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A Comparative Study of Potential Energy Curves Analytical Representations for CO, N_2, P_2, and ScF in Their Ground Electronic States

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Abstract

In this study, a detailed comparative analysis of four different potential energy functions is elaborated. These potential energy functions namely are Morse, Deng-Fan, Varshni, and Lennard-Jones. Furthermore, a mathematical representation for long-range region is elucidated. As a study case, four diatomic molecules (CO, N_2, P_2, and ScF) in their electronic ground states were chosen. Subsequently, the corresponding dissociation energy as well as some spectroscopic parameters were calculated accordingly.

Keywords: CO, N2, P2,ScF Dissociation energy, Deng-Fan ,Varshni , Morse , Lennard-Jones Potential.

دراسة مقارنة للتمثيلات التحليلية لمنحنيات طاقة الجهد للجزيئات CO, N_2، P2 ، ScF في حالاتهم الإلكترونية الأرضي

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الخلاصة

في هذه الدراسة ،تم اجراء مقارنة مفصلة لأربع دوال مختلفة لطاقة الجهد. حيث ان دوال الجهد هي Morse و Deng–Fan و Varshni و Lennard–Jones. علاوة على ذلك ، تم توضيح التمثيل الرياضي بأستخدام منطقة بعيدة المدى. كحالة دراسية، تم اختيار أربعة جزيئات ثنائية الذرة (CO و N2 و P2 و ScF) في حالاتها الأرضية الإلكترونية. بعد ذلك ، تم حساب طاقة التفكك وبعض الثوابت الطيفية للجزيئات ثنائية الذرة المذكورة اعلاه.

1. Introduction

A potential energy curve is considered an important graphical illustration in which a molecule's potential energy curve is represented as a function of the inter-atomic distance. This particular illustration, i.e. the potential energy curve, provides insights about the chemical kinetics, photo dissociation, electric charge, and several other spectroscopic properties [1-5]. Because of the limitation in Schrödinger equation solution in molecular geometry, physical approximations are needed. Herein, in 1927, Born and Oppenheirmer reported a specific approach to overcome the addressed issue [6]. This particular approximation suggests the separation between the electron and nuclear motions; since the mass of nuclei is extremely larger than that of electron, thus one may consider nuclei as a fixed position in comparison to a moving electron. Since the discovery of Born and Oppenheirmer

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approximation, a number of researchers attempted to acquire analytical representation regarding the potential energy curve as a function of the inter-nuclear space. As such, these representations often demanded to be mathematically easy as well as precisely reproducing experimental and theoretical data. The potential energy curve produces a deep understanding about a molecular system structure; where the minimum value of a potential curve represents a diatomic molecule bond length, while the force constant is provided via its second derivative, after which the rotational and vibrational energy level can be evaluated. Continuously, higher-ordered derivatives are needed for the estimation of the so-called anharmonicity constant [7, 8].

In the literature, there are over 50 analytical representations in which four functions were selected for the current study. These functions namely are: Morse, Deng-Fan, Varshni, and Lennard-Jones. Furthermore, the potential energy curves as well as the dissociation energies of CO, N_2, P_2, and ScF are investigated in details.

2. Theory

A dissociation energy, or the bond dissociation energy, is defined as the essential energy needed in the endothermic procedure to break a bond and subsequently form two molecular or atomic fragments, whereby each molecular or atomic possesses a single electron of the original collective pair. Herein, a potential energy curve height, which is just above the minimal vibrational level, is equivalent to the work needed to dissociate that particular molecule. This is defined as the dissociation energy (D_o), where another form of dissociation energy is represented by the term (D_e). The correlation between the two forms of dissociation energy can be expressed in the following relation [7, 9]:

$$D_e = D_0 + G(0) \tag{1}$$

herein, the term $G(0)$ is given by Equation (2) as follows:

$$G(0) = \omega_e/2 - \omega_e X_e/4 + \omega_e y_e/4 \tag{2}$$

where the term (ω_e) represents the harmonic oscillator, while $\omega_e x_e$ is the enharmonic oscillator. Consequently, in terms of molecular constant, Equation (3) is utilized to estimate the value of D_e.

$$D_e = \omega_e{}^2/4\omega_e X_e \tag{3}$$

One of the functions utilized in this study is the Morse representation, which was invented by Morse in 1929 [10]. The Morse potential/representation is given by Equation (4) as described below:

$$V(x) = D_e{}^{-\alpha x}(e^{-\alpha x} - 2) \tag{4}$$

where parameter x, known as the displacement distance, is represented in accordance with Equation (5).

$$x = R - R_e \tag{5}$$

where R is the bond length, while R_e represents the equilibrium bond length. Herein, when the value of $x = 0$, then the function achieves minimum value of $V = -D$, yet if $x \rightarrow \infty$, then $V \rightarrow 0$.

