2.1 INTRODUCTION:

The purpose of this chapter is to give a brief account of recent developments in interatomic force models in solids. These models provide a simple nomenclature and an easily visualized picture, which describes the inter-relation of electronic polarization and short-range forces in solids. It is clear from the quantitative success of the models that this inter-relation is important and these models appear to be well established as tool for the study of perturbed lattice in ionic and covalent crystals. Interpretation of experimentally determined phonon dispersion curves in terms of microscopic theory is still far from being completed. A number of phenomenological models have been developed to understand the structure of these curves.

The formal treatment of lattice dynamical theory preceded the development of modern quantum theory since it was formulated by Born and Von Karman [1] (BVK) in year 1912. A large number of dynamical models have been proposed on the basis of BVK theory and used to
compute the eigen (or phonon) frequencies and eigen vectors of the ionic and other crystals. The important models, among them are:

i) Rigid-Ion Model [2-3] (RIM)

ii) Rigid-Shell Model [4-6] (RSM)

iii) Valence-Force-Field Model [7-11] (VFFM)

iv) Phenomenological Dipolar Models [12-17]

v) Pseudopotential Model [66-68]

2.2 Rigid-Ion Model (RIM):

The foundation for the study of lattice dynamics was laid by Born [1]. This model was used by Lyddane and Herzfeld [48] in their calculation on the vibration spectra of alkali halides. Kellermann [2-3] made a detailed study of the lattice vibrations of NaCl structure on the basis of this model. He assumed that the ions are regarded as the rigid (or undeformable) and unpolarizable point ions or spherically rigid -ions (plus and minus) and they are prevented from collapsing under their mutual Coulomb attraction by the presence of short-range overlap repulsion. Hence this model is often called the rigid ion (or point ion) model.

When the lattice is distorted during vibrations, the ions get displaced and may be represented by dipoles placed at the perfect lattice sites. This causes a change in the lattice energy due to dipole-dipole
interactions summed over all the lattice sites in the solid. Since this interaction is of long-range in character, it is difficult to truncate the summation at any point due to slow convergence. This difficulty was overcome by Kellermann using the technique proposed by Ljwald [18] for the calculation of Modelung energy. According to the picture of RIM, the potential energy of interaction of pair of ions separated by a distance $|\vec{r}| = |\vec{r}^0 (l'k') - \vec{r}^0 (lk)|$ in chapter 1 is given by

$$\phi_{kk'}(r) = \phi_{kk'}^{(C)}(\vec{r}) + \phi_{kk'}^{(R)}(\vec{r})$$

$$\phi_{kk'}^{(C)}(\vec{r}) = \frac{1}{2} \sum_{lk} \sum_{l'k'} Z_k e Z_{l'} e \frac{Z_k e Z_{l'} e}{|\vec{r}|} + \phi_{kk'}^{(R)}(\vec{r})$$

Where $\phi_{kk'}^{(C)}(\vec{r})$ is the Coulombic-contribution of the potential energy and $\phi_{kk'}^{(R)}(\vec{r})$ is the short-range overlap repulsion contribution. The matrix elements correspondingly may be divided into Coulombic and short-range non-Coulombic parts. Here $Z_k e$ and $Z_{l'} e$ are the charges on $k^{th}$ and $k'^{th}$ ions respectively. Thus from equation (1.6)

$$\phi_{\alpha\beta}(lk, l'k') = \phi_{\alpha\beta}^{(C)}(lk, l'k') + \phi_{\alpha\beta}^{(R)}(lk, l'k')$$

In view of (2.1), the matrix elements are

$$D_{\alpha\beta}(\vec{q}, kk') = D_{\alpha\beta}^{(C)}(\vec{q}, kk') + D_{\alpha\beta}^{(R)}(\vec{q}, kk')$$
From the definition of $\phi^{(c)}$ the Coulombic part may be written as

$$D^{(c)}_{\alpha\beta}(q, kk') = Z_k e C_{\alpha\beta}(q, kk') Z_k e$$ ......(2.4a)

Where the elements of the Coulombic matrix $C(q)$ may be written as

$$C_{\alpha\beta}(q, kk') = \frac{1}{\sqrt{m_k m_{k'}}} \sum_l \frac{\delta^2|\vec{r}^0(l'k') - \vec{r}^0(lk)|^{-1}}{\alpha u_{\alpha} (lk) \alpha u_{\beta} (l'k')} \exp\left(i\vec{q}.\left(\vec{r}^0(l'k') - \vec{r}^0(lk)\right)\right)$$ ......(2.4b)

The expression for $D^{(R)}_{\alpha\beta}(q, kk')$ will be of the general type defined by

$$D^{(R)}_{\alpha\beta}(q, kk') = \frac{1}{\sqrt{m_k m_{k'}}} \sum_l \phi^{(R)}_{\alpha\beta}(l k, l'k') \exp\left(i\vec{r}^0(l'k') - \vec{r}^0(l, k)\right)$$ ......(2.5)

$$= R_{\alpha\beta}(q, kk')$$

Thus the matrix $D(q)$ can be written as

$$D(q) = (ZCZ + R)$$ ......(2.6)

Where $Z$ is a $(3n \times 3n)$ diagonal matrix formed from the ionic charges with elements

$$Z_{\alpha\beta}(k k') = Z_k e \delta_{\alpha\beta} \delta_{kk'}$$ ......(2.7)

$C$ and $R$ are $(3n \times 3n)$ diagonal matrices corresponding to the Coulomb and short-range (SR) non-Coulombic parts respectively. In view of (1.12) the equation of motion for RIM is

$$\omega^2(q) U(q) = (R + ZCZ) U$$ ......(2.8)
This is rather a simple equation and is merely the matrix formulation of Kellermann's theory. This leads to the following characteristic equation

\[(R + ZCZ) - \omega^2 I = 0\]  

\[\ldots \ldots \ldots (2.9)\]

Which can be solved for the frequencies \(\omega_j(\vec{q})\). The determinant given by (2.9) is of the order 6 for a cubic diatomic crystals. Since the Coulombic interaction in (2.1) being long-range in nature is not feasible to evaluate the series (2.4b) directly. In fact it does not tend to a unique value as \(\vec{q} = 0\), but to a value, which depends on the relative directions of \(\vec{q}\) and the electrical polarization associated with the mode concerned. Kellermann's [3] technique for solving this convergence problem shall be discussed in Chapter 3.

The acoustical modes in long wavelength limit are directly related to the elastic constants of a solid. The calculations based on the rigid-ion model lead to the Cauchy-relation, which provides equality between the elastic constants \(C_{12}\) and \(C_{44}\). But experimental observations show that the two elastic constants are different and such a relation is not satisfied though the discrepancies in the case of all alkali halides except LIF are small.
The Cauchy-discrepancy \( (C_{12} \neq C_{44}) \) implies the existence of many-body forces arising either from anisotropy in the electron distribution or angle bending. The former effect was thoroughly investigated by Lowdin [19-21] to solve the problems of Cohesion and elastic properties. From his studies Lowdin confirmed the existence of many-body interactions and Lundqvist [22-26] incorporated such forces in the study of the lattice dynamics of the ionic crystals.

While considering the dielectric properties of the ionic crystals, we know that these give a close relation with the long wave optical vibrations but it is seen that the theoretical curves for optical branches show much variation with the experimental dispersion curves. Hence, the rigid-ion model fails in explaining the dielectrical behaviour of the crystals. As this model considers the ion to be rigid and unpolarizable, the high frequency (optical) dielectric constant \( \varepsilon_\infty \) must be equal to unity for all ionic crystals. Experimentally it is found to be incorrect, for example, the observed value of \( \varepsilon_\infty \) for NaCl is 2.25.

