Chemical Physics Letters 591 (2014) 69–77

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

An accurate pair potential function for diatomic systems

Jianing Colin Xie [a,d,1], Tapas Kar [a,*], Rui-Hua Xie [b,c,*]

[a] Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322, USA
[b] Department of Applied Physics, Xi'an Jiaotong University, Xi'an 710049, China
[c] Department of Physics, Hubei University, Wuhan 430062, China
[d] A & M Consolidated High School, College Station, Tx 77840, USA

ARTICLE INFO

Article history:
Received 26 August 2013
In final form 4 November 2013
Available online 11 November 2013

ABSTRACT

Based on the molecular-orbital theory for a simplest single-electron diatomic system, we have developed a unique functional form for pair potentials. We have demonstrated that the diatomic potential thus constructed is able to adequately describe a stable as well as meta-stable diatomic system with a good accuracy for all relevant internuclear distances.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The interaction potential is of fundamental importance for understanding the static and the dynamic properties of gases, liquids and solids. Within the Born–Oppenheimer approximation, the solution of the Schrödinger equation for a diatomic system leads to a set of internuclear potentials $E(R)$ [1–6; 7, where R is the internuclear distance. Clearly, an analytical formula for the potential E (R) is much easier to deal with than the energy values corresponding to a series of values of R, such as are provided by *ab initio* or quantum Monte Carlo calculations [2,6]. Many applications in fact require such an analytical form, in which one or more parameters are left to be evaluated [1–6; 7]. At present, it seems impossible to deduce a manageable analytical expression for the function E (R) from the first principles of the theory (even modern mathematical methods are of little help), and one has to turn to empirical approaches to looking for analytical potential function forms with fitting parameters [1,2,5,6]. Although numerous attempts to analytically model diatomic potentials have been made [1–8], these analytical potentials are usually applied to describing either strongly or weakly bound, neutral or singly-charged bound diatomics, and often lose their validity for small, intermediate, or relatively large internuclear distances [2,5–7]. Thus, great effort has been devoted to the construction of hybrid potentials, which use different functions for different R-regions [5,6,9].

For practical applications, it is necessary to build analytical potential functions E (R) [2,10,11], which satisfy the three basic criteria [2,10] and are able to adequately describe short-, intermediate-, and large-R regions [2]. As well as these, a desirable characteristics [2,10] is that analytical formula E (R) be flexible enough to describe a unique function having a local maximum as well as a local or global minimum. To achieve these criteria and characteristics defined for a favorite pair potential, we have developed a five-parameter pair potential function for diatomic systems. We demonstrate that this new potential form satisfies the required criteria and characteristics and is able to represent the pair–potential curves of stable or meta-stable diatomic systems. As an example, we have successfully applied it to describe strongly bound molecules H_2^+, H_2, and LiH, weakly bound van der Waals molecule He_2, and meta-stable diatomic dication BeH^{++}. The vibrational energies of H_2, LiH and He_2 calculated by using this new model potential reach a good accuracy for all relevant ranges of the internuclear distances.

2. Five-parameter model potential

2.1. Analytical potential functional form

To build a model potential, the choice of the functional form is of great importance. Based on the molecular orbital theory for the ground-state H_2^+, we have recently found an analytical functional form that is able to model the diatomic potentials [10]. To see how we introduce parameters into the analytical function, we briefly present the analytical functional form here. The associated Hamiltonian for simplest single-electron diatomic system H_2^+ is given by [12]

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}, \tag{1}$$

where atomic units are used and r_A (r_B) denotes the distance between the single electron and nucleus A (B). By considering a s-type trial function of H_2^+, the energy of the bonding orbital can be exactly written as (in atomic units) [12]

* Corresponding authors. Address: Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322, USA (T. Kar), Department of Applied Physics, Xi'an Jiaotong University, Xi'an 710049, China (R.-H. Xie).

E-mail addresses: tapas.kar@usu.edu (T. Kar), rhxie@mail.xjtu.edu.cn, jrhxie@yahoo.com (R.-H. Xie).

[1] Permanent address: 106 Walcourt Loop, College Station, TX 77845, USA.

0009-2614/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cplett.2013.11.004

$$E(R) = E_\infty + \frac{J_1(R) + K_1(R)}{1 + S_0(R)}, \tag{2}$$

where $E_\infty = -\frac{1}{2}$ is the total energy of the system at the infinite internuclear distance $R = \infty$, and $J_1(R)$, $K_1(R)$ and $S_0(R)$ are defined by [12]

$$J_1(R) = \langle \phi_0^A | \left(-\frac{1}{r_B} + \frac{1}{R} \right) | \phi_0^A \rangle = e^{-2R} \left(1 + \frac{1}{R} \right); \tag{3}$$

$$K_1(R) = \langle \phi_0^A | \left(-\frac{1}{r_A} + \frac{1}{R} \right) | \phi_0^B \rangle = e^{-R} \left(\frac{1}{R} - \frac{2}{3} R \right); \tag{4}$$

$$S_0(R) = \langle \phi_0^A | \phi_0^B \rangle = e^{-R} \left(1 + R + \frac{1}{3} R^2 \right), \tag{5}$$

known as the Coulomb, exchange, and overlap integrals (note: $|\phi_0\rangle = e^{-r}/\sqrt{\pi}$, the 1s-orbital of H atom), respectively.

The resultant analytical curve of this function Eq. (2) is presented in Figure. 1(a). It reads an energy minimum $E_{\min} = -0.56483$ Hartree at an equilibrium internuclear distance $R_e = 1.323$ Å, and satisfies the necessary criteria and characteristics for building a good diatomic potential [10]. In comparison with accurate data [13,14], this analytical potential–energy curve Eq. (2) for the ground-state H_2^+ should be quantitatively improved over all the internuclear distances R. In the following, two theoretical approaches are presented to see how the quantitative improvement of the potential curve is achieved.

One well-known approach is based on *ab initio* method [5,6]. For this one-electron system H_2^+, the self-interaction-free Hartree–Fock method is exact (apart from small basis set errors) [15]. That is, the potential energy curve for the ground-state H_2^+ should approach the exact solution in the limit of infinite basis set size [15]. Thus, if one increases the basis set size (for example, including *polarization* and even *diffuse* functions in the trial function), then the potential curve of the ground-state H_2^+ should be improved significantly in all the regions of R. In Figure 1a, we demonstrate the effect of basis set size by using Hartree–Fock (HF) method implemented in the GAUSSIAN 09 electronic structure package [16]. It is seen that the numerical potential curve for the ground-state H_2^+ is greatly improved and approaching to the most accurate data [13,14] as the basis size is increased from GAUSSIAN-type basis set 3-21G (2 sets of GAUSSIAN functions in the valence region), to 6-31G (d,p) (including polarization p and d functions), and then to 6-311+G (3df,2pd) (including 2p and 1d polarization functions and diffuse functions) [16].

