CHAPTER I

OPTICAL POLARIZABILITY AND DIAMAGNETIC SUSCEPTIBILITY
OF SEMICONDUCTORS
ABSTRACT

In Chapter I, a general introduction to the semiconductors and the optical studies in them is given. A brief review of the parameter polarizability and its determination by both theoretical and experimental methods is outlined. Methods of evaluating diamagnetic susceptibility from polarizability is also described.
1.1 OPTICAL STUDIES IN SEMICONDUCTORS:

1.1.1 INTRODUCTION:

The study of the propagation of light through matter, particularly solid matter, comprises one of the important and interesting branches of optics. The many and varied optical phenomenon exhibited by solids include selective absorption, dispersion, double refraction, polarization effects. Many of the optical properties of solids can be understood on the basis of classical em theory. The most direct and perhaps the simplest method for proving the band structure of semiconductors is to measure the absorption spectrum. In the absorption process, a photon of a known energy excites. Emission of radiation is the inverse of the absorption process. Most of the transitions that are considered as examples of absorption mechanisms can occur in the opposite direction and produce a characteristic emission. However, there is an important difference between the information one can obtain by absorption and by emission in a semiconductor. The absorption process can involve all the states in the semiconductor i.e., states on either side of the Fermi level, resulting in a broad spectrum where as
the emission process couples a harmonic band of states containing thermalized electrons with a narrow band of empty states containing thermalized holes and hence produce a narrow spectrum. Under special conditions, the electron hole pair can recombine radiative and non-radiative transitions. The main requirement for emission is that the system need not be at equilibrium and the deviation from equilibrium requires some form of excitation. Electric excitation gives rise to electroluminescence. Whereas optical excitations (via absorption) produce photoluminescence. Excitation with an electron beam causes cathodoluminescence. Triboluminescence is the emission of light in response to mechanical excitation.

1.1.2 CLASSIFICATION OF SOLIDS INTO CONDUCTORS, SEMICONDUCTORS AND DIELECTRICS:

Physical properties of solids, (of which the main being electric properties), are determined by the degree of filling of the energy bands rather than by the process of their formation. From this point of view, all crystalline bodies can be divided into two quite different groups. i.e., (i) Conductors and (ii) Semiconductors and dielectrics.
CONDUCTORS:

The first group includes substances having a partially-filled band in their energy spectrum above the completely filled energy bands. A partially filled band is observed in alkaline metals whose upper band is formed by unfilled atomic levels, and in alkaline earth crystals with a hybrid upper band formed as a result of the overlapping of filled and empty bands. All substances belonging to the first group are conductors.

The second group comprises of substances with absolutely empty bands above completely filled bonds. This group also includes crystals with diamond type structures, such as silicon, germanium, grey tin diamond itself. Many chemical compounds also belong to this group this group, for example metal oxides, carbides, corundum ($\text{Al}_2\text{O}_3$) metal nitrides and others. The second group of solids includes Semiconductors and dielectrics.

In principle, there is no difference between semiconductors and dielectrics. The division in the second group into Semiconductors and dielectrics is quite arbitrary and is determined by the width $E_g$ of the forbidden energy gap separating them completely. Filled band from the empty band. Substances with forbidden band widths $E_g \leq 2$ ev belong to the semiconductor subgroup. Germanium ($E_g \approx 0.7$ ev), silicon ($E_g \approx 1.2$ ev), Galium Arsenide ($E_g \approx 1.5$ ev)
and Indium Antimonide (\(E_g \approx 0.2 \text{ ev}\)) are typical semiconductors. Substances for which \(E_g > 3 \text{ ev}\) belong to dielectrics. Well-known dielectrics include corundum (\(E_g \approx 7 \text{ ev}\)), diamond \((E_g > 5 \text{ ev})\), Boron Nitride \((E_g \approx 4.5 \text{ ev})\) and others. The arbitrary nature of the division of second group of solids into dielectrics and semiconductors is illustrated by the fact that many generally known dielectrics are now used semiconductors. For example, silicon carbide with its forbidden band width of about \(3 \text{ ev}\) is now used in semiconductor devices. Even such a classical dielectric as diamond is being investigated for a possible application in semiconductor technology.

1.1.3 SEMICONDUCTORS AT PRESENT AND IN FUTURE:

Semiconductors burst impetuously into 20th century science and technology. Their extremely low energy consumption, the remarkable compactness of devices due to very dense packing of elements in circuits, and high reliability mean they are the most important materials in electronics, radioengineering and science, space exploration would have been impossible without semiconductor devices, since the requirements of small size, low weight and energy consumption are especially stringent for the space craft equipment. Microelectronics has opened new prospects for
the development of semiconductor technology. It has become possible to replace semiconductor devices assembled from separate elements by the integrated circuits. Modern technology allows designers to create $10^2$ elements per cm of surface. By using the layered structures developed during last years (metal-nitride-dielectric semiconductor), $10^2$ circuits that can store information can be placed per mm of surface. The information can be readout not only with the help of electric signals but also using laser radiation obtained, for example, from semiconductor injection lasers.

