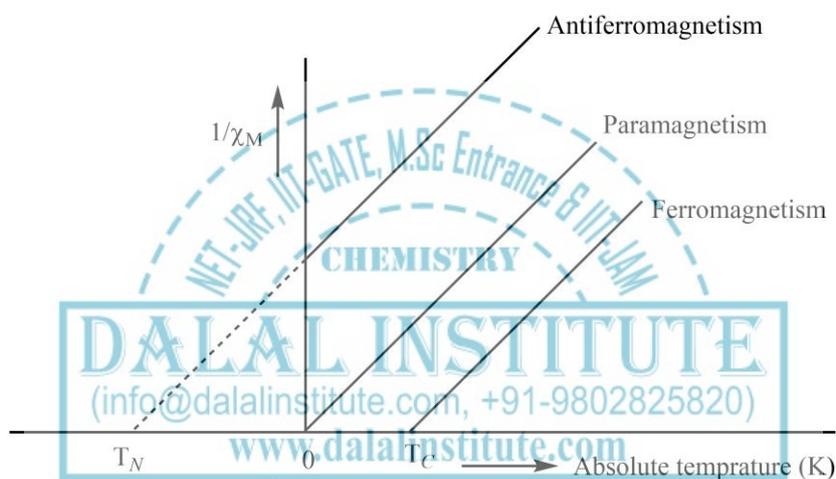


Figure 2. The plot of reciprocal of magnetic susceptibility vs temperature for normal paramagnetic, ferromagnetic and antiferromagnetic materials.

Thus, for ferromagnetic and antiferromagnetic materials, the value of θ is generally labeled 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 the electron gives rise to the orbital magnetic moment (μ_l), and the spin motion generates the spin magnetic moment (μ_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 the Bohr model, the electron is considered as a negatively charged hard-sphere that spins about its own axis as well as revolves around the positively charged heavy center of the atom. The pictorial representation of the rise of the magnetic moment by these two kinds of motion is shown below.

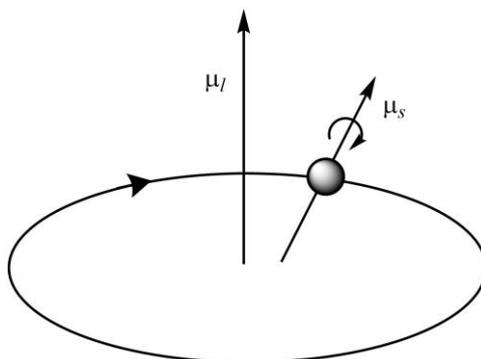


Figure 3. The generation of orbital magnetic moment (μ_l) and spin magnetic moment (μ_s) from prewave mechanical quantum theory.

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 (μ_l): 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 (μ_l) can be given as:

$$\mu_l = iA = \left(\frac{e\omega}{2\pi c}\right)\pi r^2 \quad (12)$$

Where e is the electronic charge, ω 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 the angular momenta of an orbiting electron is given by the following relation.

$$L_{\text{quantum mechanical}} = \sqrt{l(l+1)} \frac{h}{2\pi} \quad (13)$$

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 (ω) and moment of inertia (I).

$$L_{\text{classical}} = I\omega \quad (14)$$

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

$$L_{\text{classical}} = mr^2\omega \quad (15)$$

Now, it is a well-known fact that all values of the 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 analogs.

$$mr^2\omega = \sqrt{l(l+1)} \frac{h}{2\pi} \quad (16)$$

Or

$$\omega r^2 = \sqrt{l(l+1)} \frac{h}{2\pi m} \quad (17)$$

Putting the value of ωr^2 from equation (17) into equation (12), we get

$$\mu_l = \frac{e}{2e} \left(\sqrt{l(l+1)} \frac{h}{2\pi m} \right) \quad (18)$$

$$\mu_l = \sqrt{l(l+1)} \left(\frac{eh}{4\pi mc} \right) \quad (19)$$

$$\mu_l = \sqrt{l(l+1)} \text{ B.M.} \quad (20)$$

Comparing equation (20) and equation (13), we can conclude that the magnitude of magnetic moment (μ_l) 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 (μ_l and L) are collinear but oriented in the 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 (μ_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 (μ_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's splitting factor or the "g" value.

$$\frac{\mu_s}{S} = \frac{\mu_s}{\sqrt{s(s+1)}} = g \quad (21)$$

$$\mu_s = g\sqrt{s(s+1)} = 2\sqrt{s(s+1)} \text{ B.M.} \quad (22)$$

Where s is the quantum number defining the 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 moments 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 the resultant spin and resultant orbital motions do couple, and the overall magnetic moment will be obtained from “ J ” i.e. total angular momentum quantum number. The phenomena like diamagnetism, paramagnetism, or ferromagnetism arise as a result of alignments and interactions of these 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 the externally applied magnetic field. Thereafter, we can discuss the cause or interaction responsible for such behavior. In some material, the atomic-scale magnetic moments do not interact with each other; while in some cases the strong interaction may lead to a 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 an external magnetic field, the number of magnetic lines of force passing through the substance is less than the number of 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 substances and are repelled by the external magnetic field.

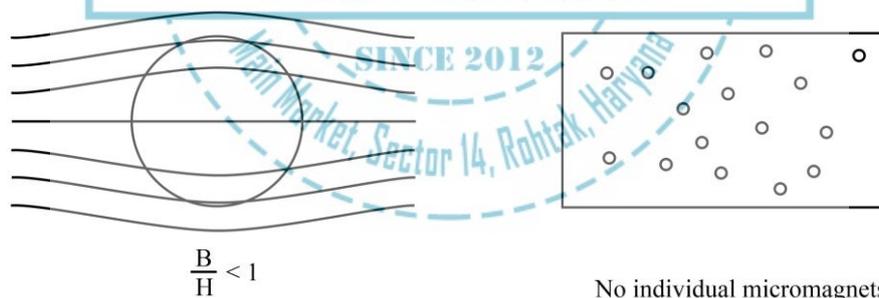


Figure 4. The behavior of a diamagnetic body in the externally applied magnetic field and corresponding magnetic domain.

Diamagnetic substances do not have unpaired electrons, and therefore the magnetic moment produced by one electron is canceled 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 an external magnetic field, the number of magnetic lines of force passing through the substance is more than the number of 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 substances and are attracted by the external magnetic field.

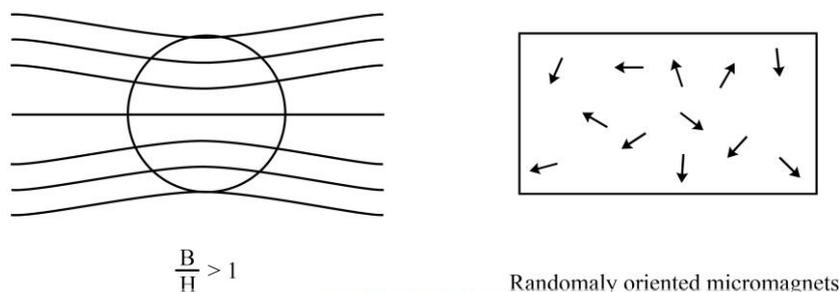


Figure 5. The behavior of a paramagnetic body in the externally applied magnetic field and corresponding magnetic domain.

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 the temperature of the system.

3. Ferromagnetic materials: When some substances are placed in the external magnetic field, the number of magnetic lines of force 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 substances and are strongly attracted by the external magnetic field.

