CHAPTER 2

MOLECULAR POLARIZABILITIES AND DIAMAGNETIC SUSCEPTIBILITIES
This chapter deals with the introduction to optical polarizability (Principal, Bond and Mean Molecular polarizability) and diamagnetic susceptibility. Various methods of the determination of mean molecular polarizability are briefly outlined. The evaluation of diamagnetic susceptibility from Mean Molecular polarizability and other theoretical approaches to evaluate diamagnetic susceptibility are presented.
2.1 MOLECULAR POLARIZABILITY

2.1.1 Introduction

When an oscillating electric vector of a beam of light interact with molecule, it will get polarized. Hence an optic moment is induced in the molecule and then the molecule behaves like an oscillating dipole, since the electric vector is oscillatory. Now, the molecule of the medium becomes polarized and the induced optic moment (P), and the intensity of the electric field (E) are related as

\[ P = \alpha E \]  \hspace{1cm} ... \hspace{1cm} (2.1)

where

\[ E = E_0 \cos 2\pi vt \]

\[ \alpha = \text{Constant of proportionality i.e, induced optic moment in the molecule per unit incident electric vector and is called polarizability.} \]

In isotropic media, '\( \alpha \)' has the same value in all directions and hence is a scalar, while in anisotropic media it has different values in different directions and thus becomes a tensor of second rank, as per Silberstein\(^1\) using rectangular space fixed co-ordinate systems, the nine tensor components (here after denoted as 'b's) are written in the form of matrix as

\[ \alpha = b = \begin{pmatrix} b_{xx} & b_{xy} & b_{xz} \\ b_{yx} & b_{yy} & b_{yz} \\ b_{zx} & b_{zy} & b_{zz} \end{pmatrix} \]  \hspace{1cm} ... \hspace{1cm} (2.2)
For an optically inactive molecule, \( \alpha \) is a symmetrical tensor i.e., 
\[ b_{xy} = b_{yx}, \ b_{yz} = b_{zy}, \ b_{zx} = b_{xz} \]
so that six independent elements are present in its matrix. This concept of anisotropy in the polarizability of a molecule is simply born out from experiments on light scattering, refractivity and other related phenomena.

### 2.1.2. Principal Polarizabilities

A coordinate system which has three mutually perpendicular directions 
OX, OY, OZ can be fixed in every molecule (Fig. 2.1) such that when the incident field acts along any one of the directions, the corresponding induced moment also acts along the same direction and the equations such as

\[
\begin{align*}
P'_x &= b_{xx}E'_x \\
P'_y &= b_{yy}E'_y \\
P'_z &= b_{zz}E'_z
\end{align*}
\]

... (2.3)

hold good. Here all the non-diagonal terms of the tensor vanish and diagonal terms \( b_{xx}, b_{yy}, \) and \( b_{zz} \) exist. These are called "principal coefficients of polarizability". They are represented by \( b_1, b_2 \) and \( b_3 \).

Gans and Bottcher\(^2\) suggested that it is convenient to visualize the molecule geometrically as a polarizability ellipsoid (Fig. 2.2). Hence polarizability can be described by three orthogonal semi-axes \( OX', OY' \) and \( OZ' \). These three semi-axes may be identified with coefficients \( b_1, b_2 \) and \( b_3 \). These
Fig. 2.1. Molecule in coordinate frames of references
Fig. 2.2. Molecular polarizability ellipsoid
coefficients of polarizability measure the moments when $E_{X'}, E_{Y'}$ and $E_{Z'}$, act respectively along $OX'$, $OY'$ and $OZ'$. Then the polarizability ellipsoid can be written as

$$\frac{X^2}{b_1^2} + \frac{Y^2}{b_2^2} + \frac{Z^2}{b_3^2} = 1 \ldots \quad (2.4)$$

and all points are represented by the co-ordinates on the surface of the ellipsoid. This may be viewed as imaginary end points of moment vectors induced, when unit field is successively applied to the molecule in all possible orientations.

The principal co-efficient of polarizability $b_1$, $b_2$ and $b_3$ appear in many fields of study such as optical and electrical phenomena and in the particular refractivity light scattering, dielectric polarization and Kerr effect. They can be evaluated from quantitative measurements made on the above properties. The average of the principal polarizability coefficients is known as mean molecular polarizability or average polarizability ($\alpha_M$) and is related directly to electronic polarization $eP$ by the expression

$$eP = \frac{4\pi N}{3} \alpha_M \ldots \quad (2.5)$$

2.1.3. Bond Polarizability

According to Mayer and Otterbein individual chemical bonds may be associated with polarizabilities along their lengths and in the two perpendicular directions (transverse and vertical) to the bonds. These bonds may be associated
with a polarizability ellipsoid with the three coefficients \( b_L \), \( b_T \) and \( b_V \) as its semiaxes. Here \( b_L \) is the longitudinal link polarizability, \( b_T \) is the transverse link polarizability in the plane of the molecule or group containing the link and at right angles to the link and \( b_V \) is the link polarizability normal to the plane. These are assumed to set up the molecular polarizability in an additive manner.