In the previously discussed Morse potential function, as the bond length becomes close to zero, the function goes to a relatively huge value. The aforementioned insufficiency of Morse function is mainly due to small wave function. Therefore, in order to solve this insufficiency, the Morse potential was altered in a number of attempts. The Deng-Fan potential function is considered as a modified Morse potential function, often called as a generalized Morse potential function [11]. This function is known to be qualitatively alike to the pre-described Morse function, yet it possesses the right asymptotic performance as the inter-nuclear space becomes close to zero [11, 12].

The defined Deng-Fan potential function for a particular diatomic molecule was suggested by two scientists, namely Deng and Fan, as represented in Equation (6).

$$V(r) = P_1 + \frac{P_2}{e^{ar}-1} + \frac{P_3}{(e^{ar}-1)^2} \tag{6}$$

whereby

$$P_1 = D_e \tag{7}$$

$$P_2 = -2D_e(e^{ar_e} - 1) \tag{8}$$

$$P_3 = D_e(e^{ar_e} - 1)^2 \tag{9}$$

herein, a represents the potential well range and r_e signifies the equilibrium inter-nuclear space.

In addition to the earlier discussed Deng-Fan energy potential function, another attempt to overcome Morse energy potential function shortcoming is the Varshni energy potential function [13]. In Vaeshni proposal, seven energy potential functions were proposed, whereby one of them is described as shown in Equation (10) [13, 14].

$$V(r) = D_e\left\{1 - \frac{r}{r_e}\exp[-\beta x]\right\}^2 \tag{10}$$

where $x = (r - r_e)$.

Continuously, the parameter β is given through the following equation:

$$\beta = \left[\frac{8\pi^2\mu(\omega_e x_e)c}{h}\right]^{1/2} \tag{11}$$

herein, D_e, r_e, and β possess similar physical importance as utilized in Morse potential function. In the meanwhile, the terms represent the reduced mass, light speed, and Planck constant, respectively [13].

Finally, the Lennard-Jones potential function, which is expressed in Equation (12), has been used widely to study various systems [15].

$$V(r) = D_e[(r_e/r)^6 - 1]^2 \tag{12}$$

3.Results and discussion

The spectroscopic parameters of the employed diatomic molecules, including CO, N_2, P_2, and ScF in their ground electronic states ($^1\sum^+$), are presented in Table-1. It should be mentioned that the dissociation energy (D_e) is calculated using Equation (3), whereby the obtained results are also listed in Table-1.

Table 1-Spectroscopic parameters of CO, N_2, P_2, and ScF in their electronic ground states

Molecules	$\boldsymbol{\omega_e}$ (cm^{-1})	$\boldsymbol{\omega_e x_e}$ (cm^{-1})	$\boldsymbol{m_1}$ (g/mol)	$\boldsymbol{m_2}$ (g/mol)	$\boldsymbol{r_e}$ (A°)	$\boldsymbol{\alpha}$ (A°)	$\boldsymbol{\beta}$	$\boldsymbol{D_e}$ *(cm^{-1})*
CO	*2134*	*13.7*	*12.0107*	*15.999*	*1.1333*	*1.8677*	*2.3616×10^{10}*	*83101*
N_2	*2356*	*14.3*	*14.0067*	*14.0067*	*1.1012*	*2.56*	*2.4378×10^{10}*	*97041*
P_2	*788*	*2.9*	*30.9737*	*30.9737*	*1.9017*	*1.351*	*1.6325×10^{10}*	*53530*
ScF	*717*	*3.7*	*44.9559*	*18.9984*	*1.7857*	*1.46102*	*1.7124×10^{1}*	*34736*

It can be clearly observed from Table-1 that the calculated dissociation energies of the introduced diatomic molecules are 83101, 97041, 53530, and 34736 cm^{-1} for CO, N_2, P_2, and ScF, respectively, at their electronic ground states. The results obtained were found to be in agreement with the experimental values previously reported [16, 17].