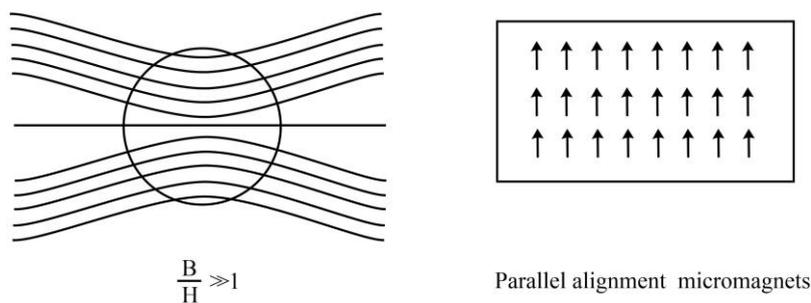


Figure 6. The behavior of a ferromagnetic body in an externally applied magnetic field and corresponding magnetic domain.

Ferromagnetic substances do have unpaired electrons, and therefore there is a net magnetic moment possessed by individual constituents. However, a 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 an external magnetic field, the number of magnetic lines of force 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.

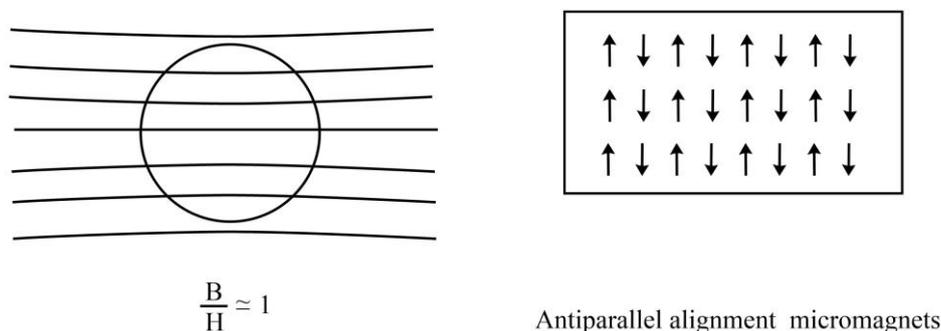


Figure 7. The behavior of an antiferromagnetic body in an externally applied magnetic field and corresponding magnetic domain.

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, a special interaction of these micro-magnets makes them orient antiparallel to each other yielding a very small value of positive magnetic susceptibility. The antiferromagnetic susceptibility usually depends on the temperature of the system only, though the dependence on field strength is also observed sometimes.

❖ Gouy'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.

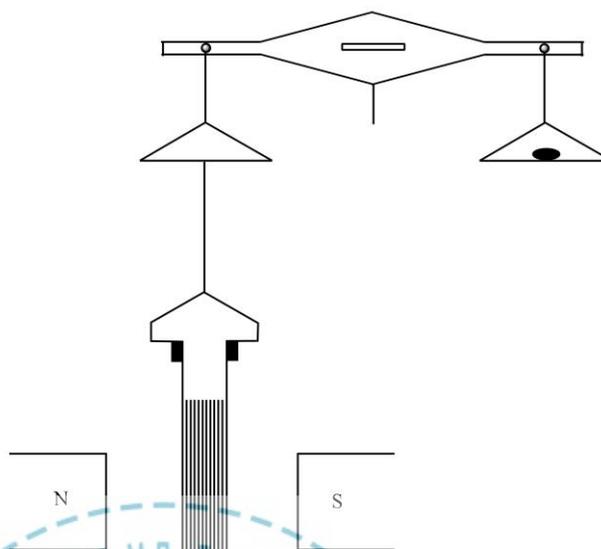


Figure 8. The schematics of Gouy balance.

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:

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

where B/H is called the magnetic permeability of the material and K is the magnetic susceptibility per unit volume (I/H). The Gouy's method includes the measurement of force on the sample by the 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:

$$dF = \mu^{\circ} H K dV \frac{dH}{dx} \quad (24)$$

Where μ° 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's 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 Gouy's 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 center 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).

$$F = \mu^{\circ} A K \left[\frac{H^2}{2} \right]_0^H \quad (25)$$

$$F = \frac{\mu^{\circ} A K H^2}{2} \quad (26)$$

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.

$$F = g \Delta w \quad (27)$$

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

$$g \Delta w = \frac{\mu^{\circ} A K H^2}{2} \quad (28)$$

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, equation (28) takes the form:

$$g \Delta w' = \frac{\mu^{\circ} A (K - K') H^2}{2} \quad (29)$$

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

$$K = \frac{2g \Delta w'}{\mu^{\circ} A H^2} + K' \quad (30)$$

Converting from volume susceptibility (K) to mass susceptibility (χ) leads to:

$$\chi = \frac{K}{\rho} = \frac{KV}{W} = \frac{2g \Delta w' V}{\mu^{\circ} A H^2 W} + \frac{K' V}{W} \quad (31)$$

$$\chi = \frac{\beta \Delta w'}{W} + \frac{K' V}{W} \quad (32)$$

$$\chi = \frac{(\alpha + \beta \Delta w')}{W} \quad (33)$$

Where $\alpha = K'V$ is a correction constant incorporated for the air replaced by the sample, $\beta = (2gV)/(\mu^{\circ} A H^2)$ 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 α , β and δ 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 emphasize 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 Gouy's balance, then suspend the empty tube from the balance and measure its weight (W_1). Now turn on the electromagnets to desired magnetic field strength and reweigh the tube (W_2). The force on the Gouy's tube, δ , is thus $\delta = W_2 - W_1$. The value will be negative because the tubes are generally diamagnetic and are pushed out of the magnetic field.

ii) Calculation of α : Fill the water in Gouy's tube to the required marking and weigh it, this will give the value of W_3 . 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, $V = (W_3 - W_1)/1.00$, where the changes in weight should be expressed in grams. Now, $\alpha = K'V$ or $\alpha = 0.029 \times (W_3 - W_1)$ 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. The most commonly used calibrants are $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$ and $\text{Hg}[\text{Co}(\text{SCN})_4]$. 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, T_1 , and then fill the tube to the required height with the calibrant and weigh it with the magnetic field off (W_4) and on (W_5). For $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$, use $\chi = 3172/T$ in 10^{-6} c.g.s units; while for $\text{HgCo}(\text{SCN})_4$ the $\chi = 4985/(T+10)$ in 10^{-6} in c.g.s unit can be used at temperature T . Using this χ then $\beta = (\chi W - \alpha)/\Delta w'$, where $\Delta w' = (W_5 - W_4) - \delta$ in mg and $W = (W_4 - W_1)$ 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 depend upon the precision of its theoretical results with the experimental one. The theoretical and experimental routes 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 the experiment directly. The experimental determination of magnetic moment (μ) requires the measurement of magnetic susceptibility (χ) first. This experimental value of paramagnetic susceptibility is then used to find the value of the magnetic moment by using a certain quantum mechanical correlation. Now as we know that the experimentally measured molar paramagnetic susceptibility (χ_M) is actually the sum of paramagnetic (χ_M^P) and

diamagnetic (χ_M^D) susceptibilities. Hence, the actual value of paramagnetic susceptibility is obtained by subtracting the diamagnetic susceptibility from the experimentally measured susceptibility.

$$\chi_M = \chi_M^P + \chi_M^D \quad (34)$$

$$\chi_M^P = \chi_M - \chi_M^D \quad (35)$$

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 these orbits 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 atoms ($\chi_M^{D-atomic}$) can be calculated using equation (36).

$$\chi_M^{D-atomic} = -\frac{N e^2}{6mc^2} \sum_{i=1}^{i=n} \langle r_i^2 \rangle \quad (36)$$

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 $\langle r_i^2 \rangle$ is the mean square radius of the i th electron. Therefore, the larger the number of the electrons in an atom, the 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 atoms ($\chi_M^{D-atomic}$) and diamagnetic susceptibility per mole of bonds (χ_M^{D-bond}). The $\chi_M^{D-atomic}$ and χ_M^{D-bond} are generally labeled as Pascal's constants.