Another well-known theoretical approach is the polarization approximation. Under this approximation, Tang and Toennies [17–19] have developed a systematic and successful procedure to take account of exchange energies for calculating the interatomic potentials of the ground-state H_2^+. For this single electron system, the plane in the middle of the two protons divides the space into two parts, and the exchange energy can be interpreted as a result from the electron hopping back and forth across this plane. The "*exchange*" therefore refers to the exchange of two protons. If the first-order exchange energy $\epsilon_{\text{exch}}^{(1)}$ is used, the energy of the

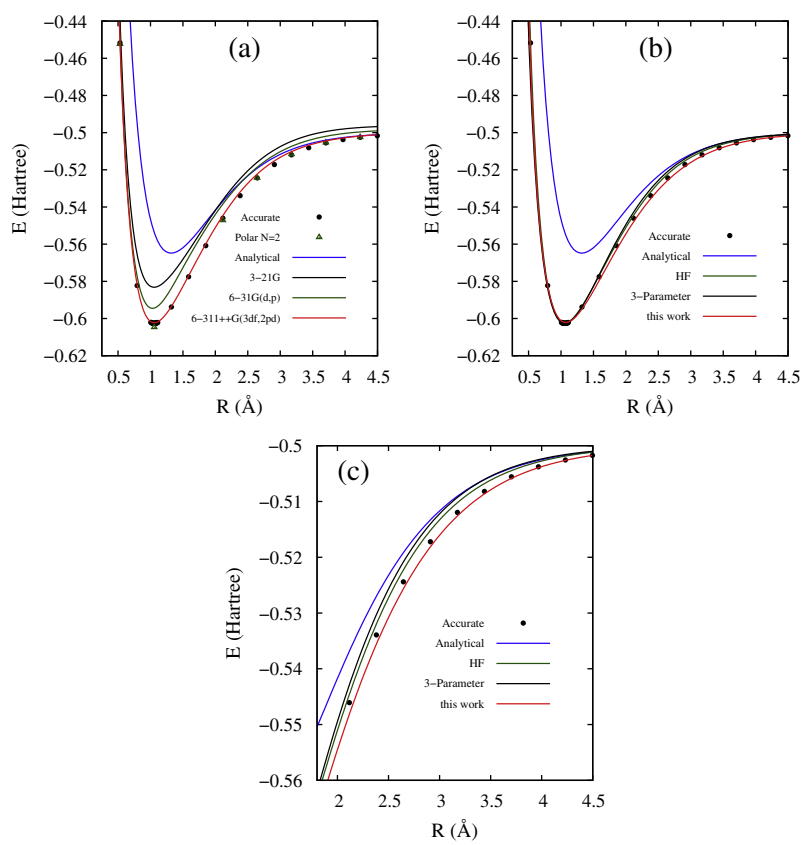

Figure 1. The potential energy curve of the ground-state H_2^+. (a) Analytical function Eq. (2) (blue line), HF/3–21G (black line), HF/6–31G (d,p) (green line), HF/6–311++G (3df,2pd) (red line), and the 2*nd*-order polarization approximation (green triangle, Ref. [18]). (b,c) Analytical function Eq. (2) (blue), three-Parameter model potential (black, $\alpha = 1.0511106, \beta = 0.91703424, \gamma = 2.25$, Ref. [10]), five-Parameter model potential (red, this Letter, $\alpha = 0.95, \beta = 0.669, \gamma = 0.965, n = 6.0$, and $\zeta = 0.11$), and HF/6–311++G (3df,2pd) (dark green). The filled dots are the most accurate data [13,14]. The equilibrium distance R_e and minimum energy E_{min} in the three- and five-prameter model potentials are fitted to 1.0574 Å and −0.60263 Hartree, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ground-state H_2^+ for the first-order polarization approximation can be written in the following form in atomic units [10]

$$E(R) = E_{\text{polar}}(R) - [1 - S_0(R)]\epsilon_{exch}^{(1)}(R), \tag{6}$$

where $E_{\text{polar}}(R) = E_\infty + J_1(R)$ and $\epsilon_{exch}^{(1)}(R) = [S_0(R)J_1(R) - K_1(R)]/[1 - S_0^2(R)]$. In fact, it can be shown that Eq. (6) is equivalent to the analytical equation Eq. (2). Moreover, for the Nth-order polarization approximation, the energy of the ground-state H_2^+ can be written as $E(R) = E_{\text{polar}}(R) - (1 - \sum_{n=0}^{N-1} S_n(R))\epsilon_{\text{exch}}(R)$, where $E_{\text{polar}}(R) = E_\infty + \sum_{n=1}^{N} \epsilon_n(R)$ ($\epsilon_n(R)$ is the polarization energy series) and $S_n(R)$ is the n-th order overlap integral. Details for this part are presented in the Appendix B of the supporting material of Ref. [10]. As shown in Figure 1a and Table 1, the energy of the ground-state H_2^+ under the polarization approximation is getting closer to the exact values as the perturbation order N is increased.

2.2. Five-parameter model potential

Motivated by the *ab initio* calculations with polarization and diffuse functions included and by the polarization approximation approach with the increase of the perturbation order N, we have recently constructed a simple three-parameter model potential (in atomic units) [10] for diatomic systems based on the analytical function Eq. (2), i.e.

$$E(R, \alpha, \beta, \gamma) = E_\infty + \frac{J_1(R, \gamma) + K_1(R, \alpha, \beta)}{1 + S_0(R)} \tag{7}$$

with

$$J_1(R, \gamma) = e^{-2\gamma R}\left(1 + \frac{1}{R}\right), \tag{8}$$

$$K_1(R, \alpha, \beta) = e^{-\alpha R}\left(\frac{1}{R} - \beta R\right), \tag{9}$$

and $S_0(R)$ is given in Eq. (5). As shown in Tables 1 and Figure. 1(b), the three-parameter model potential [10] for the ground-state H_2^+ agrees well with the most accurate data [13,14] for a set of parameters ($\alpha = 1.0511106, \beta = 0.91703424, \gamma = 2.25$) [10]. This shows that the three parameters α, β and γ can be properly adjusted so that contributions of both the polarization and exchanging energies can be accounted for in an much efficient way, thereby achieving in effect the same goal as that of using a larger basis set (e.g., 6–311++G (3df,2pd)) in the trial wave function of H_2^+ [10].

