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## Comparative study of few diatomic empirical potential functions

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**Abstract:** The diatomic potential function suggested by Zavitsas and Dimitreva-Zenevich are explored further. A modification in Zavitsas potential function is suggested. The extended Rydberg and H-H potential functions along with Zavitsas, modified Zavitsas and D-Z potential are used to construct the PE curves of the ground states of CO and I<sub>2</sub>. Study of percentage deviations from RKR curves show that the Zavitsas function is a better agreement to the RKR curves.

**Key words:** diatomic functions, empirical potentials, modified Zavitsas function, D-Z function.

### I. Introduction

The empirical potential energy functions of diatomic molecules are one of the topics of interest in the study of diatomic molecular spectra. There are number of empirical potential functions suggested from time to time, which involve the spectroscopic constants derived from the vibrational and rotational analysis of the molecular spectra. Apart from the classic functions suggested by Morse [1], Rydberg [2], Kratzer [3], Lippincott [4], Hulbert-Hirschfelder (H-H) [5], there are few other functions like Tietz [6], Hua [7], Mattera [8]. Varshni [9] etc. Various combinations of potential functions like Morse, Rydberg and Kratzer [10-14] were tried but none of them was found satisfactory. Goodisman [15] and Erkoc [16], have reviewed and reported number of potential functions in their papers. Few of them are used for computer simulations of condensed matter properties. Lim [17] has applied the potential functions to various problems like loading and deformation studies. An energy consistent potential function was suggested by Sun and Feng [18]. Based on the numerical solutions of Schrodinger's equation, Heidari and Beg [19] have shown better accuracy of the H-H function compared to other empirical potential functions. Timothy Royappa and others [20] have recently taken the survey of 21 potential functions comprising old and new potential functions and concluded that the functions involving more parameters generally produce closer fits to Rydberg – Klien – Rees – Vanderslice (RKR) curves.

In the present study the potential functions suggested by Zavitsas [21] and Dimitreva-Zenevich (D-Z) [22] are applied for the construction of potential energy curves of ground states of CO and I<sub>2</sub> as they have large number of vibrational levels and the molecular constants are also known at higher accuracy. The potential functions suggested by Murrell and Sorbie [23-24] usually known as extended Rydberg function used in present work and all they are compared with RKR curves for their performance.

### II. Potential energy functions

The Morse [1] potential energy function is modified by various workers [25-30]. In fact the Hulbert-Hirschfelder [5] potential is an extension of Morse function and gives fair results. Zavitsas also modified the Morse function, which is explored further in the present work. In this function the electronegativities of constituent atoms forming a diatomic molecule are used. It will not be out of place here to mention a potential energy function suggested by Szoke and Baitz [31] where in also the electronegativities were used.

The Dimitreva-Zenevich (D-Z) [22] potential function was compared by Bhartiya and Behere [32] with the extended Rydberg potential function but for the calculation of anharmonicity constants for number of molecules using the formulae given by Varshni [9]. The Zavitsas potential [21] curve for the electronic state of any molecule has to be constructed in two parts viz  $r < r_e$  and  $r > r_e$ . Where  $r_e$  is equilibrium internuclear distance and  $r$  is instantaneous value. So also the D-Z potential, which has to be constructed in two parts  $y < y_m$  and  $y > y_m$ . (See further explanations). In both cases i.e. D-Z potential function and extended Rydberg function, one has to solve the quartic equation for getting required parameters. All these similarities tempted us to investigate these functions in detail. The comparison of the H-H and extended Rydberg potential function with RKR curves for the ground states of the diatomic Aluminium halides was reported in our earlier studies [33].