Continuously, the acquired potential curves using Equation (4) through Equation (12) are reported. Herein, Figure- 1 illustrates the potential energy curves of the CO as a diatomic molecule using Morse, Deng-Fan, Varshni, and Lennard-Jones potential representations. It can be clearly observed from Figure- 1 that the demonstrated potential energy curves reach minimum values when $r = 1.15$ (A^o). This mainly occurs when $r \to r_0$ whereby the dissociation energy approaches zero. Concurrently, the dissociation energy, within Morse, Varshni, and Lennard-Jones potential representations, reach a saturation value when r becomes approximately 3 (A^o) and higher. However, this observation was not perceived in the case of Deng Fan function. The current findings are in a good agreement with other reported outcomes in regard to Morse and Varshni potentials [16, 18].

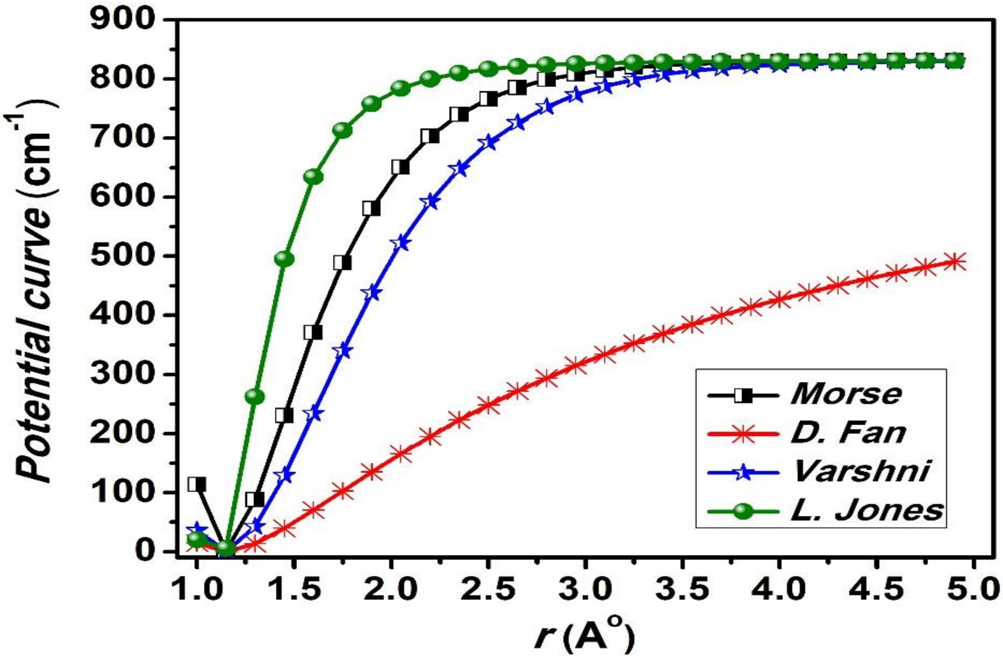

Figure 1-Potential energy curves of CO in its electronic ground state using Morse, Deng-Fan, Varshni, and Lennard-Jones potential functions.

Figure- 2 demonstrates the potential energy curves of N_2 using all four introduced functions. As can be noticed, in general, the evaluation of the employed diatomic molecules revealed that three of the introduced potential functions (Morse, Deng-Fan, and Lennard-Jones) reached a maximum/saturation value where $r \geq 3.5A^o$. However, this was not the case when Varshni potential function was applied. This could be attributed to the differences in the spectroscopic parameters of N_2 molecule which directly influence the calculated potential function. Furthermore, the term $\mathrm{r} \rightarrow \mathrm{r_o}$ was noticed when $\mathrm{r} = 1.15\mathrm{A^o}$, while the experimental value was reported as $1.0975A^o \mp 0.0001$ [19]. This was found to be in a good agreement with the previously discussed CO molecule with respect to the applied potential energy functions. The reported outcomes are in a good agreement with previous findings [7, 17].