In this regard the work was stated with view to see if optical polarizability (which is a useful parameter in the elucidation of properties of liquids and liquid crystals) can be used as a tool to study optical properties of solids in general and semiconductors in particular. The fundamental properties like refractive index, susceptibility etc. do not show much variation with the size of the sample [ex: $\kappa_{\text{simple crystal}} = \kappa_{\text{amorphous powder}}$]. But any how they do offer useful way of understanding the behaviour of semiconductors and many theoretical studies taking the semiconductor under isolation coincide mostly with the amorphous state or near thinfilm state study of the system.
Of the properties chosen primarily to characterize semiconductors, polarizability and susceptibility show near constant values from bulk-thinfilm-amorphous states and are very nearly represented by theoretical approaches. As such a study of polarizability and susceptibility of these other related properties is presented.
1.2 OPTICAL POLARIZABILITY AND SUSCEPTIBILITY:

1.2.1 INTRODUCTION

As the well established and much reputed theory of MAXWELL'S observes; a light wave is identified with pulsating vectors (one electric and the other magnetic), which are at right angles to each other and they are perpendicular to the direction of propagation of the light wave. In elucidating and explaining the observed optical phenomena the electric component is customarily associated with the light vector though in the process the magnetic vector can also be used. This is because, it is the electric vector that causes the intensity effects more than its counter part. As JENKINS & WHITE put forward in their 'Fundamentals of optics': "Presumably also the electric vector is the one that affects the retina of the eye. In this sense, therefore the electric wave is the part that really constitutes light and magnetic wave, though no less real, is no less important.

When such a beam of light is incident on a transparent material medium of refractive index different from that of the surroundings, the medium gets polarized.
Suppose a light wave of electric intensity \( E = E_0 \cos(2\pi t) \) goes past a molecule in the medium, it induces an optic moment in the molecule and the latter behaves like an oscillating dipole, since the incident light vector \( E \) is oscillatory. The resulting dipole moment is \( eb \), so that the relation between dipole moment and applied field is

\[
p = eb = aE
\]

\[\text{...... (1.1)}\]

The induced moment \( P \) will be proportional to the intensity of the incident electric field \( E \) and is given by

\[
P = \alpha E
\]

\[\text{...... (1.2)}\]

where \( \alpha \), the constant of proportionality, is the moment induced in the molecule per unit incident electric field; and it is called the 'polarizability' of the molecule.

Molecules are necessarily less symmetrical than atoms. This raises the possibility of an induced dipole moment not parallel to the electric field that induced it. The polarizabilities of mono atomic ions and atoms are generally believed to be independent of field direction. But according to SILBERSTEIN,[1]. When two isotropic atoms \( A \) and \( B \) are held together as in a diatomic molecule the resulting system \( A-B \) is not isotropically polarizable.
If a unit field acts successively along and perpendicular to the line of centres A-B, it will induce primary moment parallel and perpendicular to the line of centres respectively in both atoms A and B. Each primary moment induced in the atom, will produce a secondary moment in its neighbour. In the first case, the secondary moments will add to the primary moments, while in the second case they oppose the primary moments. Hence the polarizability along the line of centres exceeds that in the transverse direction making the polarizability of A-B anisotropic. Hydrogen molecule is an example of this behaviour.

In general many of the molecules are optically anisotropic and therefore the polarizability \( \alpha \), acquires directional property. The polarizability of a molecule is not simply a scalar in most cases. It is a tensor of second rank, with a set of co-efficients that express a linear dependence of the components of the one vector \( p \) on those of another \( E \). This involves nine co-efficients, and might be written in this way.

\[
P = \alpha_{xx} E + \alpha_{xy} E + \alpha_{xz} E
\]

\[
P = \alpha_{yx} E + \alpha_{yy} E + \alpha_{yz} E
\]

\[
P = \alpha_{zx} E + \alpha_{zy} E + \alpha_{zz} E
\]

\[\text{(1.3)}\]
It can be proved that, the polarizability tensor has only six of the nine coefficients as independent.

\[ \alpha_{xy} = \alpha_{yx}, \quad \alpha_{xz} = \alpha_{zx} \]

and \[ \alpha_{yz} = \alpha_{zy} \] ........ (1.4)

The symmetry of the tensor expresses a most remarkable physical fact that a field \( E \) applied in the \( x \) direction always causes a \( Z \) components of polarization exactly equal to the \( x \) component of polarization that would be caused by an equal field applied along the \( Z \) direction. This is true even for a molecule that has no symmetry. This is termed as 'reciprocity principle'.

