

# CHAPTER - I

INTERACTION POTENTIAL FUNCTIONS FOR DIATOMIC MOLECULES

# 1.1 POTENTIAL ENERGY CURVES<sup>1-3</sup>

The atoms forming diatomic molecule are in simple harmonic oscillations along the line joining the nuclei. In classical mechanics the vibratory motion of two atoms can be reduced to a single mass point vibrating about equilibrium position. The potential energy of such a mass point is found to be a quadratic function of the change in internuclear distance  $(r-r_e)$ . The potential energy curve is a parabola (A) as shown in Fig. 1.1. The frequency of oscillation of the single mass point is given by

$$v_{osc} = (1/2\pi) \sqrt{k/\mu}$$
 ....(1.1)

where k is the force constant and  $\mu$  is the reduced mass. Quantum mechanically the Schrodinger's equation involving the potential energy of single mass point is solved to yield the discrete energy values as given by,

E (v) = (v + 
$$1/2$$
) h  $v_{osc}$  ....(1.2)

where v is the vibrational quantum number which takes integral values 0, 1, 2 .... In the lowest vibrational state (v=0) the oscillator possesses a finite energy known as 'zero point energy.'

The term values of oscillator are given by,

G (v) = (v + 
$$1/2$$
)  $\omega$  ....(1.3)

where  $\omega = v_{osc}/c$  = vibrational frequency in cm<sup>-1</sup>. The allowed transitions are governed by the selection rules  $\Delta v = \pm 1$ . All

these transitions superpose on each other to predict a single line in the vibrational spectrum of the harmonic oscillator model.

simple harmonic oscillator model fails The to explain the following facts. In real diatomic molecules the restoring force for compression and extension is not the same. The bond between two atoms strongly resists compression as seen from the relative compressibility of the solids. On the other hand, the attractive force between two atoms becomes zero when these are separated by an infinite distance. The potential energy for large atomic separation attains a constant value as shown by the curve B the symmetry of P.E. curve A does not (Fig.1.1). However, explain these facts. Further overtones and combination terms observed in the vibrational spectra cannot be predicted by the model. Experimentally vibrational energy level separation decreases with increase in v, but the model calculates equal spacing of energy levels. In order to take into account these observed facts, anharmonic oscillator model is used.

On anharmonic oscillator model the potential energy of a diatomic molecule is to a first approximation given by the function.

$$U(r) = f (r-r_e)^2 - g (r-r_e)^3 \qquad \dots (1.4)$$

where  $g \leq f$ .

This approximation is effective if  $(r-r_e)$  is not too large. For still better approximation, higher power terms in  $(r-r_e)$  should

be added to eq.(1.2). This introduction of anharmonicity in molecular vibrations can explain the occurence of overtone and fundamental bands in the vibrational spectrum.

Quantum mechanically the term values of anharmonic oscillator are given by,

$$G(v) = \omega_{e}(v + 1/2) - \omega_{e}X_{e}(v + 1/2)^{2} + \omega_{e}y_{e}(v + 1/2)^{3}$$
.....(1.5)

where  $\underset{e}{\omega}_{e} X_{e}$  and  $\underset{e}{\omega}_{e} y_{e}$  are the anharmonicity constants with  $\underset{e}{\omega}_{e} X_{e} < \underset{e}{\omega}_{e}$  and  $\underset{e}{\omega}_{e} y_{e} < \underset{e}{\omega}_{e} X_{e}$ . For g > 0,  $\underset{e}{\omega}_{e} X_{e} > 0$ , while  $\underset{e}{\omega}_{e} y_{e}$  may be positive or negative. Eq. (1.5) shows that energy levels of the anharmonic oscillator are not equidistant but their separation decreases slowly with increasing v.For v=0, we get 'zero point energy' as given below.

$$G(0) = (1/2) \omega_e - (1/4) \omega_e X_e + (1/8) \omega_e y_e \dots (1.6)$$

If the energy levels are referred to this lowest level as zero, we obtain

$$G_{o}(v) = \omega_{o}v - \omega_{o}x_{o}v^{2} + \omega_{o}y_{o}v^{3} \qquad \dots (1.7)$$

where,

$$\omega_{o} = \omega_{e} - \omega_{e} X_{e} + (3/4) \omega_{e} y_{e}$$
$$\omega_{o} X_{o} = \omega_{e} X_{e} - (3/2) \omega_{e} y_{e} + \dots$$
$$\omega_{o} y_{o} = \omega_{e} y_{e} + \dots$$

The allowed transitions are governed by the selection rules  $\Delta v = \pm 1, 2, 3, \ldots$  Among these  $\Delta v = \pm 1$  predict the most intense line in the spectrum, while  $\Delta v = \pm 2, \pm 3$ , give transitions with rapidly decreasing intensity.