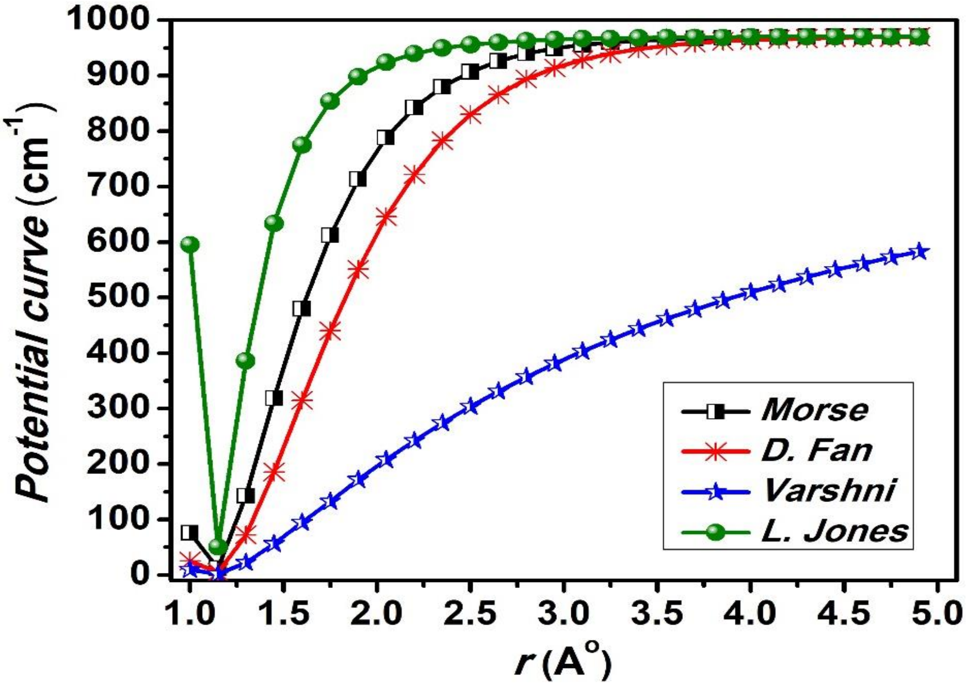

Figure 2- Potential energy curves of N_2 in its electronic ground state using Morse, Deng-Fan, Varshni, and Lennard-Jones potential functions.

Subsequently, the calculated potential energy curves using Morse, Deng-Fan, Varshni, and Lennard-Jones potential function for P_2 diatomic molecule are demonstrated in Figure- 3. As demonstrated in the figure, the term $r \rightarrow r_o$ was observed at $r = 1.85A^o$ for all applied potential energy functions. It should be mentioned that the experimental value of the P_2 bond length was reported to be $189.5A^o$ [20]. Continuously, the calculated potential curves reach a maximum/saturation value at $r > 3A^o$; yet in the case of Deng-Fan potential function, a continuous increment along the x-axis ($r \geq 1.85\ to\ 5A^o$) was observed. Herein, the diatomic molecule (P_2) revealed a quite different value of the term $r \rightarrow r_o$ in comparison to both CO and N_2 molecules. However, the current study findings are in well-agreement with previous reports [17].

In Figure- 4, the potential energy curves using all four demonstrated potential functions for ScF diatomic molecule are elucidated. The estimated potential energy curves, in regard to Morse, Varshni, and Lennard-Jones representations, exhibited a maximum and/or saturation value when $r \geq 3.5A^o$. However, the calculated values are much smaller than those obtained using CO, N_2, and P_2 molecules. It can be also noticed that the potential curve using Deng-Fan function has a lower value in comparison to the other three potentials. Finally, the term $r \rightarrow r_o$ was perceived at $r = 1.75A^o$, whereby the reported experimental bond length value was found to be $1.811A^o$ [21].