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

	$\chi_M^{D-atomic}$ ($10^{-6} \text{ cm}^3 \text{ mol}^{-1}$)			χ_M^{D-bond} ($10^{-6} \text{ cm}^3 \text{ mol}^{-1}$)	
H	-2.9	Fe ²⁺	-12.8	C=C	+5.5
C	-6.0	Ni ²⁺	-12.8	C≡C	+0.8
C (aromatic)	-6.2	Co ²⁺	-12.8	C=N	+8.2
N	-5.6	Cu ²⁺	-12.8	C≡N	+0.8
N (aromatic)	-4.6	Mg ²⁺	-5.0	N=N	+1.8
O	-4.6	Zn ²⁺	-15.0	N=O	+1.7
Cl	-20.1	Ca ²⁺	-10.4	C=O	+6.3

The calculation of χ_M^D using Pascal's constants can be exemplified by taking the case of pyridine and acetone.

i) Molar diamagnetic susceptibility (χ_M^D) for pyridine: The contributions from diamagnetic susceptibility per mole of atoms ($\chi_M^{D-atomic}$) and diamagnetic susceptibility per mole of bonds (χ_M^{D-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.

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

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

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

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

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

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

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

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

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

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

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 (χ_M^P) can be obtained from equation (35). Nevertheless, χ_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 the ground state and excited state under the effect of an externally applied magnetic field. From the quantum mechanical description of magnetism, the magnitude of paramagnetic susceptibility can be given as follows:

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

Where μ_{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

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^P T} \text{ B.M.} \quad (37)$$

➤ **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 analogous 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:

$$\mu_{\text{eff}} = \sqrt{4S(S+1) + L(L+1)} \text{ B. M.} \quad (38)$$

Hence, the relationship shown in the equation (38) does not consider 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 $^{2S+1}L_J$ state. This situation is pretty much analogous 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:

$$\mu_{\text{eff}} = g\sqrt{J(J+1)} \text{ B. M.} \quad (39)$$

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

$$g = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)} \quad (40)$$

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) contributes but the resultant orbital motion is quenched: In this case, the orbital motion contribution to the effective magnetic moment is completely quenched and μ_{eff} is calculated using spin only formula. Therefore, the effective magnetic moment should be calculated as:

$$\mu_{\text{eff}} = \sqrt{4S(S+1)} \text{ B. M.} \quad (41)$$

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

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B. M.} \quad (42)$$

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.).

Metal centre	Ground state	$\mu_{\text{eff}} = [4S(S+1)+L(L+1)]^{1/2}$	$\mu_{\text{eff}} = g[J(J+1)]^{1/2}$	$\mu_{\text{eff}} = [4S(S+1)]^{1/2}$	μ_{eff} (experimental)
Ti ³⁺	² D _{3/2}	3.00	1.55	1.73	1.7 – 1.8
V ³⁺	³ F ₂	4.47	1.65	2.85	2.7 – 2.9
Cr ³⁺	⁴ F _{3/2}	5.20	0.70	3.87	3.7 – 3.9
Mn ³⁺	⁵ D ₀	5.48	0	4.90	4.8 – 4.9
Fe ³⁺	⁶ S _{5/2}	5.92	5.92	5.92	5.7 – 6.0
Fe ²⁺	⁵ D ₄	5.48	6.71	4.90	5.0 – 5.6
Co ²⁺	⁴ F _{9/2}	5.20	6.63	3.87	4.3 – 5.2
Ni ²⁺	³ F ₄	4.47	5.59	2.87	2.9 – 3.5
Cu ²⁺	² D _{5/2}	3.0	3.55	1.73	1.8 – 2.1

The results clearly indicate that the experimental value of μ_{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 behavior 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 the orbital magnetic moment. However, valence bond theory does not provide any sophisticated explanation for the qualitative and quantitative nature of the quenching of orbital magnetic moment. The orbital contribution to the magnetic moment and its behavior under different ligand fields will be rationalized on the basis of crystal field theory in the forthcoming sections of this chapter.

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

❖ Magnetic Properties of Free Ions

The resultant magnetic behavior 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 from 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 ($^{2S+1}L_J$). Consequently, the effective magnetic moment will be given by equation (43) as:

$$\mu_{\text{eff}} = g\sqrt{J(J+1)} \text{ B. M.} \quad (43)$$

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

$$g = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)} \quad (44)$$

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:

$$\mu_{\text{eff}} = g\sqrt{S(S+1)} \text{ B. M.} \quad (45)$$

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

$$\mu_{\text{eff}} = 2\sqrt{S(S+1)} \text{ B. M.} \quad (46)$$

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

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B. M.} \quad (47)$$

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

This type of magnetic behavior 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.

Metal ion	Electronic configuration	Ground state term symbol	Gyromagnetic ratio	$\mu_{\text{eff}} = g[J(J+1)]^{1/2}$	μ_{eff} (experimental)
La ³⁺	f^0	¹ S ₀	–	0	0
Ce ³⁺	f^1	² F _{5/2}	6/7	2.54	2.3 – 2.5
Pr ³⁺	f^2	³ H ₄	4/5	3.58	3.4 – 3.6
Nd ³⁺	f^3	⁴ I _{9/2}	8/11	3.62	3.5 – 3.6
Pm ³⁺	f^4	⁵ I ₄	3/5	2.68	2.7 – 2.8
Sm ³⁺	f^5	⁶ H _{5/2}	2/7	0.84	1.5 – 1.6
Eu ³⁺	f^6	⁷ F ₀	–	0	3.4 – 3.6
Gd ³⁺	f^7	⁸ S _{7/2}	–	7.94	7.8 – 8.0
Tb ³⁺	f^8	⁷ F ₆	3/2	9.72	9.4 – 9.6
Dy ³⁺	f^9	⁶ H _{15/2}	4/3	10.63	10.4 – 10.5
Ho ³⁺	f^{10}	⁵ I ₈	5/4	10.60	10.3 – 10.5
Er ³⁺	f^{11}	⁴ I _{15/2}	6/5	9.57	9.4 – 9.6
Tm ³⁺	f^{12}	³ H ₆	7/6	7.63	7.1 – 7.4
Yb ³⁺	f^{13}	² F _{7/2}	8/7	4.50	4.4 – 4.9
Lu ³⁺	f^{14}	¹ S ₀	–	0	0

The results clearly indicate that the experimental values of μ_{eff} for most of the lanthanide ions are pretty much comparable to their theoretical counterparts. However, the magnetic moment for Eu³⁺ and Sm³⁺ calculated using equation (43) are zero, suggesting them as diamagnetic which is quite strange as they are actually having a considerable amount of paramagnetism. This is obviously due to the fact that the energy difference between their ground state term and the first excited state is comparable to thermal energy i.e. $\Delta E \approx kT$. Therefore, even at room temperature, a part of the total population of Sm³⁺ and Eu³⁺ 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).

➤ **Magnitude of L-S Coupling in 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 the 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 neighboring levels. Mathematically, the magnetic susceptibility will be given as follows:

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

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-Weiss law. The theoretical 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 in 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+1}L 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:

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

Hence, the relationship shown in the equation (49) does not consider 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:

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

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

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

Where S is the spin multiplicity and n is the number of unpaired electrons. The equations (50, 51) are also called as spin only formulas 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 behavior, 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.