Neglecting cubic terms the separation of successive absorption bands ( in  $cm^{-1}$  ) is given by,

The first and second differences between successive absorption bands determine vibrational constants  $\omega_{p}$  and  $\omega_{p}X_{p}$ .

A real molecule cannot be strictly a rigid rotator while it is vibrating as evidenced by the observed fine structure of rotation bands of diatomic molecules. So it is regarded as a nonrigid rotator i.e. a rotating system consisting of two mass points connected by a massless spring. In such a system, the centrifugal force causes increase in internuclear distance with increasing rotation. On this model the rotational terms are given by,

$$F(J) = BJ(J+1)-DJ^2(J+1)^2$$
 ....(1.9)

The rotational constant D depends on the vibrational frequency of the molecule through the relation

$$D = 4 B^2 / \omega^2 \qquad \dots \dots (1.10)$$

As  $\omega >> B$ , D << B so that we may neglect the departure of the molecule from the model of rigid rotator. By considering a vibrating rigid rotator, the rotational constant  $B_v$  in the vibrational state v is given by,

where  $B_e$  = the equilibrium rotational constant and  $\alpha_e$  = the rotation vibration coupling constant. Similarly by taking into account the nonrigidity effect we can express the higher order rotational constant  $D_V$  as,

$$D_V = D_e + \frac{\beta}{e} (v + 1/2) + \dots (1.12)$$

where  $\beta_{P}$  is the higher order spectroscopic constant.

#### Description of P.E. Curve

For equilibrium distance  $(r_e)$ , the potential energy has a minimum value and diatomic molecule is in physically stable state. In this state repulsive and attractive forces between the charged nuclei are balanced. If the internuclear distance decreases the repulsion increases which leads to a sharp rise in potential energy. When the atoms are drawn apart, the potential energy again increases due to superior electronic binding force. The potential energy approaches a limiting value as the internuclear distance tends to infinity. The height of asymptote gives the limiting value of potential energy called the 'Dissociation energy' denoted by  $D_e$  and  $D_o$  in Fig. (1.2).  $D_o$  is the dissociation energy with respect to zero point energy state, while  $D_e$  is dissociation energy as referred to vibrationless state. The dissociation energy (heat of dissociation) is the amount of work done to separate the atoms to an infinite distance.

The correct representation of a potential energy curve determines the molecular structure. It gives the detailed information about the important molecular data listed below.

- 1. The minima of the curves determine the bond length which decides the stability of the molecule.
- 2. The second derivative of potential energy with respect  $d^2 U/dr^2$ ) ( gives the force distance to constant and determines the vibrational and rotational levels of а (1.3) shows the relation between molecule. Fig. force constant and dissociation energy in hydrogen halides  $^3$ .
- 3. The anharmonic constants are evaluated from the third and higher order derivatives of U.
- 4. Potential energy curves are useful to apply Franck Condon principle to the radiative transitions, dissociation and predissociation processes.
- 5. Potential energy curves are helpful in studying many problems like gas kinetics, steller structure and recent astrophysical problems.
- 6. The determination of dissociation energies is of great interest in thermochemistry, combustion physics and

astrophysics. The dissociation energies also play а quantitative problem of valency fundamental role in i) ii) Statistical calculations of equilibria at high temperatures. iii) Chemical bonding and many other problems.

#### **1.2 DETERMINATION OF POTENTIAL ENERGY CURVES**

Potential energy curves for diatomic molecules fall mainly into two categories, one with appreciable minima (bound states) and the other exhibiting a very shallow minimum or none at all (repulsive states). We shall study only the bound state curves.