Overall, this three-parameter model potential [10] has been shown to be a favorite representation of the potential curves of diatomic systems by a unique "approximate" potential curve [11]. It has been successfully and extensively applied to describe over 200 stable or meta-stable diatomic systems [10] (including weakly bound van der Waals diatomic complexes, for example, CdNe, NaAr, and CaHe, and meta-stable diatomic dications, for example, BeH^{++}, AlH^{++}) over a significantly wide range of internuclear distances (To be noted, the mentioned 200 cases are presented in Figs. A and B, and Tables 1–8 of the supporting material of Ref. [10]). Nevertheless, the overall accuracy of this three-parameter potential needs to be further improved, in particular in the large-R portion as shown in Figure 1c of the potential for the ground-state H_2^+.

On the other hand, as demonstrated above, polarization and diffusion functions play an important role in a good description of the diatomic potential. Thus, the nth-order overlap integral $S_n(R)$ (see Appendix B in the supporting material of Ref. [10]) should be taken into account in the construction of a model potential function. In general, more parameters introduced in a potential function imply greater flexibility and the great possibility of a closer representation of a true potential function of E (R). In this sense, the three-parameter model potential [10] is further improved by introducing two more parameters, i.e., ζ and n into the function K (R, α, β), and the parameter α into the overlap-integral function $S_0(R)$. Thus, we have constructed a five-parameter potential form in atomic units

$$E(R, \alpha, \beta, \gamma, \zeta, n) = E_\infty + \frac{J_1(R, \gamma) + K_1(R, \alpha, \beta, \zeta, n)}{1 + S_0(R, \alpha)} \tag{10}$$

with

$$K_1(R, \alpha, \beta, \zeta, n) = e^{-\alpha R}\left(\frac{\zeta}{R^n} - \beta R\right), \tag{11}$$

$$S_0(R, \alpha) = e^{-\alpha R}\left(1 + R + \frac{1}{3}R^2\right), \tag{12}$$

and $J_1(R, \gamma)$ is the same as Eq. (8). When $\alpha = \gamma = \zeta = n = 1$ and $\beta = 2/3$, Eq. (10) turns to Eq. (2). In the large-R limit, where the atomic electron clouds do not overlap considerably, the interaction energy of an atomic pair is given by the well-known multipolar dispersion expansion. In this limit, the three-parameter model potential [10] approaches E_∞ exponentially, a feature different from the one suggested by the multipolar dispersion expansion. Thus, in the exchange integral $K(R, \alpha, \beta)$, we introduce two new parameters ζ and n to the 1/R term. That is, the **1/R** term is replaced by ζ/R^n to account for the effect of polarization and diffusion functions. To account for the effect of the sum $\sum_{n=0}^{N-1} S_n(R)$ of the N-order overlap integral $S_n(R)$, we introduce the same parameter α in $K_1(R, \alpha, \beta, \zeta, \eta)$ to the exponent term in $S_0(R)$.

As shown in Tables 1 and Figure 1(b) and (c), the five-parameter model potential for the ground-state H_2^+ agrees well with the most accurate data [13,14] for a set of parameters ($\alpha = 0.95, \beta = 0.669, \gamma = 0.965, n = 6.0$, and $\zeta = 0.11$). To be noted, R_e and dissociation energy $D_e = E_\infty - E_{min}$ (the minimum energy $E_{min} = E(R = R_e)$) are fitted to the most accurate data: [13] 1.0574 Å and 0.10263 Hartree, respectively. We find that the five-parameter model potential performs much better in the large-R region than the three-parameter model potential [10] and has almost the same quality as the *ab initio* HF/6–311++G (3df,2pd) calculation.

3. Application

Based on the polarization approximation, the ground-state potentials $E(E_{polar}, \epsilon_{exch})$ of H_2 [4] (details are also given in section I (2) in Appendix B of Ref. [10]) and other multi-electron diatomic

Table 1
The potential energies E (R) (in units of Hartree) derived by using polarization approximation approach, three-parameter model potential ($\alpha = 1.0511106, \beta = 0.91703424, \gamma = 2.25$) [10], and five-parameter model potential (this Letter, $\alpha = 0.95$, $\beta = 0.669$, $\gamma = 0.965$, $n = 6.0$, and $\zeta = 0.11$) for H_2^+ at the nuclear–nuclear distance R = 1.0, 2.0, and 4.0 Bohr. Perturbation results are adapted from Ref. [17], accurate results are from Ref. [13], and the relative errors between theoretical and accurate results are given in the parenthesis.

R	N = 1 [17]	N = 2 [17]	N = 3 [17]	3-Parameter [10]	this work	Accurate [13]
1.0	−0.2884 (36.17%)	−0.4406 (2.48%)	−0.4403 (2.55%)	-0.4724 (4.36%)	−0.4610 (2.04%)	−0.4518
2.0	−0.5538 (8.10%)	−0.5876 (2.49%)	−0.5994 (0.53%)	-0.60263(0.01%)	−0.6021 (0.08%)	−0.6026
4.0	−0.5369 (1.68%)	−0.5427 (0.62%)	−0.5445 (0.29%)	-0.5429 (0.59%)	−0.5482 (0.38%)	−0.5461

systems [19] (details are also given in Sections I (3) and I (4) in Appendix B of Ref. [10]), when expressed in terms of the polarization and exchange energies, can take a form similar to Eq. (6) derived for H_2^+, despite that their origins of the exchange energy are totally different. Motivated by these known theoretical results, we have applied extensively the three-parameter model potentials to about 200 other diatomic systems [10], for which experimental or *ab initio* data are available in the literature. All these studied cases by using the three-parameter model potentials are presented in Figs. A and B, and Tables 1–8 of the supporting material of Ref. [10]. For the five-parameter model potential, we select 4 representative cases, H_2, LiH, He_2, and BeH^{++}, and report these results in this communication. In Ref. [10] and this Letter, the dissociation energy D_e is fitted exactly to accurate literature data, and the average relative error and root mean square error for fitting R_e to accurate literature data are 0.02% and 0.017%, respectively.

