

## An Empirical Five-Parameter Potential Energy Function of Stable Diatomic Molecules

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**ABSTRACT.** A good deal of information about the structure of diatomic molecules is contained in their potential energy curves. One of the methods of constructing the potential curves is the use of an empirical potential function. This type of function is fitted to an algebraic expression and its parameters are related to the spectroscopic constants, the bond length  $r_e$ , the force constant  $k_e$ , the vibrational-rotational coupling  $\alpha_e$ , the anharmonicity constant  $\omega_e x_e$ , and the dissociation energy  $D_e$ .

A number of three-parameter functions are found in literature but no much work has been done on five-parameter function. Hülbert-Hirschfelder function is an extension of Morse function where the repulsion part of Morse function has been modified. We are doing an exercise of modifying the Morse function by taking various forms of either the attractive branch or both the attractive and repulsive branches.

We make potential curve calculation of fifteen molecular states with this function and make comparative study with those of Morse and Hülbert-Hirschfelder functions. We present the plots of these curves and also calculate the absolute deviations by calculating the percentage error.

### 1. Introduction

Knowledge of internuclear potential curves is of fundamental importance in a wide variety of fields ranging from gas kinetics to stellar structure. There is a need for accurate potential curves for the different electronic states of diatomic molecules. The Schrödinger equation for a molecule is

$$\hat{H} \Psi = E \Psi \quad (1.1)$$

where the Hamiltonian operator for a diatomic molecule is

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN} \quad (1.2)$$

Here  $\hat{T}_N$  and  $\hat{T}_e$  stands for the kinetic energy operators for the nuclei and electrons, respectively.  $\hat{V}_{ee}$  is the electron-electron repulsion term,  $\hat{V}_{eN}$  is the electron-nuclear repulsion term. On the validity of the Born-Oppenheimer approximation, we can separate the Schrödinger equation of a molecule into two parts and write a complete wavefunction  $\Psi$  as

$$\Psi(\mathbf{r}, \mathbf{R}) = \Psi_N(\mathbf{R}) \Psi_e(\mathbf{r}, \mathbf{R}) \quad (1.3)$$

and

$$\hat{H}_e \Psi_e = E_e \Psi_e \quad (1.4)$$

then

$$(\hat{H}_N + E_e) \Psi_N = E \Psi_N \quad (1.5)$$

Here  $\Psi_n$  depends only on the nuclear co-ordinates.  $E_e$  is the electronic energy which is a function of the internuclear distance  $r$ . We understand that

$$\hat{H}_N = \hat{T}_N + \hat{V}_{NN} \quad (1.6)$$

$$\hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} \quad (1.7)$$

Eq. (1.5) can be written as

$$(\hat{T}_N + \hat{V}_{NN} + E_e) \Psi_N = E \Psi_N \quad (1.8)$$

The sum  $(\hat{V}_{NN} + E_e)$  is termed as the potential energy function written to be

$$U = \hat{V}_{NN} + E_e \quad (1.9)$$

For a diatomic molecule it is simply a function of the internuclear distance  $r$  and represented by a typical potential curve as shown in figure (1).

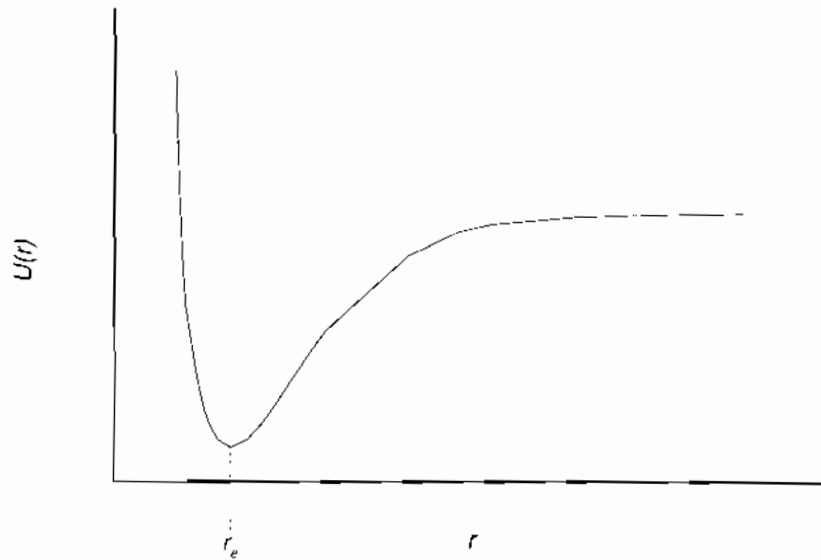


Fig. (1): A typical potential energy curve.