### III. The Zavitsas potential function

The function suggested by Zavitsas [21] is modification of Morse function is given as:

$$U_{(Z)} = D_e [1 - \exp(-\beta_{\pm} x)]^2 \quad (1)$$

Where  $x = r - r_e$  and  $D_e$  is dissociation energy. In the Morse function  $\beta$  is constant throughout, but here this  $\beta_{\pm}$  changes.  $\beta_+$  is used for  $r > r_e$  and  $\beta_-$  is used for  $r < r_e$ .

$$\beta_+ = \beta_M (1 + a_1 u^{1/2} + a_2 u^n + a_3 u^{3n} + a_4 u^{5n}) \quad (2)$$

$$\beta_- = \beta_M (1 + m u^{1/2}) \quad (3)$$

$\beta_M$  is Morse constant given by the expression

$$\beta_M = (2\pi^2 c \mu \omega^2 / h D_e)^{1/2} = 0.006513 \omega_e (\mu / D_e)^{1/2} = 8.486 (k_N)^{1/2} \quad (4)$$

Where  $k_N$  denotes normalized force constant  $k_N = k_e / D_e$  ;

$$k_e = 4\pi^2 \mu \omega^2 = (5.8923 \times 10^{-7}) \mu \omega^2 \text{ milli dynes/A}^0 \quad (5)$$

$$u = [1 - \exp(-\beta_M x)]^2 \quad (6)$$

$$m = -0.025 r_e + 0.70 \exp(-7.41 \times 10^3 k_N r_N) / (z_1 z_2) + 0.042 |(\Delta \chi)| \quad (7)$$

$r_e$  is equilibrium internuclear distance and  $r_N$  is  $(r_e / D_e)$

$|(\Delta \chi)|$  is difference between the electronegativities of two atoms forming a diatomic molecule

$$n = 0.70 - 0.03 r_e + 0.096 / ((1 \times 10^3) k_N r_N - 0.3) + 0.55 (\Delta \chi)^2 / r_e^{1/2} \quad (8)$$

$$a_1 = -0.32 m; a_2 = 0.15; a_3 = 0.2 - 0.6 m; \text{ and } a_4 = (0.21 - 3m) \times |(\Delta \chi)|^2$$

#### IV. Modified Zavitsas function

In the potential function given by equation (1) to equation (8) few anomalies are conspicuous. The quantities  $m$  and  $n$  should be dimensionless but the terms  $-0.025 r_e$  in expression of  $m$  (7) and  $-0.03 r_e$  in expression of  $n$  (8) are not dimensionless as the numbers are multiplied by  $r_e$  having dimension of length. The quantities  $k_N$  and  $r_N$  are also expected to be dimensionless but they are not. In order to overcome these difficulties we tried to take  $r_N = r_e D_e$  ( $D_e$  in  $\text{cm}^{-1}$  and  $r_e$  in cm) and instead of  $k_N$  given by Zavitsas we used  $\Delta$ , a Sutherland parameter defined as  $\Delta = k_e r_e^2 / 2 D_e$  when  $k_e$  is in dynes  $\text{cm}^{-1}$  and  $D_e$  is in ergs. This parameter  $\Delta$  is a dimensionless number. The  $10^3$  factor appearing in the expression of  $m$  and  $n$  are excluded as we are not converting the millidynes to dynes etc. Another modification is in the last terms of  $n$  which overweighs due to  $r_e^{1/2}$  as it is in the denominator. We excluded it from equation 8 and Morse constant is taken as

$$\beta_M = 0.1277 \times 10^8 \omega_e (\mu / D_e)^{1/2} \quad (9)$$

With these modifications the expression of  $m$  and  $n$  are as follows.

$$m = -0.025 r_N + 0.70 \exp(-7.41 \Delta) / (z_1 z_2) + 0.042 |(\Delta \chi)| \quad (10)$$

$$n = 0.70 - 0.03 r_N + (0.096 / (\Delta - 0.3)) + 0.55 (\Delta \chi)^2 \quad (11)$$

#### V. The Dimitreva-Zenevich (D-Z) potential function

A simple analytical approximation for diatomic potential function is suggested by Dimitreva and Zenevich[22] which is as follows.

$$v_1(y) = a_0 y^2 / [1 - (a_1 y / 3)]^3 \quad \text{for } y \leq y_m \quad \& \quad (12)$$

$$v_2(y) = D_e - [C / r_e^6 (1 + y)^6] \quad \text{for } y \geq y_m \quad (13)$$

The boundary conditions of slopes yield the quartic equation in  $y_m$

$$y_m \{ (-5 a_1 y_m^2 / 3) + [8 + (a_1 / 3) y_m] + 2 \} = 6 [1 - (a_1 y_m / 3)]^4 \times D_e / a_0 \quad (14)$$