3.1. How to determine the model potential parameters

Before proceeding with the application, we present here how to determine the five parameters in the five-parameter model potential. The procedures are given below:

1. Step 1: Follow one of the three approaches, which are presented in Appendix C in the supporting material of Ref. [10], to determine the parameters α, β and γ in the three-parameter model potential Eq. (7). We have determined the three parameters (α, β, γ) of 211 diatomic systems and listed the determined values in Table 1 in the supporting material of Ref. [10]. In nearly 200 cases, we follow Approach 1 (see Appendix C in the supporting material of Ref. [10]). The case studies for weakly bounded diatomic systems such as He_2, NaAr, CdNe, SrHe, CaHe, BaHe, LiHe use Approach 2 [10]). We have not tried Approach 3 in the case study.
2. Step 2: Set the α value determined above into Eq. (12) (i.e., $S_0(R, \alpha)$ in the five-parameter potential Eq. (10)) and let $\zeta = 1$ and $n = 1$. At this point, the equilibrium point (E_{min}, R_e) of the potential curve may be away from the accurate one (note: this curve is not very far away from the determined three-parameter potential curve).
3. Step 3: Turn to tune the parameters ζ and n and pull the equilibrium point (E_{min}, R_e) back to the accurate one.Step 4: Further tune all five parameters to get better agreement between the five-parameter potential curve and the available RKR (Rees–Klein–Rydberg [2]) points or *ab initio* potential–energy curves. At this step, it may need some trial-and-error steps and experience to quickly find the fitting parameters (As shown in this Letter, the determined values of the three parameters (α, β, γ) in the five-parameter potentials for the studied cases H_2^+, H_2, LiH, He_2 and BeH^{++} are not far from those determined by using the three-parameter model potential). A totally objective or even black-box approach is however not available yet (NOTE: user may use Nonlinear Least Square Program to determine the parameters).

For convenience, we briefly present here Approach 1 mentioned above. For diatomic systems for which experimental or *ab initio* data are already available, we obtain the three parameters of α, β, and γ in the three-parameter model potential Eq. (7) as follows:

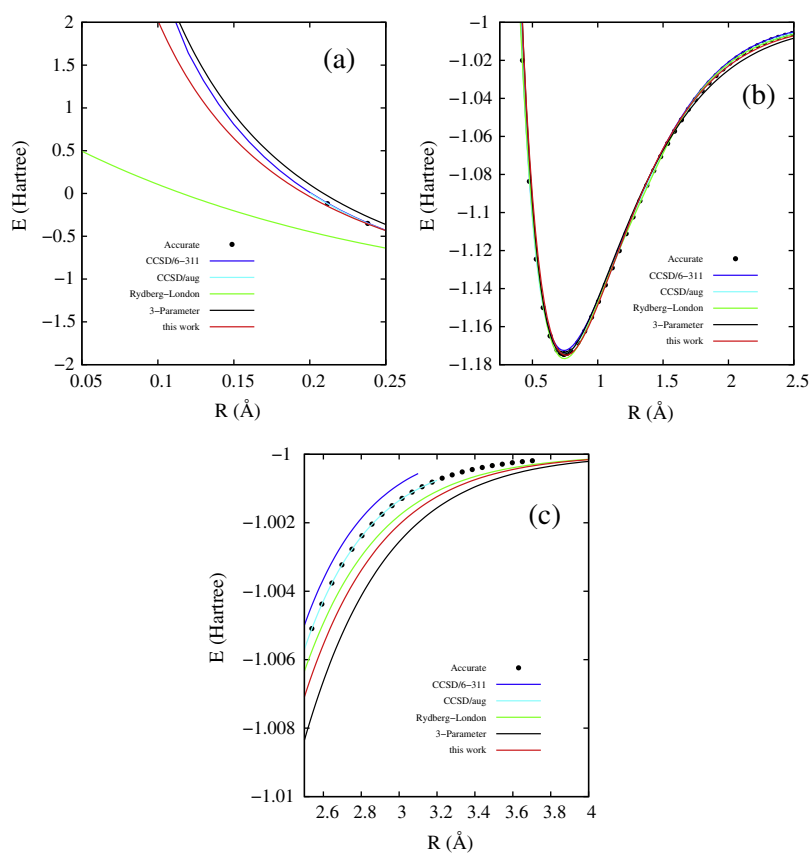

Figure 2. The comparison between five-parameter model potential (Red line, this Letter, $\alpha = 1.519, \beta = 2.0478, \gamma = 1.785, n = 0.795$, and $\zeta = 1.005$), three-parameter model potential (Black line, $\alpha = 1.5065756, \beta = 2.48475652, \gamma = 1.45$, Ref. [10]), hybrid Rydberg–London potential (Green line, Ref. [9]), CCSD/6–311++G (3df,2pd)(Blue line, Ref. [10]), CCSD/aug-cc-pV5Z (Cyan line), and the most accurate data (filled circles, Ref. [21]) for the ground-state H_2. (a) Short-R region $R = 0.05 \sim 0.25$ Å; (b) Intermediate-R region $R = 0.25 \sim 2.5$ Å; (c) Large-R region $R = 2.5 \sim 4$Å. The equilibrium distance R_e and minimum energy E_{min} in the three- and five-parameter model potentials are fitted to 0.7412 Å and −1.1744746 Hartree, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

1. First, the dissociation energy $D_e = E_\infty - E_{min}$ (E_{min}: the minimum energy at R_e) from experiments or other approaches, such as *ab initio* methods, imposes a constraint as two adjusting parameters, for example, α and γ, are scanned.
2. Then, the known value of R_e is used to obtain a second constraint condition, i.e., $\frac{dE}{dR}(R = R_e) = 0$. This gives the third parameter β. There might be many possible sets of α, β, and γ that meet the two constraints associated with D_e and R_e. Based on the two steps, we have provided a Fortran program in the supporting materials of Ref. [10] to obtain roughly the three parameters α, β and γ (Readers may contact us directly for the Fortran code).
3. Finally, we further tune the parameters until good agreement between the three-parameter potential curve and the available RKR [2] or Dunham [2] or *ab initio* results is reached. In this paper, we have listed the determined values of three parameters (α, β, γ) in the three-parameter model potential Eq. (7) for the studied cases H_2^+, H_2, LiH, He_2 and BeH^{++}.

The last step is subjective in the sense that different standards for the agreement (between the model potential curve and the known results) will give slightly different results. Establishing a common objective standard for all the molecules studied is virtually impossible. In some cases, e.g., for meta-stable diatomic systems, defining a quantitative criteria for good agreement is even less useful because the overall agreement in the shape of the potentials is more important than the agreement at a few internuclear distances. In addition, we found a simple rule that may be useful for determining the parameters as α and γ are tuned on a finer and finer scale: (1) if γ is fixed at some value and the value of α increases (decreases), then the equilibrium distance is seen to decrease (increase); and (2) if α is fixed at some value, then varying the value of γ changes the width and depth of potential well.

