

CHAPTER - 2
VARIOUS COMBINATIONS OF ANALYTICAL
POTENTIAL FUNCTIONS

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Varshni¹ discussed the limitations of different potential energy functions suggested by Kratzer, Morse, Rydberg and several others. In order to improvise the applicability of these functions, a number of attempts have been recently made to formulate their linear combinations. The idea of superposition might have taken from the ionic potential functions reviewed in the Chapter 1. These potentials necessarily consists of a combination of attractive and repulsive terms for the potential energy of a diatomic molecule. In this chapter, first we will take a brief survey of various combinations of potential functions reported in the literature. Then we will present a number of new combination potentials suggested in the present work.

2.1 MK POTENTIAL The first attempt to formulate the hybrid potential from the analytical functions was made by Raghuwanshi and Sharma². They put forward a linear combination of Morse and Kratzer functions and referred to it as MK potential.

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

where a is the potential parameter. By Varshni's method they obtained the expression for the rotational constant

$$\alpha_e = [(a^3 r_e^3 - a^2 r_e^2 + 1) / (a^2 r_e^2 + 1)] (6B_e^2 / \omega_e) \quad (2)$$

In general the potential curve of Eq (1) lies well below the individual Morse, and Kratzer curves. The percentage errors-

in α_e values calculated for a few diatomic molecules were found to have large magnitudes. However, a good agreement was seen between the calculated and experimental Δ and F values.

2.2 MR POTENTIAL

Iyer and Sharma³ have suggested the following linear combinations of Morse and Rydberg potentials:

Potential I:

$$U(r) = -(D_e/2) \{ 1 + (b/2)(r-r_e) \} \exp[-b(r-r_e)/2] + (D_e/2) \{ 1 - \exp[-b(r-r_e)] \}^2 - (D_e/2) \quad (3)$$

Potential II:

$$U(r) = -(D_e/2) \{ 1 + b(r-r_e) \} \exp[-b(r-r_e)] + (D_e/2) \{ 1 - \exp[-b(r-r_e)] \}^2 - (D_e/2) \quad (4)$$

By Varshni's method they obtained expressions for α_e and $\omega_e x_e$:

Potential I:

$$\alpha_e = [0.873 \Delta^{\frac{1}{2}} - 1] 6B_e^2 / \omega_e \quad \text{and} \quad \omega_e x_e = [4.34 \Delta] W / \mu_A r_e^2 \quad (5)$$

Potential II:

$$\alpha_e = (.833 \Delta^{\frac{1}{2}} - 1) 6B_e^2 / \omega_e \quad \text{and} \quad \omega_e x_e = (5.416 \Delta) W / \mu_A r_e^2 \quad (6)$$

Where the symbols have their usual meanings.

Iyer and Sharma claimed that the values of α_e and-

$\omega_e x_e$ calculated by them are superior to those i) calculated by Varshni for Morse and Rydberg potential functions separately. ii) calculated by Raghuwanshi and Sharma² on MK potential. Iyer and Sharma also noted that the combination² of Morse and Kratzer does not show any appreciable improvement over the Morse function due to the unsuitability of the Kratzer potential. However, they found that for the overall representation of the potential energy curves the MR combination is more suitable.

2.3 RK POTENTIAL

Varma and Jha⁴ proposed a linear combination of Rydberg and Kratzer potential functions

$$U(r) = -D_e [1 + b \rho] \exp[-b \rho] + D_e [\rho / r]^2 - D_e \quad (7)$$

Where $\rho = r - r_e$ and $b = [(k_e / D_e) - (2 / r_e^2)]^{1/2}$

They have reported the expression for α_e only

$$\alpha_e = \left[\frac{2b^3 r_e^3 + 12}{3(b^2 r_e^2 + 2)} - 1 \right] \frac{6B_e^2}{\omega_e} \quad (8)$$

The calculated α_e values were found closer to the respective experimental values than those calculated separately for Morse, Rydberg and Kratzer functions. The average % error was the least. Further the values of r_{\min} and r_{\max} calculated from this function were also in better agreement to those calculated from the true potential energy curve.

