Modified Rosen-Morse potential-energy model for diatomic molecules

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By employing the dissociation energy and the equilibrium bond length for a diatomic molecule as explicit parameters, we generate an improved expression for the generalized Woods-Saxon potential. It is exactly shown that the generalized Woods-Saxon potential and the well-known Rosen-Morse potential are the same empirical potential-energy function for diatomic molecules. Based on the measure of inner-shell radii of two atoms, we propose a modified Rosen-Morse potential-energy model. Evaluation of the average deviations from the experimental data is carried out on six molecules. The modified Rosen-Morse potential is found to be more accurate than the Morse and Rosen-Morse potentials in fitting experimental data for the six molecules examined.

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I. INTRODUCTION

There has been a growing interest in constructing a universal empirical potential-energy function for diatomic molecules in chemistry physics [1–18]. The reason is that the analytical potential-energy function is the most comprehensive and compact way to summarize what we know about a molecule. The more parameters in an analytical potential-energy function, the better that the function will fit experimental data. However, the simple analytical potential functions with fewer parameters have been used in many computational chemistry software, programs such as SHAPES [19], UFF [20], and ESFF [21]. The first simple empirical analytical potential function proposed by Morse [1] has been employed in a wide variety of problems in chemical physics, such as molecular spectroscopy [22], molecular dynamics simulation [23–27], adsorption [28], phase transition [29], thermal transport [30], etc. Rong *et al.* [22] used the Morse potential models to study transition frequencies and intensities in a series of diatomic molecules and polyatomic molecules. With the help of the Morse potential-energy model, Mauro and Varshneya performed multiscale modeling of $GeSe_2$ glass structure [23]. Hu *et al.* used the Morse potential to treat the bond stretch of iodine molecules, and investigated reversible controlling the orientation of iodine molecules embedded in the AlPO4-11 crystals [25]. In revealing the angular symmetry of chemical bonds by atomic force microscopy, Welker and Giessibl used the empirical Morse potential to describe the bonding energy of a diatomic molecule [26]. Numerous contributions have been made to expand the original Morse potential model and apply it in different fields [31–40].

Efforts have been made to evaluate the accuracy of numerous empirical analytical potential models in terms of fitting experimental data [41–45]. Relationships of potential parameters among various empirical potential functions have

also been investigated [46–49]. Recently, equivalence of some empirical analytical potential functions have received attention. By employing the dissociation energy and the equilibrium bond length for a diatomic molecule as explicit parameters, improved expressions have been generated for the Rosen-Morse, Manning-Rosen, Schiöberg, and Tietz potential-energy functions [50–52]. It is found that the Manning-Rosen potential, Schiöberg potential, and Deng-Fan potential are identical [50,51]. It is also found that the Wei potential and the well-known Tietz potential function are the same solvable empirical potential function [52].

Motivated by the recent works about the equivalence of some empirical potential-energy functions, we attempt to investigate the equivalence between the generalized Woods-Saxon potential [53] and the well-known Rosen-Morse potential [3] for diatomic molecules. Based on the concept of inner-shell radii of two atoms, the modified Rosen-Morse potential model is proposed and the accuracy tests are carried out on six diatomic molecules.

II. EQUIVALENCE OF THE GENERALIZED WOODS-SAXON POTENTIAL AND THE ROSEN-MORSE POTENTIAL

An empirical internuclear potential function $U(r)$ should satisfy the following conditions:

$$\left.\frac{dU(r)}{dr}\right|_{r=r_e} = 0, \tag{1}$$

$$U(\infty) - U(r_e) = D_e, \tag{2}$$

$$\left.\frac{d^2U(r)}{dr^2}\right|_{r=r_e} = k_e = \mu\omega_e^2, \tag{3}$$

where D_e is the dissociation energy, r_e is the equilibrium bond length, μ is the reduced mass of a diatomic molecule, and ω_e denotes the equilibrium harmonic vibrational frequency.

