CHAPTER - 2

INTERIONIC POTENTIALS

In this chapter we discuss the interionic potentials. The cohesive energy of an ionic solid in specified thermodynamic conditions is defined as internal energy of solid relative to the state of the free ions at the absolute zero temperature. The crystal energy $w$ can be expressed in the following form (Born and Mayer 1932, Huggins and Mayer 1933, Huggins 1937).

$$W = W_e + W_{rep} + W_v \quad \ldots \ldots \ (2.1)$$

Where $W_e$ is the electrostatic or madelung energy $W_{rep}$ the short range overlap repulsive energy and $W_v$ the Van der waals (Vdw) energy. The largest contribution arises from the electrostatic potential, the other terms contribute only 20 to 30 percent of the total energy. However the repulsive forces becomes very strong at short distances in order to maintain the crystals in equilibrium. If we neglect the vdw forces and consider the repulsive interaction only up to nearest neighbour then the interatomic force model reduces to the initial form of the simple Born model (Tosi 1964).

2.1 Madelung Energy :-

The interaction energy of the point like charges $Z_p e$ and $Z_p e$ pertaining to the ion in the $1^{th}$ cell and to the $p^{th}$ ion in the reference cell is
The corresponding electrostatic energy of the crystal per molecule is then given by

$$W_0 = \frac{1}{2N} \sum_{p,p'} Z_p Z_{p'} \frac{e^2}{|r_1 + r_p - r_{p'}|} \tag{2.2}$$

where the superscript prime in summation indicates that the case \( l = 0 \) is executed for \( P = P' \) and \( N \) is the number of molecules in the unit cell. Equation (2.2) can be written in the form

$$W_0 = -\frac{Z e^2 \alpha_M}{R} \tag{2.3}$$

Where \( Z \) is the largest common factor of the \( Z_p \) and \( Z_{p'} \) and \( R \) is the interionic distance, the madelung constant \( \alpha_M \) referred to the characteristic length \( R \), is defined as

$$\alpha_M = -\frac{R}{2N} \sum_{p,p'} \phi_p \psi (r_{p'}) \tag{2.4}$$

where \( \phi_{p'} = Z_p / Z \) and

$$R \psi (r_{p'}) = \sum_1 \sum_p \frac{\phi_p}{|r_1 + r_p - r_{p'}| / R} \tag{2.5}$$

\( R \psi \) is the electrostatic self potential at the crystal at the lattice point \( r_{p'} \) the ionic charges are measured in the unit of \( Z e \) and interionic distance in units of \( R \). It is clear from equ. (2.4) and (2.5) that the madelung constant is independent of the absolute value of ionic charge and of the absolute value of the cell edges, it
depends only the crystal structure, there are several methods for the evaluation of madelung constant (Madelung 1913, 1921). These methods have been reviewed excellently by Tosi (1964) for different crystal structures. The madelung energy increases with decreasing interionic separation and tends to contact the lattice. The contraction proceeds on until the neighbouring ions begins to interpenetrate and the repulsive forces become strongly operative.

2.2 REPU SIVE ENERGY :-

The equilibrium condition for a solid can be satisfied only if the interatomic forces become repulsive at small interatomic distances. The short range repulsion between atoms is connected with the role of pauli's exclusion principle is opposing overlap of closed electron shells. The problem of interaction between two hydrogen like ions has been studied by Heitler and London (1927) and by Pauling (1928). A quasi exponential form of repulsive energy of the two closed-shell atoms is also consistent with the result of first order perturbation calculations for the interaction of the two helium or neon atoms in their ground state (Slater 1928, Bleick and Mayer 1934).