Taking \( XY_2 \) bent symmetric molecule as an example, when \( YXY = 2\theta \), each bond, X-Y will have the coefficients of polarizability \( b_{L,XY} \), \( b_{T,XY} \), \( b_{V,XY} \). Then the principal coefficients of \( XY_2 \) bent molecule can be expressed in terms of the bond polarizability components as

\[
\begin{align*}
    b_{1,XY} &= 2 \left[ b_L^{XY} \cos^2 \theta + b_T^{XY} \sin^2 \theta \right] \\
    b_{2,XY} &= 2 \left[ b_T^{XY} \cos^2 \theta + b_L^{XY} \sin^2 \theta \right] \\
    b_{3,XY} &= 2 \left[ b_V^{XY} \right]
\end{align*}
\]

and

\[
\begin{align*}
    b_{1,XY} &= 2 \left[ b_L^{XY} \cos^2 \theta + b_T^{XY} \sin^2 \theta \right] \\
    b_{2,XY} &= 2 \left[ b_T^{XY} \cos^2 \theta + b_L^{XY} \sin^2 \theta \right] \\
    b_{3,XY} &= 2 \left[ b_V^{XY} \right]
\end{align*}
\]

Then the mean polarizability \( \alpha_M = \frac{b_1+b_2+b_3}{3} \) of the \( XY_2 \) bent symmetrical molecule can be given as

\[
\alpha_M = \frac{2}{3} \left[ b_L + b_T + b_V \right]^{XY}
\]

Sachasse\(^4\), Wang\(^5\), Denbigh\(^6\), LeFevre and LeFevre\(^7\) and Bunn and Dauberry\(^8\) estimated the numerical values of \( b_L \), \( b_T \) and \( b_V \) for many bond ellipsoids by taking the following arguments.
1. $b_l \neq b_T = b_V$. Bond polarizabilities are cylindrically symmetrical for single bonds. $b_l \neq b_T \neq b_V$ are most asymmetric in nature of double bonds and $b_l \neq b_T = b_V$ for the triple bonds. The triple bond satisfies the cylindrically symmetrical nature as in the case of single bonds.

2. The value of bond polarizability coefficients of a particular bond like C-C can be taken to remain constant indifferent molecules containing structural configuration under identical electronic environment.

Considering the above conditions, the mean polarizability $\alpha_M$ for a $XY_2$ molecule can be written as

$$\alpha_M = \frac{2}{3} (b_l + 2b_T)^{XY} \quad \ldots \quad (2.7a)$$

provided it has only single bonds, satisfying the cylindrical symmetry requirements. However, in the case of CO$_2$, the X-Y link becomes double bond and it becomes very difficult to solve the equation for mean polarizability, without any approximation, because the number of unknowns will be more. LeFevre school estimated the bond polarizabilities of many bonds in different environments (in their reviews)$^{9,10}$ by taking the C-H bond to be isotropically polarizable.

2.1.4. Methods for the evaluation of Mean Molecular Polarizability

There are different methods for determination of mean molecular polarizability ($\alpha_M$). They are (1) Method based on Lippincott-δ-function potential
model (2) Molecular vibration method (3) Refractometric Method (4) Magneto Optic Rotation Method.

The first two methods are theoretical. They are based on quantum mechanical approach and vibrational spectroscopic parameters respectively and the remaining two are experimental methods. Refractometric method deals with refractivity measurements while Faraday rotation method is based on the principle of magneto-optic rotation. The discussion of the above methods is given below briefly.

2.1.4.1. Lippincott - δ - function Potential Model Method

This method is based on quantum mechanical approach. The δ-function potential was proposed by Frost and modified by Lippincott and Stutmann. In brief, their method consists in evaluating

1. The parallel bond components from the δ-function model.

2. Correction to the parallel components form non-bonded region electrons.

3. Perpendicular bond components from atomic δ-function polarizabilities and

4. Mean molecular polarizabilities.

All these aspects are discussed in detail below.

1. Parallel bond components from the atomic δ-function model

The parallel bond components are obtained from the contributions from two sources (1) bond region electrons (2) non-bond region electrons, according to
the valance bond interpretation. The bond region contributions are calculated by using a linear combination of the atomic $\delta$-wave functions of the atoms involved in the bond and the expectation value of electronic position are squared $<x^2>$, towards the bond axis. The bond region parallel component of polarizability can be expressed as

$$\alpha_{ijp} = 4n A_{12} (1/a_0) (<x^2>)^2 \quad \ldots \quad (2.8)$$

where $A_{12}$ is the root mean square $\delta$-function strength of the two nuclei, $a_0$ is the radius of the first Bohr orbit of the atomic hydrogen, 'n' is the bond order and $<x^2>$ is the mean square position of bonding electron, given as

$$<x^2> = \left[ \frac{R^2}{4} + \frac{1}{2C_{R12}^2} \right]^2 \quad \ldots \quad (2.9)$$

Here $R$ is the inter molecular distance of the equilibrium position, $C_{R12}$ is dependant on $\delta$ - function strength and is expressed as

$$C_{R12} = \left[ (n_1 n_2 N_1 N_2)^{1/2} (A_1 A_2)^{1/2} \right] \quad \ldots \quad (2.10)$$

$n_1, n_2$ are the principal quantum numbers, $N_1$ and $N_2$ are twice the column number in periodic table and $A_1, A_2$ are the $\delta$-function strengths of atoms 1 and 2 respectively.

In the case of bond of hetero nuclear type, a polarity correction is needed to account for the ionic character. Then,

$$\alpha_{ijp} = \sigma \alpha_{ijb} \quad \ldots \quad (2.11)$$

where
σ = \exp\left[-\frac{(X_1 - X_2)^2}{4}\right], is the degree of covalency and X₁ and X₂ are the Pauling's electronegatives of atom 1 and 2 respectively.