2.4 MRK POTENTIAL

Behere⁵ attempted a combination of Morse, Rydberg and Kratzer potentials

$$U(r) = D_e \left\{ [1 - \exp(-a \rho)]^2 - [1 + b \rho] \exp(-b \rho) + (\rho^2 / r^2) + 1 \right\} \quad (9)$$

Where $\rho = r - r_e$. The potential parameters a and b are given by

$$a^2 = k_e / 2D_e \quad \text{and} \quad b^2 = k_e / D_e$$

The following expressions for α_e and $\omega_e x_e$ were obtained.

$$\alpha_e = \left\{ [0.6869 (\Delta - 1)^{3/2} / \Delta] + (2 / \Delta) - 1 \right\} 6B_e^2 / \omega_e$$

$$\omega_e x_e = \left\{ 3.8272 \Delta - 14.7316 - (18.0184 / \Delta) + (52.9228 / \Delta^2) \right. \quad (10)$$

$$\left. + (42.1232 (\Delta - 1)^{3/2} / \Delta^2) \right\} W / \mu_A r_e^2$$

The % errors calculated for various molecules were found to be considerably large. Also the average percentage errors were maximum as compared with those obtained by other combination potentials. Behere therefore concluded that a combination of more than two individual potentials is worse in evaluating the α_e and $\omega_e x_e$ values.

2.5 IMPROVED MR POTENTIAL

Birajdar et al⁶ re-examined the MR potential due to-

Iyer and Sharma³. They found that the derivations for α_e and $\omega_e x_e$ were incorrect. The corrected expressions are as given below :

MR Potential (I)

$$\alpha_e = [1.2346 \Delta^{\frac{1}{2}} - 1] 6B_e^2 / \omega_e \quad \text{and} \quad \omega_e x_e = 11.65 \Delta W / \mu A r_e^2 \quad (11)$$

MR Potential (II)

$$\alpha_e = [1.0264 \Delta^{\frac{1}{2}} - 1] 6B_e^2 / \omega_e \quad \text{and} \quad \omega_e x_e = 8.247 \Delta W / \mu A r_e^2 \quad (12)$$

Birajdar et al also proposed a new potential function which combines Morse's and Rydberg's potentials

$$U(r) = (D_e/2) \{ [1 - \exp(-a\rho)]^2 - (1 + b\rho)\exp(-b\rho) + 1 \} \quad (13)$$

Where the potential parameters are related by $a = b/\sqrt{2} = \sqrt{(k_e/2D_e)}$

Using this potential they obtained

$$\alpha_e = [0.9714 \Delta^{\frac{1}{2}} - 1] 6B_e^2 / \omega_e \quad (14)$$

$$\omega_e x_e = 7.655 \Delta W / \mu A r_e^2 \quad (15)$$

The average % errors in α_e and $\omega_e x_e$ calculated from Eqs (14) & (15) were found to be considerably less as compared to those estimated using Eqs (11) & (12) for MR Potentials I & II. Birajdar et al therefore claim the superiority of the MR potential suggested by them over those proposed by Iyer and Sharma³.

2.6 RE-EXAMINED MK POTENTIAL

Birajdar and Behere⁷ reinvestigated the MK potential proposed by Raghwanishi and Sharma². They noted that in order to make $U(r_e)=0$ the last term $-2D_e$ in MK potential can be omitted without affecting the derivatives of α_e and $\omega_e x_e$. Further they obtained the following expression for $\omega_e x_e$ not reported earlier by Raghwanishi and Sharma²:

$$\omega_e x_e = \{ 8 \Delta^{-31} + (2/\Delta) + (45/\Delta^2) + [60(\Delta-1)^{3/2}/\Delta^2] \} W/\mu_A r_e^2 \quad (16)$$

The average % error in $\omega_e x_e$ of randomly selected molecules was found to be much less than that evaluated on Morse function alone.

Table 2-1 contains the expressions for F and G functions for different combination potentials discussed above.

2.7 AIM OF THE PRESENT STUDY

We have already summarized the results of the comparative studies of various potentials carried out by Varshni¹ and Steele et al⁸. Varshni¹ found that the analytical functions due to Morse, Poschl-Teller, Rosen-Morse, Frost-Musulin, Rydberg and Lippincott give the α_e and $\omega_e x_e$ values in the increasing order of accuracy. Varshni's third, sixth and seventh functions are also successful in this respect. For over all representation of the P.E curves, the Rydberg, Varshni III-

and Varshni VI functions were found to be most successful.

Steele et al⁸ found that Linnett, Lippincott and Rydberg functions yield minimum percentage errors in the estimates of α_e and $\omega_e x_e$ values. However, a function evaluating satisfactory α_e and $\omega_e x_e$ values does not necessarily show a good reproducibility of P.E curves e.g. Linnett. On the other hand a function like Hulburt and Hirschfelder gives nearly the best fit of the potential for all the molecules considered. The Frost-Musulin potential does not give any appreciable improvement over the Morse curve, while Rydberg potential is a distinct improvement.