1.2.2 PRINCIPAL POLARIZABILITIES:

It has been an observed fact that each and every molecule possess three mutually perpendicular directions which can be tentatively designated as \( OX, OY \) and \( OZ \) (Fig.1.1), in such a manner that when the incident field acts along any one of them the corresponding induced moment also acts along the same direction and the equations represented below holds good.
Fig. 11. Molecule in coordinate frames of reference.
All the non-diagonal terms of the tensor components in this representation vanish and the diagonal terms $b_1$, $b_2$ and $b_3$ are called the 'Principal co-efficients of polarizability'. These are extremely important in the investigation of optical properties of molecules.

In addition it is convenient to visualize the molecule geometrically as a polarizability ellipsoid (GANS & BOTTCHER) and there is ample scope to describe the polarizability ellipsoid mathematically by three orthogonal semi-axes. These three semi-axes may be identified with the co-efficients $b_1$, $b_2$ and $b_3$ which measure the moments induced when the unit field acts respectively collinear with them. The expression for polarizability ellipsoid can be written as

$$P' = b_1 E_{x'}$$
$$P' = b_2 E_{y'}$$
$$P' = b_3 E_{z'}$$

\[ ...... (1.5) \]
and points are presented by the coordinates on the surface of the ellipsoid. When unit field is successively applied to the molecule in all possible orientations, all the points on the surface of the ellipsoid may be viewed as imaginary end-points of induced moment vectors.

There is clear distinction between spherically symmetrical molecules and less symmetrical molecules. The directions of action of the inducing field and the induced moments of spherically symmetrical molecules are always collinear, whereas the direction of action of induced moments of less symmetrical molecules depends on the orientation of the molecule in the field i.e., the field induces component moments parallel and perpendicular to itself. The perpendicular components of the induced moments will become zero when the molecule fixed coordinating system coincides with the laboratory fixed coordinating system. Then the parallel components will be $b_1$, $b_2$ or $b_3$ respectively.
The direction of the applied field and that of the induced moment are not said to be the same as explained above, in any general case. For, if a unit field acts at an angle $\theta$ (Fig.1.2) with $b_1$ direction in the $b_1$-$b_2$ plane then the respective components are moments induced in the two directions $b_1$ and $b_2$ are $b_1 \cos \theta$ and $b_2 \sin \theta$. Usually the resulted induced moment differs in its direction from that of the incident field direction as shown in Fig.(1.3). To be precise it will make an angle $\tan^{-1} \left( \frac{b_2 \tan \theta}{b_1} \right)$ with the $b_1$ direction.

The applications of principal co-efficients of polarizability $b_1,b_2$ and $b_3$ are found in many fields of study such as refractivity, light scattering, dielectric polarization and kerr effect. Quantitative measurements made on the above properties were used to evaluate the principal co-efficients of polarizability, and the average of these co-efficients $\left( b_1 + b_2 + b_3 \right)/3$ is often termed as mean polarizability or average polarizability ($\alpha$) and is related directly to electric polarization $E^P$ by the expression

$$E^P = 4\pi N\alpha/3$$
Fig. 1.2 Molecular polarizability ellipsoid
1.2.3 BOND POLARIZABILITIES:

A suggestion, that individual chemical bonds may be associated with polarizabilities along their lengths and in the two perpendicular (transverse and vertical) directions, and each chemical bond may be described as a polarizability ellipsoid with three co-efficients designated by $b_L$, $b_T$ and $b_V$ as its semi-axes, was first made quantitatively by Mayer & Otterbein [3] in 1931. $b_L$ is known as longitudinal link polarizability, $b_T$ is the link polarizability in the plane of the molecule or group containing the link and at right angles to it and $b_V$ is the one normal to the plane. These are assumed to constitute the molecular polarizability in an additive manner.