2. **Non-bonded Region Electron contribution**

It has been observed that the calculated values of \( \alpha_{ij}^{\parallel\parallel} \) (for bonds containing electrons in the non bonded region) are usually smaller than the observed values. To compensate this drawback, a correction based on Linnet's\(^{13}\) model is proposed and is given by the equation (2.12) as

\[
\alpha_{ij}^{\parallel\parallel} = \sum_j f_j \alpha_j \quad \ldots (2.12)
\]

where \( f_j \) is the fraction of the non-bonded electrons of the \( j \)th atom and \( \alpha_j \) is its atomic polarizability. Thus for a poly atomic molecule, the parallel component of polarizability can be written as

\[
\alpha_{ij}^{\parallel\parallel} = \sum_i \sigma_i \alpha_{ij}^{\parallel\parallel\parallel} + \sum_j f_j \alpha_j \quad \ldots (2.13)
\]

or

\[
\alpha_{ij}^{\parallel\parallel} = \alpha_{ij}^{\parallel\parallel\parallel} + \alpha_{ij}^{\parallel\parallel\parallel\parallel} \quad \ldots (2.14)
\]

3. **Perpendicular Bond components**

An isolated atom possesses three degrees of freedom. While combining to form molecules, two degrees of freedom are lost in forming a bond and hence the two perpendicular components of polarizability of a molecule are written as
Here $\alpha_j$ and $X_j$ are the atomic polarizability and electro-negativity of the atom respectively and $n_{df}$ is the number of degrees of freedom and is given by the equation.

$$n_{df} = (3N - 2n_b)$$ \hspace{1cm} (2.16)

where $N$ is the number of atoms, $n_b$ is the number of bonds in the compound. The exceptions to this rule are linear as well as planar molecules since in these molecules the common atom does not lose the second degree of freedom and hence $n_{df}$ is taken as

$$(3N - 2n_b +1)$$ \hspace{1cm} (2.17)

4. **Mean Molecular Polarizability**

Considering the above three contributions, the mean molecular polarizability of poly atomic molecule is written as

$$\alpha_M = \frac{1}{3} \left( \Sigma \alpha_{||P} + \Sigma \alpha_{||n} + \Sigma' 2 \alpha_{\perp} \right)$$ \hspace{1cm} (2.18)

or

$$\alpha_M = \frac{1}{3} (\Sigma \alpha_{||} + \Sigma' 2 \alpha_{\perp})$$ \hspace{1cm} (2.19)

With this expression the mean molecular polarizability can be estimated with an accuracy of 10% or better depending upon the accuracy of structural data used in calculations.
2.1.4.2 Molecular Vibration Method

The principal coefficients of polarizability necessary for the conformation analysis are generally computed from a knowledge of bond polarizability and molecular structure. But in these computations the number of unknowns are more than the number of equations which can be formulated. Hence several approximations are to be made in computing the bond polarizability coefficients. In an attempt to reduce the number of unknowns several empirical relations involving force constants were proposed by Fripiat\textsuperscript{14}, Matossi\textsuperscript{15}, Torkington\textsuperscript{16}, Tolksmith\textsuperscript{17} and Brandt\textsuperscript{18}.

The polarizability of a molecule is associated with its vibration. When a molecule is displaced from its equilibrium position, the equilibrium is restored by a restoring force, which per unit displacement was found to be proportional to the square of the frequency of vibration. Thus one can expect a relation between polarizability and force constant 'K'. One such a relation was proposed by Fripiat\textsuperscript{14}, which reads as

\[ K = A + \frac{B}{\alpha_0} \] \hspace{1cm} (2.20)

A and B are constants for a given series of compounds. 'A' depends on the nature of the bond and represents force designated as 'quantique'. \( \frac{B}{\alpha_0} \) represents the contribution from the electronic deformability of ions. LeFevre and Narayana Rao\textsuperscript{19} proposed a general method of computing atomic polarizabilities from stretching (K) and bending (K\textsubscript{s}) force constants. Their relation for XY\textsubscript{2} bent symmetric type molecule with YXY = 2\( \theta \) is given as
\[ \lambda P = \frac{4\pi N\mu^2 \sin^2 \theta}{9K_0} + \frac{8\pi N\epsilon^2 \cos^2 \theta}{9K} + \frac{8\pi N\epsilon^2 \sin^2 \theta}{9K} \frac{p^2}{r^2} \]  

... (2.21)

where \( \mu \) is bond moment.

Almost all the above relations are empirical and are not applicable to a wide variety of molecules with a reasonable accuracy. In an attempt to develop a more general method, Rao and Murthy\(^{20}\) have derived an equation relating longitudinal \( (b_L) \) and transverse \( (b_T) \) bond polarizabilities with the stretching force constant '\( K \)'.

They proposed another empirical relation between polarizability and mean amplitude of vibration. The details are as follows.

**Relation - 1**

LeFevre et al.\(^{21}\) have attributed the observed molar Kerr constant and depolarization factor in spherically symmetric molecules (e.g. Methane) to the deviations in sphericity which arises out of the distortions in bond angles brought in by external electric field. The observed electric birefringence and hence molar Kerr constant have been accounted for by a temperature independent term \( \theta_3 \). They defined \( \theta_3 \) as

\[ \theta_3 = \frac{8}{5} (B_1 + C) \]  

... (2.22)
where

\[
B_1 = \frac{\mu^2}{18 K_\delta^2} [b_{1L} - b_{1T}]
\]  

\[
C = \left( \frac{2 \mu e}{9 K_\delta} \right) \left( \frac{db_{1L}}{dr} - \frac{db_{1T}}{dr} \right)
\]

Here 'μ' is bond moment, 'e' is effective charge and \((db_{1L} / dr), (db_{1T} / dr)\) are longitudinal and transverse bond polarizability derivatives with respect to the internuclear separation 'r'.