Among the combination potentials discussed in the previous sections, MK potential is not satisfactory as compared to Morse potential. Also MRK potential fails to evaluate accurate α_e and $\omega_e x_e$ values. The failure of these two combination potentials, as we understand, is due to the following reasons: (1) The simple Morse function though 'overworked in many branches of investigation' gives a poor performance as has been noted by Varshni¹. A suitable modification is therefore needed to improvise the same. (2) Kratzer function is not applicable to molecular problems¹ as it predicts the abnormal result $\Delta=1$ for Sutherland's parameter which value is not found in any diatomic molecule.

On the other hand the combinations of Rydberg potential with others are more successful e.g. MR and RK potentials are more suitable for the overall representation of the P.E. curves and for estimating accurate α_e and $\omega_e x_e$ values. The reason is due to the fact that¹ Rydberg function is at the top in evaluating α_e and $\omega_e x_e$ in order of increasing accuracy and in reproducing the P.E. curves.

With a view to further improvise the general performances of individual Morse and Rydberg potentials, we have tried, in the present work, various combinations of these functions with other functions.

2.8 PRESENT WORK

We have suggested two hybrid potentials involving generalized Morse, Kratzer and Rydberg potentials, three combinations of Rydberg function with Varshni's and Lippincott's functions and one superposition function due to Varshni's second and sixth potentials.

2.8.1 Generalized Morse and Rydberg (GMR) potential

$$U(r) = D_e [1 - \exp(-b\rho)]^2 - D_e [1 - (1 + b\rho) \exp(-b\rho)] \rho^3 \exp(-b\rho) \quad (17)$$

where $\rho = (r - r_e)/r_e$. It satisfies the three necessary criteria of Varshni. The first term is a slight modification of Morse-

potential, while the second term represents a more generalized form of Rydberg potential. After simplification Eq(17) takes the following form:

$$U(r)=D_e[1-\exp(-b \rho)]^2+D_e[(1+b \rho) \rho ^3 \exp(-2b \rho)] -D_e \rho ^3 \exp(-b \rho) \quad (18)$$

The first two terms of this equation constitute a potential which is similar to Hulburt-Hirschfelder potential. The GMR potential is one of a class of possible potential functions of the form.

$$U(\rho)=D_e \{ [1-\exp(-b\rho)]^2 + \rho ^3 \exp(-b\rho)F(\rho) \} \quad (18a)$$

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

For a variety of $F(\rho)$ values, the necessary criteria $U(0)=0$ and $U(\infty) = D_e$ are satisfied. We have chosen

$$F(\rho)=[-1+(1+b\rho)\exp(-b\rho)] \quad (18b)$$

By putting $F(\rho) = C(1+b\rho)\exp(-b\rho)$ in Eq (18a) Hulburt-Hirschfelder Potential can be obtained.

In general, one may get $F(\rho)=n+\exp(-b\rho)(1+b\rho)$ and find the best n value which would lead to the best performance of the potential function given by Eq(18a). This potential therefore needs to be further examined.

By following Varshni's method¹ we obtained the expressions given below:

$$U^{II}(r_e) = 2D_e b^2 / r_e^2 \text{ with } b = (\Delta)^{\frac{1}{2}}$$

$$U^{III}(r_e) = -6D_e b^3 / r_e^3 \text{ and } U^{IV}(r_e) = 2D_e b(7b^3 + 3) / r_e^4$$

$$\alpha_e = (\Delta^{\frac{1}{2}} - 1) 6B_e^2 / \omega_e \quad (19)$$

$$\text{and } \omega_e x_e = [8\Delta - (3/\Delta^{\frac{1}{2}})] W / \mu_A r_e^2 \quad (20)$$

It is interesting to note that Eq(19) is exactly the same as that given by Morse, while G function in Eq(20) differs by a factor of $3/\Delta^{\frac{1}{2}}$

2.8.2 Generalized Morse and Kratzer(GMK) potential

Raghuwanshi and Sharma² directly combined Morse and Kratzer potentials to formulate their MK potential. We have considered Varshni's first and fifth functions which are the generalizations of Morse and Kratzer potentials respectively. With a view to formulate a three-constant potential function we used only one potential parameter (n).

$$U(r) = D_e \{ 1 - \exp[-n(r^2 - r_e^2) / 2r_e^2] \}^2 + D_e \{ 1 - (r_e/r)^n \}^2 \quad (21)$$

It satisfies the three criteria. Varshni's method leads to

$$U^{II}(r_e) = 4D_e n^2 / r_e^2 \text{ with } n = (\Delta/2)^{\frac{1}{2}}$$

$$U^{III}(r_e) = -12D_e n^3 / r_e^3 \text{ and } U^{IV}(r_e) = 2D_e n^2 (14n^2 + 6n + 14) / r_e^4$$

$$\alpha_e = [(\Delta/2)^{\frac{1}{2}} - 1] 6B_e^2 / \omega_e \quad (22)$$

$$\omega_e x_e = [4 \Delta - 3(\Delta/2)^{\frac{1}{2}} - 7] W / \mu_A r_e^2 \quad (23)$$

In Eq (21), a term $\pm D_e$ can be added to bring the minimum of potential energy curves at zero value.