3.2. The simplest multi-electron molecule H_2

The hydrogen molecule has been one of the most favorite systems used for testing quantum theory and for testing other theoretical methods or calculations. For this two-electron system, the *exchange* can be interpreted as a result of an exchange of the two electrons. The potential energy function for its ground state is also given by Eq. (6) [19]. This shows that both H_2^+ and H_2 bonding can be understood in a similar fashion, despite that the origin of the exchange energy is totally different. That also explains why both H_2^+ and H_2 have been important prototypes for theoreticians to acquire a physical understanding of the nature of chemical bonding. Therefore, we first study H_2, the simplest multi-electron system.

In Figure 2, we compare the five-parameter model potential ($\alpha = 1.519, \beta = 2.0478, \gamma = 1.785, n = 0.795$, and $\zeta = 1.005$) with 3-parameter model potential ($\alpha = 1.5065756$, $\beta = 2.48475652$, $\gamma = 1.45$) [10], hybrid Rydberg–London potential [9], advanced *ab initio* CCSD [20] (couple cluster method with single and double excitation) calculation, and the most accurate literature data [21] for the ground-state H_2. For advanced *ab initio* CCSD calculations, we use two basis sets [16]: 6–311++G (3df,2pd) and aug-cc-pV5Z (Augmented correlation-consistent core-valence basis sets up to septuple-zeta quality). In the large-R region (see Figure 2c), we found that the five-parameter model potential performs much better than the 3-parameter model, and is close to the hybrid Rydberg–London potential. In the short-R region (see Figure 2), the five- and three-parameter model potentials are close to the accurate data and CCSD/6–311++G (3df,2pd) calculations, and are much better than the hybrid Rydberg–London potential. In the intermediate-R region (Figure 2b), all model potentials have quite similar performance, agreeing well with the accurate data. To be noted, CCSD calculation is improved greatly in the large-R region as a larger basis set aug-cc-pV5Z is used.

The vibrational energies for the ground-state H_2 calculated by using the three- and five-parameter model potentials are summarized in Tables 2 and compared with experiment. In total, we have obtained 15 vibrational levels as observed in experiment [22]. It is found that the calculated vibrational energies by using the five-parameter model potential reach a relative error of about 5% for 13 vibrational levels ($v = 0 \sim 12$) in comparison with experiment [22], and are significantly improved in the large-R region of the diatomic potential in comparison with the vibrational energies [10] obtained by using the three-parameter model potential.

3.3. The smallest neutral heteropolar molecule LiH

Lithium hydride has been the object of intense theoretical and spectroscopic studies since LiH represents the smallest neutral heteropolar molecule. Its simple electronic structure makes the molecule one of the favorite subjects for testing different quantum-chemical techniques. In this Letter, we also take the lithium hydride LiH as the second example.

In Figure 3a and b, we compare the five-parameter potential ($\alpha = 0.871, \beta = 1.9650, \gamma = 0.294, n = 0.265$, and $\zeta = 1.188$) with the three-parameter potential ($\alpha = 0.8885591$, $\beta = 1.51479003$, $\gamma = 0.345$) [10], *ab initio* CCSD/6–311++G (3df,3pd) calculation, and the most accurate RKR experimental data [23] for the ground state LiH. In the large-R region, as shown in Figure 3b, we find that the five-parameter model performs better than the three-parameter model, and even better than CCSD/6–311++G (3df,2pd) calculation. Table 3 summarizes the calculated vibrational energies for two isotopes ^{7}LiH and ^{7}LiD by using the five- and three-parameter model potentials. In comparison with RKR experimental data [23], we find that the accuracies of the computed vibrational energies for both ^{7}LiH and ^{7}LiD by using the five-parameter model reach a good accuracy over the whole range of the internuclear distances. In the large-R region, the calculated vibrational energies are significantly improved in the five-parameter model than in the three-parameter model.

3.4. Weakly bound diatomic molecules

Weakly bound diatomic molecules are of great interest to both theoreticians and experimentalists. Such weak interactions are the

Table 2
The calculated vibrational energies for the ground state H_2 using 3-parameter model ($\alpha = 1.5065756, \beta = 2.48475652, \gamma = 1.45$) [10], and 5-parameter (this work, $\alpha = 1.519, \beta = 2.0478$, $\gamma = 1.785, n = 0.795$, and $\zeta = 1.005$) potentials. The value in the parenthesis is the relative error of the present calculation from experiment [22]. Dissociation energy $D_e = 4.74763$ eV.

v	Exp. [eV]	3-Parameter model [eV]	This Letter [eV]
0	−4.4774	−4.4628 (0.33%)	−4.4849 (0.17%)
1	−3.9615	−3.9218 (1.00%)	−3.9500 (0.29%)
2	−3.4747	−3.4166 (1.67%)	−3.4457 (0.83%)
3	−3.0166	−2.9465 (2.32%)	−2.9724 (1.46%)
4	−2.5866	−2.5111 (2.92%)	−2.5307 (2.16%)
5	−2.1847	−2.1099 (3.42%)	−2.1211 (2.91%)
6	−1.8110	−1.7427 (3.77%)	−1.7442 (3.69%)
7	−1.4661	−1.4093 (3.87%)	−1.4008 (4.46%)
8	−1.1508	−1.1097 (3.57%)	−1.0916 (5.14%)
9	−0.8665	−0.8439 (2.61%)	−0.8178 (5.62%)
10	−0.6153	−0.6123 (0.49%)	−0.5804 (5.68%)
11	−0.4000	−0.4155 (3.88%)	−0.3806 (4.84%)
12	−0.2245	−0.2543 (13.27%)	−0.2203 (1.89%)
13	−0.0945	−0.1301 (37.67%)	−0.1013 (7.16%)
14	−0.0174	−0.0452 (159.77%)	−0.0264 (51.78%)