Rearranging (2.24), we get

\[
d(b_{1L} - b_{1T}) = \frac{9 K_\delta C}{2 \mu e} K \cdot dr
\]  

Integration of this equation needs the understanding of the variation of \(K, K_\delta\) and \(\mu\) with respect to 'r'. The variation of bending force constant \((K_\delta)\) with internuclear distance ('r') is so small that it can be neglected. From the electromagnetic interaction point of view, any variation in 'μ' with respect to 'r' is imperceptible and hence can be treated as constant. But the variation of 'K', with 'r' is perceptible and many empirical relations relating them were proposed. According to Gordy\(^{22}\), the relation between 'K' and 'r' is

\[
K = a N \left( \frac{X_1 X_2}{r^2} \right)^{3/4} + B
\]  

... (2.26)
where $X_1$, $X_2$ are electronegativities of atoms forming the bond length $r$ and 'N' is bond order. 'a' and 'b' are Gordy's constants. Substituting (2.26) in (2.25) and integrating we get

$$
\begin{align*}
\frac{9}{2} K_0 c 
\end{align*}

(b_l - b_T) = \frac{(3b - 2K) r + \varepsilon}{2 \mu_e} \ldots \ (2.27)
$$

$\varepsilon$ is an integration constant. As $r \to 0$, $b_l - b_T$ vanishes much faster than the $b_l$ and $b_T$ values themselves and hence $\varepsilon = 0$.

On further integrating the equation (2.27) and simplifying, we get

$$
\begin{align*}
b_l - b_T &= A \left[ \left( X_B, X_C \right)^{1/2} \left( aN/(K-b) \right)^{2/3} \right] \ldots \ (2.28)
\end{align*}
$$

where $K$ is the stretching force constant, $X_B$ and $X_C$ are electronegativities of the atoms $B$ and $C$ (in the bond $BC$). ‘a’ and ‘b’ are Gordy’s constants. ‘$N$’ is the bond order and $S = [K/(3b - 2K)]$ is a dimensionless parameter. ‘$A$’ is characteristic constant.

Rao and Murthy have evaluated the values of R.H.S. of equation (2.28) in SH, CH, CCl and C Br bonds and compared them with the values of Denbigh$^6$ and LeFevre$^{21}$. They found that the parameter ‘$A$’ plays a significant role and is characteristic of the bond under consideration.

It is given by

$$
\begin{align*}
A &= 0.1 \left[ \frac{(i j)_Y}{(i j)_X} \right] \ldots \ (2.29)
\end{align*}
$$
Here \((i \ j)\) refers to the product of row and column numbers of an atoms \(X\) and \(Y\) in periodic table. 'Y' is more electronegative than 'X'.

**Relation - II**

In equation (2.28) there are two unknowns namely \(b_L\) and \(b_T\). Hence another equation is necessary to solve for \(b_L\) and \(b_T\). Rao and Murthy's study of the literature on mean amplitudes of vibration and bond polarizabilities revealed that both these parameters depend on the bond strength variation with internuclear distance. In the case of \(C-X\) (\(X = \text{Cl, Br, I, F}\)) bonds, the mean bond polarizability was observed to increase linearly with the mean amplitude of vibration. Based on this observation Rao and Murthy have proposed an empirical relation between mean polarizability of a bond and its mean amplitude of vibration. The relation is

\[
 b_L + 2b_T = CP^i (j)^n \gamma (\sigma x_{12})
\]

(2.30)

Here \(C\) is constant equal to \(5.24 \times 10^{-15} \text{ cm}^2\), \(P\) is characteristic of the apex atom \(B\), (in polyatomic molecule) and more electronegative atom in the bond (of diatomic molecule) and is equal to 1.0, 1.2, 1.3, 1.4 and 1.5 according as the apex atom belongs to 2nd, 3rd, 4th, 5th and 6th row in the periodic table. \(n = \pm 1\) according as the bond under study is a hydride or nonhydride bond. \(\gamma\) is saturation factor i.e. fraction of the valence electrons in more electronegative atom taking part in bonding. From (2.28) and (2.30), it is now possible to evaluate longitudinal \((b_L)\) and transverse \((b_T)\) bond polarizabilities of each bond in the molecule. Then the average polarizability of the molecules is given by
\[ \alpha_M = \frac{\sum K}{3} n_i (b_{1i} + 2 b_{T}) \] ... (2.31)

where \( n_i \) is the number of bonds of type 'i'. Rao et al., Murthy et al., Subbaiah et al. have used this method to evaluate \( b_{1i}, b_{T} \) and \( \alpha_M \) of a few bio and synthetic polymers. The same method has been extended to liquid crystals also.

2.1.4.3 Refractometric Method

There are number of instruments used for the determinaiton of refractive index (\( n \)), an important parameter of the substance. \( n \) can be used for various studies. Bauer et al. have given detailed description of different methods and their relative accuracies. LeFevre had discussed the correlation between refractive index and other molecular properties like molecular refraction, atomic and ionic refraction etc. Baccaredda and Schiavionto utilised refractometry in the study of the crystallinity of polymers. The refractive index can also be used for the evaluation of molecular polarizability and Lorentz-Lorentz relation for molar fraction at infinite wavelength (electronic polarization) is given as

\[ [R]_\infty = L^P = \left( \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \right) \frac{M/\rho}{3} = \frac{4\pi N}{3} \left( \frac{b_1 + b_2 + b_3}{3} \right) \]

\[ = \frac{4\pi N}{3} \alpha_M \] ... (2.32)

On further simplification, the above equation for mean polarzability reads as
\[ \alpha_M = \frac{3}{4\pi N} \left( \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \right) \frac{M}{\rho} \quad \cdots \quad (2.33) \]

where \( N \) the Avagadros number, \( M \) is molecular weight, \( \rho \) is the density and \( n_\infty \) is refractive index at infinite wavelength. From Cauchy's refraction \( n_\infty \), the refractive index at infinite wavelength (of source of radiation) pertaining to the state of static field is given as

\[ n_\infty = \left( \frac{n_1 \lambda_1^2 - n_2 \lambda_2^2}{\lambda_1^2 - \lambda_2^2} \right) \quad \cdots \quad (2.34) \]