The well-known Woods-Saxon potential plays an important role in nuclear physics since it can be used to model the interaction between a neutron and heavy nucleus. The

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generalized Woods-Saxon potential is formed by the standard Woods-Saxon potential with an extra term, which is given by [54]

$$U_{\text{GWS}}(r) = -\frac{U_0}{1 + e^{\frac{r-r_0}{b}}} - \frac{C e^{\frac{r-r_0}{b}}}{\left(1 + e^{\frac{r-r_0}{b}}\right)^2}, \quad (4)$$

where the parameter U_0 is the potential depth, r_0 is the width of the potential, b is the surface thickness, which is adjusted to the experimental values of ionization energies, and C is an adjustable parameter proposed by Berkdemir *et al.* [54] Gönül and Köksal [55] investigated the *s*-wave solutions of the Schrödinger equation and Klein-Gordon equation with the generalized Woods-Saxon potential. By using the super-symmetric quantum-mechanics method, Berkdemir *et al.* [56] studied approximately analytical solutions of the Schrödinger equation with the centrifugal barrier term for the generalized Woods-Saxon potential.

Here, we adopt the generalized Woods-Saxon potential to model the interaction for diatomic molecules. Substituting the expression of the generalized Woods-Saxon potential $U_{\text{GWS}}(r)$ given in Eq. (4) into condition (1), we obtain

$$r_e = r_0 + \ln\left(-\frac{U_0 - C}{U_0 + C}\right) b. \quad (5)$$

By using condition (2) and expression (5), we obtain the relation

$$0 - \left[-\frac{U_0}{1 - \frac{U_0-C}{U_0+C}} + \frac{C(U_0-C)}{(U_0+C)\left(1 - \frac{U_0-C}{U_0+C}\right)^2} \right] = D_e. \quad (6)$$

Solving Eqs. (5) and (6) for U_0 and C, we obtain

$$U_0 = D_e\left(1 - e^{\frac{2(r_e-r_0)}{b}}\right), \quad (7)$$

$$C = D_e\left(e^{\frac{2(r_e-r_0)}{b}} + 2e^{\frac{r_e-r_0}{b}}\right). \quad (8)$$

We add one term D_e to the right hand of expression (4). This only produces an energy of zero at the potential minimum, i.e., $U_{\text{GMS}}(r_e) = 0$, and does not affect the physical properties of the original generalized Woods-Saxon potential-energy function. Substituting expressions (7) and (8) into expression (4) and making some algebraic simplifications, we can rewrite the generalized Woods-Saxon potential in the following form:

$$U_{\text{GWS}}(r) = D_e\left(1 - \frac{e^{\frac{r_e-r_0}{b}} + 1}{e^{\frac{r-r_0}{b}} + 1}\right)^2. \quad (9)$$

In 1932, Rosen and Morse [32] proposed a potential function for polyatomic molecules,

$$U_{\text{MR}}(r) = B \tanh(r/d) - C \sec h^2(r/d). \quad (10)$$

This potential function possesses a minimum value at $r_0 = -\tanh^{-1}(B/2C)$ in the case of $|B| < 2C$. The Rosen-Morse potential can be used to study polyatomic vibrational states such as the vibrational states of the NH_3 molecule [3].

It can also be used to model the diatomic interactions [45]. The Rosen-Morse potential can also be expressed in the form of [50]

$$U_{\text{RM}}(r) = D_e\left(1 - \frac{e^{2r_e/d} + 1}{e^{2r/d} + 1}\right)^2. \quad (11)$$

If we replace $1/b$ by $2/d$, expression (9) becomes entirely the form of expression (11). Thus one can say that the generalized Woods-Saxon potential and the standard Rosen-Morse potential are the same empirical potential function for diatomic molecules.

III. MODIFIED ROSEN-MORSE POTENTIAL-ENERGY MODEL

Frost and Musulin [56] suggested that there exists an approximation universal relation between a reduced potential-energy function and a reduced internuclear distance for diatomic molecules. The reduced potential-energy function $U_{\text{reduced}}(r)$ and reduced internuclear distance r_{reduced} are defined as [56]

$$U_{\text{reduced}}(r) = \frac{U(r)}{D_e}, \quad (12)$$

$$r_{\text{reduced}} = \frac{r - r_{ij}}{r_e - r_{ij}}, \quad (13)$$

where r_{ij} is a constant for a given diatomic molecule and is a measure of the inner-shell radii of two atoms. The parameter r_{ij} can be calculated by using the relation [56]

$$r_{ij} = r_e - \sqrt{\frac{K D_e}{k_e}}, \quad (14)$$

where the parameter K is a dimensionless constant, which is given by

$$K = \frac{d^2 U_{\text{reduced}}(r)}{dr_{\text{reduced}}^2}\bigg|_{r_{\text{reduced}}=1}. \quad (15)$$