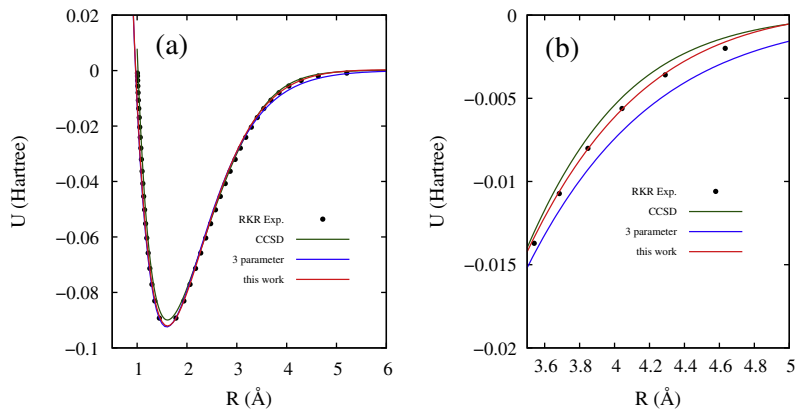

Figure 3. The comparison between five-parameter model potential (red, this work, $\alpha = 0.871, \beta = 1.9650, \gamma = 0.294, n = 0.265$, and $\zeta = 1.188$), three-parameter model potential (blue, $\alpha = 0.8885591$, $\beta = 1.51479003, \gamma = 0.345$, Ref. [10]), CCSD/6–311++G (3df,2pd)(black, Ref. [10]), and the RKR experimental data (filled circles, Ref. [23]) for the ground state LiH: (a) full scale and (b) large-R region. The potential energy $U(R) = E(R) - E_{\infty}$. The equilibrium distance R_e and minimum energy $U_{\min}$ in the three- and five-prameter model potentials are fitted to 1.5950 Å and −0.092435 Hartree, respectively.

Table 3
The calculated vibrational energies for isotopes ^{7}LiH and ^{7}LiD using the three-parameter model potential ($\alpha = 0.8885591$, $\beta = 1.51479003, \gamma = 0.345$) [10] and five-parameter model potential (this work, $\alpha = 0.871$, $\beta = 1.9650, \gamma = 0.294, n = 0.265$, and $\zeta = 1.188$). The value in the parenthesis is the relative error of the numerical calculation from experiment [23]. Dissociation energy $D_e = 2.515$ eV.

	^{7}LiH			^{7}LiD		
v	3-Parameter [eV]	5-Parameter [eV]	Exp. [eV]	3-Parameter [eV]	5-Parameter [eV]	Exp. [eV]
0	−2.4283 (0.02%)	−2.4092 (0.81%)	−2.4287	−2.4502 (0.03%)	−2.4303 (0.84%)	−2.4509
1	−2.2594 (0.03%)	−2.2425 (0.78%)	−2.2601	−2.3222 (0.05%)	−2.3044 (0.81%)	−2.3233
2	−2.0949 (0.11%)	−2.0805 (0.79%)	−2.0971	−2.1976 (0.06%)	−2.1811 (0.72%)	−2.1989
3	−1.9355 (0.21%)	−1.9232 (0.84%)	−1.9395	−2.0751 (0.12%)	−2.0603 (0.83%)	−2.0775
4	−1.7812 (0.34%)	−1.7706 (0.94%)	−1.7873	−1.9555 (0.19%)	−1.9423 (0.87%)	−1.9593
5	−1.6321 (0.50%)	−1.6229 (1.06%)	−1.6403	−1.8387 (0.29%)	−1.8269 (0.93%)	−1.8440
6	−1.4884 (0.67%)	−1.4801 (1.23%)	−1.4985	−1.7249 (0.40%)	−1.7142 (1.02%)	−1.7318
7	−1.3502 (0.85%)	−1.3424 (1.42%)	−1.3618	−1.6140 (0.52%)	−1.6043 (1.12%)	−1.6224
8	−1.2175 (1.03%)	−1.2099 (1.64%)	−1.2302	−1.5062 (0.65%)	−1.4972 (1.24%)	−1.5160
9	−1.0906 (1.17%)	−1.0829 (1.87%)	−1.1035	−1.4014 (0.79%)	−1.3929 (1.39%)	−1.4125
10	−0.9696 (1.26%)	−0.9612 (2.12%)	−0.9820	−1.2998 (0.91%)	−1.2916 (1.54%)	−1.3117
11	−0.8545 (1.27%)	−0.8451 (2.34%)	−0.8655	−1.2013 (1.04%)	−1.1932 (1.71%)	−1.2139
12	−0.7456 (1.13%)	−0.7349 (2.53%)	−0.7541	−1.1061 (1.14%)	−1.0978 (1.89%)	−1.1189
13	−0.6431 (0.77%)	−0.6308 (2.67%)	−0.6481	−1.0141 (1.24%)	−1.0055 (2.08%)	−1.0268
14	−0.5471 (0.07%)	−0.5328 (2.69%)	−0.5475	−0.9255 (1.27%)	−0.9163 (2.25%)	−0.9374
15	−0.4577 (1.10%)	−0.4412 (2.54%)	−0.4527	−0.8403 (1.25%)	−0.8304 (2.41%)	−0.8509
16	−0.3753 (3.05%)	−0.3563 (2.16%)	−0.3642	−0.7586 (0.80%)	−0.7477 (2.23%)	−0.7647
17	−0.3001 (6.27%)	−0.2785 (1.38%)	−0.2824	−0.6805 (0.92%)	−0.6684 (2.68%)	−0.6868
18	−0.2322 (11.47%)	−0.2081 (0.11%)	−0.2083	−0.6060 (0.54%)	−0.5925 (2.76%)	−0.6093
19	−0.1721 (20.43%)	−0.1455 (1.84%)	−0.1429	−0.5352 (0.06%)	−0.5202 (2.76%)	−0.5349
20	−0.1200 (37.14%)	−0.0915 (4.53%)	−0.0875	−0.4682 (0.95%)	−0.4515 (2.66%)	−0.4638
21	−0.0764 (73.64%)	−0.0467 (6.16%)	−0.0440	−0.4051 (2.25%)	−0.3866 (2.43%)	−0.3962
22				−0.3459 (4.09%)	−0.3255 (2.04%)	−0.3323
23				−0.2908 (6.79%)	−0.2685 (1.38%)	−0.2723
24				−0.2400 (10.75%)	−0.2157 (0.44%)	−0.2167
25				−0.1934 (16.58%)	−0.1673 (0.87%)	−0.1659
26				−0.1513 (25.56%)	−0.1236 (2.56%)	−0.1205
27				−0.1138 (40.32%)	−0.0848 (4.50%)	−0.0811

ultimate test for both theoretical methods and basis sets. The pair potentials themselves can be used by theoreticians to model systems using molecular dynamics and by spectroscopists to aid in the analysis of spectra. Here, we take He_2 as the third example.