If one considers a molecule of $XY\textsuperscript{2}$ bent symmetric type with $YXY = 2\theta^\circ$, where each bond $X-Y$ in the molecule is characterized by the co-efficients of polarizability $b_{XY}$, $b_{XY}^L$, $b_{XY}^T$, $b_{XY}^V$, the principal co-efficients of polarizability of the $XY$ type bent symmetrical molecule can be expressed as a sum of the bond polarizability components resolved along three principal directions fixed in the molecule.
Hence,

\[ b_{XY} = \frac{2}{3} \left( b_L \cos \theta + b_T \sin \theta + b_V \right) \]

and \[ b_{XY}^2 = 2 \left( \frac{XY}{b} \right) \]

Now the mean polarizability \( \alpha \) is given by

\[ \alpha = \frac{2}{3} \left( b_L + b_T + b_V \right)^{XY} \]  \( \ldots (1.7) \)

For many bond ellipsoids, the numerical values for their semi-axes have been estimated by SACHSSE [4], WANG [5], DENBIGH [6], LEFVRE & LEFVRE [7], & BUNN & DAUBENY [8] taking into consideration the following arguments.
(1) For single bonds $b \neq b = b$, and they are cylindrically symmetrical and for double bonds $b \neq b \neq b$ and they are most asymmetric in nature and for triple bonds $b \neq b \neq b \neq b$ and they satisfy the symmetry requirements as in the case of single bonds.

(2) For bonds like C-C, the numerical values of the bond polarizability dimensions can be taken to remain constant in different molecules containing this structural unit under similar electronic environment.

For XY molecule, the mean polarizability $\alpha$ with these imposed conditions will become

$$\alpha = \frac{2}{3} \left( \frac{b + 2b}{L^T} \right)_{XY} \quad \text{...(1.8)}$$

provided it has only single bonds, thus satisfying the cylindrical symmetry requirement.
1.3 EVALUATION OF OPTICAL POLARIZABILITY:

1.3.1 METHOD BASED ON LIPPINCOTT 6-FUNCTION POTENTIAL MODEL:

For the evaluation of optical polarizabilities, FROST model wave functions [9] have gained much importance. LIPPINCOTT [10] improved the one-dimensional S-function potential model of FROST and applied it to evaluate the potential energy of an n-electron system. AMDS & YOFFE [11] utilized the FROST model wave functions and perturbation theory to evaluate mean polarizability. LIPPINCOTT & STUTMAN [12] developed a semi-empirical 6-function potential model and utilized the method for the evaluation of mean polarizabilities of several polyatomic molecules. LIPPINCOTT, NAGARAJAN & STUTMAN [13] classified a series of molecules according to residual number of degrees of freedom. BERAN & KEVAN [14] studied several classes of compounds such as fluorine and perfluoro carbons, alkylhalides, ethers etc., and suggested that the LIPPINCOTT method has the appeal of being readily extendable to complex molecules and to new molecules (for which no experimental data exists), since the method yields fairly reliable results with modest accuracy.
The model assumes that at each atom there exists a potential which is infinite and everywhere else the potential is zero. The integral of the potential over all space, however, is finite and equal to a parameter which we call the 'δ-function strength' or reduced electronegativity. At each atom then, a δ-function wave function is generated representing the probability amplitude of the electron for this isolated atom. These δ-function atomic orbitals then are linearly combined to form molecular orbitals with the restriction that two atoms may interact at a time and only when bonds are believed to exist between the atoms. The major advantage of a δ-function model lies in its one-dimensional nature, if we consider each bond to be a separate one-dimensional entity, and, since the potential as a non-zero value at only two points along any given bond. Hence we get non-trivial solutions for these problems.

For n-electron system the potential energy is taken to be the sum of single δ-function potentials, each having the following form for a diatomic system

\[ V = - \left[ A \delta \left( X - a/2 \right) + A \delta \left( X + a/2 \right) \right] \quad \text{........ (1.9)} \]
in which, \( X \) is the coordinate of motion along the inter nuclear axis, \( a \) is the function spacing, \( A \) and \( A \) are the \( \delta \)-function strengths or reduced electro negativities (REN'S) for nucleus 1 and 2 respectively, \( g \) is the unit \( \delta \)-function strength and \( (X) \) is a \( \delta \)-function.

The properties of \( \delta \)-function are

\[
\delta (X) = 0 \quad \text{when} \quad X = 0
\]

\[
\delta (X) = \infty \quad \text{when} \quad X = 0
\]

\[
\int_{-\infty}^{\infty} \delta (X) \, dx = 1
\]

for any argument of \( X \).

For the case in question thus the potential is zero everywhere except at the \( \delta \)-function positions, i.e., \( X = a/2 \) and \( X = -a/2 \).

Reduced electro negativity values are, in principle, obtained from the separated atom energies and the equation

\[
A = \left( -\frac{2}{1} E \right)^{1/2}
\]

\[\text{......... (1.10)}\]

is derived using the \( \delta \)-function model.
The $6$-function strength or reduced electronegativity, $C$, is defined as

$$C = \frac{1}{2} \left( A \langle n N \rangle \right) \quad (1.11)$$

for the homonuclear situation. Where $A$ is $6$-function strength, $n$ is bond order (principal quantum number and $N$ is twice the column number in the periodic table. The parameter $R$ is the bond length, $X$ and $X$ are the Pauling electronegativities [15] of atoms $P$ and $Q$ in the bond $P-Q$.