In the Born model the repulsive energy in an ionic crystal is not calculated from first principles. Instead, a simple functional dependence on the distance between the ion is assumed and the potential parameters are determined from crystal data. In the early work on cohesion of ionic crystals, the Born repulsive energy was assumed to vary as an inverse power of the distance between ions, as follows,
\[ W_p = \frac{-B}{r^n} \quad \text{............. (2.6)} \]

and the parameters \( B \) and \( n \) can be determined directly for each salt from the equation of state and its volume derivative. In most applications of the Born model the repulsive energy between two closed shell ions has been assumed to vary exponentially with their separation. The evaluation of cohesive energy of an ionic crystal requires then the determination of just two repulsive parameters only if the total repulsive energy, as a function of the nearest neighbour distance \( r \) is written in the form

\[ W_{rep} = B \exp \left( -\frac{r}{\rho} \right) \quad \text{............... (2.7)} \]

The parameters \( B \) and \( \rho \) can be derived from the equation of state and its volume derivative. Taking explicit account of the repulsions of the second neighbours in an ionic crystal composed of two bravais lattices of ions, the contribution of the Born repulsive energy to lattice energy per molecule can be written as follows (Tosi 1964).

\[ W_{rep} = Mb_{\pm} \exp \left( -\frac{r_{\pm}}{\rho} \right) + \frac{1}{2} M' \left( b_{++} + b_{--} \right) \exp \left( -\frac{r_{\pm}}{\rho'} \right) \quad \text{..... (2.8)} \]

here \( M \) and \( M' \) are the number of first and second neighbours and \( r' \) is the distance between the second neighbours. \( b_{ij} \) are the repulsive strength parameters. The hardness parameter corresponding to inverse power form and exponential form determined from experimental ultrasonic data are given in table (2.1).

Recently Narayan and Ramaseshan (1974, 1976) have postulated a very attractive hypothesis for the repulsive potential in ionic
solids. According to this hypothesis an ion may be considered to be a soft sphere whose radius is a function of the corresponding force acting on it. The repulsion between ions arise from the increase in their internal energy when compressed together. The internal energy of the ion can be expressed as the function of its radius. In the framework of this picture the repulsive potential \( W_{\text{rep}} \) between two unlike ions in a binary crystal can be written as

\[
W_{\text{rep}} = W_+ (r_+) + W_- (r_-) \quad \ldots \ldots (2.9)
\]

where \( W_+ \) and \( W_- \) are function of \( r_+ \) and \( r_- \), the radii of two ions.

In the NR treatment ionic radii are defined such that

\[
r = r_+ + r_- \quad \ldots \ldots \ldots (2.10)
\]

Where \( r \) is the nearest neighbour distance, since the ionic radii are not strictly additive, equation (2.10) will imply a slight variation in the radius of an ion from crystal to crystal. It is also evident from equ. (2.9) that the repulsive energy is a function of \( r_+ \) and \( r_- \). On the other hand in the Born-Mayer-Heggins type treatment the ionic radii are taken as constants.

For a given \( r \) there is according to equ. (2.10) still one internal degree of freedom viz. the radius of one of the ions. We have one further relation expressing the internal equilibrium of the lattices. This arises from the minimization of the energy of the crystal with respect to its internal coordinates \( r_+ \) and \( r_- \). Physically we can picture this as the two ions pushing against each other and so adjusting their radii that the forces they exertion each other are
balanced. This requires the condition

$$\frac{dW_+(r_+)}{dr_+} = \frac{dW_-(r_-)}{dr_-} \quad \ldots \ldots \quad (2.11)$$

The total lattice energy per molecule of a binary ionic crystal can now be written as

$$W = -\frac{\alpha e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + W_+(r_+) + W_-(r_-) \quad \ldots \ldots \quad (2.12)$$

Because of relations (2.10) and (2.11) $r_+$ and $r_-$ are function of $r$. In view of this fact the quantities $\frac{dW}{dr}$, $\frac{d^2W}{dr^2}$ etc. are still meaningful. The repulsion potential expressed by equ. (2.9) does not specify the change to be made when an ion occurs in different structures for this an additional postulate is proposed according to which the energy of compression of an ion was local to the points of contact with its neighbours and originated, essentially from the local compression and distortion. Thus the repulsion energy caused by nearest neighbours for a given radius of the ion is directly proportional to the number of the nearest neighbours $M$, i.e.,