The refractive indices at four wavelengths have been included by Sellemeier in his studies. Accordingly when the refractive indices \( n_1, n_2, n_3, n_4 \), of a substance are available at four wavelengths \( \lambda_1, \lambda_2, \lambda_3, \lambda_4 \) respectively, \( n_\infty \) is given by

\[ n_\infty^2 = \left( \frac{(n_3^2 \lambda_3^2 - n_4^2 \lambda_4^2)(n_2^2 - n_1^2) - (n_1^2 \lambda_1^2 - n_2^2 \lambda_2^2)(n_4^2 - n_3^2)}{(\lambda_2^2 - \lambda_1^2)(n_4^2 - n_3^2) - (\lambda_4^2 - \lambda_3^2)(n_2^2 - n_1^2)} \right) \quad \cdots \quad (2.35) \]

The arithmetical tediousness of equation (2.35) is comparatively seldom justified by the accuracy of the results.

A new dispersion relation of Murthy et al.\textsuperscript{35,36} has been found useful in getting molecular polarization, ORD and MORD and that gives

\[ n_{\infty} = (1 - \beta/\alpha) \]
where \( \beta, \alpha \) are the slope and intercept of the curve \((1/n-1)\) and \(1/\lambda^2\).

2.1.4.4 Magneto Optic Rotation Method

Faraday, while studying the effect of magnetic field on properties of matter, observed that the plane of polarization of linearly polarized light was rotated after passing through a Zena glass placed between the poles of an electromagnet. Further he noticed that all substances exhibit the magnetic rotatory polarization, a phenomenon similar to the natural optical activity. Therefore, it is possible to study the properties of matter by the application of polarized light techniques, under the influence of magnetic fields. These observations led to the well-known Faraday Verdet law, which reads as

\[
R = \delta HI \quad \ldots \quad (2.36)
\]

The proportionality constant \( \delta \) is known as Verdet constant. The Faraday effect has been observed in the radio wave, microwave, infrared, visible ultraviolet and X-ray regions by several investigators in the respective fields. According to Buckingham and Stephens,\(^3^7\) a medium causes optical rotation when its refractive indices for right and left circularly polarized components of plane polarized light, \(n_r\) and \(n_l\) are unequal. In the case of natural optical activity, this results from the very low symmetry either in the individual molecules or in a crystal of unit cell. In magnetic optical rotation, the inequality is created by magnetic field, the right and left handed circular motions about \(H\) being inequivalent. In regions of absorption, the absorption coefficients of the two
components of the circularly polarized light $K'$ and $K''$ also differ in the presence of magnetic fields, giving rise to magnetic circular dichroism.

The molar theory utilising magneto optic rotation was first developed by deMallemann\textsuperscript{38} and it was modified by Rao and Murthy\textsuperscript{39} to suit the estimation of mean polarizability from a knowledge of Verdet constants of the substances. Their expression for polarizability reads as

$$\alpha_M = \left( \frac{c' n M P \delta'}{\rho(n^2 + 2)^2 (1 - \Delta'/2)} \right)^{1/2}$$  \hspace{1cm} (2.37)

where

$$c' = \frac{9 e \lambda^2}{8 \pi^3 N}$$

is constant, $P$ is the effective number of electrons, $\delta'$ the Verdet constant of the substance and $\Delta'$ is the optical anisotropy of the substance and $M$ and $\rho$ refer to the molecular weight and density of the substance under consideration. Since the optical anisotropy factors for most of the substances are vanishingly small, Rao and Murthy\textsuperscript{39} concluded that the factor $(1 - \Delta'/2)$ can be safely neglected can be safely neglected without any observable deviation in the value of $\alpha_M$. Their modified equation is given as

$$\alpha_M = \left( \frac{c' n M P \delta'}{\rho(n^2 + 2)^2} \right)^{1/2}$$  \hspace{1cm} (2.38)
This facilitates the determination of mean polarizability from the magneto optic rotation studies and forms another useful experimental technique to study the mean polarizability. This method has been successfully used by Rao et al. and Murthy et al. for determining the polarizabilities of few alkyl halides, substituted benzenes, naphthalene, phenol and their substituents and a few other ring compounds.

2.1.4.5 Mean Polarizability through Bond refractions

Extensive work has been done on refractions of atoms and ions. LeFevre and steel have estimated the bond refractions (Rao’s) at infinite wavelengths utilising dispersion measurements. Using the bond refractions Murthy developed an empirical relation to estimate the mean molecular polarizability which reads as

\[
\alpha_M = \frac{3}{4\pi N} \sum_i (R_{\infty})_i
\]  

(2.39)

Here \( N \) is the Avagadro’s number, \( \sum R_{\infty} \) is the summation of bond refractions of various bonds present in the molecule.

But, \( R_{\infty} \) corresponds to the bond refractions at infinite wavelength in the isolated state that needs some correlation due to the presence of electrons not taking part in bonding. So it can be written as

\[
\alpha_M = \frac{3}{4\pi N\gamma} \sum_i (R_{\infty})_i
\]  

(2.40)
where $\gamma$ is saturation factor equal to $(0.9)^n$ where 'n' reveals the number of unsaturated bonds or rings present in the molecule.

The above relation is successful in the case of simple and complex molecular systems.

2.2. DIAMAGNETIC SUSCEPTIBILITY

2.2.1 Introduction

Magnetic susceptibility, a measure of extent to which a material is either attracted or repelled by a magnetic field, is commonly determined by measuring the force exerted on a sample by a field of known strength. It is defined as the ratio of the intensity of magnetization 'I' induced in any medium to the strength of the applied field 'H'.

