

❖ 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

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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.

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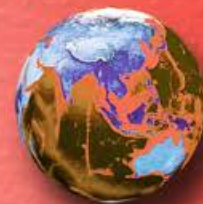
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