$$W_\pm (r_\pm) = M \Phi_\pm (r_\pm) \quad \ldots \ldots \quad (2.13)$$

The actual manner of causing the distortion on any ion is immaterial in the treatment of Narayan and Ramaseshan. Thus the same compression function can be used for nearest as well as next nearest neighbours. The only difference is that the radius for the two cases will be different. In binary crystals like alkali halides, next nearest neighbours are identical ions and so, by symmetry, the boundary between them lies at the mid point between their centres. The
total repulsion potential extended up to second neighbours can be written as

\[ W_{rep} = M \left[ \Phi_+ (r_+) + \Phi_- (r_-) \right] + M' \left[ \Phi_+ \left( \frac{r'}{2} \right) + \Phi_- \left( \frac{r'}{2} \right) \right] \] ............ (2.14)

where \( M \) is the number of the next nearest neighbours and \( r' \) is the distance between next nearest neighbours. This approach of expressing the repulsive potential with the help of equation (2.14) is at variance with the Born-Mayer-Huggins treatment where different weights to \( ++, +-, -+ \) and \(- -\) interactions have been given by introducing the B factors due to Pauling (1928). If we adopt an exponential function for the repulsive potential then we can re-express equation (2.14) as follows:

\[ W_{rep} = M \left[ A_+ \exp \left( - \frac{r_+}{\rho_+} \right) + A_- \exp \left( - \frac{r_-}{\rho_-} \right) \right] + M' \left[ A_+ \exp \left( - \frac{r'}{2\rho_+} \right) \right. \\
\left. + A_- \exp \left( - \frac{r'}{2\rho_-} \right) \right] \] ............ (2.15)

In each compound there are four unknown parameter viz. \( A_+, A_-, \rho_+, \rho_- \). By using the experimental values of interionic separation \( r \) and compressibility \( K \) at the pressures. Theoretical and experimental support for the ion dependant parameters \( \rho_+ \) and \( \rho_- \) has been provided by Gilbert (1968), Ida (1976), Shanker and Agarwal (1980). Values of \( \rho_+ \) and \( \rho_- \) derived from different methods are given in table 2.2.

2.3 Van der Waals Energy :-

The most direct evidence of the existence of the Van der
Waals (vdw) potentials is the fact that rare gases can be condensed into the solid state. The attractive binding in rare gas solids and also in many organic crystals arises mainly from the vdw interactions. In fact it was first shown by London (1930) from quantum mechanical treatment that a dipole-dipole attractive potential, varying as the inverse sixth power of the distance, existed between all atoms and ions. This attractive potential is generally known as the Vdw dipole-dipole energy. Most typical ionic crystals like alkali halides and alkaline-earth-chalcogenides are composed of closed shell ions which are identical with rare gas atoms as far as the outermost electronic configuration is concerned. Such a similarity is responsible for the existence of the ionic crystals, however, there are electrostatic forces which are relatively of much longer range. For this reason vdw interaction in ionic solids are considered to be short range forces (Tosi 1964).

It has been evident from numerous investigations (May 1937, 1938, Dheer and Sharan, 1967, Ree and Holt 1973, Catlow et al, 1978, Sangster and Atwood 1978, Andzelm and Pielat 1977, 1978) that the vdw interactions play an important role in determining the cohesive, elastic, dielectric and lattice dynamical properties of ionic solids. The vdw interactions are also of considerable importance in studies of defect energies (Boswarva and Lidiard 1967), surface energies (Benson and Benson 1955) and for those properties which involve the higher order volume derivatives of the potential energy (Hollinger and Borsch 1976). In recent times there have been many attempts (Haff 1966, Lynch 1967, Boswarva 1970, Ladd 1974, Winslow 1975, Jain et al.1976, Narayan...
1977, Shanker et al. 1978, Kapoor and Jain 1978) to calculate vdW potentials in ionic solids. The common features of all this work is that the calculated vdW potential are significantly larger than the values estimated by Mayer and Coworkers (Mayer 1933, Mayer and Levy 1933, Mayer and Helmholtz 1932). The calculation of the vdW potentials performed by various coworkers either depend on the use of London-Margenau (LM) formulae based on the perturbation treatment (London 1930, Margenau 1939) or make use the slater - Kirkwood (sk) variational theory (Slater and Kirkwood 1931). There is another useful formula originally due to Kirkwood (1932) and Muller (1936). The formula will be called as KM formula in the present text.