A theoretical calculation for the potential energy function involves the solution of Eq. (1.4). Accurate potential energy function can be calculated by *ab initio* methods for

relatively small molecules. For large systems, the calculation becomes prohibitive both in terms of computer time and storage requirements. We therefore need other alternative methods.

The Rydberg-Klein-Rees (RKR) (Rydberg, 1933; Klein, 1932; Rees, 1947) method is the one widely used method employing the experimental vibrational and rotational levels. The major disadvantage of this method is that the potential curve can be constructed only in the region for which sufficient spectroscopic data is available.

## 2. Empirical potential function

Another procedure is, then, suggested where an empirical function is fitted to a certain algebraic expression of the form.

$$U(r) = U(r_e) + (r - r_e) \left. \frac{dU}{dr} \right|_{r=r_e} + \frac{(r - r_e)^2}{2!} \left. \frac{d^2U}{dr^2} \right|_{r=r_e} + \frac{(r - r_e)^3}{3!} \left. \frac{d^3U}{dr^3} \right|_{r=r_e} + \dots \quad (2.1)$$

This function obeys the following conditions:

- The function should go to infinity as  $r$  goes to zero.
- It should pass through a minimum at some value of  $r$ .
- It should approach a finite limiting value as  $r$  goes to infinity.

We can therefore apply the following conditions to evaluate the parameters of the potential function in terms of molecular constants. For three-parameter function the conditions are

$$U_\infty - U(r_e) = D_e \quad (2.2)$$

$$\left. \frac{dU}{dr} \right|_{r=r_e} = 0 \quad (2.3)$$

$$\left. \frac{d^2U}{dr^2} \right|_{r=r_e} = k_e \quad (2.4)$$

In four and five parameters functions these conditions are extended to

$$\left. \frac{d^3U}{dr^3} \right|_{r=r_e} = k_e X \quad (2.5)$$

$$\left. \frac{d^4U}{dr^4} \right|_{r=r_e} = k_e Y \quad (2.6)$$

where  $X$  and  $Y$  are related to  $\alpha_e$  and  $\omega_e x_e$  respectively by the relations (Varshini, 1957)

$$X r_e = -3 \left[ \frac{\omega_e x_e}{6B_e^2} + 1 \right] \quad (2.7)$$

$$Y r_e^2 = \frac{5}{3} X^2 r_e^2 - 8 \frac{\omega_e x_e}{B_e} \quad (2.8)$$

We also make use of Sutherland parameter  $\Delta$  in our calculations which is

$$\Delta = \frac{k_e r_e^2}{2D_e} \quad (2.9)$$

A number of three- to four- parameter functions are found in literature (Morse, 1929; Rosen & Morse, 1932; Pöschl G. and Teller E., 1933; Linnett, 1940; Linnett, 1941; Lippincott, 1953; Hua, 1990; Fayyazuddin & Rafi, 1995). We are proposing a new five-parameter function.

### 3. The proposed five-parameter function

The general form of the proposed function is

$$U(x) = D_e \left[ f(x) e^{-2ax} - 2g(x) e^{-ax} \right] + D_c \quad (3.1)$$

where

$$f(x) = 1 + a_2 x^2 \quad (3.2)$$

$$g(x) = 1 + \frac{a_2}{2} x^2 + b_1 x^3 \quad (3.3)$$

and  $x = r - r_e$ .