Three general methods exist for obtaining curves for the bound state of diatomic molecules :

1. RKRV method<sup>5</sup>

2. Dunham method<sup>6</sup> and,

3. Method based on empirical potential functions.

#### 1.2.1 RKRV Method

RKRV method is a WKB approximation with which The one obtains reliable potential energy curves from the measured vibrational and rotational constants of the diatomic molecule. In this method classical turning points on the potential energy curve are calculated from experimentally known vibrational energy levels. One major disadvantage of the method is that the potential curve can be constructed numerically only in the region for which spectroscopic available. sufficient data are There are many

modified versions of this method found in the literature. We quote below a few of them.

Vaidyan and Santaram<sup>7</sup> proposed a modification of RKRV method to obtain true turning points rapidly with sufficient accuracy. In this method the internuclear distance r corresponding to energy U(r) of the molecule is represented by an equation of the form

$$Y(r) = mr + C.$$

which represents a straight line. Two  $r_{min}$  and two  $r_{max}$  values from RKRV data are needed to evaluate m and c values. The method is also extended to electronic states whose  $\omega_e X_e$  is not very large.

However, the method has disadvantages due to reasons quoted below.

- 1. It is very laborious,
- 2. It can be efficiently used only when sufficient spectroscopic data is known,
- 3. It cannot be applied with accuracy for lower vibrational states.

Recently Reddy and Reddy<sup>8</sup> have further modified the method due to Vaidyan and Santaram. They have given a procedure in which r values from RKRV are not needed to evaluate the true turning points. Instead the consecutive term values corresponding to v = 3 and 4 are sufficient. They have obtained

the following relations :

$$M_{\pm} = \ln \left[ \left( \frac{\omega}{e}^{\pm} (4 \omega_{e} X_{e} U_{4})^{1/2} \right) / (r_{4} - r_{3}) \dots (1.13) \right]$$
  
where  $(r_{4} - r_{3}) = \left[ \left( \frac{b_{1}}{2 \sqrt{g}} - \frac{b_{2}}{2\sqrt{g}_{2}} \right) K + (\sqrt{g_{1}} - \sqrt{g_{2}}) \pm (X_{4} - X_{3}) \right] r_{e}$   
 $\dots (1.14)$ 

in which  $b_1 = 3.75/h_1 - b'/h_1^2 + 135 P^2$   $g_1 = 18 P^2 + 1/h_1$   $h_1 = 1 - 3 m$  b' = 3.75 - 12.15 m  $b_1 = (2.917/h_2) - (b''/h_2^2) + 82 P^2$   $g_2 = 14 P^2 + (1/h_2)$   $h_2 = 1 - (7 m/3)$  h'' = 2.917 - 7.35 m  $x_4 - x_3 = P (0.501 + 5 K + 43.1 K^2)$   $P = (B_e/\omega_e)^{-1/2}, m = \omega_e/\omega_e$ and  $K = \omega_e X_e/\omega_e$ For  $r > r_e$ ,  $\ln \left[ \omega_e - (4\omega_e X_e U_3)^{1/2} \right] = m_+ r_3 + C_+ \dots (1.15)$ 

For 
$$r < r_e$$
,  $\ln \left[ \bigcup_e + (4 \bigcup_e X_e \bigcup_3)^{1/2} \right] = m_r_3 + C_....(1.16)$   
For  $r_{\pm}, r_3 = \left[ (b_2 K/2 \sqrt{g_2}) + \sqrt{g_2} \pm P (3.74166 + 10.9132 K + 49.273 K^2) \right] r_e$  ....(1.17)

Knowing the values  $m_{\pm}$  from eq. (1.13) and  $C_{\pm}$  from eqs.(1.15) and (1.16) one can evaluate true turning points rapidly by varying 'U' value in the Vaidyan and Santaram relation. There is a printing mistake in the eq.(5) of Reddy and Reddy<sup>8</sup> for  $r_3$ . The R.H.S. should be multiplied by  $r_e$  as correctly given in the above eq. 1.17.