For heteronuclear systems,

$$C_{R_{12}} = \left( \frac{C_C}{R_1 R_2} \right)^{1/2}$$

$$C_{R_{12}} = \left[ \left( \frac{n n N N}{1 2 1 2} \right)^{1/2} \left( \frac{A A}{1 2} \right) \right]^{1/2}$$

An attempt to test the validity of the $6$-function by calculating mean polarizabilities of diatomic and polyatomic molecules was made by LIPPINCOTT & STUTMAN the method consisted in evaluating.
(a) The parallel bond components from the 6-function model,

(b) Corrections to the parallel components from the non-bond region electrons,

(c) The perpendicular bond components from the atomic 6-function polarizabilities and

(d) The mean molecular polarizability.

The details of the evaluation of these components are discussed below.

(a) The Parallel Component:

According to the valence bond interpretation (1) bond region electrons and (2) non-bond region electrons contribute mainly towards bond parallel components. The bond region electron contributions are calculated using a linear combination of atomic 6-function wave functions representing the two atoms involved in the bond; i.e., the expectation value of electronic position squared $\langle x^2 \rangle$ along the bond axis and this is used to obtain the bond region polarizability.
\[ \alpha_{ib} = 4 \pi A_{12} \left( \frac{1}{a_0} \right) (\langle x^2 \rangle) \quad \ldots \ldots (1.12) \]

Where \( A_{12} \) is the root-mean square 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 \( \langle x^2 \rangle \) is the mean square position of a bonding electron and may be expressed as

\[ \langle x^2 \rangle = \left[ \frac{R}{4} + \frac{1}{2(\text{C})} \right] \quad \ldots \ldots (1.13) \]

Here \( R \) is the internuclear distance at the equilibrium position.

A polarity correction is necessary to produce the ionic character in the bond which is of heteronuclear type and is given by

\[ \alpha_{bp} = \alpha_{ib} \cdot \sigma^- \]

where \( \sigma^- = \exp \left[ -\frac{(X_1 - X_2)^2}{4} \right] \]

in which \( X_1 \) and \( X_2 \) are paulings electronegativities of atoms 1 and 2 respectively.
(b) NON-BOND REGION ELECTRON CONTRIBUTION:

The non-bond region contribution to the polarizability \( \alpha_{nn} \) is given as

\[
\sum \alpha_{jn} = \sum f_j \alpha_j \quad \ldots \ldots \quad (1.14)
\]

\( f_j \) is the fraction of the non-bonded electrons of the \( j \)th atom and \( \alpha_j \) is its atomic polarizability. Usually \( f_j \) is calculated on the basis of the outer valence electrons not taking part in bonding, and the basis for such calculation is the LEWIS-LANGMUIR octet rule modified by LINNET [16] as the double quartet of electrons.

For polyatomic molecule, the parallel component of polarizability comes out to be

\[
\sum \alpha_{II} = \sum \alpha_{II,n} + \sum \alpha_{II,p} \quad \ldots \ldots \quad (1.15)
\]

(c) THE PERPENDICULAR COMPONENT:

Since the \( \delta \)-function model is essentially one dimensional in nature, it is necessary to obtain the perpendicular component by a contrived but justifiable
approach. In this regard a detailed discussion was done by LIPPINCOTT & STUTMAN [12]. According to this approach, every isolated atom is allowed to possess three degrees of polarizability freedom, and every bond which is formed between two atoms removes two of these degrees of freedom, with the exception that (1) if two bonds are formed from the same atom and exist in a linear configuration, then only three atomic degrees of freedom are lost and (2) if three bonds are formed in the same atom and exist in a plane, then only five atomic degrees of freedom are lost.

The contribution to the perpendicular component of polarizability is given by

\[
\sum_\text{f} 2\alpha_\perp = nd \left[ \frac{\sum_j X_j \alpha_j^2}{\sum_j X_j^2} \right] \quad \ldots \ldots \ (1.16)
\]

where \( nd \) is the number of residual atomic polarizability degrees of freedom and \( \alpha_j \) and \( X_j \) are the atomic polarizability and electro negativity of the \( j \)th atom respectively.