$I \alpha H$ or $I = KH$

or

$K = I/H$ ... (2.41)

Here $K$ is proportionality constant, and is called the magnetic susceptibility per unit volume and depends on the material of the body. The susceptibility has the same values in all directions in case of an isotropic body, while in anisotropic materials, it is different along the three principal magnetic axes. The measurements on their powdered samples give the average of the three values. The elegant reviews of Selwood\textsuperscript{45}, Mulay\textsuperscript{46} give the complete details of the fundamentals, theory and applications of susceptibility.
In case of diamagnetic susceptibility, the intensity of magnetization induced in a body by an applied field will be less than that produced in vacuum by the same field and hence, the susceptibilities are shown with a negative sign. Practically, all organic and inorganic compounds with exception of free radicals and compounds of transition elements are diamagnetic. In general the susceptibilities of diamagnetic substances is independent of temperature (with some exemptions) and of field strength (for smaller magnetic fields). Any significant change in diamagnetic susceptibility with temperature in most cases may be attributed to a change in the physical or chemical structure of the material.

The diamagnetic susceptibilities and molecular polarizabilities are important factors in the evaluation of several kinetic properties in positive ion chemistry. Also, the molecular polarizability and diamagnetic susceptibility find application in the evaluation of electron ionization cross-sections, which has much importance in mass spectroscopic studies of compounds.

2.2.2 Mean Polarizability and Diamagnetic Susceptibility

Attempts to correlate mean polarizability and diamagnetic susceptibility are recorded in literature. For many systems of near-spherical symmetry (for example the noble gases, some ionic crystals and even some branched aliphatic hydrocarbons), Kirkwood and Vinti observed an approximate proportionality between diamagnetic susceptibility and the square root of mean polarizability. The work by Gans and Mrowka led to a rather more complicated relationship between the diamagnetic susceptibility and mean polarizability. The work of
Amos and Yoffe\textsuperscript{50} has established a simplified relation between diamagnetic susceptibility and mean polarizability as

\[
\chi_M = \frac{1}{4} (N\alpha_M)^{1/2} \quad \ldots \quad (2.42)
\]

where \( N = 2n \), \( n \) being the number of electrons.

Due to the many limitations in the above methods, it is planned to develop another empirical relation between diamagnetic susceptibilities and mean polarizabilities. From the measured values of diamagnetic susceptibilities and mean polarizabilities of methyl chloride and some of its higher homologous it is observed that the additive nature of mean polarizability and diamagnetic susceptibility is alike (Fig. 2.3). The graph drawn between the experimental values of mean polarizability versus diamagnetic susceptibility for a few molecular systems (Fig. 2.4) shows a general tendency of linearity instead of being non-linear (as expected by Kirkwood and Amos and Yoffe expressions). The graphs drawn between diamagnetic susceptibility and mean polarizability and diamagnetic susceptibility and square root of mean polarizability (Fig. 2.5) clearly indicates that there is only linear relationship between mean polarizability and diamagnetic susceptibility. Further, it is clearly known that the \( \chi_M \) as well as \( \alpha_M \) depend on the effective number of free electrons which will be free to take part in magnetic and optical interactions. In view of these considerations a semi-empirical relation was proposed by Rao \textit{et al.}\textsuperscript{47} which is given as

\[
\chi_M = -(\gamma m \sigma') \alpha_M \quad \ldots \quad (2.43)
\]
Fig. 2.3. Molecular polarabilities and diamagnetic susceptibilities of Alkyl chlorides
Fig. 2.4. Molecular polarizabilities and diamagnetic susceptibilities of a few molecular systems.
Fig. 2.5. Linear and Nonlinear relationships between polarizability and susceptibility
Here $y = (0.9)^n$ represents the saturation factor of the molecule with 'n' denoting the number of unsaturated bonds or rings present in the molecule, $\sigma'$ is the degree of covalency of the characteristic group which is given by the equation

$$\sigma' = (\sigma_1^{1/n_1} \sigma_2^{1/n_2} \ldots \sigma_p^{1/n_p})^{1/2} \quad \ldots \quad (2.44)$$

where $\sigma_1, \sigma_2, \ldots, \sigma_p$ are the Pauling's percentage covalency characters of the bonds present in the characteristic group. $n_1, n_2, \ldots, n_p$ are the bond orders of the various bonds present in the characteristic group.

$m$, is a characteristic constant which is equal to $0.72 \times 10^{19}$ CGS units per unit volume.

The equation (2.43) takes the following two forms depending on whether the compound is saturated or unsaturated.

For all saturated compounds

$$\chi_m = -0.72 \times 10^{19} (\sigma') (\alpha_M) \quad \ldots \quad (2.45)$$

For all unsaturated compounds

$$\chi_m = -0.72 \times 10^{19} (0.9)^n (\sigma') (\alpha_M) \quad \ldots \quad (2.46)$$

$\sigma'$ for various classes of compounds can be calculated using the above equations as follows.

In any alkyl halide the characteristic bond will be the C-X bond and for higher numbers of the series, the C-C bond will also be an important linkage. Therefore for $\text{C}_2\text{H}_5\text{Cl}$ the degree of covalence is taken as a geometric mean of the Pauling's percentage covalency factors of C-C and C-Cl bonds.
\[ \sigma_{c_{211},c_1} = \left[ \sigma_{c-c} \sigma_{c-c_1} \right]^{1/2} \]
\[ = (1 \times 0.93941)^{1/2} \]
\[ = 0.96923 \]

\( \gamma \) in this case will be equal to one because these type of compounds are completely saturated (i.e. \( n = 0 \)).