2.8.3 Varshni's Second and Sixth [V(II & VI)] Potential

Varshni's second potential function is unsuitable for calculating α_e and $\omega_e x_e$ values, while his sixth function is seen to be the most accurate function in this respect¹. In order to improvize the performance of second function, we have linearly combined it with the relatively successful sixth function

$$U(r) = D_e \{ 1 - (r/r_e) \exp[-a(r-r_e)] \}^2 + D_e \{ 1 - (r/r_e) \exp[-a(r-r_e)] \}^2 \quad (24)$$

In this combination we have used only one potential parameter 'a' to have a simple three-constant potential function. By following Varshni's method we got

$$U^{II}(r_e) = 4D_e (a^2 r_e^2 + 1) / r_e^2 \quad \text{with } a = [(\Delta/2) - 1] / r_e$$

$$U^{III}(r_e) = -12(D_e / r_e^3) [a^3 r_e^3 + 3a r_e + 1] / r_e^3$$

$$U^{IV}(r_e) = (4D_e / r_e^4) [7a^4 r_e^4 + 42a^2 r_e^2 + 36a r_e + 18]$$

$$\alpha_e = [(x^3 - x^2 + 3x) / (x^2 + 1)] 6B_e^2 / \omega_e \quad (25)$$

$$\omega_e x_e = [(8x^6 + 41x^4 - 6x^3 + 75x^2 + 54x - 3) / (x^4 + 2x^2 + 1)] W / \mu_A r_e^2 \quad (26)$$

Where $x = [(\Delta/2) - 1] = a r_e$

2.8.4 Rydberg and Lippincott (RL) Potential

As per Varshni¹, Rydberg potential is found to be nearly at the top in evaluating α_e and $\omega_e x_e$ values accurately. It is also a successful function for overall representation of P.E. curves. However, Lippincott function is found to give most accurate values for $\omega_e x_e$ only. It is not that satisfactory in estimating α_e and representing the P.E. curves. It is therefore felt that the performance of Lippincott function for the latter purpose can be improved by combining it with the Rydberg function. In this combination also we have made use of a single potential parameter 'b'

$$U(r) = -D_e [1 + b(r - r_e)] \exp[-b(r - r_e)] + D_e \left\{ 1 - \exp[-b(r - r_e)]^2 / r \right\} \quad 27$$

According to Varshni's method we obtain

$$U^{II}(r_e) = (D_e b / r_e) [b r_e + 2] \quad \text{with} \quad b = (\sqrt{1 + 2\Delta} - 1) / r_e$$

$$U^{III}(r_e) = -2D_e b (b^2 r_e^2 + 3) / r_e^2$$

$$U^{IV}(r_e) = D_e b [3b^3 r_e^3 - 12b r_e + 24] / r_e^3$$

$$\alpha_e = \left\{ [2b r_e - 3] b r_e / [3b r_e + 6] \right\} \quad 6B_e^2 / \omega_e \quad 28$$

$$\omega_e x_e = \left\{ (11b^4 r_e^4 - 18b^3 r_e^3 + 156b^2 r_e^2 + 46) / 3(b r_e + 2)^2 \right\} \quad W / \mu_A r_e^2 \quad 29$$

2.8.5 Rydberg and Varshni's Second[RV(II)]Potential

We have seen earlier that Rydberg potential is the

most suitable one for both the calculations of α_e and $\omega_e x_e$ and representation of P.E. curves, while Varshni's second potential is unsuitable.¹ In order to upgrade the general performance of the latter function we have tried its combination with Rydberg potential

$$U(r) = -D_e \{ 1 + b(r-r_e) \exp [-b(r-r_e)] \} + D_e \{ 1 - (r_e/r) \exp [-b(r-r_e)] \}^2 \quad (30)$$