Another defect of rigid-ion model is that the values of the longitudinal optical frequency \( \varepsilon_{LO} \) obtained by this theory and by LST (Lyddane-Sacks Teller) relation [27]
The $\frac{\omega_{\text{LO}}}{\omega_{\text{TO}}} = \sqrt{\frac{\varepsilon_0}{\varepsilon_\infty}}$ differ widely. In (2.10) $\varepsilon_0$ is low frequency (static dielectric constant) [28,29]

Szigeti [28,29], while discussing the dielectric properties of alkali halides obtained two important relations namely.

$$m\omega_{\text{TO}}^2 \left( \frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2} \right) = \frac{6a}{K} \ldots \ldots (2.11a)$$

and

$$\varepsilon_0 - \varepsilon_\infty = \frac{(\varepsilon_0 + 2)^2 4\pi Ne_s^2}{9m\omega_{\text{TO}}^2} \ldots \ldots (2.11b)$$

where $N$ is the number of ion pairs per unit volume, $m$ is the reduced mass of an ion pair and $K$ is the compressibility, $e_s^*$ is Szigeti effective charge of well known Szigeti relation [28,29] given by (2.11 b).

It is seen that experimental quantities fail to satisfy the relation (2.11 b). Szigeti [28,29] suggested a replacement of $K$ by the effective compressibility and $e$ by the effective charge $e_s^* (=<e)$ respectively. The ratio $e_s^*/e$ is found to be less than unity, while X-ray diffraction studies show that ionic charges of the alkali halides (except LiF and NaF) are not much different from effective ionic charges. So Szigeti [28,29] suggested that apart from the ionic and electronic polarization, there is some further
polarization due to mutual distortions of neighbor overlap. The effect can be described in terms of charge in the overlap region. These dipoles are dipoles”.

**2.2.1 MODIFIED RIGID-ION MODEL (MRIM):**

This model was first proposed by Vetelino and Mitra [30] and later on developed by their coworkers [31-33] is essentially a rigid-ion model which incorporates (a) the short-range central and non-central interactions and (b) the long-range Coulomb interactions among ions of appropriate effective ionic charge which ensures a proper LO-TO mode splitting. The development of this model is thus based on the concept of Szigeti effective charge [28-29]. The expressions for the crystal energy and secular equation corresponding to MRIM are almost the same as those given, respectively, by (2.1) and (2.6) except the difference in the definition of ionic charge (Ze) and the extension of short-range forces upto second and sometimes third neighbour ions.

The MRIM contains in all five parameters (i) An effective ionic charge Ze, (ii) non-central forces (α, β) for first neighbour, (iii) central second neighbour force constant assuming same for cation-cation and anion interactions and (iv) central third neighbour force constant. These
parameters are determined with the use of three elastic constants and two zone-centre optic mode frequencies.

The effective ionic charge in MRIM is given by

\[(Ze)^2 = \frac{m V_s}{4\pi} \left( \omega_{LO}^2 (\Gamma) - \omega_{TO}^2 (\Gamma) \right) \] ……(2.12a)

\[(Ze)^2 = \frac{m V_s}{4\pi} \omega_{TO}^2 (\Gamma) (\varepsilon_0 - \varepsilon_\infty) / \varepsilon_\infty \] ……(2.12b)

where \(m\) is reduced mass and \(V_a\) is atomic volume.

It is interesting to note that the relation (2.12) is not very much different from the corresponding Szigeti relation [28,29] if one uses \(\varepsilon_\infty = 1\). Also, the values calculated for the effective ionic charges from (2.12) are not much different from the Szigeti, effective charge for most of the crystals.

2.3 RIGID SHELL MODEL:

In the past there has been considerable success in the application of the Rigid Shell Model (RSM) picture to describe the lattice vibrations of ionic or covalent crystals. Dick and Overhauser [16] originally developed the model to calculate the effective ionic charge \(e^*\), which is the measure of the strength of the electric dipole absorption of infrared radiation by the crystal lattice vibrations. The value of \(e^*\) for diatomic
crystals is defined in terms of experimentally determined quantities using Szigeti's relation.

The effective electric field acting on the ion is

$$E_{\text{eff}} = E + \frac{4\pi}{3} P$$

where $E$ is the macroscopic electric field in the crystal; $P$ is the macroscopic polarization and $4\pi/3$ $P$ is Lorentz field. The Lorentz field is believed to be valid for cubic diatomic crystal, composed of ions having rare gas configuration, such as alkali halides.

In the shell model each ion has a rigid core formed by the nucleus and the inner tightly bound electrons. The core is surrounded by a 'rigid' shell of electrons, each shell being bound to its core by an ideal spring. Adjacent shells also interact with each other via springs. As a result of the shell-shell interaction, the ions deform during vibration, i.e., there is a displacement of the electron shell relative to the ion core. This leads to an additional dipole moment polarizability of the ion. Since the polarizability of the negative ion is usually greater than that of the positive ion, the net contribution of the additional moments is opposite to the moment arising from the displacements of the cores. One also takes into account the exchange charge in the region of overlap of the electron orbitals. The exchange charge which is positive, arises from the redistribution of
electrons in the region of overlap; such redistribution occurs because of
Pauli exclusion principle. During a lattice vibration the exchange charge
also makes a contribution to the dipole moment.

Later, it was Cochran [4-6] who developed shell model into a
theoretical scheme to study the lattice dynamics of crystals. He used the
model to study the dispersion curves of germanium and found that the
theoretical dispersion curves were in fair agreement with the experimental
dispersion curves. Cochran [4-6] and Woods et al. [34] used a simplified
version of the shell model to study the dispersion curves of NaI. An
experimental investigation of the dispersion relations for sodium iodide has
given results in good agreement with calculations based on shell model,
despite the fact that the theory contains no parameter which may be
adjusted to fit the data obtained by neutron spectroscopy, while the shell
model might be expected to be less satisfactory for an element having
strongly directed bonds.

The use of the shell model gives the atom the property of
polarizability in an electric field and of distortion. Polarizability under the
influence of short-range forces acting through both cores and shells. The
lattice vibrations, therefore, induce electric field in the crystal. The
existence of dipole moments is ascertained by the infrared absorption of
germanium and these moments result in a long-range interaction between ions. The fact that the shells are taken to be coupled to nearest-neighbour shells, and to have negligible mass, introduces a further long-range force of a non-electrostatic character. The electrostatic interaction in germanium has been taken by Lax to be a quadrupole interaction because, although dipole moments may exist on the atoms during vibration, the total dipole moment of the crystal must vanish because of the space-group symmetry of germanium.

In setting up the equation of motion of the particles in the unit cell we have to consider separately the interactions between the cores, between the shells, and between shells and cores. These give rise to additional terms in the expression for the force constants and one obtains twelve equations of approximation, we get only six vibrational frequencies corresponding to each phonon wave vector.