This can be simplified as

$$A y_m^4 + B y_m^3 + C y_m^2 + D y_m + E = 0 \quad (15)$$

Where  $A=1$ ,  $B = (22.5 a_0 / D_e a_1^3) - 12 / a_1$ ,  $C = (54 / a_1^2) - 108 (a_0 / D_e a_1^4) - 4.5 a_0 / D_e a_1^3$

$D = - [108 / a_1^3 + 27 (a_0 / D_e a_1^4)]$  &  $E = 81 / a_1^4$

Where  $a_0$  and  $a_1$  are Dunham coefficients given as  $a_0 = (\omega_e^2 / 4 B_e)$  and  $a_1 = [-1 - (\alpha_e \omega_e / 6 B_e^2)]$

Where the symbols carry their usual meanings.

The quartic polynomial in  $y_m$  gives four roots. The smaller +ve root is selected and this value of  $y_m$  helps to calculate  $C$  which is required in expression of  $v_2(y)$ .

$$C = \frac{a_0 y_m \left[ \left( 2 + \frac{a_1 y_m}{3} \right) \right] (1 + y_m)^7 r_e^6}{\left\{ 6 \left[ 1 - \left( \frac{a_1 y_m}{3} \right) \right]^4 \right\}} \quad (16)$$

These formulae are used in the calculation of PE curves of ground state of CO and  $I_2$ .

#### VI. Extended Rydberg function

Huxley and Murrell [23-24] have suggested the potential function resembling to Rydberg potential function and therefore named as extended Rydberg potential function.

$$U_R(r) = D_e - D_e \{ 1 + a_1 \rho + a_2 \rho^2 + a_3 \rho^3 \} e^{(-a_1 \rho)} \quad (17)$$

Where  $\rho = r - r_e$  and  $a_1, a_2, a_3$  are constants not to be confused with Dunham coefficients.

This potential function gives good fit to RKR curves and is employed by Behere et al [34] to construct the PE curves of alkaline earth halide molecules. To calculate  $a_1, a_2$  and  $a_3$  we need the force – field parameters which are :

$$f_2 = 4\pi^2 m \omega_e^2 c^2 \quad (18)$$

$$f_3 = (3 f_2 / r_e) [1 + (\alpha_e \omega_e / 6 B_e^2)] \quad (19)$$

$$f_4 = (f_2/r_e^2) \{ 15[1 + (\alpha_e \omega_e / 6B_e^2)] - [8 \omega_e x_e / B_e] \} \quad (20)$$

Where  $f_n$  are the  $n^{\text{th}}$  derivative of the potential at the equilibrium distance  $r_e$ .

The first step is to solve the following quartic equation for  $a_1$

$$D_e a_1^4 - 6f_2 a_1^2 - 4f_3 a_1 - f_4 = 0 \quad (21)$$

If the roots are real, then since  $f_4$  is always positive there must be one or three positive roots of equation (21). For acceptable equation the largest positive root gives the best result. In some cases, it was observed by Huxley and Murell [24] that the solution of equation (21) has one +ve, one -ve and a pair of complex conjugate roots whose real part is largest than the real +ve root and whose imaginary part is small.

By differentiating equation (21) we get,

$$a_2 = (1/2) [a_1^2 - (f_2/D_e)] \quad (22)$$

$$a_3 = a_1 a_2 - (a_1^3/3) - (f_3/6D_e) \quad (23)$$

In such cases the more suitable values of  $a_1$  would be the real part of these complex roots and if this is substituted in equation (21) equation (22) and (23) will give +ve values of  $a_2$  and  $a_3$ . Once  $a_1$  is known then all other parameters can be calculated. The real part of complex root is not of course an exact root of equation (21) and  $f_4$  is derived from the resulting potential according to the following expression,

$$f_4 = D_e [3a_1^4 - 12a_1^2 a_2 + 24a_1 a_3] \quad (24)$$

The programme was designed by Behere and extended Rydberg potential energy curves were successfully drawn for the ground states of several molecules.