In case of an ester the characteristic group is

\[
\begin{array}{c}
\text{C} \\
\text{O} \\
\text{O}
\end{array}
\]

These compounds have one first order and one second order C-O bonds in the characteristic group. For the above compounds the degree of covalency is calculated as

\[ \sigma' = \left[ \sigma_{c-o} \sigma_{c-o} \right]^{1/2} = [(0.778827)3^2]^{1/2} \]
\[ = 0.92705 \]

For this class of compounds \( \gamma = 0.9 \) because there is only one unsaturated bond in the molecule (i.e. \( n = 1 \)).

In the case of a ketone, the characteristic group is C = O. The degree of covalency is given as

\[ \sigma' = (\sigma_{c-o})^{1/2} = (0.778827)^{1/2} = 0.88251 \]

In the same way the degree of covalency and saturation factor can be calculated for any characteristic bonds present in the molecules.
2.2.3 Evaluation of diamagnetic susceptibility - Pascal's method

Pascal\textsuperscript{51}, from his vast study on a very large number of compounds, concluded that magnetic susceptibilities could be represented by the expression

\[ \chi_m = n_A \chi_A + \lambda' \]  \hspace{1cm} \text{(2.47)}

where \( n_A \) is the number of atoms of susceptibility \( \chi_A \) in the molecule and \( \lambda' \) is a constitutive correction depending on the nature of the bonds between the atoms. In this expression, \( \chi_A \) is the empirical constant derived from the measured susceptibilities. At first glance, this whole procedure looks rather dubious especially in connection with \( \lambda' \). It cannot be denied, however, that considerable success has been achieved by use of Pascal's constants and that they often afford means of estimating susceptibilities where no other methods are available.

Pascal's constants for the elements, are given in Table 2.1 and list of constitutive correction constants in Table 2.2. Pascal found that the positions of oxygen with respect to carbon atoms in the molecule introduced another constitutive correction. He referred to 'tertiary,' and 'quaternary' (C\(_3\) and C\(_4\)) carbon atoms as those in which three or four valences respectively are attached to carbon, regardless of the actual number of surrounding carbon atoms. For instance, a tertiary carbon atom is the one designated (*) in the group

\[
\begin{array}{c}
\text{C} \\
\text{C—C—X} \\
\text{C}
\end{array}
\]
TABLE 2.1

Atomic susceptibility constants of Pascal

<table>
<thead>
<tr>
<th>Atom</th>
<th>( \chi_a \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-6.00</td>
</tr>
<tr>
<td>H</td>
<td>-2.93</td>
</tr>
<tr>
<td>N(open chain)</td>
<td>-5.57</td>
</tr>
<tr>
<td>N(closed chain)</td>
<td>-4.61</td>
</tr>
<tr>
<td>N Monoamide</td>
<td>-1.54</td>
</tr>
<tr>
<td>N Diamide, imide</td>
<td>-2.11</td>
</tr>
<tr>
<td>O Alcohol or ehter</td>
<td>-4.61</td>
</tr>
<tr>
<td>O Aldehyde or ketone</td>
<td>+1.72</td>
</tr>
<tr>
<td>O Carboxyl group</td>
<td>-3.36</td>
</tr>
<tr>
<td>O Aldehyde or ketone</td>
<td>+1.73</td>
</tr>
<tr>
<td>Cl</td>
<td>-20.10</td>
</tr>
<tr>
<td>F</td>
<td>-11.50</td>
</tr>
<tr>
<td>Br</td>
<td>-30.60</td>
</tr>
<tr>
<td>I</td>
<td>-44.60</td>
</tr>
<tr>
<td>S</td>
<td>-15.00</td>
</tr>
<tr>
<td>Se</td>
<td>-23.00</td>
</tr>
<tr>
<td>B</td>
<td>-7.00</td>
</tr>
<tr>
<td>Si</td>
<td>-13.00</td>
</tr>
<tr>
<td>P</td>
<td>-10.00</td>
</tr>
<tr>
<td>As</td>
<td>-21.00</td>
</tr>
</tbody>
</table>
### TABLE 2.2

Constitutive correction constants

<table>
<thead>
<tr>
<th>Group or structure</th>
<th>$\chi \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C</td>
<td>5.50</td>
</tr>
<tr>
<td>C=C</td>
<td>0.80</td>
</tr>
<tr>
<td>C=C-C=C</td>
<td>10.60</td>
</tr>
<tr>
<td>N=N</td>
<td>1.85</td>
</tr>
<tr>
<td>C=N</td>
<td>8.15</td>
</tr>
<tr>
<td>-C=N</td>
<td>0.80</td>
</tr>
<tr>
<td>Benzene</td>
<td>-1.40</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>-3.00</td>
</tr>
<tr>
<td>$C_3^a$, $C_3^b$, $C_3^c$</td>
<td>-1.30</td>
</tr>
<tr>
<td>$C_4^a$, $C_4^b$, $C_4^c$, $C_4^c$</td>
<td>-1.55</td>
</tr>
<tr>
<td>$C_3^a$, $C_4^b$</td>
<td>-0.50</td>
</tr>
<tr>
<td>C in mono cyclic system</td>
<td>-0.24</td>
</tr>
<tr>
<td>C in bicyclic systems such as the two of</td>
<td>-3.10</td>
</tr>
<tr>
<td>the atoms in naphthalene</td>
<td></td>
</tr>
<tr>
<td>Mono chloro derivative</td>
<td>+3.10</td>
</tr>
<tr>
<td>Dichloro derivative</td>
<td>+4.30</td>
</tr>
<tr>
<td>Pyrimidine ring</td>
<td>+6.50</td>
</tr>
<tr>
<td>Purine ring</td>
<td>+9.90</td>
</tr>
</tbody>
</table>
a quaternary carbon atom

\[ C - C^* = C \]

A tertiary carbon atom in the alpha position with respect to an oxygen group is designated \( C_3^* \).