Let the cores of the positive and negative ions be represented as particle 1 and 2 and their shells as particle 3 and 4 respectively. Two ions have been replaced by shells of charges $Y_1 e$ and $Y_2 e$ and cores with charges $X_1 e$ and $X_2 e$ respectively. Hence,

\[(X_1 + Y_1)e = Z_1 e \quad \ldots\ldots(2.14)\]

\[(X_2 + Y_2)e = Z_2 e \quad \ldots\ldots(2.15)\]
Where $Z_1e$ and $Z_2e$ are the net charge on first and second ion. Further the neutrality of the charge requires

$$(X_1 + X_2 + Y_1 + Y_2)e = 0 \quad \ldots \ldots (2.16)$$

Where $e = |e|$ = electronic charge. As the shells are free to move relative to their core, one can understand the electronic polarization to arise from the electronic dipole moment

$$p(lk) = Y_ke(U^s(lk) - U^c(lk)) \quad \ldots \ldots (2.17)$$

Where $Y_ke$ is the charge on the shell of the ion (lk). The electronic dipole moments ($p$) are determined by both long- and short-range forces and they thus have two contributions. One arising from long-range electrostatic forces and the other from short-range (distortion) polarization mechanism. Thus by writing $P_k$ for $p(lk)$, for convenience, we can express

$$P_k = P^e_k + P^d_k \quad \ldots \ldots (2.18)$$

The harmonic potential energy per unit cell is

$$\phi_{RSM} = \frac{1}{2} \sum_{lk} \sum_{l'k'} \frac{Z_k Z_{l'} e^2}{r(lk, l'k')} + \sum_{k} \frac{P_k^2}{a_k} - \sum_{k} P_k \left( E^m_k + \frac{1}{2} E^p_k \right) + \frac{1}{2} \sum_{lk} \sum_{l'k'} \left[ \frac{1}{Y_k} \right] \left[ \frac{P_k}{Y_k} + \frac{P_k'}{Y_{k'}} \right] \quad \ldots \ldots (2.19)$$

Where $E^m_k$ is the monopole electric field at the ion (lk) of monopole charge $Z_k e$ due to all other ions. $E^p_k$ is the dipoles electric field for the dipoles at site (lk). The prime over the summation means exclusion
of the terms with $l_k = l'_k$, is defined by $\alpha_k = (Y_{ke})^2 / K_k$ where $K_k$ is core-shell spring constant of $k^{th}$ ion.

The equation of motion can be derived from above potential energy and written as,

$$\omega^2 (\bar{q}) m U = (R + ZCZ) U + (T + ZCY) W \quad \ldots \ldots (2.20a)$$

$$0 = (T' + YCZ) U + (S + YCY) W \quad \ldots \ldots (2.20b)$$

The shell masses have been assumed to be negligible in writing (2.20b), $Y$ is a $(3n \times 3n)$ dynamical matrix of shell charge ($Y_{ke}$ with its elements) $Y_{\alpha \beta} (k k') = Y_{ke} \delta_{\alpha \beta} \delta_{kk'}$, $Z$ is the charge matrix defined by (2.7). $U$ and $W$ are $3n$-component column matrices represented by the core and relative core-shell displacements, such that $U(lk) = U^c (lk)$ and $W (lk) = [U^s (lk) - U^c (lk)]$. $R$, $T$, and $S'$ ($T^t$ being the transpose conjugate of $T$) are the short-range core-core, core-shell and shell-shell interaction matrices such that [34]

$$R = D + S + 2F \quad \text{and} \quad T = S + F$$

with $D$, $S$ and $F$ representing $(3n \times 3n)$ matrices due to various interactions. The elements of the $(3n \times 3n)$ matrix $S$ are defined as [6].

$$S_{\alpha \beta} (q, kk') = S_{\alpha \beta} (q, kk') + K_k \delta_{\alpha \beta} \delta_{kk'} \quad \ldots \ldots (2.21a)$$
such that \( S' = S + K \) with \( S \) as the SR shell-shell interaction matrix (3n x 3n) and \( K \) as the diagonal matrix (3n x 3n) specified by the core-core spring force constant \( K_k \). \( C \) is the same Coulomb interaction matrix (3n x 3n) as defined by (2.4b).

In order to reduce the number of parameters, the short-range forces are assumed to act entirely through the shells. i.e., \( R = T = S \). The elimination of \( W \) from (2.20a) and (2.20b) gives

\[
\omega^2 (\vec{q}) m \mathbf{u} = D(\vec{q}) \mathbf{u}
\]

(2.21b)

where the dynamical matrix corresponding to the rigid shell model (RSM) is

\[
D(\vec{q}) = (R + ZCZ) - (T + ZCY)(S + K + YCY)^{-1} (T^\dagger + YCS)
\]

(2.22a)

The first term on the right hand side corresponds to RIM. Thus the second term represents explicitly the additional contributions arising from the electronic polarization. This term involves three and four-body forces between the ions even if the individual \( R, T \) and \( S \) involve only two-body forces. A substitution of the dynamical matrix (2.22a) in the secular determinant and its solution will yield 3n vibration frequencies \( \omega_j^2 (q) \) corresponding to each phonon wave vector (\( q \)). Along the principal symmetry directions \( \Delta, \Sigma, \Lambda \) this determinant reduces to lower order determinant (2 x 2) for diatomic cubic crystals similar to
The equivalent of a SM treatment was first applied to zinc-blende structure by Tolpygo [35]. His treatment was based on a potential energy expression, which omitted the shell-shell interactions at a time when the importance of these terms was not yet realized. Kaplan and Sullivan[36] have corrected this omission and have included second nearest neighbours in their treatment. They gave expressions for eleven - experimental quantities. The three elastic constants the piezoelectric constant, the high and low frequency dielectric constants and five special lattice frequencies at centre and boundary of Brillouin zone Without second nearest neighbours these expressions contain eleven parameters. Omitting second nearest neighbours Kaplan and Sullivan [36] have obtained the value of eleven parameters for GaAs and ZnS.

Kushwaha [37] incorporated the bond-bending interaction within the framework of RSM and studied the lattice dynamics of ionic and partially ionic (zinc-blende) crystals. Although bond-bending force shell model (BBFSM) involves 14 parameters for zinc-blende structure, yet it provides an adequate and interesting insight regarding the interactions without ionic and partially ionic crystals.
2.4 VALENCE FORCE FIELD MODEL (VFFM):

2.4.1 INTRODUCTION:

Valence force fields have been extensively used in the analysis of the vibrational spectra of molecules in the gaseous state. Various attempts have been made to study the dynamical behaviour of solids with the application of valence force field. Herman [36] and Pope [39] to study the lattice dynamics of the elemental semiconductors (germanium and silicon). Singh and Dayal [40] have also studied the lattice dynamics of elemental semiconductor on the basis of VFF. First time, the idea of VFF has been introduced by Terent [7] for crystals. Nakayama and Oduima [8,9] have also studied triagonal selenide on the basis of VFF. The application of VFF to the lattice dynamics of sphelarite and Wurtzite ZnS has been also done by Numovici and Birman [10]. Earlier, general valence force field (GVFF) has been proposed by Musgrave and Pope [11] to the case of diamond type lattices. The classical approach to the problem of molecular structure assumes that the molecule consists of mass points, having some electrical properties and bound together by forces of various kinds. Let us use the mass weighted Cartesian displacement coordinates to describe the molecular system of N atoms. In terms of the time derivatives of these coordinates the kinetic energy T is,
where \( q_i \) represents one of the mass weighted cartesian displacement coordinates. The potential energy will be some function of the displacement and therefore for small values of the displacements, the potential energy \( \phi \) may be expressed as a power series in the displacement \( q_i \):

\[
2\phi = 2\phi_0 + 2\sum_{i=1}^{3N} \left( \frac{\partial \phi}{\partial q_i} \right) q_i + 2\sum_{i,j=1}^{3N} \left( \frac{\partial^2 \phi}{\partial q_i \partial q_j} \right) q_i q_j + \text{higher terms} \quad \ldots (2.23b)
\]

or

\[
2\phi = 2\phi_0 + 2\sum_{i=1}^{3N} \phi_i q_i + \sum_{i,j}^{3N} \phi_{ij} q_i q_j + \text{higher terms} \quad \ldots (2.23b)
\]

