

P R E F A C E

In this Dissertation the author has reported the theoretical research investigations made by him during the last one year, in the Department of Physics, Shivaji University, Kolhapur on (i) the determination of the bound state Potential energy curves for a number of diatomic molecules by using six new combination potential functions suggested by him and (ii) the evaluation of the rotational-vibrational coupling constant (α_e) and the anharmonicity constant ($\omega_e x_e$) along with the Varshni's F and G functions by employing Varshni's method. The dissertation also includes a study on a few ionic P.E. functions suggested by the author for the alkali hydride and halide diatomic molecules. The dissertation consists of five chapters.

In Chapter 1 , a survey of potential energy curves for diatomic molecules and various methods to determine the same has been taken. At the outset, an outline of the basic theory leading to the formation of potential energy curves is given and the importance of these curves in the determination of molecular structure is discussed. Next the methods of determination of the potential energy curves are explained, particularly the RKR method and its recent modifications have been given in detail. Then we have discussed the empirical potential functions employed for the representation of potential energy curves. First the necessary and the desirable criteria required for a good potential function

are cited. Then various potential functions reported in the literature have been explained in somewhat detail. In each case, the expression for potential energy is given and the merits and the demerits are also mentioned. Then follows the evaluation of potential parameters and testing of a potential function for its suitability. Next a brief survey of ionic potential energy functions has been taken.

At the end of Chapter 1 we have outlined the Varshni's method¹ useful to obtain expressions for the rotational-vibrational coupling constant and the anharmonicity constant. Further Varshni's comparative study of various potential functions has been summarized along with its conclusions. Also the comparative study of Steele et al² has been briefly surveyed with its findings.

The various combinations of well known potential energy functions form the subject matter of Chapter 2. In the first half of this Chapter, we have described the recent attempts to formulate hybrid potential functions from the superposition of Morse, Rydberg and Kratzer potentials. In each case the expressions for potential energy, potential parameter α_e and $\omega_e x_e$ constants have been listed. The relative advantages and disadvantages of these combination functions are also mentioned at length.

(1) Varshni Y.P. Rev Mod.Phys **29**, 664 (1957)

(2) Steele D. and Lippincott E.R. 'Rev. Mod. Phys' **34**, 2 p.239 (1962)

A few attempts found in literature to improvize the above combination potentials are also described.

In the second half of Chapter 2 we have given the details of our study on superposition potentials. In the beginning we have explained the aim of the present study. From the earlier comparative studies^{1,2} it was revealed that the simple Morse function gives rather a poor performance and the Kratzer function is not applicable to molecular problems. Due to these reasons the combinations involving Morse and Kratzer functions are not satisfactory. On the otherhand the combinations of Rydberg potential with others are more successful because Rydberg function evaluates α_e and $\omega_e x_e$ values with maximum accuracy and gives almost correct reproduction of the P.E curves¹. With a view to further improvize the general performances of individual Morse and Rydberg potentials, we have attempted, in the present work, various combinations of these potential functions as given below:

- 1) Generalized Morse & Rydberg (GMR) potential:

$$U(r) = D_e [1 - \exp(-b \rho)]^2 - D_e [1 - (1 + b \rho) \exp(-b \rho)] \rho^3 \exp(-b \rho)$$

$$\text{Where } \rho = (r - r_e / r_e)$$

- 2) Generalized Morse and Kratzer (GMK) potential:

$$U(r) = D_e \{ 1 - \exp[-n(r^2 - r_e^2)/(2r_e^2)] \}^2 + D_e \{ 1 - (r_e/r)^n \}^2$$

(iii)

(3) Varshni's Second and Sixth[V(II & VI)] potential:

$$U(r) = D_e \{1 - (r_e/r) \exp[-a(r-r_e)]\}^2 + D_e \{1 - (r/r_e) \exp[-a(r-r_e)]\}^2$$

(4) Rydberg and Lippincott (RL) potential:

$$U(r) = -D_e \{1 + b(r-r_e) \exp[-b(r-r_e)]\} + D_e \{1 - \exp[-b(r-r_e)^2/r]\}^2$$

(5) Rydberg and Varshni's Second [RV(II)] potential:

$$U(r) = -D_e \{1 + b(r-r_e) \exp[-b(r-r_e)]\} + D_e \{1 - (r_e/r) \exp[-b(r-r_e)]\}^2$$

(6) Rydberg and Varshni's Sixth [RV(VI)] Potential:

$$U(r) = -D_e \{1 + b(r-r_e) \exp[-b(r-r_e)]\} + D_e \{1 - (r/r_e) \exp[-b(r-r_e)]\}^2$$

In each case the expressions for potential parameters, F & G functions and α_e and $\omega_e x_e$ constants have been obtained by Varshni's method.