#### Franck-Condon Factors and r-Centroids

The intensities of diatomic molecular bands in electronic spectra are governed by the overlap integral the square of which is known as the Franck-Condon factor<sup>1</sup>

$$q_{\mathbf{v}'\mathbf{v}''} = \int \psi_{\mathbf{v}'\mathbf{v}''} \psi_{\mathbf{v}''} dr \Big]^2 \qquad \dots \dots (1.18)$$

where  $\frac{\Psi}{V}$  and  $\frac{\Psi}{V}$  are the wavefunctions of the upper and lower vibrational levels between which transitions occur. The average internuclear separation associated with the transition is known as the r-centroid and is defined by

$$\widetilde{\mathbf{r}}_{\mathbf{V}'\mathbf{V}''} = \int \Psi_{\mathbf{V}'} \mathbf{r} \quad \Psi_{\mathbf{V}''} \, d\mathbf{r} / \int \Psi_{\mathbf{V}'} \Psi_{\mathbf{V}''} \, d\mathbf{r} \quad \dots \quad (1.19)$$

A knowledge of r-centroids is useful for the determination of electronic transition moment of the band system.

#### 1.2.2 Dunham's Method

Dunham<sup>6</sup> assumed a potential energy curve of the form

$$U(r) = a_0 X_1^2 (1 + \sum_{n=1}^{\infty} a_n X_1^n) \dots (1.20)$$

where  $X_1 = (r-r_e)/r_e$ . By employing well known expression for the energy levels of a diatomic molecule viz.

$$E_{\mathbf{v},\mathbf{j}} = \sum_{\mathbf{j}=\mathbf{0}}^{\infty} \sum_{\mathbf{j}=\mathbf{0}}^{\infty} y_{\mathbf{i}\mathbf{j}} [\mathbf{v} + 1/2)^{\mathbf{i}} \left[ \mathbf{J} (\mathbf{J}+1) \right]^{\mathbf{j}} \dots (1.21)$$

We can relate the coefficients  $a_i$ 's eq. (1.20) to the coefficients  $y_{ij}$ 's determined from the experimental rotational vibrational constants. This method has certain advantages and disadvantages.

#### **Advantages**

- Using eq. (1.20) the wave equation can be solved to a very good degree of accuracy.
- 2. Accurate potential energy curve close to the minimum is obtained with the help of eq.(1.20).
- 3. The method is flexible.

#### Disadvantages

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The most serious drawback is that the potential energy curve becomes divergent as r tends to +  $\infty$  for  $0 \leq r \leq \infty$ . So the method must be used carefully for higher vibrational levels.

Simons<sup>9</sup> and Thakkar<sup>10</sup> have proposed a new alternative to the Dunham method. They assumed the same type of power series expansion, but instead of  $X_1$  substituted the quantity  $X_2 = (r-r_e)/r$ . This potential also suffers from certain drawbacks. At smaller r (r  $\approx$  ( $r_e/2$ ) or less ) potential energy curve has oscillatory behaviour and it converges very slowly.

#### **1.2.3 Semiempirical Potential Energy Functions**

Another general method<sup>11</sup> to determine potential energy curve is based on semiempirical potential functions. In this a certain type of algebraic expression is assumed for a potential curve, and the parameters in it are evaluated from the energy spectroscopic constants. known The requirements for а good potential are listed below.

- 1. It must have minimum number of parameters.
- 2. It must be adequately close to the dispersion forces at large internuclear distances.
- 3. It should obey Varshni's criteria.<sup>4</sup>

Most of the potentials are constructed in terms of three parameters which depend on the bond dissociation energy  $(D_e)$  equilibrium internuclear distance  $(r_e)$  and the vibrational force constant  $(k_e)$ . These molecular constants are most readily obtained from the study of band spectrum of a diatomic molecule. It is well known that the more the number of parameters in a potential, the greater is its ability to produce RKRV curve. So potential with four or five parameters should be constructed in such a way that the fourth and fifth parameters are expressed in terms of the remaining three. We can develop such a potential in terms of constants  $D_e$ ,  $r_e$ ,  $k_e$ ,  $\alpha_e$ (rotation vibration coupling constant) and  $\omega_e X_e$  (anharmonicity constant). The last two are expressed in terms of  $D_e$ ,  $r_e$ ,  $k_e$ .

A large variety of analytical functions meeting with the above requirements have been suggested to this date.

Morse Function<sup>12</sup>

$$U = D_{e} \left[ 1 - \exp(-a(r - r_{e})) \right]^{2} \dots (1.22)$$

where a is potential parameter. It satisfies Varshni's criteria at r = 0; however, it yields large finite value instead of infinity.