By choosing, the zero of energy so that the energy of the equilibrium configuration is zero \( \phi_0 \), may be eliminated. Furthermore, when all the \( q \)'s are zero, the atoms are all in their equilibrium positions so that the energy must be a minimum for \( q_i = 0, i=1,2,3 \) —Therefore

\[
\left( \frac{\partial \phi}{\partial q_i} \right)_0 = \phi_i = 0 \quad \text{for } i = 1,2,\ldots,3N \quad \ldots (2.24)
\]

For sufficiently small amplitudes of vibration, the higher terms (cubic, quartic, etc., in the \( q \)'s) can be neglected,

\[
2\phi = \sum_{i,j=1}^{3N} \phi_{ij} q_i q_j \quad \ldots (2.25)
\]
In which $\phi_{ij}$ are the force constants given by

$$\phi_{ij} = \left( \frac{\partial^2 \phi}{\partial q_i \partial q_j} \right)_{o} \hspace{1cm} (2.26)$$

with

$$\phi_o = \phi_p \hspace{1cm} (2.25b)$$

In many cases, however, it is more convenient to introduce a new, set of $3N-6$ coordinates $S_1, S_2, \ldots, S_{3N-6}$ which are defined by means of the six conditions and $3N-6$ relations. Such coordinates are known as internal coordinates* because they describe the internal configuration of the molecule without regard for its position as a whole in space.

**2.4.2 POTENTIAL FUNCTION:**

To obtain an expression for the potential energy of molecules, it becomes essential to make certain approximations about the nature of the forces operating between atoms of the molecules. This helps in determining the force constants of the molecules. One of the simplest approximations used for the potential energy of the molecules is the central forces approximation. It is assumed that the forces holding the atoms in their equilibrium positions act only along the lines joining pairs of atoms and that every pair of atoms is connected by such a force. This type of force function would result if the molecule were held together by purely
ionic interactions. In practice, this approximation has not been particularly successful and is now of little use.

**2.4.3 VALENCE FORCE APPROXIMATION:**

Another approximation which is at once free of the objection raised against central forces for linear molecules, and also more compatible with chemical ideas regarding interatomic forces is the so-called valence force approximation. In this case the forces considered are those, which resist the extension or compression of valence bonds, together with those, which oppose the bending or torsion of bonds. For ammonia, the potential function would be,

\[ 2\phi = \sum_i F_i r_i^2 + \sum_{i<j}^3 \sum_{a}^3 F_{a} \alpha_{ij}^2 \]  \hspace{1cm} (2.27)

where \( r_i \) is the extension of a bond and \( \alpha_{ij} \) is the distortion of the valence angle between bonds \( i \) and \( j \).

The simple valence force field can be generalized by the inclusion of one internal coordinate due to the changes in other coordinates. The resulting potential function is known as the General Valence Force Field (GVFF).

Another approach for molecules, which resists treatment by simple potential function was proposed by Urey and Bradley [41], who suggested the use of a mixed potential function. The potential function
known as Urey Bradley valence field is the combination of a simple valence force field and the central interaction terms between non-bonded atoms. In physical terms, this sort of the potential function seeks to take into account the van der Waals forces between non-bonded atoms.

The Urey-bradley valence force field [41] (UVFF) is assumed to describe the forces operating inside the covalent solids or the solids, which crystallize in zinc-blende structure. Considering the cubic ZnS crystal lattice, the potential energy of such crystal under UVFF approximation is written as,

\[ 2\phi = \sum r \alpha (\delta r) + \sum \mu_1 (\delta r, \delta \theta) + \sum \mu_2 (\delta r, \delta \theta) + \sum \gamma_1 (\delta \theta) + \sum \gamma_2 (\delta \theta) \ldots (2.28) \]

Summation extends over bond lengths and bond angles. \( \alpha \) is the force constant corresponding to Zn-S bond extension, \( \mu_1 \) is the force constant associated with non-bonded second-neighbour Zn-Zn central-interaction, \( \mu_2 \) is the force constant associated with non-bonded second neighbour S-S central interaction, \( \gamma_1 \) and \( \gamma_2 \) represent the force constants associated with the bending of the bond angles S-Zn-S and Zn-S-Zn.

Following the method of Wilson et. al. [42], the Urey-Bradley valence coordinates are transformed into atomic displacement coordinates. This transformation enables one to express the potential energy in terms of the components of the displacements of atoms of the
crystal. Contributions to potential energy from other neighbours except first and second neighbours have been ignored.

2.4.4 TRANSFORMATION RELATIONS:

The potential energy of the lattice under UVFF is expressed in terms of the internal coordinates which are unaffected by translations or rotations of the molecule as whole. These are particularly important because they provide the most physically significant set for use in describing the potential energy of the molecule. The kinetic energy, on the other hand, is more easily set up in terms of cartesian displacement coordinates of the atoms. The interatomic distances or the angles between chemical bonds or both are applicable in the case of atoms or molecules of solids having infinitesimal amplitude of vibration, hence all displacements can be considered infinitesimal and only first order or linear terms need be evaluated. Let \( S_t \) represent one of the 3N-6 internal coordinates and \( \xi_i \) represents one of the cartesian displacement coordinates [80].

Then,

\[
|S_t| = \sum_{i=1}^{3N} B_{ti} \xi_i
\]

(2.29)

Where, \( t = 1, 2, \ldots, 3N-6 \). Coefficients \( B_{ti} \) are the constants determined by the geometry of the molecule. Instead of using three cartesian coordinates to describe the displacement of an atom, it is
convenient to introduce a vector $\bar{\rho}_a$ for each atom $\alpha$ whose components along the three axis directions are the $\xi, \xi', \xi''$ for that atom. Similarly it is useful to group the coefficient $B_i$ for a given $S_t$ into sets of three, each set $B_i, B_i', B_i''$ being associated with a given atom $\alpha$. These quantities can be considered as the components of a vector $\bar{s}_{i\alpha}$ associated with the atom $\alpha$ and with internal coordinate $S_t$. Then equation (2.29) can be written as [81]

$$|\bar{s}_t| = \sum_{\alpha=1}^{N} \bar{s}_{i\alpha} \bar{\rho}_\alpha$$

.....(2.30)

This equation can be used to obtain the relation between the change in bond length, bond angles and displacement of atoms. Furthermore, simple rules can be worked out for writing down the vectors $\bar{s}_{i\alpha}$. The physical meaning of vector $\bar{s}_{i\alpha}$ is as follows: Let all atoms except atom $\alpha$ be in equilibrium positions. The direction of $\bar{s}_{i\alpha}$ is the direction in which a given displacement of atom $\alpha$ will produce the greatest increase of $S_t$, the magnitude of $\bar{s}_{i\alpha}$ is equal to the increase in $S_t$, produced by unit displacement of the atom in this most effective direction. These statements follow from consideration of (2.30) above.

The simple type of coordinates in terms of which the potential functions for most molecules are usually expressed will now be worked out in detail. We should remember that the internal coordinate $S_t$ either refers
to bond stretching or valence angle bending.