Considering the effect of inner-shell radii of two atoms for diatomic molecules, we modify the standard Rosen-Morse potential-energy function. The standard Rosen-Morse potential-energy function should be replaced by its modified version,

$$U_{\text{MRM}}(r) = D_e\left(1 - \frac{e^{\frac{2(r_e-r_{ij})}{d}} + 1}{e^{\frac{2(r-r_{ij})}{d}} + 1}\right)^2. \quad (16)$$

The potential parameter r_{ij} appearing in expression (16) is given in expression (14). In the presence of K as a constant, expression (16) has also three independent parameters. The modified Rosen-Morse potential function is still a three-parameter potential-energy model.

In 1929, Morse [1] proposed the first three-parameter empirical potential-energy function for diatomic molecules, which is given by

$$U_{\text{M}}(r) = D_e\left(1 - \frac{e^{\alpha r_e}}{e^{\alpha r}}\right)^2. \quad (17)$$

The Morse potential function has been widely used in many fields.

IV. EVALUATION OF THE GOODNESS-OF-FIT TO THE EXPERIMENTAL DATA

In this section, we assess the accuracy of the Morse, Rosen-Morse, and modified Rosen-Morse empirical potential-energy functions for diatomic molecules. Employing condition (3), we can obtain the expressions for the parameter α and d appearing in the Morse potential $U_M(r)$, Rosen-Morse potential $U_{RM}(r)$, and modified Rosen-Morse potential $U_{MRM}(r)$, respectively,

$$\alpha_M = \sqrt{\frac{k_e}{2D_e}}, \tag{18}$$

$$d_{RM} = 2\left[\sqrt{\frac{k_e}{2D_e}} + \frac{1}{r_e}W\left(r_e\sqrt{\frac{k_e}{2D_e}}e^{-r_e\sqrt{\frac{k_e}{2D_e}}}\right)\right]^{-1}, \tag{19}$$

$$d_{MRM} = 2\left[\sqrt{\frac{k_e}{2D_e}} + \frac{1}{r_e - r_{ij}}W\right. $$
$$\left. \times\left((r_e - r_{ij})\sqrt{\frac{k_e}{2D_e}}e^{-(r_e - r_{ij})\sqrt{\frac{k_e}{2D_e}}}\right)\right]^{-1}, \tag{20}$$

where W is the Lambert W function, which satisfies $z = W(z)e^{W(z)}$.

Taking the experimental values of D_e, r_e, and ω_e as inputs, and choosing $K = 4.00$ as a rounded average value [56], we determine the potential parameters α and d for three potential functions. The experimental values of D_e, r_e, and ω_e for six diatomic molecules are listed in Table I. Diatomic interaction potentials can be inferred from the spectroscopy data by three general methods: (1) the Wentzel-Kramers-Brillouin (WKB) Rydberg-Klein-Rees (RKR) approach [57–59], (2) the WKB-based Dunham approach [60], and (3) the direct potential fit (DPF) method [35]. The diatomic potential curve can be deduced from spectroscopic measurements through the RKR approach. Steele *et al.* [42] pointed out that a more stringent criterion is the ability of a function to predict the potential-energy curve, as judged by agreement with known RKR points. The DPF approach greatly reduces the numbers of parameters required to reproduce the data, and it directly provides a quantum-mechanically accurate physical model for the system [38]. The RKR and DPF approaches are applicable normally to electronic states that are well characterized spectroscopically over a wide range of vibrational energy [18]. In the present work, we apply the experimental RKR and DPF data for the diatomic potential-energy curves. The experimental RKR data points and the experimental DPF data
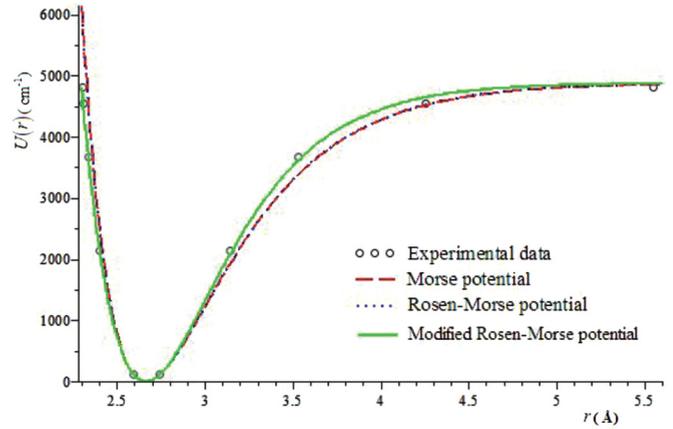