It is found that this function is not suitable for randomly chosen molecules. Though this simple function has been very widely used, it gives rather a poor performance in many branches.

## Hulburt - Hirschfelder Function<sup>13</sup>

It is a modified form of Morse function given as,

$$U = D_{e} \left[ (1 - \exp(-x)^{2} + cx^{3}(\exp(-2x))(1+bx) \right]$$
....(1.23)

where X =  $\frac{\omega_e (r - r_e)}{2 r_e (B_e D_e)^{1/2}}$  and,

b,c are simple algebraic functions of the five spectroscopic constants.

#### **Rydberg Function**

Rydberg<sup>14</sup> proposed U ( r ) = D<sub>e</sub> ( 1 + b $\rho$  ) exp ( - b $\rho$  ) The function is similar to the hydrogen atom wave function. It satisfies criteria 1 and 2 but does not become infinite at r=0, though it attains a large value. Its performance is better in predicting transition probabilities of  $C_2$  molecule than that of Morse and Hulburt-Hirschfelder functions.

#### Linnett Function

 $Linnett^{15}$  suggested the function.

$$U(r) = (a/r^{m}) - b \exp(-nr)$$

where m and n are constants for a given state of the molecule, while the parameters a and b are given by,

.

$$a = \frac{r_e^m D_e nr_e}{(m - nr_e)}$$
$$b = \frac{m a e^{hr}e}{n r_e^{m+1}}$$

#### Lippincott Function

as

Lippincott<sup>16</sup> proposed a potential to a first approximation

$$U = D_{e} \left[ 1 - \exp \left( 1 - \frac{n^{2}}{2 r} \right) \right]$$

where n =  $k_e r_e / D_e$ At r = 0, U =  $D_e$ r =  $r_e$ , U = 0 r = $^{\infty}$ , U =  $D_e$  Lippincott et al<sup>16</sup> evaluated  $\omega_e x_e$  values in terms of n which is empirically given by,

$$n = n_0 (I/I_0)_A^{1/2} (I/I_0)_B^{1/2}$$

where  $(I/I_0)_{A,B}$  are the ionization potentials of atoms A and B respectively relative to these of the corresponding atoms in the same row and first column of the periodic table.

The value of  $\alpha_e$  on this potential was found to be zero and hence Lippincott et al<sup>16</sup> modified it in the following manner.

$$U = D_{e} \left[ 1 - \exp(-ne^{2}/2 r) \right] \left[ 1 + a f(r) \right]$$
  
where  $af(r) = -a (r_{e}/r)^{6} \left[ 1 - \exp(-b^{2} nr^{11}/2r_{e}^{12}) \right]^{1/2} + a(r_{e}/r)^{12} \left[ 1 - \exp(-b^{2} nr^{11}/2r_{e}^{12}) \right]$ 

They obtained the expressions

$$D_{e} = \omega_{e}^{2} / 2 \operatorname{nr}_{e}B_{e}$$

$$\alpha_{e} = ab (\operatorname{nr}_{e} / 2)^{1/2} 6 B_{e}^{2} / \omega_{e}$$

$$\omega_{e}x_{e} = 1.5 B_{e} \left[ 0.25 + (\operatorname{nr}_{e} / 4) + ab (\operatorname{nr}/2)^{1/2} + (5a^{2}b^{2} - ab^{2}) \operatorname{nr} / 2 \right]$$

For most of the molecules ab and b are found to be nearly constants from which the values of  $\substack{\alpha \\ e}$  and  $\substack{\omega \\ e} \substack{x \\ e}$  were calculated in agreement with the experimental values.

#### Varshni Functions

Varshni<sup>4</sup> has proposed seven new potential functions. Most of these are the modifications of Morse, Rydberg and Lipincott functions. Varshni's functions V(II), V(IV), V(V) are not applicable whereas the remaining are better in performance.

#### Noor Mohammad Functions

Noor Mohammad<sup>17</sup> proposed some potential functions of much better forms than most of the three parameter potentials already known. These potentials though much improved in quality, are still unlikely to predict true potential curves. These are divided into two types.