❖ Orbital Contribution: Effect of Ligand-Field

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

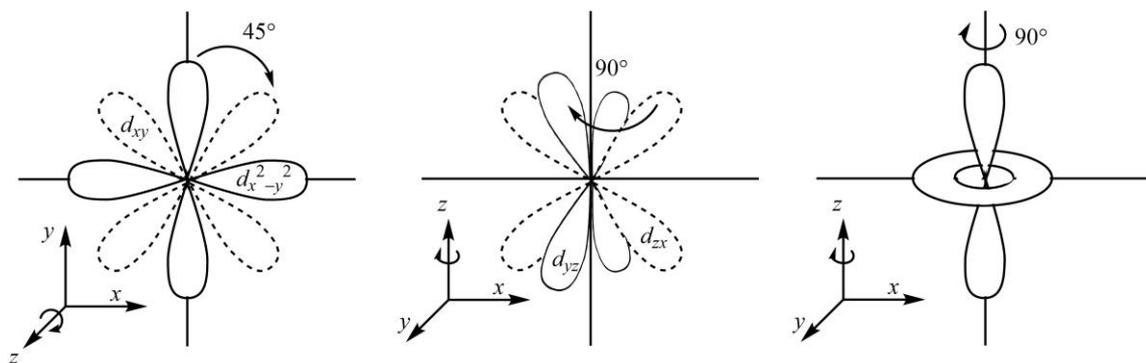


Figure 9. The circulation of electron density in a partially filled d -subshell about the z -axis.

It is also worthy to mention that the resultant orbital angular momentum would exist only if the degenerate set of interconvertible orbitals is unsymmetrically occupied. Though we already know that the generation of the orbital magnetic moment was 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 a ring, the ends of the wire coil would be in a different location after the rotation. The prerequisite for a non-zero orbital motion is exactly the same. Any spherically symmetric distribution of electron density would not result in an orbital angular momentum (like a single electron in s -orbital or multi-electron cloud with S state).

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

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

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

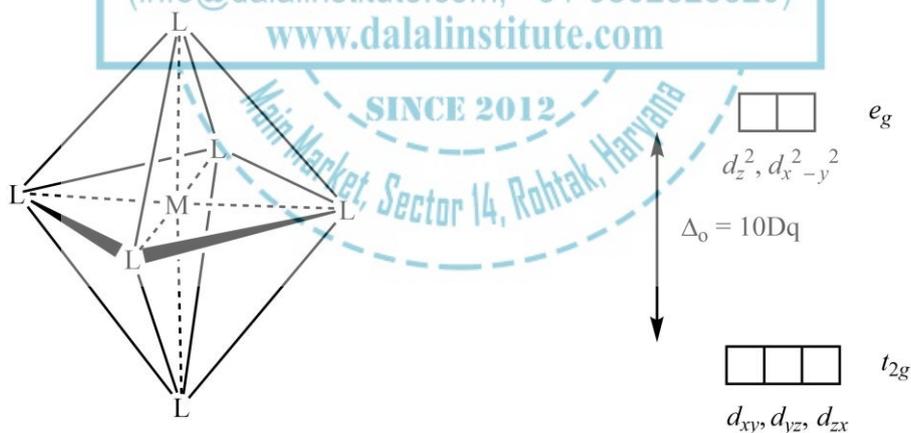


Figure 10. The octahedral coordinative environment of transition metal center and corresponding crystal field splitting pattern of d -subshell.

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

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

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

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

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

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

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

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

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

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

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\mu_{\text{eff}} = \mu_{\text{s.o.}} \left(1 - \alpha \frac{\lambda}{\Delta} \right) \quad (52)$$

Where $\mu_{\text{s.o.}}$ is the spin-only magnetic moment, λ is the spin-orbital coupling parameter, and Δ is the energy between ground (A or E) and the excited state (T). It is also worthy to remember that the sign of the spin-orbital coupling parameter is negative for more than half field configurations while positive for less than half-filled electronic configurations. The α is a constant whose value depends upon the spectroscopic ground state term; value is 0 for ${}^6\text{S}$ (${}^6\text{A}_1$), 2 for ${}^2\text{D}$ (${}^2\text{E}$) and ${}^5\text{D}$ (${}^5\text{E}$), and 4 for ${}^3\text{F}$ (${}^3\text{A}_2$) and ${}^4\text{F}$ (${}^4\text{A}_2$) ground state terms. The calculation of the effective magnetic moment for all these three cases is given below.

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

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

$$\mu_{\text{eff}} = \mu_{\text{s.o.}} \left(1 - 0 \times \frac{\lambda}{\Delta} \right) \quad (53)$$

$$\mu_{\text{eff}} = \mu_{\text{s.o.}}$$

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^6 low-spin complexes and putting $\mu_{s.o.} = 0$, value of $\Delta = 10Dq$ and α as zero in equation (52), we get

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

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

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

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

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

$$\mu_{\text{eff}} = \mu_{s.o.} \left(1 - 2 \times \frac{\lambda}{10Dq} \right) \quad (55)$$

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

$$\mu_{\text{eff}} = \mu_{s.o.} \left(1 - 2 \times \frac{|\lambda|}{10Dq} \right) \quad (56)$$

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

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

$$\mu_{\text{eff}} = \mu_{s.o.} \left(1 - 2 \times \frac{\lambda}{10Dq} \right) \quad (57)$$

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

$$\mu_{\text{eff}} = \mu_{s.o.} \left(1 + 2 \times \frac{|\lambda|}{10Dq} \right) \quad (58)$$

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

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

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

$$\mu_{\text{eff}} = \mu_{\text{s.o.}} \left(1 - 4 \times \frac{\lambda}{10Dq} \right) \quad (59)$$

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.

$$\mu_{\text{eff}} = \mu_{\text{s.o.}} \left(1 - 4 \times \frac{|\lambda|}{10Dq} \right) \quad (60)$$

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

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

$$\mu_{\text{eff}} = \mu_{\text{s.o.}} \left(1 - 4 \times \frac{\lambda}{10Dq} \right) \quad (61)$$

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.

$$\mu_{\text{eff}} = \mu_{\text{s.o.}} \left(1 + 4 \times \frac{|\lambda|}{10Dq} \right) \quad (62)$$

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

➤ *Temperature Independent Paramagnetism (TIP)*

In the previous section, we concluded that owing to the A_1 symmetry of the ground state and zero unpaired electron, the strong field complexes of d^6 configuration should be diamagnetic in nature. In other words, there should be no spin-only or the orbital magnetism in spin paired complexes d^6 metal ions. However, that is not hundred-percent true because there are some complexes that have neither the spin nor the orbital degeneracy, yet show weak paramagnetism. Consider the case of MnO_4^- or $[\text{Co}(\text{NH}_3)_6]^{3+}$, which do not have unpaired electron (no spin degeneracy) and are lacking ground Mulliken state of T-symmetry (no orbital degeneracy); suggesting zero spin-only and zero orbital magnetism. Nevertheless, both of these compounds are weakly paramagnetic in nature. This exceptional behavior can be attributed to the existence of a low-lying excited state which does have the necessary orbital degeneracy and is still a singlet. When the external magnetic field is applied, some of the excited state mixes itself into the ground state resulting in a perturbed ground state that possesses some of the properties of the excited one. The experiments have shown that these complexes have small orbital paramagnetism, which at times, is enough to cancel out the inherent diamagnetism. This kind of paramagnetism is also called temperature-independent paramagnetism due to its non-reliance on the thermal population of Boltzmann levels.