The dipole-dipole (d-d) energy term which arise from interaction between induced dipole moments of different atoms, actually is the first term in an infinite series of rapidly converging terms. The next term, which was investigated by Margenau varies inversely as the eighth power of the distance between atoms, this term is called the dipole - quadrupole (d-q) interaction because it is interpreted as arising from the interaction of a dipole moment on one atom with a quadrupole on the other. The next term in the sequence, which varies inversely as the tenth power of interatomic distance is called quadrupole - quadrupole (q-q) term. The g-g term is negligible in ionic crystals, and in the present thesis we discuss only d-d and d-q interactions. The mathematical original details of d-d and d-q interactions have been given at sufficient length by previous authors (Tosi 1964, Mayer 1933, Margenau 1939, Klein and Venables 1976). The total Vdw energy is written as -
\[ W_v = - \frac{C}{r^6} - \frac{D}{r^8} \] \hspace{1cm} \text{(2.16)}

where \( C \) and \( D \) are d-d and d-q constants which can be expressed in terms of pair coefficients \( C_{ij} \) and \( D_{ij} \), as follows:

\[ C = S_{+-} C_{+-} + S_{++} C_{++} + S_{--} C_{--} \] \hspace{1cm} \text{(2.17)}

\[ D = T_{+-} d_{+-} + T_{++} d_{++} + T_{--} d_{--} \] \hspace{1cm} \text{(2.18)}

Where \( S_{ij} \) and \( T_{ij} \) are the lattice sums. The subscripts \(+-, ++\) and \(--\) represents cation-anion cation-cation and anion-anion interactions, various methods for calculating the vdw energies are based on three different theories, viz. (i) London-Margenau (LM) formulation based on the perturbation treatment, (ii) Slater-Kirkwood (Sk) variational theory, (iii) Kirkwood-Muller (KM) formulation. The expression for the coefficients \( C_{ij} \) and \( D_{ij} \) based on these theories are as follows:

**LM Theory** -

\[ C_{ij} = \frac{3}{2} \alpha_i \alpha_j \frac{E_i E_j}{E_i + E_j} \] \hspace{1cm} \text{(2.19)}

\[ D_{ij} = \frac{9}{4} \frac{C_{ij}}{d^2} \left[ \frac{\alpha_i E_i}{N_i} + \frac{\alpha_j E_j}{N_j} \right] \] \hspace{1cm} \text{(2.20)}

**Sk Theory** -

\[ C_{ij} = \frac{3}{2} \frac{e \hbar}{m^{1/2}} \frac{\alpha_i \alpha_j}{\left( \frac{\alpha_i}{N_i} \right)^{1/2} + \left( \frac{\alpha_j}{N_j} \right)^{1/2}} \] \hspace{1cm} \text{(2.21)}
\[ d_{ij} = \frac{27 \hbar^2 \alpha_i \alpha_j}{8m} \left[ \left( \frac{\alpha_i}{N_i} \right)^{1/2} + \left( \frac{\alpha_j}{N_j} \right)^{1/2} \right]^2 \left( \frac{i}{N_i} \right)^2 + \frac{2\alpha_i \alpha_j}{3} \left( \frac{N_i}{N_j} \right) + \left( \frac{\alpha_j}{N_j} \right) \right] \] ...... (2.22)

**KM Theory**

\[ C_{ij} = \frac{-6mc^2}{N_0} \chi_i \chi_j \left( \frac{\chi_i}{\alpha_i} + \frac{\chi_j}{\alpha_j} \right) - 1 \] ...... (2.23)

\[ d_{ij} = \frac{-9mc^2}{e^2 N_0} \left( \frac{\chi_i}{N_i} + \frac{\chi_j}{N_j} \right) \] ...... (2.24)

Where \( e \) and \( m \) are the charge and mass of an electron, \( K \) is Planck's constant divided by \( 2\pi \), \( c \) the velocity of light. \( \chi \), \( E \), and \( N \) are, respectively, the polarizabilities, molar susceptibilities, characteristic-excitation energies, and effective number of electrons in ions \( i \) and \( j \). The mathematical assumption implied in the derivation of Equations (2.19 to 2.24) are discussed below.