### 2.4.5 BOND STRETCHING:

Let the internal coordinate $S_t$ represent the increase in the distance between the atom 1 and 2. It is obvious that the most effective direction to displace the end atoms is along the line connecting them, but in directions away from each other. Furthermore, the vectors $\mathbf{s}_t$ and $\mathbf{s}_t$ should here be unit vectors. For the coordinate $S_t$, all other vectors $\mathbf{s}_\alpha$ ($\alpha \neq 1, 2$) are zero since displacements of other atoms will not effect $S_t$.

It is often convenient to express the vectors $\mathbf{s}_t$ in terms of unit vectors along certain of the interatomic connecting lines, for example, along the chemical valence bonds. Hence for bond stretching (see equation 2.30) the internal coordinate $S_t$, can be expressed as,

$$|\mathbf{S}_t| = \sum_{\alpha=1}^{N} \mathbf{s}_{\alpha} \cdot \mathbf{P}_\alpha$$

Let $\mathbf{e}_{21}$ be the unit vector directed from atom 2 towards the atom 1. Similarly, let $\mathbf{e}_{12}$ be the unit vector directed from atom 1 towards the atom 2. Clearly,

$$\mathbf{s}_{11} = \mathbf{e}_{12} = -\mathbf{e}_{21}, \quad \mathbf{s}_{12} = \mathbf{e}_{21}$$

Hence, from equation (2.31)
If \( u_1, v_1, w_1 \) and \( u_2, v_2, w_2 \) be the components of \( \vec{\rho}_1 \) and \( \vec{\rho}_2 \), along x, y and z axes, respectively, then

\[
\vec{\rho}_1 = \vec{i}u_1 + \vec{j}v_1 + \vec{k}w_1 
\]

and

\[
\vec{\rho}_2 = \vec{i}u_2 + \vec{j}v_2 + \vec{k}w_2 
\]

Where \( \vec{i}, \vec{j}, \vec{k} \) are the unit vectors along x, y and z axes, respectively. Let \( \lambda_{12}, \mu_{12} \) and \( v_{12} \) are the direction cosines of \( \vec{e}_{12} \) with respect to x, y and z axes.

\[
\vec{e}_{12} = \vec{i}\lambda_{12} + \vec{j}\mu_{12} + \vec{k}v_{12}
\]

Let \( |\Delta \vec{r}_{12}| \) represent the change in the radial distance between the atom 1 and 2, \( \Delta \vec{r}_{12} \) is the proper internal coordinate \( S_t \) to be transformed. Thus,

\[
|\Delta \vec{r}_{12}| = |(\vec{i}\lambda_{12} + \vec{j}\mu_{12} + \vec{k}v_{12})(\vec{i}(u_2 - u_1) + \vec{j}(v_2 - v_1) + \vec{k}(w_2 - w_1))|
\]

or

\[
|\Delta \vec{r}_{12}| = \lambda_{12}(u_2 - u_1) + \mu_{12}(v_2 - v_1) + v_{12}(w_2 - w_1)
\]

This equation represents the internal coordinate \( |\vec{S}_t| = |\Delta \vec{r}_{12}| \) bond stretching in terms of components of the displacements of atoms and the direction cosines of bond joining the atom 1 and 2.
2.4.6 VALENCE ANGLE BENDING:

The change in the angles of the valence bonds can be expressed in terms of the direction cosines of the bonds with respect to a given coordinates system and the components of the displacements of atoms. For this let us suppose that there are three bonded atoms 1, 2 and 3 (Fig. 2.1). The angle between the 3,1 and 3,2 at atom 3 is $\phi$. This time the change $\Delta \phi$ in $\phi$ is the internal coordinate $\vec{s}_1$. The bond length can be represented by $|\vec{r}_{31}|$ and $|\vec{r}_{32}|$. In this case the vector $\vec{s}_{11}$ will be perpendicular to the bond $|\vec{r}_{31}|$ and directed outwards. The magnitude $|\vec{s}_{11}|$ is equal to $1/|\vec{r}_{31}|$. Similarly the vector is perpendicular to $|\vec{r}_{32}|$ bond and directed outwards. The magnitude $|\vec{s}_{12}|$ is equal to $1/|\vec{r}_{32}|$. The $\vec{s}_{13}$ vector for apex atom 3 is the sum of the vectors $\vec{s}_{11}$ and $\vec{s}_{12}$ with the reverse sign. Hence,

$$\vec{s}_{13} = - (\vec{s}_{11} + \vec{s}_{12})$$

(2.38)

These $\vec{s}$ vectors can be written in terms of unit vectors along the bond. Let $\vec{e}_{31}$ and $\vec{e}_{32}$ be the unit vectors from the apex angle $\phi$ along the bonds $|\vec{r}_{31}|$ and $|\vec{r}_{32}|$ respectively. It can be easily shown that

$$\vec{s}_{11} = \frac{\cos \phi \vec{e}_{31} - \vec{e}_{32}}{|\vec{r}_{31}| \sin \phi}$$

(2.39)
Figure 2.1 Vectors $s_1$, $s_2$ and $s_3$ for the increase in the angle $\phi$ formed by two bends.
The equations (2.37) and (2.41) are utilized to obtain the relations between the internal coordinates corresponding to bond-stretching and bond bending into the components of atomic displacement coordinates. These equations are of principal importance for the setting up of the secular, equation of any lattice under UVFF approximation.

2.4.7 APPLICATION OF UVFF FORMULATION TO ZINC BLENDE CRYSTALS:

In zinc-blende crystals, each atom has four nearest atoms of opposite type and twelve atoms (next nearest neighbours) of the same type (Table 1.1). If the bond length between atoms is denoted by \(|\vec{r}_o|\), then the value of each of \(|\vec{r}_{31}|\) and \(|\vec{r}_{32}|\) of equation (2.41) will be equal to \(r_o\). Thus,

\[ |\vec{r}_o| = |\vec{r}_{31}| = |\vec{r}_{32}| \]

The problem of transformation is simplified by taking one of the atoms of the crystals lattice at the origin of the coordinates system. The new expression for the internal coordinates \(S_i\) corresponding to bond-bending is obtained by substituting values of \(s_{12}, s_{13}, s_{14}\) in equation 2.31.
The equation (2.42) is reduced in terms of the direction cosine and the components of displacement of 1, 2, and 3. Thus, on simplification.

\[ S_t \Delta \phi_{132} = \frac{\cos \phi}{|\vec{r}_0| \sin \phi} \left( (\lambda_{31} u_1 + \mu_{31} v_1 + v_{31} w_1) - (\lambda_{32} u_2 + \mu_{32} v_2 + v_{32} w_2) \right) \]

\[ + \frac{1}{|\vec{r}_0| \sin \phi} \left( (\lambda_{23} u_1 + \mu_{23} v_1 + v_{23} w_1) - (\lambda_{32} u_2 + \mu_{32} v_2 + v_{32} w_2) \right) \]

\[ + \frac{1 - \cos \phi}{|\vec{r}_0| \sin \phi} \left( (\lambda_{31} - \lambda_{23}) u_3 + (\mu_{31} - \mu_{23}) v_3 + (v_{31} - v_{23}) w_3 \right) \] .......(2.43)