Varshni's method leads to

$$U^{II}(r_e) = D_e [3b^2 + (4b/r_e) + (2/r_e^2)] \quad \text{with} \quad b = (\sqrt{6\Delta - 2} - 2)/3r_e$$

$$U^{III}(r_e) = -D_e [8b^3 + (18b^2/r_e) + (24b/r_e^2) + (12/r_e^3)]$$

$$U^{IV}(r_e) = D_e [17b^4 + 56(b^3/r_e) + 120(b^2/r_e^2) + 144(b/r_e^3) + (72/r_e^4)]$$

$$\alpha_e = [(8x^3 + 9x^2 + 12x + 6)/(9x^2 + 12x + 6)] 6B_e^2/\omega_e \quad (31)$$

$$\omega_e x_e = \left[\frac{5(8x^3 + 18x^2 + 24x + 12)^2}{3(3x^2 + 4x + 2)^2} - \frac{(17x^4 + 56x^3 + 120x^2 + 144x + 72)}{(3x^2 + 4x + 2)} \right] \frac{W}{\mu A r_e^2} \quad (32)$$

Where $x = br_e$

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

According to Varshni¹ his sixth potential function is the most accurate one in calculating α_e values and representing P.E. curves. Regarding the evaluation of $\omega_e x_e$ it is found

to be the next successful function to the Lippincott and Rydberg potentials. Hence its appropriate combination with Rydberg potential would further increase the accuracy of the results. We have attempted the following combination:

$$U(r) = -D_e \{1+b(r-r_e) \exp [-b(r-r_e)]\} + D_e \{1-(r/r_e) \exp [-b(r-r_e)]\}^2 \quad (33)$$

Varshni's method gives

$$U^{II}(r_e) = D_e [3b^2-(4b/r_e)+(2/r_e^2)] \quad \text{with} \quad b=[(\sqrt{6\Delta}-2)+2]/3r_e$$

$$U^{III}(r_e) = -D_e [8b^3-18(b^2/r_e)+(12b/r_e^2)]$$

$$U^{IV}(r_e) = D_e [17b^4-56(b^3/r_e) + (48b^2/r_e^2)]$$

$$\alpha_e = \left[\frac{2b(4b^2r_e^3-9br_e^2+6r_e)}{3(3b^2r_e^2-4br_e+2)} - 1 \right] \frac{6B_e^2}{\omega_e} \quad (34)$$

$$\omega_e x_e = \left[\frac{20b^2(4b^2r_e^2-9br_e+6)^2}{3(3b^2r_e^2-4br_e+2)^2} - \frac{b^2(17b^2r_e^2-56br_e+48)}{(3b^2r_e^2-4br_e+2)} \frac{W}{\mu_A} \right] \quad (35)$$

2.9 CONCLUDING REMARKS

Using the above suggested hybrid potentials we have calculated the potential energy curves and the rotational-vibrational coupling constants and anharmonicity constants for a number of diatomic molecules which were randomly chosen.

In the next Chapter 3 we have reported the potential energy curves in comparison with those obtainable on other well-known potential functions and by the RKR method.

Table 2.1
Comparison of F and G expressions

Potential	Expression for F	Expression for G
1) M.K.	a) $[\frac{(\Delta-1)^{3/2}}{\Delta} - \Delta + 2]$	b) $[8\Delta - 31 + (2/\Delta) + (45/\Delta^2) + 60 \frac{(\Delta-1)^{3/2}}{\Delta^2}]$
2) R.K	a) $\{ [2(\Delta-1)^{3/2} - 3\Delta + 6]/3\Delta \}$	$\{ (5/3)[2(\Delta-1)^{3/2} + 6] \frac{\Delta^2}{\Delta} - 6 \frac{[(\Delta-1)^2 + 6]}{\Delta} \}$
3) MR(I)	0.873 $\Delta^{1/2} - 1$	4.34 Δ
4) MR(II)	0.833 $\Delta^{1/2} - 1$	5.416 Δ
5) MRK	$\{0.6869(\Delta-1)^{3/2}/\Delta + (2/\Delta) - 1\}$	$\{3.8272\Delta - 14.7316 + (18.0184/\Delta) + (52.9228/\Delta^2) + [42.1232(\Delta-1)^{3/2}/\Delta^2]\}$
6) Imp. MR(I)	1.2346 $\Delta^{1/2} - 1$	11.65 Δ
7) Imp MR(II)	1.0264 $\Delta^{1/2} - 1$	8.247 Δ
8) ^C New MR	0.9714 $\Delta^{1/2} - 1$	7.655 Δ

Note: a) Rewritten/derived in present work
b) Ref(7)
c) Ref(6)
d) 'Imp' means improved

M-Morse, K-Kratzer, R-Rydberg, Δ -Sutherland's Parameter

R E F E R E N C E S

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