The ground state wave function \( \psi \) of the closed shell atom can be written by a Slater determinant for \( N \) electrons

\[ \psi = (N!)^{-1/2} \det \begin{bmatrix} \psi_1 & \psi_2 & \ldots & \psi_N \end{bmatrix} \] ...... (2.25)

To define the polarizability, one can write the perturbing potential as

\[ \nu = F \sum_{p=1}^{N} Z_p \] ...... (2.26)

Where \( F \) is the electric field along the \( Z \) axis. The variational wave function \( \psi \) is taken to be
\[
\psi' = \psi + \sum_{\lambda=1}^{N} a_{\lambda} \phi_{\lambda} \quad \ldots \ldots (2.27)
\]

\[
\phi_{\lambda} = (N!)^{-1/2} \det [\psi_1, \psi_2, \ldots, \psi_N] \quad \ldots \ldots (2.28)
\]

and

\[
\psi_{\lambda} = \frac{Z_{\lambda}}{\psi} \psi_{\lambda} F_{\lambda} \quad \ldots \ldots (2.29)
\]

where \( F_{\lambda} \) is either unity of function such as \((1 + C_1 r + C_2 r^2)\). The following three quantities need to be defined:

\[
h_{\lambda} = \langle \psi^* \mid \sum_{\mu} \phi_{\mu} \rangle \quad \ldots \ldots (2.30)
\]

\[
\phi_{\lambda, \mu} = \langle \phi^* \mid H \mid \phi_{\mu} \rangle - E_0 g_{\lambda, \mu} \quad \ldots \ldots (2.31)
\]

\[
g_{\lambda, \mu} = \langle \phi^* \mid \phi_{\mu} \rangle \quad \ldots \ldots (2.32)
\]

Where \( H \) is the complete Hamiltonian for the unperturbed system and the usual quantum mechanical integral over all space are inciated. The energy change upon imposing the field is

\[
h' = 2F \sum_{\lambda} a_{\lambda} h_{\lambda} + \sum_{\lambda} \sum_{\mu} a_{\lambda} a_{\mu} Q_{\lambda, \mu} \quad \ldots \ldots (2.33)
\]

which is to be minimized with respect to each \( a \),

\[
-\frac{\partial h'}{\partial a_{\lambda}} = 0 = 2Fh_{\lambda} + 2 \sum_{\mu} a_{\mu} Q_{\lambda, \mu} \quad \ldots \ldots (2.34)
\]

From determinant theory, the solution is is

\[
a_{\lambda} = -A_{\lambda} F \quad \ldots \ldots (2.35)
\]

and the minimized energy is
The expression for polarizability is

\[ \alpha = - \frac{2h'}{F^2} = 2 \sum A_\lambda h_\lambda \quad \ldots \ldots (2.37) \]

it is assumed that the \( \psi_\lambda \) are orthogonal to all \( \psi_\lambda \). This assumption is not necessarily true although the \( F_\lambda \) can be selected to make it true. Then,

\[ g_{\lambda\mu} = 0 \text{ if } \lambda \neq \mu \quad \ldots \ldots (2.38) \]

The calculation of \( Q \) is more complex. If \( F_\lambda \) in Eqn. (2,29) is unity and Hartee wave-functions are used \( Q_{\lambda\lambda} = \frac{1}{2} \). This value was taken as an approximation by previous workers (Slater and Kirkwood 1931, Eggenhoffner et al. 1982). The off-diagonal \( Q_{\lambda\mu} \) terms which have been neglected previously are not without significance. \( A_\lambda \) in equ. (2.35) is given by,

\[ A_\lambda = \frac{-h}{\sum_{\mu} Q_{\lambda\mu}} \quad \ldots \ldots (2.39) \]