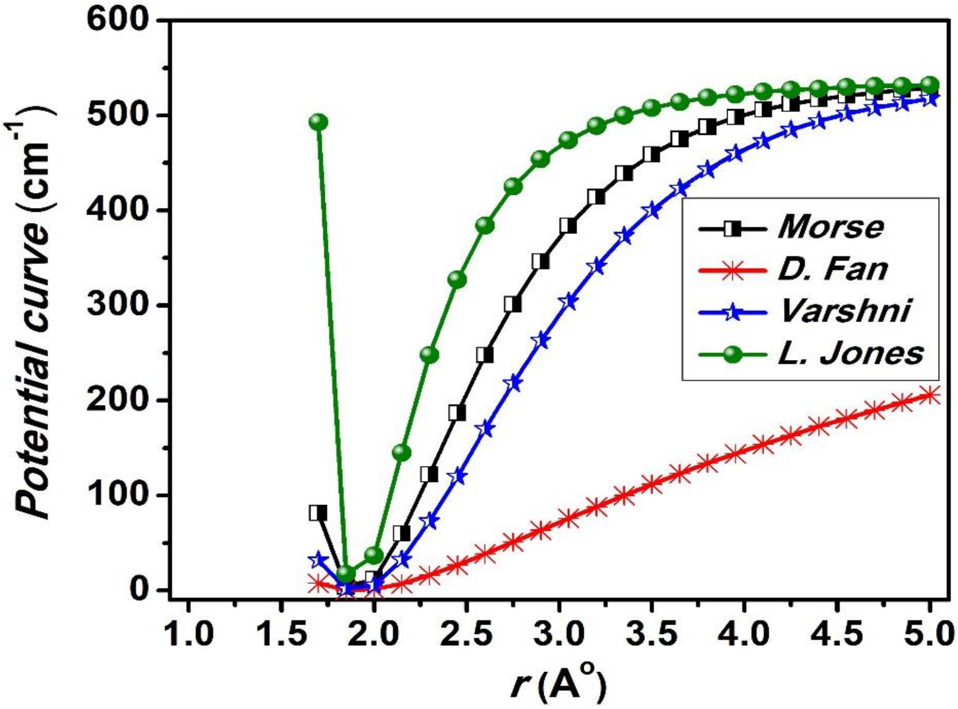

Figure 3- Potential energy curves of P_2 in its electronic ground state using Morse, Deng-Fan, Varshni, and Lennard-Jones potential functions.

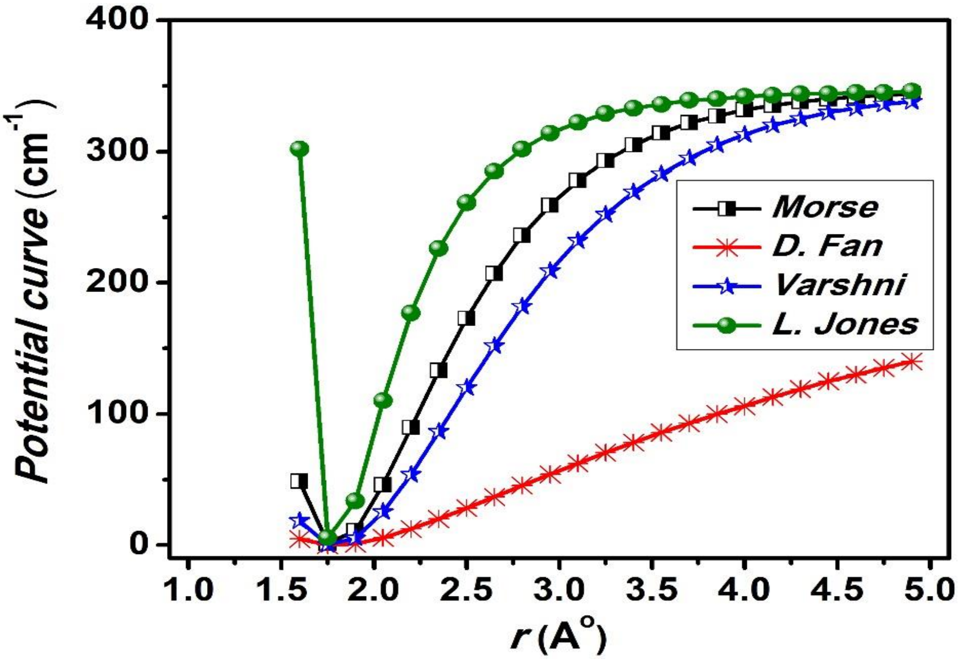

Figure 4- Potential energy curves of ScF in its electronic ground state using Morse, Deng-Fan, Varshni, and Lennard-Jones potential functions.

Conclusions

A comparative analysis representation using four potential energy functions was successfully demonstrated for different diatomic molecules, namely CO, N_2, P_2, and ScF, in which a mathematical representation for long-range along the x-axis was utilized. Moreover, these diatomic molecules were envisaged in their electronic ground state. In particular, an upright agreement between the introduced functions (Morse, Deng-Fan, Varshni, and Lennard-Jones) was achieved with some dissimilarities. Furthermore, the value of (r) was reported for all mentioned diatomic molecules. Additionally, the stated outcomes were found to be in a well-agreement with previously published data.

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