An extensive discussion of Pascal's constants is given by Bhatnagar and Mitra\textsuperscript{52} tables and critical discussions are given by Gray and Farquharson\textsuperscript{53}, and Pacault\textsuperscript{54} has proposed an exhaustive review. The support for the Pascal's method is given by excellent agreement between observed susceptibilities of tetra substituted ureas and calculated values for the normal carbamido structures of these compounds. Similarly successful arguments are applied by Clow\textsuperscript{55-57} to many substituted ureas, carbon dioxide, carbon oxysulphide, carbon disulphide, several thioureas and a rather large number of sulphur compounds.

### 2.2.3.1 Modified Pascal's Method

Pascal and co-workers\textsuperscript{58} have revised the Pascal's incremental susceptibility data in order to reduce the number of constitutive correction and to minimize the error. Gupta\textsuperscript{51} has observed that this method gives better values than the previous set. Pascal \textit{et al.} have realised the importance of bond concept of susceptibility and worked out the bond susceptibility data for number of bonds.
2.2.3.2 Haberditzl's Atomic and Bond incremental systems

Haberditzl has\textsuperscript{59,60} have developed the atomic and bond incremental systems based on the following concept to overcome the difficulties in universalizing the Pascal's method.

1. For inner shell core electrons, the increments are calculated on Quantum mechanical basis.

2. The bonding electron increments were determined empirically with the aid of the increments calculated in (1) above.

The theoretical basis of a general incremental system for hydrocarbons based on primary, secondary and tertiary etc., carbon atoms along with the sample calculations are given by Haberditzl \textit{et al}\textsuperscript{61}. These constants have been modified by Dauben's \textit{et al}.\textsuperscript{62} and Mital \textit{et al}.\textsuperscript{63} (Table 2.3).

2.2.3.3 Guoy Method

To measure diamagnetic susceptibility, several techniques have been developed and are in use. The information obtainable from the magnetic measurements is both qualitative and quantitative.

The methods are (1) Guoy method, (2) The Quinke method, (3) The Faraday method (4) The Curie chenevean balance (5) The Rankine balance and (6) The others methods based on magnetic resonance. All these methods are discussed in the reviews of Selwood\textsuperscript{45} and Mulay and Mulay\textsuperscript{64} and Mulay\textsuperscript{46}. Recently Spencer and Zara\textsuperscript{65} described magnetic susceptibility measurements using a laser pendulum apparatus.
### TABLE 2.3

Value of structural element increments of the Haberditl system

<table>
<thead>
<tr>
<th>Structural element</th>
<th>$\chi_m$ $\times 10^6$ cm$^3$ mole$^{-1}$</th>
<th>Structural element</th>
<th>$\chi_m$ $\times 10^6$ cm$^3$ mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C* - C*</td>
<td>2.4</td>
<td>C* $\pi$ C*</td>
<td>2.2</td>
</tr>
<tr>
<td>C* - N*</td>
<td>3.2</td>
<td>C* $\pi$ N*</td>
<td>2.2</td>
</tr>
<tr>
<td>C* - O*</td>
<td>2.8</td>
<td>N* $\pi$ O*</td>
<td>2.2</td>
</tr>
<tr>
<td>N* - N*</td>
<td>3.2</td>
<td>N* - H</td>
<td>3.6</td>
</tr>
<tr>
<td>C* - H</td>
<td>3.2</td>
<td>C* - C</td>
<td>2.6</td>
</tr>
<tr>
<td>C* - H(terminal)</td>
<td>3.6</td>
<td>N* $\pi$ N*</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>Core electrons</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.15</td>
<td>0</td>
<td>0.08</td>
</tr>
<tr>
<td>N</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Lone pairs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N*</td>
<td>0.15</td>
<td>O*</td>
<td>1.75</td>
</tr>
<tr>
<td><strong>Groups</strong></td>
<td></td>
<td>Van Vleck' Correction</td>
<td></td>
</tr>
<tr>
<td>CH$_3$ on C</td>
<td>1.45</td>
<td>C = O</td>
<td>-6.0</td>
</tr>
<tr>
<td><strong>Benzene substitution increments</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$</td>
<td>11.3</td>
<td>OH</td>
<td>5.4</td>
</tr>
<tr>
<td>F</td>
<td>3.6</td>
<td>NH$_2$</td>
<td>8.1</td>
</tr>
<tr>
<td>Cl</td>
<td>15.2</td>
<td>N(CH$_3$)$_2$</td>
<td>35.0</td>
</tr>
</tbody>
</table>
Among these techniques the widely used method is Guoy\textsuperscript{66} method. It is a well known method over a long time. Guoy method finds wide applicability even today because of its simplicity. A comprehensive description of the theory, the setting up of the Guoy Magnetic balance, suspension of the Guoy tube, the methods of observation and the other related details are given by Selwood\textsuperscript{45} as well as by Mulay\textsuperscript{46}.

Diamagnetic susceptibilities can be calculated using the equation (2.48).

\[ -\chi_M = \frac{KM}{\rho} \quad \ldots \quad (2.48) \]

\[
\frac{M_l}{M_w} = \frac{K_l \rho_w}{\rho_l K_w}
\]

where \( \rho \) is the density, \( M \) is the molecular weight and \( K \) is the specific susceptibility. Knowing \( M_l, M_w, \rho_l, \rho_w \) and \( K_w, K_l \) can be obtained. Substituting the value of \( K_l \) in the equation (2.48) \( \chi_M \) value can be calculated.
REFERENCES