❖ Application of Magneto-Chemistry in Structure Determination

The paramagnetic susceptibility of transition metal complexes can be used to obtain information about the 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 center. The aforementioned use relies on the finding of the 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 μ_{eff} around 2.9 B.M., though they have only one unpaired electron ($t_{2g}^6 e_g^1$). Likewise, some of the high-spin Co^{2+} complexes have a μ_{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 to 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^{4+} 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 μ_{eff} for $[\text{OsCl}_6]^{2-}$ 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 the formal oxidation state of the transition metal centers. The first one is the electron delocalization and use of non-innocent ligands; for instance, the neutral $[\text{Be}(\text{bipyridyl})_2]$ 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 the metal to two bipyridyl chelate ligands. Therefore, if the ligand attached can accommodate one or more unpaired electrons in the 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, $[\text{V}(\text{CO})_6]$, is paramagnetic with one unpaired electron. However, one of the neutral dinuclear clusters of vanadium, $[(\text{Diarsine})(\text{CO})_4\text{V}-\text{V}(\text{CO})_4(\text{Diarsine})]$, 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 center in most of the complexes is pretty larger than the available thermal energy. Therefore, most of the complexes are either high-spin like $[\text{FeF}_6]^{3-}$, or low-spin like $[\text{Fe}(\text{CN})_6]^{3-}$, over a wide range temperature; which makes it quite easy to distinguish and designate their electronic configurations. Nevertheless, there are complexes in which the energy gap between high-spin and low-spin configurations is quite comparable to thermal energy, leading to a rearrangement of electron filling as a function of temperature or a 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 Ni^{2+} (d^8) 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 (d^7) 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 Ti^{3+} ion bears the unpaired electron in its $3d$ orbital; which is obviously due to the difference in Z_{eff} arising from changes in the formal charge. The surprisingly large magnetic moment of magnetically dilute $[\text{FeCl}_4]^{2-}$ complex may also be explained in terms of mixing of $3d^6$ configuration (4 unpaired electrons) with $3d^5 4s^1$ configuration due to change of Z_{eff} . The theoretical calculations suggest that the spin-orbital coupling can only increase the μ_{eff} of $[\text{FeCl}_4]^{2-}$ from 4.9 B.M. ($\mu_{\text{S.O}}$) 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 σ -bond covalency between Fe^{2+} and Cl^- ligand which decreases the charge on the metal center to an extent where a considerable contribution from the $3d^5 4s^1$ configuration (6.92 B.M.) to the $3d^6$ configuration is possible. Furthermore, spin pairing due to covalent bonding, $[(\text{Diarsine})(\text{CO})_4\text{V}-\text{V}(\text{CO})_4(\text{Diarsine})]$, can also cause μ_{eff} 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 a special treatment in such cases.

➤ **Determination of the Stereochemistry of Various Transition Metal Complexes**

One of the most valuable applications of paramagnetic susceptibility measurements is to find the stereochemical arrangements of different ligands attached to the transition metal center. 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 the 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, d^0 and d^{10} 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 the other four.

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

Weak-field		Strong-field	
Unpaired electrons / Stereochemistry		Unpaired electrons / Stereochemistry	
0 (d^0)	Symmetrical	0 (d^0)	Symmetrical
1 (d^1, t_{2g}^1)	Slightly distorted octahedron	1 (d^1, t_{2g}^1)	Slightly distorted octahedron
2 (d^2, e^2 or t_{2g}^2)	Tetrahedron or slightly distorted octahedron	2 (d^2, e^2 or t_{2g}^2)	Tetrahedron or slightly distorted octahedron
3 (d^3, t_{2g}^3)	Perfect octahedron	3 (d^3, t_{2g}^3)	Perfect octahedron
4 ($d^4, t_{2g}^3 e_g^1$)	Square-planar or tetragonal	2 or 0 (d^4, t_{2g}^4 or e^4)	Slightly distorted octahedron or tetrahedral
5 ($d^5, e^2 t_{2g}^3$ or $t_{2g}^5 e_g^2$)	Tetrahedron or perfect octahedron	1 (d^5, t_{2g}^5)	Slightly distorted octahedron
4 ($d^6, t_{2g}^4 e_g^2$)	Slightly distorted octahedron	0 (d^6, t_{2g}^6)	Perfect octahedron
3 ($d^7, e^4 t_{2g}^3$ or $t_{2g}^5 e_g^2$)	Tetrahedron or slightly distorted octahedron	1 ($d^7, t_{2g}^6 e_g^1$)	Square planar or tetragonal
2 ($d^8, t_{2g}^6 e_g^2$)	Perfect octahedron	0 ($d^8, t_{2g}^6 e_g^2$)	Square planar or tetragonal
1 ($d^9, t_{2g}^6 e_g^3$)	Square planar or tetragonal	1 ($d^9, t_{2g}^6 e_g^3$)	Square planar or tetragonal
0 (d^{10})	Symmetrical	0 (d^{10})	Symmetrical

Electronic configuration from d^1 to d^9 may or may not have a 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 of 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^8 complexes does not confirm a square-planar geometry as is also possible in a compatible tetragonal geometry. Metal complexes with d^4 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 the number of unpaired electrons is not very much reliable. Furthermore, consider the example of $[\text{Co}(\text{NO}_2)_6]^{4-}$ 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 ($\mu_{\text{eff}} = 4.85\text{--}5.2$ B.M.), while the presence of one unpaired electron in Co(II) is generally related to a square pyramidal or square planar structure ($\mu_{\text{eff}} = 2.2\text{--}2.9$ B.M.). The low magnetic moment and octahedral geometry in such cases are generally ascribed to the π -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 μ_{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+} ($t_{2g}^5 e_g^2$) guarantees a huge orbital magnetic component, making μ_{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 considers the metals d -electron cloud-only and ignores the lattice effects or effect of ions surrounding the complex ion. The stereochemical 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.

Stereochemistry	Supporting configuration	Unpaired electron	Examples	Expected magnetic profile considering orbital magnetism
Perfect octahedral	t_{2g}^3	3	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	Spin only moment of 3.88 B.M due to absence of orbital magnet.
	$t_{2g}^3 e_g^2$	5	$[\text{FeF}_6]^{3-}$	Spin only moment of 5.9 B.M due to absence of orbital magnet.
	$t_{2g}^6 e_g^2$	2	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	Spin only moment of 2.83 B.M is expected but the orbital contribution from $t_{2g}^5 e_g^3$ increases μ_{eff} due to spin-orbital coupling.
Slightly distorted octahedron	t_{2g}^1	1	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	Orbital contribution is expected yielding an effective magnetic moment exceeding 1.73 B.M.
	t_{2g}^2	2	$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	Orbital contribution is expected yielding an effective magnetic moment exceeding 2.83 B.M.
	$t_{2g}^5 e_g^2$	3	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	The orbital contribution is expected yielding an effective magnetic moment exceeding 3.88 B.M.
Square-planar or tetragonal	$t_{2g}^3 e_g^1$	4	MnF_3	Spin only magnetic moment of 4.9 B.M., and significant orbital magnetism is expected from $t_{2g}^2 e_g^2$ states.
	$t_{2g}^6 e_g^3$	1	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	Spin only magnetic moment of 1.73 B.M., and significant orbital contribution expected from $t_{2g}^5 e_g^4$.
			$[\text{Cu}(\text{NH}_3)_6]^{2+}$	Spin only magnetic moment of 1.73 B.M., and less orbital contribution expected from $t_{2g}^5 e_g^4$ states.