#### Morse Family of Curves

In this type all double exponential potentials are included. These are expressed in general by,

U (r) = 
$$D_e [1 - (r_e / r)^n \exp(-b(r^m - r_e^m)]^2$$
  
....(1.25)

where,

$$b = (s - n) / (m r_e^m)$$
 ....(1.26)

m and n are two different constants. Special potentials can be deduced from eq.(1.25) by the appropriate choice of m and n values.

Potential I (with 
$$b = b_1$$
,  $m = m_1$ , and  $n = 0$ )

$$17$$

$$U(r) = D_{e} \left[ 1 - \exp(-b_{1}(r^{m_{1}} - r_{e}^{m_{1}}) \right]^{2}$$

<u>Potential II</u> ( with  $b=b_2$ , m=2 and  $n=n_2$ )

$$U(r) = D_{e} \left[ 1 - (r_{e}/r)^{2} \exp(-b_{2}(r^{2} - r_{e}^{2})) \right]^{2}$$

Potential III ( with b=b<sub>3</sub>, m=m<sub>3</sub> and n=n<sub>3</sub>)  $U(r) = D_{e} \left[ 1 - (r_{e}/r)^{n_{3}} \exp(-b_{3}(r_{e}^{n_{3}} - r_{e}^{n_{3}})) \right]^{2}$ 

#### Rydberg Family of Curves

The potential energy curves of this category are represented by,

$$U(\mathbf{r}) = -D_{e} \left[ 1 + \beta (\mathbf{r}_{e}/\mathbf{r})^{q} (\mathbf{r}^{p} - \mathbf{r}_{e}^{p}) \right] = \exp \left[ -\beta (\mathbf{r}^{p} - \mathbf{r}_{e}^{p}) \right]$$

$$\dots (1.26)$$

where,

$$\beta = \left[ -q + (q^2 + 2s^2)^{1/2} \right] / (p r_e^p) \qquad \dots \dots (1.27)$$

and p and q are two constants which take different values thereby leading to particular potentials as given below.

Potential IV ( with  $\beta = \beta_1$ ,  $p = p_1$  and q = 0)

$$U(r) = -D_{e} \left[ 1 + \beta_{1} (r^{p_{1}} - r_{e}^{p_{1}}) \right] \exp \left[ -\beta (r^{p_{1}} - r_{e}^{p_{1}}) \right]$$

where,

$$\beta_1 = 1.414 \text{ s/ } (p_1 r_e^{p_1})$$

This potential satisfies first and second criteria of Varshni. It does not become infinite at r = 0, though it is sufficiently large at r = 0.

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<u>Potential V</u> (with  $\beta = \beta_2$ , P = P<sub>2</sub> and q = 1)

$$U(\mathbf{r}) = -D_{e} \left[ 1 + \beta_{2}(\mathbf{r}_{e}/\mathbf{r}) \cdot \mathbf{r}^{2} - \mathbf{r}_{e}^{2} \right] \times \exp \left[ -\beta_{2}(\mathbf{r}^{2} - \mathbf{r}_{e}^{2}) \right]$$
  
where,  
$$\beta_{2} = \left[ -1 + (1 + 2s^{2})^{1/2} \right] / (P_{2}/r_{e}^{1})$$

This potential satisfies all criteria of Varshni. With application of KH criteria, an average value of  $P_2$  for each molecule is obtained. The value of  $P_2$  is appropriate for reproducing RKR curve and predict  $\alpha_{e}, \omega_{e} x_{e}$  accurately.

#### 1.2.4 Combination Potentials

In the past: a number of  $attempts^{18}$  have also been made to formulate superposition potentials by combining the functions due to Kratzer<sup>19</sup> Morse<sup>12</sup> and Rydberg<sup>14</sup>.

#### **1.3 IONIC POTENTIAL ENERGY FUNCTIONS**

Dissociation energy is the energy corresponding to the convergence limit i.e. position in the spectrum where vibrational bands converge and become continuous beyond it. The dissociation energy of an electronic state  $D_0$  may be defined as the energy difference between the isolated atoms at infinite separation and the lowest vibrational level of the electronic state in question.

i.e.  $D_e = D_0 + (\text{zero point energy})$ .

However, the molecule may dissociate into two ions which may also be in excited states. This corresponding energy of dissociation is the ionic dissociation energy or the binding energy of the electronic state concerned.