In equation (2.43), \( u_1, v_1 \) and \( w_1 \) are the components of \( \vec{p}_1 \) along \( O_x, O_y \) and \( O_z \). Similarly \( u_2, v_2, w_2 \) and \( u_3, v_3, w_3 \) are the components of \( \vec{p}_2 \) and \( \vec{p}_3 \) along \( O_x, O_y \) and \( O_z \) directions, respectively. Now one of the atoms of the zinc blende crystal lattice is taken as the origin of the coordinate axes and is indexed as 'O'\(^{th}\) atom (Fig.1.1). Other atoms which are the first and second neighbours of the O\(^{th}\) atom are also indexed. Replacing 3 by 0, the internal coordinates corresponding to bond bending in terms of direction cosines and components of displacements of atoms, Therefore,

\[ |\Delta \tilde{r}_{01}| = \lambda_{01} (u_1 - u_0) + \mu_{01} (v_1 - v_0) + v_{01} (w_1 - w_0) \] .......(2.44a)
and,

$$\Delta \phi_{102} = \cos \phi / |\vec{r}_0| \sin \phi \left( (\lambda_{01} u_1 + \mu_{01} v_1 + \nu_{01} w_1) + (\lambda_{02} u_2 + \mu_{02} v_2 + \nu_{02} w_2) \right)$$

$$+ 1/|\vec{r}_0| \sin \phi \left( (\lambda_{20} u_1 + \mu_{20} v_1 + \nu_{20} w_1) + (\lambda_{01} u_2 + \mu_{01} v_2 + \nu_{01} w_2) \right)$$

$$+ \frac{1 - \cos \phi}{|\vec{r}_0| \sin \phi} \left( (\lambda_{01} + \lambda_{02}) u_0 + (\mu_{01} + \mu_{02}) v_0 + (\nu_{01} + \nu_{02}) w_0 \right) \quad \text{.........(2.44b)}$$

Using these transformation relations, all the internal coordinates corresponding to the bond-stretching, bond-bending and Van der Waals bond-stretching (central forces between non bonded atoms) are transformed into the components of the displacements of the first and second neighbours of reference atom.

Once the internal coordinates are transformed into Cartesian displacement components of atoms, the potential energy of the lattice under second neighbour harmonic approximation is expressed in terms of the direction cosines of the bonds and the components of the atomic displacements. The valence force Field inside the crystal is obtained from

$$\vec{F} = - \text{grad} \phi \quad (2.45)$$

The calculations of potential energy and hence force are made from the geometry of zinc-blende structure crystals.

2.5 Deformable Dipole Model (DDM) [12]:

The development of DDM is based on the philosophy [28-44] and postulates [12,45,46] according to which the overlap between the neighbouring ions alters, when they are relatively displaced. This results into change of charge distribution in the overlap region. This is described in terms of various multipoles, out of which only dipoles are retained in DDM and considered to reside on the ions themselves [47]. These dipoles can be identified with the mechanically induced dipoles of shell Model. A specific examination of the frame work of DDM reveals that there are three types of dipole moments. One of them arises due to the displacement dipole produced as a result of the displacement of ions as a rigid sphere. It corresponds to the ionic as a rigid sphere. It corresponds to the ionic polarization and gives rise to the coulomb potential $\phi^r(\vec{r})$ which has been treated by Kellermann [2]. The second type is the polarization dipole moment which owes its origin to the deformation of electron cloud of an ion (Ik), caused by the external electric field $\vec{E}$. The dipoles of third kind are produced due to slight distortion in the electron cloud about a given ion by its overlap with the charge distributions of the neighbouring ions. In this case the dynamical matrix can be written as

$$D(\vec{q}) = (R + ZCZ) + (- (ZC + \gamma C) (\alpha^{-1} + C)^{-1} (CZ + CY)$$

$$+ (\gamma CZ + ZC\gamma + CY))$$

\[\ldots\ldots(2.46)\]
where $R$, $Z$, $C$ are $(3n \times 3n)$ matrices. The first term is the dynamical matrix appropriate to RIM. The elements of the matrix $\gamma(\vec{q})$ are due to the deformability of ions and are given by

$$\gamma_{\alpha\beta}(kk'/\vec{q}) = \sum_I \gamma_{\alpha\beta}(lkl'k')e^{ik\cdot(r(lk)-r(l'k'))} \ldots \ldots \ldots (2.47)$$

Also $\alpha = \alpha_k \delta_{kk'} \delta_{\alpha\beta}$ is a $(3n \times 3n)$ matrix specified by the polarizabilities $\alpha_k$ of ions. It is interesting to note that if we ignore the deformability of the ions (i.e., $\gamma = 0$), then we recover the Born-Huang [44] generalization or the Lyddane-Herzfeld model [48]. In addition, if we neglect the electronic polarization (i.e., $\alpha = 0$), then we obtain the RIM.

In principle DDM introduces terms of a many-body character into the lattice potential energy.

**2.6 BOND CHARGE MODEL (BCM):**

The bond charge model developed by Martin [49,50] is an outcome of the generalization of the bond-charge Concept postulates by Philips [51]. The electronic polarization in it is assumed to arise from the bond charges (BC), which are situated at the centre of the covalent bonds and assumed to stay half way between the atoms during their movement. These BC's interact with the ion cores and with each other via a pure Coulomb-potential. The self interaction of a bond charge with itself has been excluded and this assumption is equivalent to the inclusion of the
exchange and correlation effects. Martin has regarded each BC to split into two, each half moving with one of the atoms associated with the bond. The contribution to the dynamical matrix due to the motion of these BC's against the rest of the lattice comes out to be dependent of $\mathbf{q}$ since they are not situated at the lattice sites.

The Martin's BCM is apparently very much similar to the Hardy's DDM and Suffers from several limitations which has been pointed out by Sinha [52]. Weber [13a] has extended this approach to tetrahedrally coordinated semiconductors.

Weber [13a] has derived the dynamical matrix of his BCM treating the BC'S as independent Lattice particles. The equation of motion under harmonic and adiabatic approximation is

$$m\omega^2 U = \left( (R + (4 \frac{Z^2}{\varepsilon}) C_R) U + (T - (\frac{2Z^2}{\varepsilon}) C_T) S \right) \ldots \ldots \ldots \ldots \ldots \ldots (2.48a)$$

$$0 = \left( (T' - (\frac{2Z^2}{\varepsilon}) C'_T) U + (S + (\frac{Z^2}{\varepsilon}) C_S) S \right) \ldots \ldots \ldots \ldots \ldots \ldots (2.48b)$$

where, $m$, $Z$ and $\varepsilon$ are the ion mass, the charge of the BC and dielectric constant, respectively. The hyper vectors $U$ and $S$ are the displacements of two ions and four BC'S. $R$, $T$ and $S$ are the Fourier transformed force constant matrices of the SR ion, ion – BC and BC – BC interaction. $C_R$, $C_T$, and $C_S$ denote the corresponding LR Coulomb-
matrices. The adiabatic approximation has been expressed by having put the mass of the BC'S equal to zero on the left hand side of equation (2.48b). This model involves four parameters corresponding to the four types of interactions, (i) a central potential between nn ions, (ii) Coulomb potential of point charges at the sites of the ions and the bonds, (iii) central potential between nn ions and BC'S and (iv) the interaction between two adjacent bonds described by Keating potential [53].

The key feature of this mode is that the very flat TA branches in covalent crystals are understood in terms of the weak effective ion-BC forces. Rustagi and Weber [13b] extended the adiabatic BCM to describe phonon dispersion relations and elastic properties of III- V semiconductors. A symmetry of the bond-charge position and of the force constants involving them is found to be the main consequence of ionicity.