Hence the optical polarizability is given as

\[
\alpha = \frac{1}{3} \left( \sum \alpha_\parallel + \sum_\text{f} 2\alpha_\perp \right) \quad \ldots \ldots \ (1.17)
\]
MOLECULAR VIBRATION APPROACH:

OTTERBEIN & MEYERS [3] have suggested that individual chemical bonds can be associated with the polarizability ellipsoids, the principal axes being designated as longitudinal (b_L), transverse (b_T) and vertical (b_V) polarizabilities. In most cases where single bond or double bond (to some extent) are involved, b_T = b_V and hence b_L and b_T characterized a bond. Like bond force constants, these bond polarizabilities are also invariant under identical chemical environment and hence are in general transferable. Any change in its value is due to its conformation changes and so, these polarizabilities can be used as finger prints in conformation studies of molecules. This idea has extensively been used by LEFEVRE and his co-workers [17] in their studies of conformational problems in more than hundred systems.

Using these bond polarizability and bond force constants, RAO & MURTHY [18,19] have developed an algebraic expression between (b_L - b_T) and the stretching force constant of the bond K [18,19], and put forward another relation connecting (b_L + 2b_T) with mean amplitudes of vibration of the bond [19].
The relations are given as

$$(b - b_L)^{1/2} \quad (X_a X_b)^{1/2} \quad \left(\frac{aN}{k - b}\right)^{2/3}$$

where $X_B$ and $X_C$ are the electro negativities of atoms B and C in a bond B-C and N is the bond order, K is the stretching force constant and $a$ and $b$ are GORDY'S [20] constants.

$$S = \left[\frac{k}{(3b - 2k)}\right]^1$$

is a dimensionless parameter, $A$ is a constant characteristic of the bond and is given by the relation

$$A = \left[(0.01)(i_j^B / i_j^C)\right]$$

(ij) refers to the products of the row and column numbers of the element B (or C) in the periodic table. This will give the value of $(b - b_T)$ in $10^{-23}$ cm$^3$. 
The second relation is proposed purely on empirical basis and reads as

\[
(\frac{b + 2b}{L_T}) = \left( C \cdot p \cdot \frac{\nu}{\sigma} \right) \sigma^{1/2}
\]

where \( C \) is a constant \( = 5.24 \times 10^{-16} \), \( p \) is the characteristic of the apex atom (or relatively more electro negative atom in a bond) and its values are 1, 1.2, 1.3, 1.4, 1.5 according as the apex atom belongs to 2nd, 3rd, 4th, 5th or 6th row in the periodic table. \( \nu \) is the saturation factor (= the fraction of the electrons in an atom B taking part in bonding) and \( n = +1 \) or \(-1\) according as the molecule is a hydride or non-hydride.

The bond polarizability coefficients \( b_L \) and \( b_T \) and the mean polarizability are evaluated for the semiconductors from these expressions using molecular vibration data.

### 1.3.3 NEW DISPERSION RELATION:

The derivation of the new dispersion relation and the method of evaluation of optical polarizability from new dispersion relation is discussed in chapter II.
1.3.4 OPTICAL POLARIZABILITY FROM MORB STUDIES:

The method of evaluating optical polarizability from magneto optic rotation is discussed in chapter VI where its application to determine the charge carrier concentration is presented.
1.4 DIAMAGNETIC SUSCEPTIBILITY:

When atoms and molecules interact with an external magnetic field, the motion of the electron causes an interaction with an external magnetic field which is formally similar to the interaction with an electric field. If a sample is placed in a magnetic field of strength $H$, a certain intensity of magnetization ($I$) is induced inside the sample. The ratio $I/H$ is the 'magnetic susceptibility' (per unit volume), $K$, and it depends on the material of the body. For an isotropic body the susceptibility is the same in all directions. For anisotropic body materials the susceptibilities along the three principal magnetic axes are different and the measurements on their powdered samples give the average of the three values. For diamagnetic substances generally the susceptibility is independent of temperature and field strength. Considerable changes in diamagnetic susceptibilities with temperature may be attributed to a change in the physical or chemical structure of the material.

While there are a few experimental methods of determination of diamagnetic susceptibility like GOUY'S method which are described fully in section 1.4.2. The new methods of evaluation of diamagnetic susceptibility using alternative new approaches are discussed briefly.
1.4.1 DIAMAGNETIC SUSCEPTIBILITY FROM OPTICAL POLARIZABILITY:

The importance of susceptibility ellipsoid in the stereo chemical analysis and in cotton - mountain effect needs no stress. Several workers like BAUDET, HABBERDITZEL have developed various theoretical methods to determine diamagnetic susceptibility in addition to the existing experimental methods. In a few other methods molecular polarizability is utilised in calculating susceptibility, but these methods proved to be of limited application in scope. For example, KIRKWOOD'S relation shows that susceptibility is proportional to the square root of polarizability. But from several values of diamagnetic susceptibilities and mean polarizabilities of methyl chloride and its higher homologues, it is found that the additive nature of mean polarizability and diamagnetic susceptibility is alike (Fig. 1.3). A graph drawn between the experimental values of mean polarizability vs diamagnetic susceptibility of a few molecular systems (Fig.1.4) shows a general tendency of linearity instead of being non-linear. The graphs drawn shows (Fig. 1.5) that there is only linear relationship between mean polarizability and diamagnetic susceptibility [21].
Fig. 1.3 Molecular polarizabilities and diamagnetic susceptibilities of Alkyl chlorides
Molecular polarizabilities and diamagnetic susceptibilities of a few molecular systems.
Figure 6: Linear and non-linear relationships between polarizability and susceptibility.
It is an established fact that optical polarizability and diamagnetic susceptibility depends on the effective number of electrons which will be free to take part in magnetic and optical interactions. In view of the above observations, a simple relation was suggested by RAO et al [22] and it holds good for any class of molecules.

The relation reads as

\[ \chi = -\left( \frac{\Psi}{M} \right)^{m} S \chi_{M} \]  \hspace{1cm} (1.22)

\( \Psi \) represents the saturation factor = (0.9) with \( s \) representing the number of unsaturated bonds or rings present in a molecule, \( \chi_{M} \) is the degree of covalency of the characteristic group and is given by

\[ \chi_{M} = \left( \frac{1}{n_{1}} \cdot \frac{1}{n_{2}} \cdot \ldots \cdot \frac{1}{n_{n}} \right)^{1/2} \]  \hspace{1cm} (1.23)

1, 2, ..., \( n \) are Paulings percent covalency of the various bonds present in the characteristic group and \( n_{1}, n_{2}, \ldots, n_{n} \) are the bond orders of the bonds 1, 2, ..., \( n \). \( m = 0.72 \times 10^{19} \) is a characteristic constant and it depends on whether the compound is saturated or unsaturated.
For saturated compounds

\[ \chi = -0.72 \times 10^{19} (\sigma') (\alpha) \]

and for unsaturated compounds

\[ \chi = -0.72 \times 10^{19} (0.9) (\sigma') (\alpha) \]

the value of \( \chi \) is obtained in \( 10^{-6} \) CGS emu.

1.4.2 GOUY METHOD:

Several experimental methods are in vogue for the measurement of diamagnetic susceptibility. They are GOUY method, FARADAY [23] method, and NUCLEAR MAGNETIC RESONANCE (NMR) method [24,25]. Theoretical calculations of diamagnetic susceptibilities are discussed in brief in the PASCAL'S method, PASCAL, PACAULT & HOARAN method and HABERDITZL method.
In the GOUY balance, (Fig. 1.6) a long tube divided into two regions by a septum, is suspended from one side of an analytical balance so as to hang vertically in a magnetic field. The septum is in the strongest part of the field and two ends of the tube are in regions of essentially zero field strength.

Distilled water is taken in the tube and at zero current the weight is noted. Then by increasing the current in steps of 0.5 amps the weights are noted.

Now the part of the tube upto the septum is filled with the sample to be investigated and the procedure is repeated. From this molecular susceptibility is determined. The specific or per gram susceptibility is given by

\[ \chi = \frac{k}{\text{density}} \quad \text{......... (1.24)} \]

and the molar susceptibility (\( \chi \)) is equal to

\[ \chi \times \text{molecular weight} \]

\[ \chi \]
Fig. 1.6 GUOCY MAGNETIC BALANCE
The equations for this is given as

\[ \frac{m_1}{m_2} = \frac{X_1 - X_a}{X_2 - X_a} \]  \hspace{1cm} (1.25)

where \( m_1, m_2 \) are the weights without and with magnetic field respectively. \( X_a \), the susceptibility of air can be neglected safely \((X_a = 0.3 \times 10^{-6})\) and \( X_m \), the specific susceptibility is obtained by dividing the magnetic susceptibility by its density. Finally, the molar susceptibility can be obtained by multiplying specific susceptibility with its molecular weights. The molar susceptibility is expressed in \(10^{-6}\) C.G.S. units.

1.4.3 VARIOUS SEMI EMPIRICAL APPROACHES:

1.4.3.1 PASCAL METHOD [26]:

This method is mainly based on atomic concept of susceptibility. Molecular diamagnetic susceptibilities \( X_M \) are considered to be composed of atomic susceptibility constituting the molecules given by the equation

\[ X_M = X_A + \sum \lambda \]

\( X \) is the atomic susceptibility and \( \lambda \) represents constitutive corrections for structural factors. PASCAL'S
constants for the elements are given in table I and a list of constitutive corrections in table II. PASCAL found that the position of oxygen with respect to carbon atoms in the molecule introduced another constitutive correction.