FIG. 1. (Color online) Experimental RKR data points and potential-energy functions for the $A'\,^3\Pi_2$ state of ICl.

points for the six diatomic molecules are taken from the literature: ICl [13], I_2 [13], Cs_2 [13], MgH [38], $^7Li_2$ [61], $^6Li_2$ [61]. The experimental RKR data points for the $A'\,^3\Pi_2$ state of ICl are shown in Fig. 1, which also contains the curves plotted by employing the Morse, Rosen-Morse, and modified Rosen-Morse potential-energy functions. An outlook for the range covered by the experimental RKR data points tells us that the modified Rosen-Morse potential model performed better than the original Rosen-Morse potential for the $A'\,^3\Pi_2$ state of ICl. Prior to this, the Morse potential model has been regarded as the most accurate three-parameter potential-energy model [45,62].

To evaluate the goodness of fit, we calculated the average deviations from the experimental data for the Morse, Rosen-Morse, and modified Rosen-Morse potentials. The average deviation also applied by Zavitsas [12] and Hajigeorgiou [18] is defined as

$$\sigma_{avg} = 100\frac{\sum[|U_{expt}(r) - U_{calc}(r)|]}{N_p D_e}, \tag{21}$$

where N_p is the number of experimental data points, and $U_{expt}(r)$ and $U_{calc}(r)$ are the experimentally determined potential and the empirical potential, respectively.

Table II lists the average deviations of the energies calculated using the three potential-energy functions. Comparisons of the average deviations listed in Table II tell us that the modified Rosen-Morse potential is superior

TABLE I. Experimental molecular parameters for diatomic molecules.

Molecule	State	D_e (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	Ref.
ICl	$A'\,^3\Pi_2$	4 875.52	2.665	224.57	[13]
I_2	XO^+_g	12 547.335	2.666 40	214.520 8	[13]
Cs_2	$X\,^1\Sigma^+_g$	3 649.5	6.648 0	42.020 3	[13]
MgH	$X\,^2\Sigma^+$	11 104.7	1.729 682	1 492.776 34	[18]
$^7Li_2$	$X\,^1\Sigma^+_g$	8 600	2.673 011	351.390	[18]
$^6Li_2$	$X\,^1\Sigma^+_g$	8 516.77	2.673 02	379.455 515	[31]

TABLE II. Comparison of average deviations between experimental energies and energies calculated with the three empirical potential models for the six molecules.[a]

Molecule State	ICl $A'\,^3\Pi_2$	I_2 XO^+_g	Cs_2 $X\,^1\Sigma^+_g$	MgH $X\,^2\Sigma^+$	$^7Li_2$ $X\,^1\Sigma^+_g$	$^6Li_2$ $X\,^1\Sigma^+_g$
Morse	7.77	7.67	16.67	8.84	7.76	3.37
Rosen-Morse	7.56	7.31	14.23	6.56	3.83	1.90
Modified Rosen-Morse	1.40	2.48	5.55	4.22	2.86	1.12

[a]All quantities are the average absolute deviations as a percentage of the dissociation energy.

to the standard Rosen-Morse and the Morse potential to model diatomic interaction for six diatomic molecules examined.

V. CONCLUSIONS

In this work, we construct the improved expression for the generalized Woods-Saxon potential-energy function by using the dissociation energy and the equilibrium bond length as explicit parameters. We show that the generalized Woods-Saxon potential function and the well-known Rosen-Morse potential function are the same empirical potential-energy function for diatomic molecules. Basing on the measure of inner-shell radii of two atoms, we construct the modified Rosen-Morse potential model. Choosing the experimental values for the dissociation energy, equilibrium bond length, and equilibrium harmonic vibrational frequency as inputs, we calculate the average deviations of the energies calculated

with three potential models from the experimental data for six diatomic molecules. The results show that the modified Rosen-Morse potential is superior to the original Rosen-Morse potential and the Morse potential in fitting experimental data for the six molecules examined.

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