2.7 BREATHING-SHELL MODEL (BSM):

The Breathing-shell model originally proposed by Schroder [14] and later on developed by Nusslein and Schroder [54] takes account of isotropic deformation of the electron shells as a new degree of freedom, which is equivalent to a breathing motion of the shells during lattice vibrations. It is assumed that the radius of the shell after deformation can be either smaller or greater than the actual radius of the shell. Thus, the
Ionic radius in BSM is variable and can be regarded as a new degree of freedom. The total crystal energy per unit cell for BSM is

\[ \Phi^{BSM}(\vec{r}) = \frac{1}{2} \sum_{l_k} \sum_{l'_k} Z_k Z_{l'} e^2 \left| \frac{r(l_k, l'_k)}{r(l_k, l'_k)} \right| + \frac{1}{2} \sum_{l_k} \sum_{l'_k} V(\vec{r}(l_k, l'_k)) - d(l_k) - d(l'_k) + \frac{1}{2} \sum_k n_k (d(l_k) - d_0(l_k))^2 \]  

\[ \text{\ldots\ldots\ldots\ldots\ldots (2.49)} \]

The equilibrium ionic radius \( d_0(l_k) \) of a free-ion has changed to \( d(l_k) \) due to breathing during lattice vibrations. \( N_k \) is the spring force, constant which controls the breathing of the \( k \)th ions. Introducing the potential energy in RSM frame-work of (2.20) and assuming that no kinetic energy is associated with the breathing motion (adiabatic approximation), one gets:

\[ \omega^2 (\vec{q}) m U = (R + ZCZ) U + (R + ZCY) W + QV \]  

\[ 0 = (R' + YCZ) U + (R' + K + YCY) W + QV \]  

\[ 0 = Q'(U + W) + HV \]  

\[ \ldots\ldots\ldots\ldots\ldots (2.50a) \]

\[ \ldots\ldots\ldots\ldots\ldots (2.50b) \]

\[ \ldots\ldots\ldots\ldots\ldots (2.50c) \]

\( C \) is a \((6 \times 2)\) matrix. \( K \) is a diagonal matrix appropriate to the shell-core interaction of the anions. \( H \) is the \((2 \times 2)\) dynamical matrix corresponding to the 'breathing-breathing' force constant. \( V \) is a 2-vector breathing amplitude matrix. The \((6 \times 6)\) dynamical matrix \( D(\vec{q}) \) for BSM is thus.

\[ D(\vec{q}) = (R' + ZCZ) - (R' + ZCY)(R' + K + YCY)^{-1} \]

\[ = (R'' + YCZ) \]  

\[ \ldots\ldots\ldots\ldots\ldots (2.51) \]
\[ R' = R - QH^{-1}Q' \quad \ldots \ldots \ldots (2.50) \]

\( Q \) is a 2 x 2 matrix and \( Q' \) is its transpose conjugate. Notations and their significance have been explained by Singh [55].

2.8 THE DEFORMATION SHELL MODEL [15] (DSM):

It includes the effect of electron shell deformation in terms of SR three body interactions between like particles. In equilibrium state of the lattice, the electron shells around each nucleus are described by a definite charge density function. When the ions suffer displacement from their equilibrium position, the charge density function is altered owing to the deformation the electron-shells under the influence of overlap forces. This phenomenon gives rise to a deformation energy

\[ E^D = \frac{1}{2} \sum_{lk} \alpha(k)a^2(lk) \quad \ldots \ldots (2.53) \]

where \( \alpha(k)/2 \) is the energy associated with unit deformation of the \( k^{th} \) ion, \( a(lk) \) is the deformation produced in the \( (lk) \) ion by its nearest neighbour (nn) ions. \( a(lk) \) is the largest when two unlike nn move in opposite directions, while it is zero when they move by equal amount in the same direction.

The dynamical matrix \( D(\ddot{q}) \) for DSM is

\[ D(\ddot{q}) = (R' + ZCZ) - (R' + ZCY) (R' + K + YCY)^{-1} (R'^t + YCZ) \quad \ldots \ldots (2.54) \]
where, $R' = R + D_0$, $D_0$ is a $(6 \times 6)$ deformability tensor.

2.9 CHARGE TRANSFER SHELL MODELS:

It is well known that the shells in RSM descriptions have a constant charge which does not vary during lattice vibrations. In reality, this shell charge varies linearly with the displacement of the nearest neighbours (nn). This variation occurs due to the overlap of the wavefunctions of the outer electrons of the ions. Such phenomenon can be understood as: charge-transfer (or exchange) mechanism whose employment in RSM has laid to the development of the following important models.

2.9.1 EXCHANGE CHARGE SHELL MODEL (ECM):

The short-range polarization mechanism implied in RSM has revealed that this mechanism alone is not adequate to describe the dielectric behaviour of ionic crystals. This limitation led Dick and Overhauser [16] to postulate an additional polarization mechanism owing its origin to Pauli exclusion Principle which acts to reduce the electron charge density of the ions in the overlap region and hence leads to redistribution of the charge on the ions. This gives rise to a charge depletion which may be represented as the superposition of point charge of suitable magnitude called the exchange charge considered to be located
at the centre of gravity of overlap region. The dipole moment per unit volume associated with this mechanism is called as the exchange charge polarization.

The total magnitude of this exchange charge (EC) is given by Dick and Overhauser [16]

\[ q_{EC} = \frac{r_{ss}}{e\gamma} \cdot b \exp(-r_{ss}/\rho) \quad \ldots \ldots \ldots \ldots (2.55) \]

where, \( \gamma \) is a dimensionless parameter and \( r_{ss} \) and \( r \) are the shell-shell and internuclear separations, \( \rho \) is the range parameter. These exchange charges are located on the line of the centres of the shells and at a distance \( (r_1 r_{ss}/r) \) from the positive ion cell centre with \( r_1 \) as the positive ion radius.

The exchange charge shell model (ECM) is originally proposed by Dick and Overhauser [16] and later on developed by Marston and Dick [56-58]. The crystal potential energy corresponding to ECM is expressed as

\[ \Phi_{ECM} = \Phi_{RSM} + \Phi^{EC} \quad \ldots \ldots \ldots \ldots (2.53) \]

2.9.2 VARIABLE CHARGE SHELL MODEL [17] (VCM):

The fundamental concept of this modal was developed by Feldkamp [17] for zinc-blende structure. According to this model the shell-shell charge, during vibrations, varies with the nn distance as
\[ Y(M_\mu) = Y(\mu^*) \left[ 1 + \frac{2(\mu)}{Y(\mu^*)} \sum p f(p) \left\{ R(M \mu + P) \right\} \right] \] 

where, each ion \( \mu \) is regarded to consist of a core \( \mu' \) of charge \( Z(\mu')e \) a shell \( \mu'' \) of charge \( Y(\mu'')e \) where \( e \) as the electronic charge. Here \( \left( M_{\mu'} \right) \) represents the \( \mu'' \) shell in the cell \( M \), \( f(r) \) is a function of distance \( r \) and tends to become zero as \( r \to \infty \). \( R(M \mu + P) \) is a vector distance of the nn shell \( (M + P) \) from the shell \( (M_{\mu'}) \). The overlap repulsion is taken to be central and to act only through the shells. The inclusion of charge-transfer from one shell to another has given rise three and four body forces.