So that

\[ \alpha = \frac{2}{\sum_{\mu} \sum_{\lambda} Q_{\lambda\mu}} h^2 = \frac{2Nh^2}{\sum_{\mu} Q_{\lambda\mu}} \quad \ldots \ldots (2.40) \]

Using the above approximations one can get the following expression for the dipole–dipole vdw energy.
\begin{align*}
W_{d-d} &= -\frac{6}{R^6} \left[ \sum_k \left( \frac{h_k^A}{q_k^A} \right)^2 \right] \left[ \sum_p \left( \frac{h_p^B}{q_p^B} \right)^2 \right] \left( \sum_{k_1} \frac{1}{g_{kk_1}^A} \right) \left( \sum_{q_{pq}} \frac{1}{g_{pp}^B} \right) \\
&\quad - \left( \sum_{k_1} \frac{1}{g_{kk_1}^A} \right) + \left( \sum_{q_{pq}} \frac{1}{g_{pp}^B} \right) \\
&= \ldots \ldots (2.41)
\end{align*}

Where \( R \) is the interionic separation. The quantities in braces are \( \frac{1}{2} \alpha_A \) and \( \frac{1}{2} \alpha_B \) for the two interacting atoms A and B, respectively. The energy in parentheses can be defined as

\[ E_A = \frac{\sum_{k_1} Q_{kk}^A}{q_{kk}^A} \quad \ldots \ldots (2.42) \]

the equation (2.41) takes the following form

\[ W_{d-d} = -\frac{3\alpha_A \alpha_B}{2R^6} \frac{E_A E_B}{E_A + E_B} \quad \ldots \ldots (2.43) \]

This formula was first derived by London (1930). The main assumption in driving equation (2.43) are that (i) all \( \psi_\lambda \) are orthogonal to all \( \psi_\lambda \) (ii) if \( F_{\lambda} = 1 \) and (iii) off diagonal terms \( Q_{\lambda \mu} \) do not contribute to Polarizability and dipole-dipole energy. These assumptions led to the following results.

\[ g_{\lambda \lambda} = h_{\lambda} = \langle \psi_\lambda | z^2 | \psi_\lambda \rangle \quad \ldots \ldots (2.44) \]

So that equation (2.40) and (2.42) gives

\[ \alpha_A = \frac{2\Sigma_{\lambda} h_{\lambda}^A}{E_A} = \frac{2Nh_A}{E_A} \quad \ldots \ldots (2.45) \]

from equation (2.42) and equation (2.44) we get

\[ E_A^{-1} = \frac{h^A}{\sum_{k_1} Q_{kk_1}^A} = \left( \frac{\alpha_A}{2Ne^{A}} \right)^{1/2} \quad \ldots \ldots (2.46) \]

inserting equation (2.46) in equation (2.43) and assuming that off diagonal terms do not contribute i.e. \( \Sigma Q = \frac{1}{2} \), we get
\[
W_{d-d} = -\frac{3\alpha_A \alpha_B}{2R^6} \left[ \left( \frac{\alpha_A}{N_A} \right)^{1/z} + \left( \frac{\alpha_B}{N_B} \right)^{1/z} \right]^{-1} \quad \ldots \ldots (2.47)
\]

Which is the Slater-Kirkwood formula (Salter 1931).