The Proposed function can also be written as

$$U(x) = D_e \left[ (1 + a_2 x^2) e^{-2ax} - 2 \left( 1 + \frac{a_2}{2} x^2 + b_1 x^3 \right) e^{-ax} \right] + D_c \quad (3.4)$$

To solve  $a_2$  and  $b_1$  in terms of known experimental constants we put  $a_2 = \beta a^2$  and  $b_1 = \beta' a^3$  and get from Eq. (3.4)

$$\left. \frac{d^2 U}{dx^2} \right|_{x=0} = 2D_e a^2 \quad (3.5)$$

$$\left. \frac{d^3 U}{dx^3} \right|_{x=0} = -6D_e a^3 [2\beta' + \beta + 1] \quad (3.6)$$

$$\left. \frac{d^4 U}{dx^4} \right|_{x=0} = 2D_e a^4 [7 + 18\beta - 24\beta'] \quad (3.7)$$

Eqs. (3.5), (3.6) and (3.7) can be written respectively as

$$a = \frac{\sqrt{\Delta}}{r_e} \quad (3.8)$$

$$Xr_e = -3\sqrt{\Delta} (2\beta' + \beta + 1) \quad (3.9)$$

$$Yr_e^2 = \Delta [7 + 18\beta - 24\beta'] \quad (3.10)$$

and we obtain

$$\beta' = -\frac{11}{60} - \frac{1}{60 \Delta^{1/2}} (\sqrt{\Delta} Yr_e^2 + 6\Delta Xr_e) \quad (3.11)$$

$$\beta = - \left[ 1 + 2\beta' + \frac{Xr_e}{3\sqrt{\Delta}} \right] \quad (3.12)$$

Knowing  $\Delta$ ,  $Xr_e$  and  $Yr_e^2$  from the table of constants (Table 1) we get the values of  $a$ ,  $\beta$  and  $\beta'$  for each state. We therefore are in a position to calculate the potential energy function of a molecule state from Eq. (3.1) and construct the potential energy curve.

#### 4. Potential curve calculations

We have made the potential curve calculations of 15 molecular states using the proposed empirical potential function. These curves have also been constructed for the functions of Hülbert-Hirschfelder (1941), Morse (1929) and Al-Senany (1999) of the same 15 molecular states using the same molecular constants as for the proposed function. We adopt the method of calculating the percentage error used by Steele *et al* (1962) which is

$$\text{percent error} = \frac{|U_{RRR} - U|}{D_e} \times 100 \quad (4.1)$$

We thus give the percentage error as shown in Table (2). The results show that no function gives the least absolute error for all the states. It is in this context that we find how and then new functions proposed. Figure (2) shows the potential curves of the  $2^3\Delta_g$  state of  $\text{Na}_2$  from the Morse (1929), Hülbert -Hirschfelder (1941), Al-Senany (1999) and proposed functions.

To conclude, we can say that the overall performance of the proposed function is quite close to that of Hülbert -Hirschfelder (1941).