In Figure 4, we present the five-parameter model potential curve for the ground state He_2, and compare it with CCSD/6–311++G (3df,2pd) calculation, three-parameter model potential ($\alpha = 1.313, \beta = 0.04200863, \gamma = 1.40$) [10], and accurate data [24]. We find that the five-parameter potential curve agrees well with the accurate data [24], and is improved significantly in the large-R region in comparison with the three-parameter model potential. To be noted, advanced *ab initio* CCSD/6–311++G (3df,3pd) calculation performs well in the large-R region, but is not doing well in the short-R and intermediate-R regions in comparison with the literature data and the three- and five-parameter model potentials. Certainly, in comparison with accurate data [24], this potential–energy curve calculated by using CCSD/6–311++G (3df,2pd) can be quantitatively improved over all the internuclear distances by increasing the size of basis sets, for example, aug-cc-pV5Z as shown in Figure 4.

Then, we have performed vibrational energy calculations for $^4He_2$ using the five-parameter model potential. As observed in experiment, we got one single vibrational level with the vibrational energy of −0.104218 meV, which reaches a relative error of 4% in comparison with the measured value −0.099929 meV [25], is improved over 2% in comparison with the vibration energy

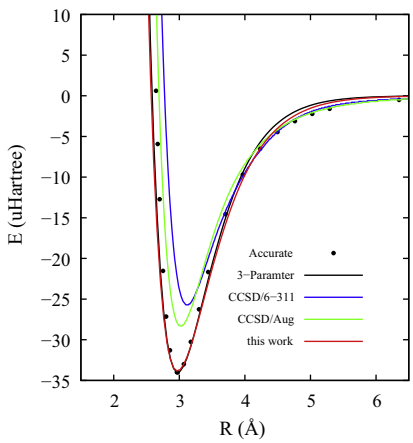

Figure 4. The comparison between five-parameter model potential (red line, this Letter, $\alpha = 1.185, \beta = 0.01391, \gamma = 1.75, n = 1.92$, and $\zeta = 1.408$), three-parameter model potential (black line, $\alpha = 1.313$, $\beta = 0.04200863, \gamma = 1.40$, Ref. [10]), CCSD/6–311++G (3df,2pd)(blue line), CCSD/aug-cc-pV5Z (green line) and the most accurate data (filled dots, Ref. [24]) for the weakly bound diatomics He_2. The potential energy $U(R) = E(R) - E_\infty$. The equilibrium distance R_e and minimum energy U_{min} in the three- and five-prameter model potentials are fitted to 2.9737 Å and −34.0 μHartree, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

−0.106599 meV calculated by using the three-parameter model potential [10], and is much better than the value −0.107 meV obtained in Ref. [24] and −0.114 meV in Ref. [4].

3.5. Diatomic dications

Diatomic dications [26] can form temporarily stable species in the gas phase even though strong Coulomb repulsion exceeds conventional bond energies. A large number of XH^{++} dications composed of first- or second-row atoms have been characterized both theoretically and experimentally [26–32]. Such species are usually thermodynamically unstable with respect to dissociation into two mono-cations, but significant kinetic stability may result if sufficiently high barriers impede fragmentation. Barriers on the potential curves usually exist due to avoided crossings between states correlating diabatically with asymptotes of repulsive (X^+ + H^+) and attractive (H + X^{++}) character. The accurate calculation of such barriers is very important for determining the lifetimes of these diatomic dications. To date, only few theoretical models [33] were specifically designed for meta-stable molecular dications [26].

As well as neutral and singly-charged diatomic systems [10] that we have extensively studied, we have found that more significantly, both the three- and five-parameter model potentials are applicable to describe the meta-stable diatomic dications. For the meta-stable dications He_2^{++}, Be_2^{++}, BeH^{++} and Mg_2^{++}, we have found that both three- and five-parameter model potentials can support 5, 18, 8 and 20 vibrational levels, respectively, which agree well with previous theoretical and experimental studies [27–29]. We also found that eight and twelve vibrational levels are observed for using the three- and five-parameter model potentials constructed for meta-stable dication BeH^{++} and AlH^{++}, respectively. The estimated lifetimes [10] for the lowest four vibrational states of BeH^{++} and those for the lowest six vibrational states of AlH^{++} are supported well by experiment [30,31]. All the dication cases that we have studied by using the three-parameter model potentials are presented in Figs. A27–A30, A55–56, A59–60, and A92–94 of the supporting material of Ref. [10].

In Figure5, we present the five-parameter potential curve for the meta-stable diatomic dication BeH^{++} ($\alpha = 0.7028$, $\beta = 1.3655, \gamma = 0.1158, n = 2.05$, and $\zeta = 2.395$), which is compared with CCSD/6–311++G (3df,3pd) calculation [10], three-parameter potential ($\alpha = 0.687, \beta = 1.43632004$, $\gamma = 0.1185$) [10], and accurate data [28,29]. It is found that the potential barrier generated by the five-parameter potential agrees well with the accurate data [27] except a slight difference around R = 4 Å, and is much more accurate than the barrier generated by the three-parameter model potential. To be noted, CCSD/6–311++G (3df,2pd) has a slight difference from the five-parameter potential model at the local minimum and local maximum. Overall, both CCSD/6–311++G (3df,2pd) and five-parameter potential model have quite similar performance.

3.6. Limitation and perspective

The term $J_1(R, \gamma)$ (i.e., Eq. (8)) in both three- and five-parameter model potentials has included only one parameter γ. In principle, one can choose multiple parameters. But as supported by this Letter and our results for more than 200 diatomic systems [10] by using three-parameter model potential, one parameter γ has already done a good job, reproducing the perturbation treatment to the polarization energy.