Table 9. Continued on the next page...

Regular tetrahedral geometry	e^2	2	$[\text{FeO}_4]^{2-}$	Spin only magnetic moment of 2.83 B.M. is expected with no orbital contribution
	$e^2 t_2^3$	5	$[\text{FeCl}_4]^-$	Spin only magnetic moment of 5.9 B.M. with no orbital magnet.
	$e^4 t_2^3$	3	$[\text{CoCl}_4]^{2-}$	Spin only magnetic moment of 3.88 B.M. with considerable orbital magnetism possibility from $e^3 t_2^4$

Though the orbital magnetism profiling is pretty useful in the determination of the 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 magnetochemistry 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 the blood. In this section, we will discuss the fundamental concepts and underlying mechanisms 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 centers cannot interact with each other due to a large distance of separation. On the other hand, the total-electron-spin of paramagnetic centers do interact through direct-exchange or superexchange interactions in magnetically concentrated substances, which is obviously due to the small inter-micromagnetic separation. In the direct-exchange, there is a coupling between nearest neighboring cations without involving any intermediary anion; while the superexchange is generally a strong magnetic exchange interaction between two nearest neighboring 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 ($\mu_{\text{S.O.}}$) as an effective magnetic moment (μ_{eff}) in these cases. The energy of total-spin interactions of paramagnetic centers (ΔE) in magnetically concentrated material can be given by the following relation.

$$\Delta E = 2J(S)_i(S)_k \quad (63)$$

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

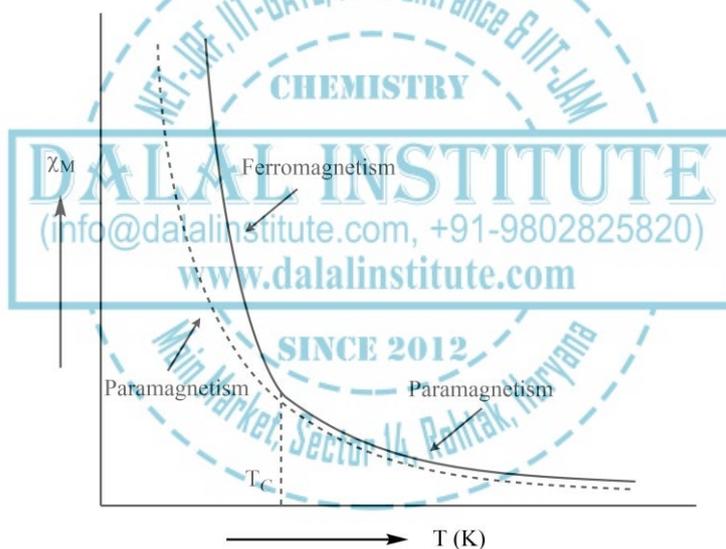


Figure 12. Plots of χ vs T for ferromagnetic and paramagnetic materials.

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 the magnetic susceptibility. Now although the ferromagnetism generally arises from direct-exchange the superexchange can also result in the same if the paramagnetic centers connected to the diamagnetic bridge are at 90° to each other. Moreover, the ferromagnetism may also arise if the two metal ions are not identical; one having an electron in e_g and the other one in t_{2g} . The corresponding modes of orbital interactions are shown below.

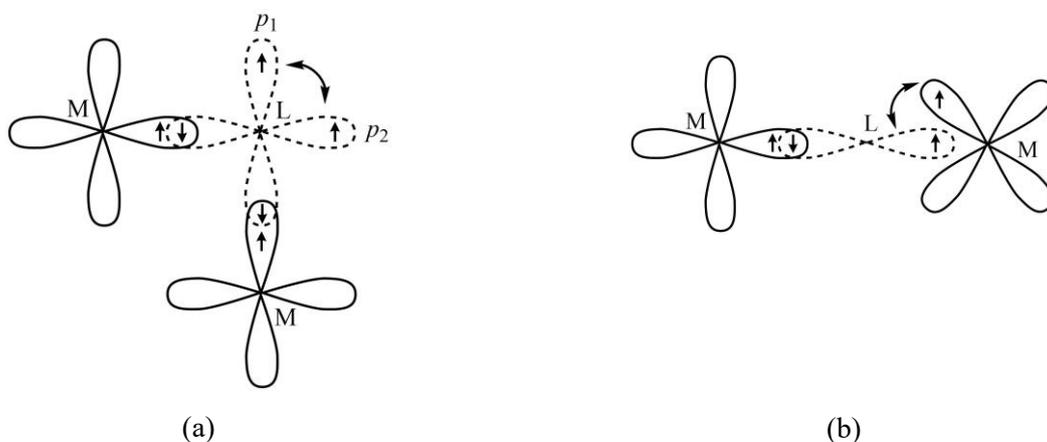


Figure 13. The ferromagnetic coupling via superexchange interactions; when (a) metal centers are at 90° , or (b) non-identical in respect of electronic configuration.

Now it's the time to discuss one of the most interesting properties of ferromagnetic materials, "the hysteresis"; which is actually responsible for the making of permanent magnets. In ferromagnetic substances, total-electron-spins of paramagnetic centers 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 a parallel alignment of individual paramagnetic centers. Now although the magnetic moments of individual paramagnetic centers 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 the applied magnetic field.

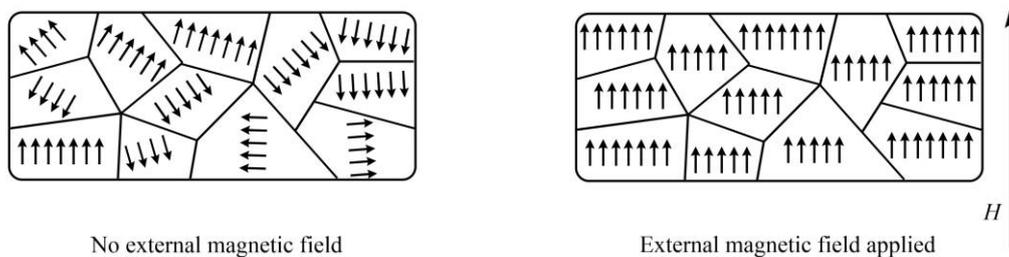


Figure 14. The alignment of magnetic domains in ferromagnetic materials when the external magnetic field is applied.

The magnitude of this domain alignment rises with the increase in the strength of the applied magnetic field, and this will continue to 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.

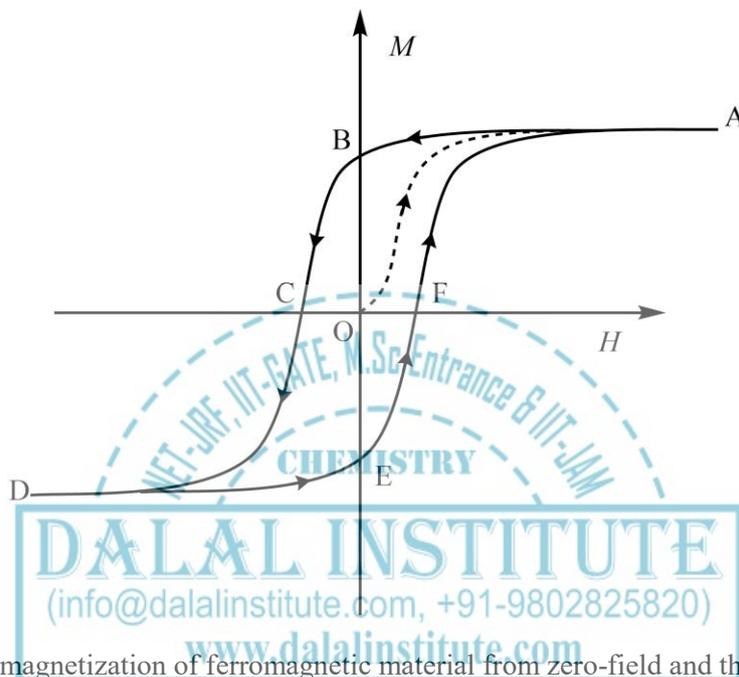


Figure 15. The magnetization of ferromagnetic material from zero-field and the hysteresis loop responsible for the retention of magnetism.