Table 1: Experimental Molecular Constants

| Molecule      | State           | $\mu_A$<br>[a] | $k_e \times 10^5$<br>(dyne/cm)<br>[b] | $r_e$ (Å)<br>[c] | $\Delta$<br>[d] | $Xr_e$<br>[e] | $Yr_e^2$<br>[f] |
|---------------|-----------------|----------------|---------------------------------------|------------------|-----------------|---------------|-----------------|
| $\text{H}_2$  | $X^1\Sigma_g^+$ | 0.5080248      | 5.794672                              | 0.741599         | 2.09575         | -4.8136       | 22.7618         |
| $\text{LiH}$  | $X^1\Sigma^+$   | 0.8812382      | 1.024434                              | 1.595584         | 3.23726         | -5.6789       | 29.6012         |
| $\text{NaH}$  | $X^1\Sigma^+$   | 0.9654996      | 0.780582                              | 1.887            | 4.40207         | -6.3406       | 35.1536         |
| $\text{KH}$   | $X^1\Sigma^+$   | 0.9824143      | 0.5631334                             | 2.2401           | 4.81701         | -6.9837       | 44.2131         |
| $\text{RbH}$  | $X^1\Sigma^+$   | 0.9960075      | 0.515025                              | 2.3668           | 4.98293         | -6.6291       | 35.4384         |
| $\text{CsH}$  | $X^1\Sigma^+$   | 1.00024        | 0.467837                              | 2.4943           | 4.95541         | -7.0652       | 45.3493         |
| $\text{Na}_2$ | $2^1\Pi_g$      | 11.4948852     | 0.071029                              | 3.74894          | 5.44991         | -6.0479       | 34.1429         |
| $\text{Na}_2$ | $2^3\Delta_g$   | 11.4948852     | 0.105047                              | 3.53654          | 4.34529         | -5.8116       | 26.9955         |
| $\text{K}_2$  | $X^1\Sigma_g^+$ | 19.481854      | 0.097952                              | 3.92443          | 8.55611         | -6.1047       | 15.4468         |
| $\text{Cs}_2$ | $X^1\Sigma_g^+$ | 66.452718      | 0.069091                              | 4.648            | 10.2995         | -6.3431       | 10.8115         |
| $\text{CaH}$  | $X^3\Sigma^+$   | 0.98303388     | 0.975833                              | 2.002500         | 7.12309         | -6.4387       | 104.9779        |
| $\text{Co}$   | $X^1\Sigma^+$   | 6.85620871     | 19.00730                              | 1.128320         | 6.73114         | -8.0918       | 54.0749         |
| $\text{ICl}$  | $X^1\Sigma^+$   | 27.414671      | 2.383668                              | 2.32091          | 18.4157         | -10.844       | 91.5536         |
| $\text{ICl}$  | $A^3\Pi^1$      | 27.4146708     | 0.7186838                             | 2.6851           | 34.2050         | -13.790       | 118.0980        |
| $\text{I}_2$  | $X^1O_g^+$      | 63.452237      | 1.719395                              | 2.6664           | 24.5339         | -11.691       | 97.6552         |

(a) From Huber and Herzberg (1979)

$$(d) \Delta = \frac{(k_e r_e^2)}{2D_e}$$

(b)  $k_e$ ,  $5.8883 \times 10^{-2} (\mu_A \omega_e)$

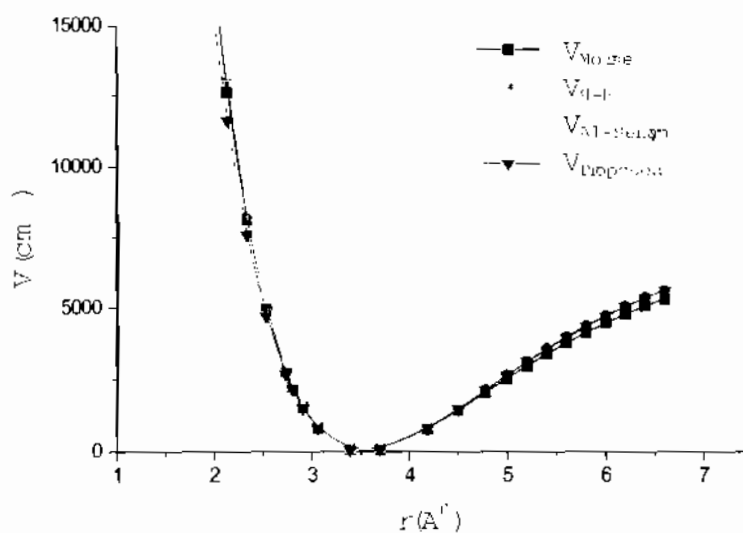
$$(e) Xr_e = -3 \left[ \frac{\omega_e \alpha_e}{6B_e^2} + 1 \right]$$