PASCAL referred to 'tertiary' \((C^3)\) and 'quarternary' \((C^4)\) carbon atoms as those in which three or four valences respectively are attached to carbon regardless of actual number of carbon atoms.

For example a tertiary carbon atom is the one designated \(C^*\) in the group

\[
\begin{array}{c}
C \\
| \\
\text{C---C---X} \\
| \\
\text{C}
\end{array}
\]

and a quarternary carbon atom

\[
\begin{array}{c}
C \\
| \\
\text{C---C} \\
| \\
\text{C}
\end{array}
\]

A tertiary carbon atom in the \(\alpha\) position with respect to oxygen group is designated as \(C^*_3\).
Ample support for the PASCAL'S method is given by the excellent agreement between the observed susceptibilities and evaluated values in case of substituted ureas, carbon dioxide, several thioureas and a number of sulphur compounds.
### TABLE I

PASCAL’S CONSTANTS OF THE ELEMENTS X 10

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-2.93</td>
</tr>
<tr>
<td>C</td>
<td>6.00</td>
</tr>
<tr>
<td>N (Open chain)</td>
<td>-5.55</td>
</tr>
<tr>
<td>N (Ring)</td>
<td>-4.61</td>
</tr>
<tr>
<td>M (Monoamide)</td>
<td>-1.54</td>
</tr>
<tr>
<td>N (Diamide, Imide)</td>
<td>-2.11</td>
</tr>
<tr>
<td>O (Alcohol, ether)</td>
<td>-4.61</td>
</tr>
<tr>
<td>O (Aldehyde, Ketone)</td>
<td>-1.62</td>
</tr>
<tr>
<td>O (Carboxyl group)</td>
<td>-3.36</td>
</tr>
<tr>
<td>F</td>
<td>6.30</td>
</tr>
<tr>
<td>Cl</td>
<td>20.10</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>
</tbody>
</table>
**TABLE II**

<table>
<thead>
<tr>
<th>SOME CONSTITUTIVE CORRECTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C = C</strong></td>
</tr>
<tr>
<td><strong>C - C</strong></td>
</tr>
<tr>
<td><strong>C = C - C = C</strong></td>
</tr>
<tr>
<td><strong>N = N</strong></td>
</tr>
<tr>
<td><strong>C = N -</strong></td>
</tr>
<tr>
<td><strong>Benzene</strong></td>
</tr>
</tbody>
</table>
1.4.3.2 PASCAL, PACAULT AND HOARAU METHOD:

The atomic susceptibility data was revised by PASCAL and his co-workers [24,27] in order to reduce the number of constitutive corrections and minimize the error and introduced correction for methyl group. The revised atomic susceptibility data and the constitutive corrections are given in the reference.

1.4.3.3 HABERDITZL METHOD [28]:

Molecular susceptibility in this method is considered to be contributed by inner shell core electrons ($\chi_{IE}$) bonding electron increments $\chi_{BE}$ and $\chi_{TT}$ electrons and it can be expressed by the equation

$$\chi = \chi_{IE} + \chi_{BE} + \chi_{TT}$$

Structural parameters are given due consideration in this approach, under the heading neighbouring bond effects. Magnetic susceptibility contributions for inner shell core electrons ($\chi_{IE}$), bonding electron increments ($\chi_{BE}$) and $\chi_{TT}$-electrons contribution ($\chi_{TT}$) calculated by HABERDITZL on a quantum mechanical basis are in literature.
This method has been improved by GUPTA and co-workers [29], to calculate the molecular susceptibilities of di and poly substituted benzenes by accounting for additional interactions between the substituents which affect diamagnetism.

1.4.3.4 SEMI EMPIRICAL METHOD OF DORFMANN [27,30]:

Following KIRKWOOD'S relation DORFMANN correlated the bond polarizability and diamagnetism. According to him

\[
\chi = -3.11 \times 10^{6} \sqrt{k \chi_{0}} + \chi_{p} \quad \ldots \ldots \quad (1.27)
\]

here \(K\) is the number of electrons and \(\chi_{0}\) is the polarizability of the symmetric system and \(\chi_{p}\) is VANVLECK'S paramagnetic term often called as 'polarization paramagnetism'.

An additional advantage of this method over previous empirical methods is that this separates successfully the measured susceptibilities into LANGEVIN & VANVLECK'S components.
In addition to the empirical methods suggested above, there are a few more methods independently developed by BROERSMA [31], TREW [32] & ANGUS [30] based on the group and bond susceptibilities concepts [34].
REFERENCES:


   Ibid. 47, 3707, 3714, (1967).


34. SRI RAMAN, S., SHANMUGA SUNDARAM, V., & SABESAN, R., J. Annamalai Univ. 27, 213-221, (1966-69).