## VII. Results and Discussion

In order to study the behaviour of all the potential functions described above, two molecules namely CO and  $I_2$  are selected. As these molecules are having deep wells and large number of vibrational levels. The spectroscopic constants used were of Farrenq [35] for CO ( $X^1\Sigma$ ) and of Ashmore and Tellinghuisen[36] for  $I_2$  ( $X^3\Pi$ ). The molecular parameters calculated are reported in Table 1.

The RKR curve, the extended Rydberg function, Zavitsas function, modified Zavitsas function; and the D-Z function are plotted for  $I_2$  and CO in figure 1 and 2 respectively. The error curves which show % deviation from RKR are also plotted below these curves at same abscissa scale. The PE curves are constructed to cover more than 98% of the potential energies. For CO % deviation is minimum for Zavitsas which is less than 1% and very high for modified Zavitsas around 6%. Extended Rydberg shows a deviation nearly 1.6%, where D-Z shows nearly 5.5% deviations. In case of  $I_2$  the Zavitsas function shows 1.9% and modified Zavitsas functions shows nearly 2.9% deviation in different regions of  $r$ . The extended Rydberg shows 1% deviation whereas D-Z shows 4.5%.

## VIII. Conclusions

Finally we conclude that the D-Z function shows slightly greater errors compared to extended Rydberg function supporting our earlier studies [34]. The Zavitsas function although logically difficult to digest, gives better result compared to our modification. But as suggested by Zavitsas it depends on the type of binding in the molecule.

| Potential function | Constants | CO $X^1\Sigma$           | $I_2$ $X^3\Pi$            |
|--------------------|-----------|--------------------------|---------------------------|
| Extended Rydberg   | $a_1$     | 3.842102                 | 4.219898                  |
|                    | $a_2$     | 2.093122                 | 5.450451                  |
|                    | $a_3$     | 1.77661                  | 3.0436                    |
| D-Z Function       | $y_m$     | 0.669282                 | 0.162297                  |
|                    | $C$       | 1076335                  | 7086400                   |
| Zavitsas           | $m$       | 0.01915                  | -0.06666                  |
|                    | $n$       | 5.935301                 | 0.649416                  |
|                    | $a_1$     | -0.00613                 | 0.02133                   |
|                    | $a_2$     | 0.15                     | 0.15                      |
|                    | $a_3$     | 0.18851                  | 0.239994                  |
|                    | $a_4$     | 0.152551                 | 0                         |
|                    | $r_N$     | 0.004358                 | 0.074324                  |
|                    | $k_e$     | 19.02013                 | 1.720618                  |
|                    | $k_N$     | 0.073469                 | 0.047963                  |
|                    | $\beta_m$ | 2.299803                 | 1.858191                  |
| Modified Zavitsas  | $m$       | 0.039897446              | $-8.36352 \times 10^{-6}$ |
|                    | $n$       | 1.180626518              | 0.673900326               |
|                    | $a_1$     | -0.01276718              | $2.67633 \times 10^{-6}$  |
|                    | $a_2$     | 0.15                     | 0.15                      |
|                    | $a_3$     | 0.176061532              | 0.200005018               |
|                    | $a_4$     | 0.081502665              | 0.210025091               |
|                    | $r_N$     | 0.000102162              | 0.000335                  |
|                    | $\Delta$  | 6.734676312              | 24.5501546                |
|                    | $k_e$     | 1902012.47               | 172061.9108               |
|                    | $k_N$     | $1.05799 \times 10^{17}$ | $6.90663 \times 10^{16}$  |
|                    | $\beta_m$ | 2.299201963              | 1.857677421               |

Table 1. Derived molecular constants for various potential functions

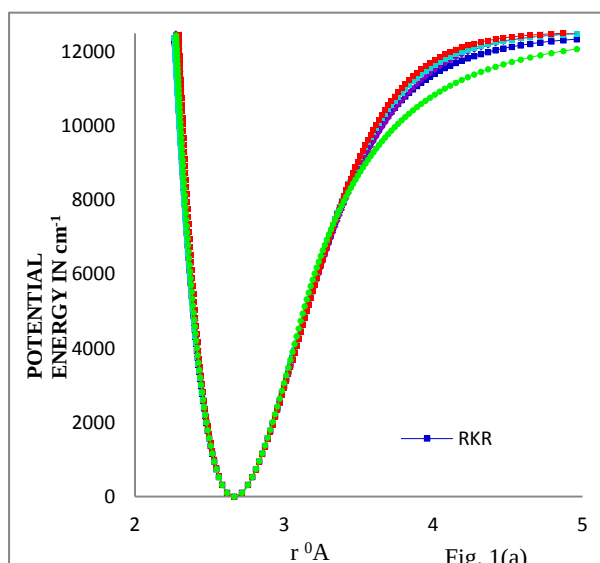


Fig. 1(a)