$$(c) r_e = \frac{(4.1061)}{\sqrt{\mu_A B_e}} \text{Å}$$

$$(f) Yr_e^2 = \frac{5}{3} X^3 r_e^2 - 8 \frac{\omega_e X_e}{B_e}$$

Table (2): The average percentage error

| Molecule        | State                                      | Morse (1929) | Hülbert - Hirschfelder (1941) | Al-Senany (1999) | Proposed |
|-----------------|--|--------------|-------------------------------|------------------|----------|
| H <sub>2</sub>  | X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> | 4.955        | 0.509                         | 13.447           | 2.784    |
| LiH             | X <sup>1</sup> Σ <sup>+</sup>              | 3.538        | 1.346                         | 14.754           | 2.145    |
| NaH             | X <sup>1</sup> Σ <sup>+</sup>              | 0.941        | 0.484                         | 4.738            | 0.743    |
| KH              | X <sup>1</sup> Σ <sup>+</sup>              | 2.106        | 4.817                         | 19.292           | 3.262    |
| RbH             | X <sup>1</sup> Σ <sup>+</sup>              | 1.320        | 1.045                         | 5.714            | 1.246    |
| CsH             | X <sup>1</sup> Σ <sup>+</sup>              | 1.091        | 2.188                         | 7.757            | 1.882    |
| Na <sub>2</sub> | 2 <sup>1</sup> Π <sub>g</sub>              | 4.624        | 1.931                         | 9.659            | 2.049    |
| Na <sub>2</sub> | 2 <sup>1</sup> Δ <sub>g</sub>              | 0.759        | 0.184                         | 2.331            | 0.169    |
| K <sub>2</sub>  | X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> | 12.485       | 0.809                         | 19.246           | 1.116    |
| Cs <sub>2</sub> | X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> | 16.719       | 0.508                         | 40.401           | 4.077    |
| CaH             | X <sup>2</sup> Σ <sup>+</sup>              | 11.723       | 11.156                        | 11.073           | 11.143   |
| Co              | X <sup>1</sup> Σ <sup>+</sup>              | 0.636        | 0.097                         | 6.128            | 0.356    |
| ICl             | X <sup>1</sup> Σ <sup>+</sup>              | 1.032        | 0.085                         | 1.371            | 0.143    |
| ICl             | A <sup>1</sup> Π <sup>1</sup>              | 8.144        | 1.419                         | 29.523           | 2.574    |
| I <sub>2</sub>  | X <sup>1</sup> Ω <sub>g</sub> <sup>+</sup> | 7.673        | 1.479                         | 25.052           | 2.640    |
| <i>Average</i>  |  | 5.183        | 1.870                         | 14.032           | 2.422    |

Fig. (2): The potential curve of the 2<sup>1</sup>Δ<sub>g</sub> of Na<sub>2</sub>.

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## دالة تجريبية لطاقة الجهد ذات خمس عوامل للجزيئات المستقرة والثنائية الذرة

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المستخلص. تتضمن منحنيات طاقة الجهد على كمية كبيرة من المعلومات عن تركيب الجزيئات ثنائية الذرة. إحدى الطرق لبناء منحنيات طاقة الجهد هي استخدام دالة جهد تجريبية. هذا النوع من الدوال يقوم على إيجاد ملائمة بين الدالة ودالة جبرية تكون لعواملها علاقة بالثوابت الفيزيائية مثل طول الرابطة بين الجزيئين  $r_e$ ، ثابت القوة  $k_e$ ، الترابط التذبذبي - الدوراني  $\alpha_e$ ، الثابت غير التوافقي  $\omega_e x_e$ ، وطاقة تفكك الجزيء  $D_e$ .

يوجد عدد من الدوال ذات الثلاث عوامل منشورة في الدوريات العلمية ولكن بندر وجود دوال ذات خمس عوامل. دالة هولبرت وهيرشفييلدر (ذات الخمسة عوامل) هي تطور لدالة مورس (ذات الثلاثة عوامل) حيث تم فيها تعديل الجزء التنافري لدالة مورس. نحن الآن نقوم بمحاولات لتطوير دالة مورس وذلك بإجراء تعديلات على الجزء التجاذبي للدالة فقط وأيضاً بتعديل كلا الجزئين التجاذبي والتنافري في آن واحد.

نحن نقوم حالياً بحساب منحنيات الجهد لخمسة عشر مستوى جزيئي باستخدام الدالة المقترحة مع إجراء مقارنة لحسابات دالتنا مع دالتي مورس وهولبرت - هيرشفييلدر. ونقدم في هذا البحث رسماً بيانياً لهذه المنحنيات وأيضاً قيم الانحراف المطلق وذلك عن طريق حساب الخطأ المئوي.