For the evaluation of dissociation and binding energies various experimental as well as theoretical methods have been developed with varying degree of accuracy. Different potential energy functions proposed for the non-ionic diatomic molecules by many workers have already been discussed in Sec. 1.2.3. The common features of all these functions is that they are expressed in terms of known dissociation energy  $(D_e)$ . As a consequence one cannot calculate the value of unknown dissociation energy from these potentials.

In an alternative approach adopted by Varshni and Shukla<sup>20</sup>, a simple potential energy function is formulated by using an attractive term of electrostatic origin and the repulsive term arising from the overlap of the outermost electrons of the two atoms or ions.Further refinements of the function can be achieved by considering the contributions due to polarization forces, Van der Waal interactions, dipole-dipole interactions etc. Such a potential function therefore, in general, consists of the following terms:  $^{20-21}$ 

i)  $(-e^2/r)$  representing charge-charge interaction, ii)  $(-e^2(\alpha_1 + \alpha_2)/2r^4) - (2e^2\alpha_1 \alpha_2/r^7)$  arising due to chargedipole interaction dipole-dipole interaction and quasielastic energy stored in the induced dipoles with  $\alpha_1$ and  $\alpha_2$  as the polarizabilities of the alkali and halide ions.

- iii) A van der Waals attraction term (  $-C/r^6$ )
- iv) Kinetic energy term representing the difference in the translational, rotational and vibrational energy between the molecule and the free ions from which it is composed.
  - v) A short range repulsive term  $\psi$  (r)

Usually the kinetic energy term is quite small and hence neglected. The repulsive term contribution is a prominent one and is calculated by considering various forms of this term. This leads to a variety of ionic potential energy functions.

Various potentials considered here have two features in common. All of them have coulombian attractive term and have two unknown constants in the repulsive term which are determined by the conditiions :

$$(dU/dr)_{r=re} = 0$$

and

$$(d^2 U/dr^2)_{r=re} = k_e$$

#### Born-Lande Potential

Born and  $Lande^{22-23}$  proposed the potential energy function

$$U(r) = -e^2/r + b/r^n$$

where b and n are constants. This potential is extensively used in investigating ionic crystals and the nature of binding in LiH molecule For alkali hydrides this potential yields very high values of  $\alpha_e$  and  $\omega_e x_e$  and very low values of binding energy (D<sub>i</sub>) and hence not suitable for alkali hydrides.

#### Born-Mayer Potential

Born and Mayer<sup>24</sup> suggested that an exponential term is preferable to take into account the repulsive interaction and is found to be satisfactory for alkali halide crystals. The potential proposed is given by,

$$U(r) = -e^2/r + B \exp(-r/\rho)$$

where B and  $\rho$  are constants. The % errors in  $\alpha_e$  and  $\psi_e x_e$  calculated on this potential are found to decrease rapidly from LiH to CsH while the % error in D<sub>i</sub> is nearly the same for all the molecules.

#### Wasastjerna Potential

Wasastjerna<sup>25-26</sup> have proposed two potential functions for alkali metal halide crystals. The simplest form of the two potentials is given by,

$$U(r) = -e^2/r + C r^7 exp (-\beta r)$$

where C and  $\beta$  are constants. This function is successful in evaluating D<sub>i</sub> values; however, it fails to evaluate  $\alpha_{e}$  and  $\omega_{e} x_{e}$ 

values accurately.

# Rittner Potential<sup>27</sup>

$$U(r) = -e^{2}/r - e^{2}(\alpha_{1} + \alpha_{2})/(2r^{4}) - (2e^{2}\alpha_{1}\alpha_{2})/(r^{7}) - C/r^{6}$$
  
+ A exp ( -r/p)

where A and  $\rho$  are repulsion constants and C is van der Waals constant. All calculated values of  $\alpha_{e}$  are negative &  $\omega_{e} x_{e}$  values are several times greater than the observed values for alkali halides. D<sub>i</sub>values are comparatively better.

#### Hellmann Potential

In order to represent the interaction between the valence electron and the core in the alkali atoms, Hellmann<sup>28</sup> proposed the following potential

$$U(r) = -e^2/r + T \exp(-\lambda/r)$$

where T and  $\lambda$  are constants. Varshni and Shukla<sup>20-21</sup> found that the potential yields satisfactory results for representing the shape of potential energy curves of alkali hydrides. However, D<sub>i</sub> values on this potential are lower than the observed ones, while the average % errors in  $\alpha_{e}$  and  $\omega_{e} x_{e}$  are reasonable.