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 complete randomization of magnetic domains, the magnetic field should be applied and then increased in the opposite direction; which, consequently, would result in a decrease of magnetization along path BC. The further increase in the magnetic field strength in the opposite direction will actually induce the magnetization of the ferromagnetic material in a reversed manner with again a saturation state, represented by the path CD. Now if the reversed magnetic field is lowered down to zero, the material would again be left with non-zero magnetization (DE). For complete randomization of “magnetic domains” along EF, an increasing applied field strength in the forward direction is needed. Finally, the further increase in the 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.

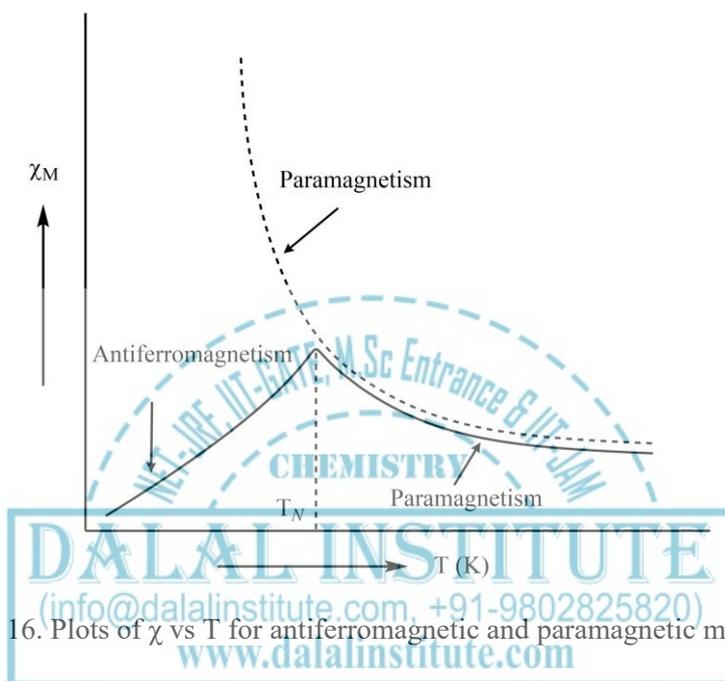


Figure 16. Plots of χ vs T for antiferromagnetic and paramagnetic materials.

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 centers wants to occur without any interference of a diamagnetic center, it would be possible only via the formation of normal covalent bond in which half-filled orbitals of the participating paramagnetic centers 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 $\text{Fe}_2(\text{CO})_9$, and the individual iron centers have one unpaired electron 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 centers in antiferromagnetic materials occurs via the mediation of a diamagnetic atom or ion. The second mechanism is so profound that even if the distance of separation between paramagnetic centers 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.

Hence, in antiferromagnetic substances, total-electron-spins of paramagnetic centers 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 centers 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 generally arises through a direct metal-metal bond like $[\text{Cu}_2(\text{OAc})_4] \cdot (\text{H}_2\text{O})_2$ and $\text{K}_4[\text{Cl}_5\text{Ru}-\text{RuCl}_5]$; however, in some compounds like $\text{K}_4[\text{Cl}_5\text{Ru}-\text{O}-\text{RuCl}_5]$, the mediation via diamagnetic center 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 a 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 behavior of a ferrimagnetic material resembles ferromagnetic materials, the ferrimagnetic materials do have an 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 the antiparallel alignment of total-electronic-spins, but unlike antiferromagnetism, they do not cancel each other completely, resulting in a permanent magnetism.

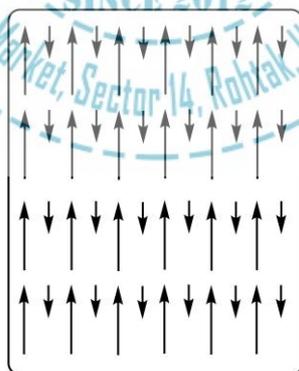


Figure 20. The ordering of total-electron-spins in Ferrimagnetic materials.

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 Neel's discovery of ferrimagnetism and antiferromagnetism in 1948, we came to know that Fe_3O_4 is actually a ferrimagnet substance.

➤ **Spin State Cross Over**

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 a quite well-known fact that metal complexes from d^4 to d^7 electronic configurations in octahedral crystal fields may result in a 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 a 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^4 – 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.

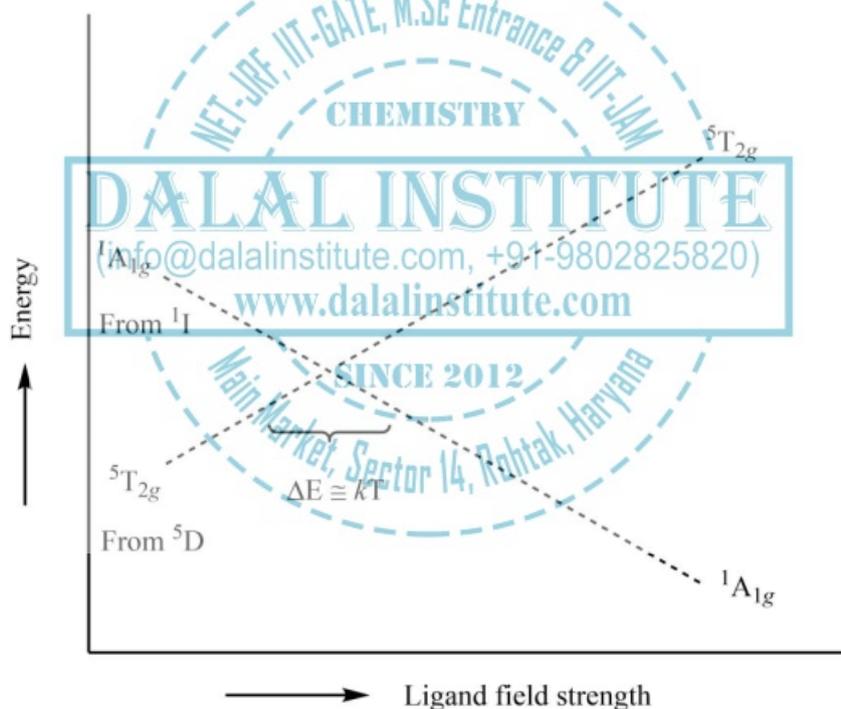


Figure 21. The partial correlation diagram of d^6 octahedral complexes showing the transformation of the ground state from ${}^5T_{2g}$ to ${}^1A_{1g}$ as the ligand-field increases.

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 the low-spin state while having four unpaired electrons in the high-spin state. Thus, a variation in the magnitude of the magnetic moment is expected as we after spin crossover. Consider the example of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$; in which the high-spin state transforms into to low-spin with the 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 $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ at 174 K suddenly drops to below 1 B.M. Similarly, the same thing does happen in $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$ but at 232 K. As the temperature is lowered than these specific temperatures, the complexes start to exist in the $^1A_{1g}$ ground state.