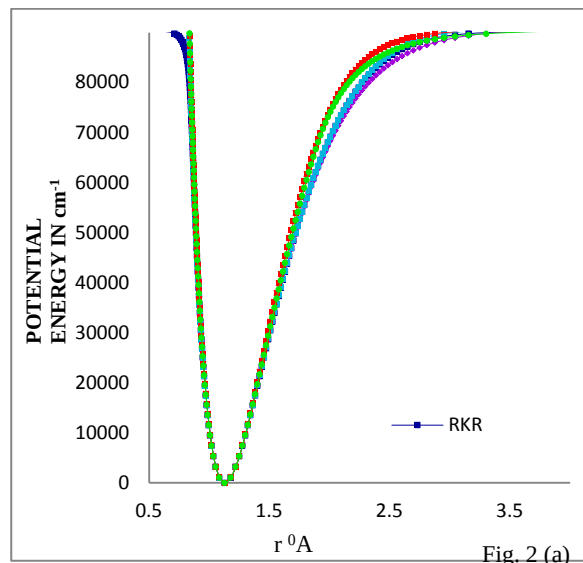


Fig. 2(a)

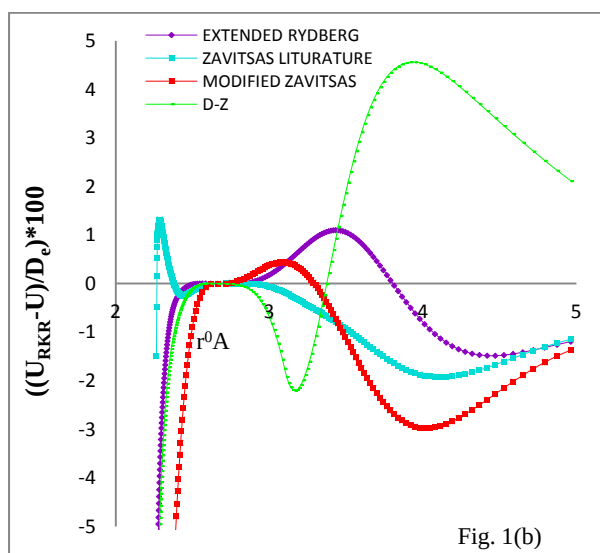


Fig. 1(b)

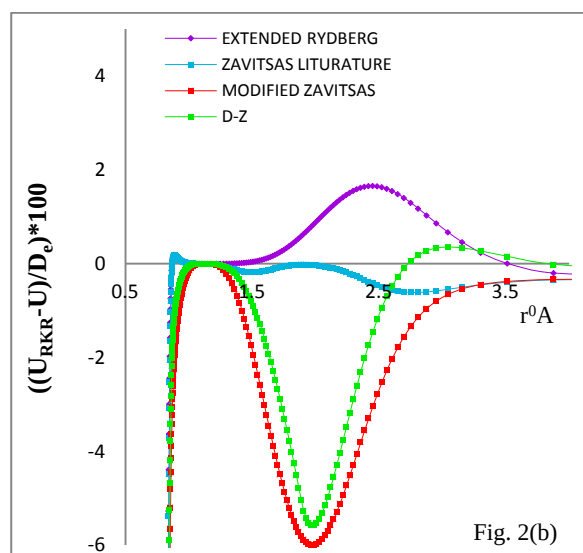


Fig. 2(b)

Fig 1 (a) PE curves (b) % Deviation for the ground state of I<sub>2</sub>

Fig 2 (a) PE curves (b) % Deviation for the ground state of CO

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