#### Varshni-Shukla Potential

Varshni and Shukla<sup>20-21</sup> proposed two potential energy functions.

$$U(r) = -e^2/r + P \exp(-kr^2)....VS I$$
  
 $U(r) = -e^2/r + S \exp(-n r)/(r^2)....VS II$ 

where P,k, S and n are the constants. Potential VS-I is reasonably statisfactory for the alkali halides. The calculated values of  $\alpha_e$  for alkali hydrides are unsatisfactory on both potentials. But the average % error in  $\omega_e x_e$  comes out to be the least on both the potentials. Also D<sub>i</sub> values are satisfactory on VS-I, while these are lower by about 10% on VS-II.

Recently Kaur et al<sup>29</sup> have critically examined the VS potentials by introducing the concept of effective charge parameter.By introduction of this concept, the results obtained are close to experimental values. Further they predicted that the potential functions yield better results than those obtained from the inverse power form for the repulsive term.

#### Harrison Potential

 $\operatorname{Harrison}^{30}$  derived a potential function quantum mechanically by taking account of various contributions arising from coulomb energy, kinetic energy and exchange energy. This potential successfully predicts crystalline state properties as well as molten state dynamics and the structural properties of alkali halides. Kumar et al $^{31}$  and Shankar et al $^{32}$  have given the modification appropriate for gaseous state. Accordingly the binding energy and vibrational constants of alkali halide molecules can be calculated through an analysis of interionic forces. On this model

binding energy is written as follows:

$$W(r) = -e^2/r - e^2(\alpha_1 + \alpha_2)/(r^4) + W_{rep} C/r^6$$

where  $\alpha_1^{\alpha}$ ,  $\alpha_2^{\alpha}$  are the electronic polarizabilities of the ions, and C is the dipole-dipole interaction coefficient. The second term is polarization energy, the third term ( $W_{rep}$ ) is a measure of repulsive energy and the last one represents van der Waals dipole dipole interaction. In the Rittner model the repulsive interaction term is taken to be simple exponential Born-Mayer type. However, this potential form is not consistant with the quantum mechanical perturbation treatment.

Recently Harrison<sup>30</sup> developed analytical form for the potential function by using quantum mechanical first principles. Within the frame work of this treatment one takes the kinetic energy, exchange energy and the coulomb energy term in the expansion of total energy of an electron gas. The following analytical form is used for cation-anion overlap repulsive energy.

$$W_{rep} = \left(n_{o} \frac{1}{\mu} 2 m\right) \left[ \overline{\mu} r \exp \left( - K \overline{\mu} r \right) \right]$$

where n\_-the repulsive strength parameter

- K -is the hardness parameter
- $\overline{\mu}$  is the arithmatical average for the two types of ions derived from valence state energies.

Using the potential parameters Kumar et al have calculated the binding energy W,  $\substack{\alpha \\ e}$ ,  $\substack{\omega \\ e}$  and the higher order spectroscopic

constants. The results obtained from Harrison potential are quite superior to those from Born-Mayer exponential form. The agreement between the calculated and experimental values is much better for higher order constants also.

#### 1.4 SUMMARY

At the outset the basic concepts leading to the description of a potential energy curve have been made clear. The importance of potential energy curves in the determination of molecular structure has also been brought out. Next the RKRV and Dunham's methods for the determination of potential energy curves are described in detail. The details regarding different analytical functions employed in the representation of P.E. curves for nonpolar diatomic molecules are briefly outlined. Finally the role of various types of ionic potential energy functions in the binding determination of energies and spectroscopic constants of polar diatomic molecules has been discussed at length.

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# FIG. 1-1 - REAL AND QUADRATIC POTENTIAL ENERGY CURVES



FIG. 1-2 - REAL P.E. CURVE WITH DIFFERENT VIBRATIONAL STATES OF A DIATOMIC MOLECULE .



FIG. 1-3 - RELATION BETWEEN FORCE CONSTANT AND DISSOCIATION ENERGY IN HYDROGEN HALIDES .