The reproducibility of potential energy curves is regarded as one of the checks to test the validity of a given analytical potential function in representing the potential energy of a diatomic molecule. Hence we have calculated the potential energy curves for a number of diatomic molecules using our proposed combination potential (given in Chapter 2) and

the results of the same have been reported in Chapter 3 . For calculation purpose we have used a WIPRO PC available in the Department of Physics, Shivaji University, Kolhapur. A random group mainly containing hydrogen, Oxygen, halogen and alkaline types of molecules has been chosen to test the reproducibility of P.E. curves. The calculated P.E curves have been compared with the RKR curves. Some of the findings of this study are listed below :

- (1) GMR and GMK potentials qualitatively overestimate the force constants of the molecules under consideration. The reproducibility of P.E. curves on these potentials is quite satisfactory in the region $r < r_e$.
- (2) Varshni's (II & VI) potential qualitatively evaluates force constant values smaller than the actual values.
- (3) RL potential predicts satisfactory values of force constants nearly agreeing with their experimental values.
- (4) The behaviour of RV(II) & RV(VI) potential curves is reasonably good in the region for $r < r_e$, these potentials give smaller values of force constants.

A given analytical function can be tested in two ways*
a) by comparing it with the experimental curve b) by comparing the calculated α_e and $\omega_e x_e$ values with the actual values. Method (a) was adopted in Chapter 3 . Method (b) is utilized

*Ref: Varshni Y.P, 'Rev. Mod. Phys.' 29 4, p 666(1957)

to test the suitability of our combination potentials and the results are reported in Chapter 4 . The condition that a satisfactory function should be capable of yielding correct α_e and $\omega_e x_e$ values is only necessary but not sufficient. A function should also be tested for its performance in the neighbourhood of $r=0$ (as was examined in Chapter 3).

In Chapter 4 , at the outset, the molecules have been grouped with a view to examine the common characteristics, if any, regarding the estimated α_e and $\omega_e x_e$ constants and F and G functions:

- Group I : CO and CH
- Group II : a)HgH, CdH, ZnH b)HI, HBr, HF, HCl
- Group III : I₂, ICl, Br₂, Cl₂
- Group IV : K₂, Li₂ and Na₂
- Group V : SO, O₂, NO, OH
- Group VI :AuAl, GeSe, P₂ and N₂

The calculations of α_e and $\omega_e x_e$ and their % errors on our various combination potentials are reported in tabular forms. Further the estimated F and G values are presented in different Tables. We have also studied the behaviour of F and G functions with the Sutherland's parameter for the said combination potentials. The study reveals the following interesting findings.

- (1) In general, it is found that there is a regular increase of α_e values as a) the atomic weights of noncarbon, nonhydrogen and non-oxygen atoms (for molecules belonging to Groups I, II & V) decrease. b) The molecular weights (for molecules of Groups III, IV & VI) decrease. However there are few exceptions.
- (2) The above mentioned general trend applies separately to the subgroups (a) and (b) of Group II mentioned above. This is due to different nature of binding in HgH, CdH and ZnH molecules belonging to subgroup (a)
- (3) The increase in $\omega_e x_e$ values also follows the above trend more or less in the same manner.
- (4) GMR and GMK potentials are found to be superior over RL and varshni (II & VI) potentials in evaluating α_e and $\omega_e x_e$ values correctly.
- (5) On the basis of average % errors in α_e and $\omega_e x_e$, we find that the GMR potential leads to the least values and hence it is the most suitable potential function. GMK and RL potentials are also satisfactory next to GMR.
- (6) F function values on GMR, GMK and RL and RV(VI) [for a few cases] are lower than those on Morse function.

It is also true in the case of G values.

- (7) In the behaviour of F and G values with Sutherland's parameter, the curves for GMR, GMK and RL potentials are represented by straight lines in very good approximation with the experimental results.

The analytical potential functions considered in the earlier Chapters are disadvantageous to evaluate unknown binding energies as they utilize dissociation energy as a known constant while estimating the potential parameters. In this respect ionic potential functions are quite useful. The last Chapter 5 deals with the calculation of binding energies using two new potential functions proposed by us:

$$\text{Potential I : } U = -(e^2/r) + B \exp(kr^{5/2})$$

$$\text{Potential II: } U = -(e^2/r) + S \log_{10}[8 + (t/r^{1/2})]$$

By the usual procedure, the following expressions were obtained for binding energies :

$$\text{Potential I : } D_i = (e^2/r_e) [2k_e r_e^3 + 5e^2] / (2k_e r_e^3 + 7e^2)$$

$$\text{Potential II: } D_i = (e^2/r_e) \left\{ 1 + [2e^2 / (2k_e r_e^3 + e^2)] \log_{10} \left[\frac{4e^2}{k_e r_e^3 + e^2} \right] \right\}$$

These expressions have been utilized to estimate the binding energies of a number of alkali halides and hydrides and heavy metal halide molecules with the help of a WIPRO PC using a suitable computer programme in Basic. The findings in the calculations are summarized below:

- (1) Potentials I and II evaluate the binding energies of beryllium and calcium halides with greater accuracy as compared to other potentials. Potential II is superior to Potential I in this respect.
- (2) Both the potentials are found to be most accurate in the calculation of binding energies of alkali hydrides (in particular HgH, CdH and ZnH molecules)
- (3) The two potentials are reasonably satisfactory to estimate the binding energies of heavy metal halides.