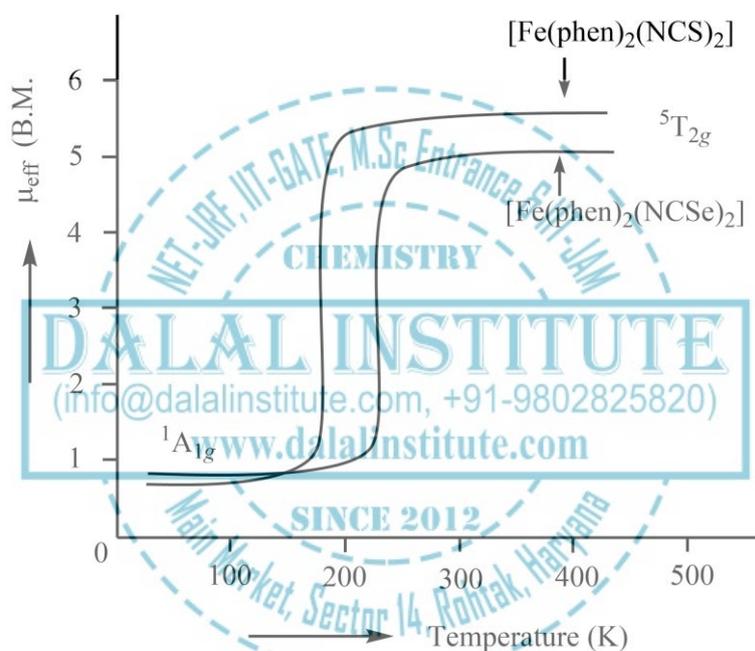


Figure 21. The partial correlation diagram of d^6 octahedral complexes.

Other examples of this include Fe^{3+} surrounded by six sulfur ligands in $[\text{Fe}(\text{S}_2\text{CNR}_2)_3]$ complex. The preference of low-spin state at lower temperatures and higher pressure can be explained in terms of the volume factor. High-spin octahedral complexes have larger volumes 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 of the lowering of temperature and increment of pressure support the lower volume, the low-spin state is also favored at the lower value of temperature. In hemoglobin, 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 Gouy'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.

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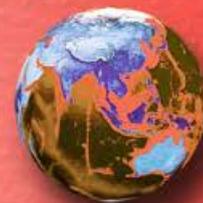
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Table of Contents

CHAPTER 1	11
Stereochemistry and Bonding in Main Group Compounds:.....	11
❖ VSEPR Theory	11
❖ $d\pi-p\pi$ Bonds	23
❖ Bent Rule and Energetic of Hybridization.....	28
❖ Problems	42
❖ Bibliography	43
CHAPTER 2	44
Metal-Ligand Equilibria in Solution:.....	44
❖ Stepwise and Overall Formation Constants and Their Interactions	44
❖ Trends in Stepwise Constants.....	46
❖ Factors Affecting Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand.....	49
❖ Chelate Effect and Its Thermodynamic Origin.....	56
❖ Determination of Binary Formation Constants by pH-metry and Spectrophotometry.....	63
❖ Problems	68
❖ Bibliography	69
CHAPTER 3	70
Reaction Mechanism of Transition Metal Complexes – I:.....	70
❖ Inert and Labile Complexes.....	70
❖ Mechanisms for Ligand Replacement Reactions	77
❖ Formation of Complexes from Aquo Ions.....	82
❖ Ligand Displacement Reactions in Octahedral Complexes- Acid Hydrolysis, Base Hydrolysis....	86
❖ Racemization of Tris Chelate Complexes	89
❖ Electrophilic Attack on Ligands	92
❖ Problems	94
❖ Bibliography	95

CHAPTER 4	96
Reaction Mechanism of Transition Metal Complexes – II:	96
❖ Mechanism of Ligand Displacement Reactions in Square Planar Complexes.....	96
❖ The Trans Effect.....	98
❖ Theories of Trans Effect.....	103
❖ Mechanism of Electron Transfer Reactions – Types; Outer Sphere Electron Transfer Mechanism and Inner Sphere Electron Transfer Mechanism.....	106
❖ Electron Exchange.....	117
❖ Problems.....	121
❖ Bibliography.....	122
CHAPTER 5	123
Isopoly and Heteropoly Acids and Salts:	123
❖ Isopoly and Heteropoly Acids and Salts of Mo and W: Structures of Isopoly and Heteropoly Anions	123
❖ Problems.....	152
❖ Bibliography.....	153
CHAPTER 6	154
Crystal Structures:	154
❖ Structures of Some Binary and Ternary Compounds Such as Fluorite, Antifluorite, Rutile, Antirutile, Cristobalite, Layer Lattices - CdI_2 , BiI_3 ; ReO_3 , Mn_2O_3 , Corundum, Pervoskite, Ilmenite and Calcite.....	154
❖ Problems.....	178
❖ Bibliography.....	179
CHAPTER 7	180
Metal-Ligand Bonding:	180
❖ Limitation of Crystal Field Theory.....	180
❖ Molecular Orbital Theory – Octahedral, Tetrahedral or Square Planar Complexes.....	184
❖ π -Bonding and Molecular Orbital Theory	198
❖ Problems.....	212
❖ Bibliography.....	213

CHAPTER 8	214
Electronic Spectra of Transition Metal Complexes:	214
❖ Spectroscopic Ground States	214
❖ Correlation and Spin-Orbit Coupling in Free Ions for 1st Series of Transition Metals.....	243
❖ Orgel and Tanabe-Sugano Diagrams for Transition Metal Complexes ($d^1 - d^9$ States).....	248
❖ Calculation of Dq , B and β Parameters	280
❖ Effect of Distortion on the d -Orbital Energy Levels	300
❖ Structural Evidence from Electronic Spectrum	307
❖ Jahn-Teller Effect	312
❖ Spectrochemical and Nephelauxetic Series	324
❖ Charge Transfer Spectra	328
❖ Electronic Spectra of Molecular Addition Compounds.....	336
❖ Problems	340
❖ Bibliography	341
CHAPTER 9	342
Magnetic Properties of Transition Metal Complexes:	342
❖ Elementary Theory of Magneto-Chemistry	342
❖ Guoy's Method for Determination of Magnetic Susceptibility	351
❖ Calculation of Magnetic Moments	354
❖ Magnetic Properties of Free Ions.....	359
❖ Orbital Contribution: Effect of Ligand-Field	362
❖ Application of Magneto-Chemistry in Structure Determination	370
❖ Magnetic Exchange Coupling and Spin State Cross Over	375
❖ Problems	384
❖ Bibliography	385
CHAPTER 10	386
Metal Clusters:	386
❖ Structure and Bonding in Higher Boranes.....	386
❖ Wade's Rules.....	401

❖ Carboranes.....	407
❖ Metal Carbonyl Clusters- Low Nuclearity Carbonyl Clusters.....	412
❖ Total Electron Count (TEC).....	417
❖ Problems.....	424
❖ Bibliography.....	425
CHAPTER 11.....	426
Metal-II Complexes:	426
❖ Metal Carbonyls: Structure and Bonding.....	426
❖ Vibrational Spectra of Metal Carbonyls for Bonding and Structure Elucidation.....	439
❖ Important Reactions of Metal Carbonyls.....	446
❖ Preparation, Bonding, Structure and Important Reactions of Transition Metal Nitrosyl, Dinitrogen and Dioxygen Complexes.....	450
❖ Tertiary Phosphine as Ligand.....	463
❖ Problems.....	469
❖ Bibliography.....	470
INDEX.....	471



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