Another useful equation for the dipole energy is that obtained by Kirkwood (1932) and Muller (1936). This contains the diamagnetic susceptibility as well as the polarizability of the individual atoms. The susceptibility per atom of a spherically symmetric system is given by

\[
\chi = -\frac{(2mc^2)^{-1} \Sigma_k (Z_k^2)}{2mc^2} \quad \ldots \ldots \ldots (2.48)
\]

where \( c \) is the velocity of light and \( m \) the electron mass. In view of (2.46) we can write for a sub shell of equivalent electrons

\[
\chi_A = -\frac{Nh^A}{2mc^2} \quad \ldots \ldots \ldots (2.49)
\]

Equations (2.45) and (2.49) imply the assumption that the same number of electrons contribute to polarizability as to susceptibility. Such an assumption has been found to be fairly satisfactory (Winslow 1975). Equations (2.45) and (2.49) yield

\[
E_A^{-1} = -(4mc^2)^{-1} \left\{ \frac{\alpha_A}{\chi_A} \right\} \quad \ldots \ldots (2.50)
\]

The dipole-dipole energy then becomes

\[
W_{d-d} = -\frac{6mc^2}{NoR^6} \chi_A \chi_B \left( \frac{\chi_A}{\alpha_A} + \frac{\chi_B}{\alpha_B} \right)^{-1} \quad \ldots \ldots (2.51)
\]

In equation (2.51) \( No \) is Avogadro number and \( \chi \) is now the molar susceptibility in cm\(^3\). The most remarkable feature is deriving
equation (2.51) is that $\Sigma$ has been eliminated. Thus the Kirkwood-Muller formula (equation 2.5) has the great advantage that it does not suffer from the uncertainties regarding the off-diagonal terms $Q_{k1}$.

**Table 2.1**

Table of repulsive hardness parameters corresponding to inverse power form and exponential form determined from experimental ultrasonic data compiled from Smith and Cain (1975).

<table>
<thead>
<tr>
<th>Crystal</th>
<th>n</th>
<th>$\rho(\text{Å}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIF</td>
<td>6.44</td>
<td>0.271</td>
</tr>
<tr>
<td>LICl</td>
<td>7.85</td>
<td>0.290</td>
</tr>
<tr>
<td>LIBr</td>
<td>8.37</td>
<td>0.294</td>
</tr>
<tr>
<td>LII</td>
<td>9.03</td>
<td>0.300</td>
</tr>
<tr>
<td>NaF</td>
<td>7.68</td>
<td>0.267</td>
</tr>
<tr>
<td>NaCl</td>
<td>8.73</td>
<td>0.288</td>
</tr>
<tr>
<td>NaBr</td>
<td>9.21</td>
<td>0.293</td>
</tr>
<tr>
<td>NaI</td>
<td>9.79</td>
<td>0.299</td>
</tr>
<tr>
<td>KF</td>
<td>8.89</td>
<td>0.271</td>
</tr>
<tr>
<td>KCl</td>
<td>9.86</td>
<td>0.290</td>
</tr>
<tr>
<td>KBr</td>
<td>10.01</td>
<td>0.299</td>
</tr>
<tr>
<td>KI</td>
<td>10.39</td>
<td>0.310</td>
</tr>
<tr>
<td>RbF</td>
<td>9.73</td>
<td>0.263</td>
</tr>
<tr>
<td>RbCl</td>
<td>10.57</td>
<td>0.284</td>
</tr>
<tr>
<td>RbBr</td>
<td>10.82</td>
<td>0.291</td>
</tr>
<tr>
<td>RbI</td>
<td>11.26</td>
<td>0.299</td>
</tr>
</tbody>
</table>
Table - 2.2

Values of $\rho_{+}$ and $\rho$ in (Å$^2$) for Alkali and halogen ions (Shanker and Agarwal 1980).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Derived from</th>
<th>Narayan and Ramaseshan (1978)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Molecular data</td>
<td>Overlap data</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>0.069</td>
<td>0.055</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.079</td>
<td>0.060</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.106</td>
<td>0.081</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>0.115</td>
<td>0.093</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>0.130</td>
<td>0.115</td>
</tr>
<tr>
<td>F$^-$</td>
<td>0.179</td>
<td>0.201</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.238</td>
<td>0.247</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>0.258</td>
<td>0.266</td>
</tr>
<tr>
<td>I$^-$</td>
<td>0.289</td>
<td>0.286</td>
</tr>
</tbody>
</table>