### 2.10 THREE BODY FORCE SHELL MODEL (TSM):

The TSM was originally developed by Singh and Verma [59] who considered interaction potential to consist of the LR Coulomb and three body interactions [22-26] and the SR overlap repulsion operative between the first and second neighbour ions. The crystal potential energy per unit cell can be written as [24]

\[ \Phi_{TSM} = \frac{e^2}{2} \sum_{lk} \sum_{l'k'} \frac{Z_k Z_{k'}}{|l k, l'k'|} + e^2 \sum_{lk} \sum_{l'k'} \phi_M^R \left( r(l k, l'k') \right) \]

\[ + \sum_{lk} \sum_{l'k'} \sum_{l''k''} e^2 r(l k, l''k') \left[ f_k \left( r(l k, l''k') \right) \right] \frac{Z_{k'}e}{r(l k, l'k')} \]

\[ \left( M \mu + P \right) \]
Here $\phi^R(r)$ is the overlap repulsion term appearing in conventional RSM. The first two terms represent the usual two-body LR Coulomb and SR overlap repulsive potentials. The last term in it is a purely three-body potential and is calculated as if a charge $e_f_k(r)$ were transferred to the ion $(l_k)$ from the neighbouring ion $(l''k'')$ which in turn interacts with charge $Z_{k'}e$ at $(l'k')$ via Coulomb's law. Here $f_k(r)$ is significant between $nn$ ions and is expressed as

$$f_k(r) = \left(Z_k/Z\right)f(r)$$

Where, $Z = Z_k$

Following the method of Woods et. al. [34], the TSM equation of motion can be written as

$$\omega^2mU = (R' + Z_mC'Z_m)U + (T' + Z_mC'Y_m)W \quad \ldots\ldots (2.59a)$$

$$\sigma = (T'' + Y_mC'Z_m)U + (S' + K + Y_mC'Y_m)W \quad \ldots\ldots (2.59b)$$

for the core and shells of the ions. Here $Z_m, Y_m$ and $m$ are $(6 \times 6)$ diagonal matrices for the modified ionic charge, the modified shell and the ionic mass; $U(=U_1,U_2)$ and $W (=W_1, W_2)$ are the amplitude vector for the core displacement and the shell-core separation, respectively. The dynamical matrix $D(\vec{q})$ is a $(6 \times 6)$ matrix and can be written as

$$D(\vec{q}) = (R' + Z_mC'Z_m) - (R' + Z_mC'Y_m)(K + R' + Y_mC'Y_m)^{-1}X$$

$$R'' + Y_mC'Z_m$$
The long-range force matrix $ZCZ$ of RSM is correspondingly replaced by its modified form

$$Z_m C' Z_m = ZCZ \left( 1 + \frac{12}{Z} r_0 \right) + D^i$$

\[\text{......}(2.61)\]

With $C$ and $D^i$ as the long-range Coulomb and three-body force matrices evaluated by Kellermann [2].

The TSM formalism for zinc-blende and cadmium fluorite structures have been partially developed by Verma and Singh [59].

The equivalence between the phenomenological dipole models, namely RSM and DDM has been established by Hardy [60] by casting an identity in the form of their potential functions and equation of motion. The physical contents of the more sophisticated dipole models abbreviated as BSK, DSM and TSM have been shown by Cochran [61] to be equivalent as the force field introduced by the charge-transfer due to displacement of an atom and is qualitatively similar to that produced due to the radial deformation of the electron shells.

This identity between BSM, DSM and TSM has also been established by rigorous mathematical derivations performed by Basu et al. [62] and Verma [63] and Various workers [64-65].
2.11 PSEUDOPOTENTIAL APPROACH:

Soma and coworkers formulated [66-68] theory for the lattice dynamics of group IV semiconductors according to the Jones-Zone Scheme proposed by Heine and Jones and also obtained the bulk properties [69] of the tetrahedrally bonded compounds in good agreement with observed data. Recently, Soma and Kagaya [73] extended the treatment by including partially ionic interactions. The dynamical matrix \( D(\vec{q},kk') \) as appearing in secular determinant consists of (i) the covalent contribution \( C_{\alpha\beta}(\vec{q},kk') \) and the ionic contribution \( I_{\alpha\beta}(\vec{q},kk') \). The ionic part is given as the sum of the electrostatic Coulomb term \( E_{\alpha\beta}(\vec{q},kk') \) and the short range repulsion term \( R_{\alpha\beta}(\vec{q},kk') \). Thus,

\[
D(\vec{q},kk') = C_{\alpha\beta}(\vec{q},kk') + E_{\alpha\beta}(\vec{q},kk') + R_{\alpha\beta}(\vec{q},kk') \quad \ldots \ldots \quad (2.62)
\]

The electrostatic term \( E_{\alpha\beta}(\vec{q},kk') \) has a long-range character and is calculated using Ewald's method [71]. The short-range repulsion term at the nearest neighbour configuration is given by

\[
R_{\alpha\beta}(\vec{q},kk') = \sum_{r=\eta} \left( \frac{\delta_{\alpha\beta}}{r^2} - \frac{r_\alpha r_\beta}{r^3} \frac{dw(r)}{dr} + \frac{r_\alpha r_\beta}{r^2} \frac{dr}{dr^2} \right) e^{i\vec{q} \cdot \vec{r}} \quad \ldots \ldots (2.63)
\]

where,

\[
\omega(r) = \lambda e^{-r/\rho} \quad \ldots \ldots (2.64)
\]
\( \lambda \) and \( \rho \) are two parameters [70]. The covalent part \( C_{ab}(\bar{q},kk') \) is defined in terms of the force constant \( \phi_{ab}(\bar{r},kk') \) such that

\[
C_{ab}(\bar{q},kk') = (1 - x) \sum_r \phi_{ab}(\bar{r},kk') e^{i\bar{q} \cdot \bar{r}}
\] .......(2.65)

where, \( x \) is the ionic fraction [71], \( \bar{r} \) is the lattice vector. In calculating \( C_{ab}(\bar{q},kk') \) force constants \( \phi_{ab}(\bar{q},kk') \) are taken up to sixth-nearest neighbours according to the expressions by Hermau [72]. The model pseudopotential of Ashcroft and the local model potential of Heine Abarenkov were used by Soma and Kagaya in calculating phonon dispersion relations of several zincblende compounds. The dielectric constant of Hubbard was considered [70,73,74].

### 2.12 DEFORMABLE BOND MODEL (DBM):

Kunc and workers [75-78] developed the deformable bond model for studying the lattice dynamical properties of zinc-blende semiconductor compounds. This model is characterised by the following interactions.

i. Each lattice site is assigned a point charge \( \pm q \), as if the binding were purely ionic. Owing to the displacements the dipoles

\[
\vec{p}_1 = + q\vec{u}_1, \quad \vec{p}_2 = - q\vec{u}_2
\] ...........(2.66)

will appear.
ii. As a consequence of the deformation of electron clouds by the shortrange forces the displacements of the first neighbour ions give rise to the electric moments

\[ \mathbf{p} = -\gamma \left( \mathbf{r}_0 (\mathbf{u}_2 - \mathbf{u}_1) / |\mathbf{r}_0|^2 \right) \] ........(2.67)

Mechanical polarization is associated with each bond. For the sake of calculation of the lattice sums it is split artificially into two parts located on the respective ends of the bond. This is done by splitting

\[ \gamma = \gamma_1 + \gamma_2 \] ...........(2.68)

iii. The total microscopic electric field polarizes the atoms and yields the dipole moments

\[ \mathbf{p}_1 = \alpha_1 \mathbf{E}_1^{\text{micro}}, \quad \mathbf{p}_2 = \alpha_2 \mathbf{E}_2^{\text{micro}} \] ...........(2.69)

where \( \mathbf{E}_{1,2}^{\text{micro}} \) are the actual microscopic fields on the cation and anion respectively, and

\[ \alpha = \alpha_1 + \alpha_2 \] ...........(2.70)

The equation represents a more or less plausible split of the electronic polarizability defined in the microscopic theory [79].

iv. All the other interactions are described as Short-range (SR) forces.
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