Based on extensive literature study, we found a number of established results about the electronic structures of diatomic systems with closed-shell and/or S-type valence constituents (atoms or ions). These diatomic systems could be good case studies of our three- and five-parameter model potentials due to the important facts: (1) the atomic densities are (approximately) spherically symmetric [34]; (2) only the outer regions of the atoms, in which the atomic densities overlap, contribute significantly to the interaction, while the region around the nuclei in which the atomic density is rapidly varying do not contribute much to the interaction energy [34]; (3) approximately, the exchange interactions between two neutral multi-electron atoms may be dominated by the exchange of a single pair of electrons at any time [19,35], and the resulting exchange energy of a multi-electron system is equal to the exchange energy of a single pair multiplied by a rather complicated angular momentum coupling constant (see Eq. (164) in Ref. [19]); (4) the asymptotic exchange energy for multi-electron diatomic ions may be due to the outer-most electron hopping between the two ionic cores, and the trial wave function can be the asymptotic wave function of the singled-out electrons [36]; (5) for a homonuclear diatomic molecule, Smirnov and Chibisov [37] found that its exchange energy is proportional to an exponent term $exp(-2\sqrt{2E_{I,A}}R)$ ($E_{I,A}$ is the ionization energy at nuclear A. See Eq. (157) in Ref. [19]). For a heteronuclear diatomic molecule, the amplitude of the wavefunction and the ionization energies $E_{I,A}$ and $E_{I,B}$ for the two atoms are different. Then, the exchange energy of a single pair of electrons is proportional to an exponent term $exp[-(\sqrt{2E_{I,A}} + \sqrt{2E_{I,B}})R]$ (see Eq. (160) in Ref. [19]), which is valid only for $E_{I,A} \approx E_{I,B}$. However, even for interactions such as LiHe where the difference between $E_{I,Li}$ and $E_{I,He}$ is a factor of 2, the formula still works (the true range of validity of the formula is still an interesting problem) [38]; and (6) between closed-shell atoms or ions, the re-arrangement of electron density is quite small [34]. Using the three-parameter model potential, we have carried out extensive studies of more than 200 diatomic systems (see the supporting material in Ref. [10]) with closed-shell and/or S-type constituents (atoms or ions whose shells are closed or whose valence shells are S-orbital), for which experimental or *ab initio* data are available. The potential curves thus determined for these diatomic systems agree with the available experimental or theoretical data, with the agreement in many cases much better than one could naively anticipate from a three-parameter potential. Moreover, we have demonstrated that the potential–energy curves of these weakly or strongly bound diatomic systems can be represented

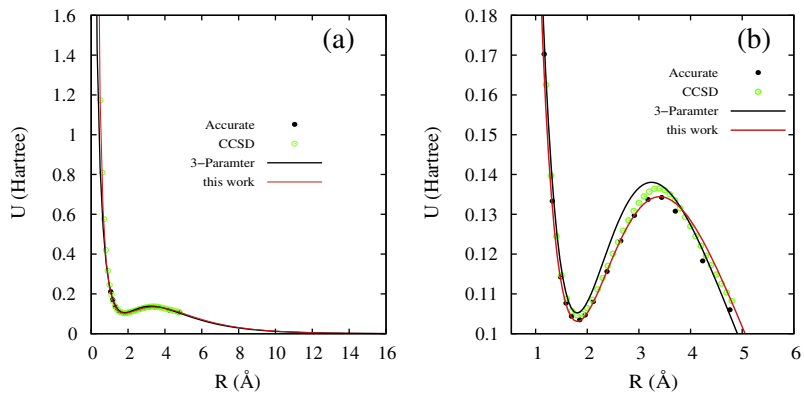

Figure 5. (a) The comparison between five-parameter model potential (Red line, this Letter, $\alpha = 0.7028, \beta = 1.3655, \gamma = 0.1158, n = 2.05$, and $\zeta = 2.395$), three-parameter model potential (Black line, $\alpha = 0.687, \beta = 1.43632004, \gamma = 0.1185$, Ref. [10]), CCSD/6–311++G (3df,3pd)(Green open circle, Ref. [10]), and the most accurate data (Black filled circle Ref. [27]) for the meta-stable diatomic dication BeH^{++}. (b) The barrier shown clearly near R = 3.5 Å. The potential energy $U(R) = E(R) - E_{\infty}$. The equilibrium distance R_e and minimum energy U_{min} of the local minimum in the three- and five-parameter model potentials are fitted to 1.8015 Å and 0.1052199 Hartree, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

by an "approximate" universal reduced potential function [11] supporting above-mentioned facts. We anticipate that our model potential provides a useful guide towards supplementing the potential curves obtained from the RKR and Dunham methods [2]. Extensions of the present approach to other types of diatomic systems are ongoing.

Molecular-modeling or simulation softwares use pair potentials chosen more for speed than for accuracy [9]. For example, they use the harmonic potential for covalently bounded pairs of neutral atoms [9] and the Lennard–Jones (LJ) potential [39] to describe the isotropic interactions in van der Waals molecules. As might be expected, the LJ potential is most successful in describing long- and short-range interactions where one of its two terms dominates, but is not sufficiently flexible to duplicate experimental results in the region of the potential well [40]. An example of this inflexibility is evident from extensive studies by differential scattering cross sections of rare-gas atoms. For these species the LJ potential approximates the repulsive wall quite well, but has a minimum that is too shallow and a long-range attraction that is too strong [40]. The Rydberg–London potential [9] is much more accurate than the harmonic potential and LJ potential, but as shown in Figure. 2(a), is much soft in the short-range interaction. In this Letter, the proposed five-parameter model potential is applicable for short-, intermediate-R and large-R regions (far beyond the equilibrium position), and is quite significantly improved in the large- and short-R regions in comparison with three-parameter model potential and Rydberg-London potential, respectively. When many-body effects are small, the five-parameter model potential might be useful in large-scale computer simulation, which has become an extremely useful tool for studying structure, dynamics, mechanism, and function of complex systems, from biology to materials science and energy technology. Surely, the asymptotic exponential behavior will present an issue for some extreme cases such as ultracold collisions for which one may consider the construction of hybrid potentials of this new potential and van der Waals potentials [5,6].

4. Conclusion

In summary, we have constructed a five-parameter pair potential function for diatomic systems. The new functional form satisfies the three basic criteria [2] for a good pair potential, is able to adequately describe short-, intermediate-, and large-R interaction regions, and is much flexible to represent a unique potential function having a local maximum as well as a local/global minimum. We have demonstrated it in stable and meta-stable diatomic systems (such as strongly bound molecules H_2^+, H_2, and LiH, weakly bound diatomics He_2, and meta-stable diatomic dication BeH^{++}). The vibrational energies of H_2, LiH and He_2 calculated by using the five-parameter model potential reach a good accuracy for all relevant internuclear distances.

JCX would like to thank Professor Jiangbin Gong for providing the Fortran program for computing the vibrational energies of the studied diatomic systems.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2013.11.004.

References

[1] D. Steele, E.R. Lippincott, J.T. Vanderslice, Rev. Mod. Phys. 34 (1962) 239.
[2] J. Goodisman, Diatomic Interaction Potential Theory, vol. 1, Academic Press, New York, 1973.
[3] J.S. Winn, Acc. Chem. Res. 14 (1981) 341.
[4] K.T. Tang, J.P. Toennies, C.L. Yiu, Phys. Rev. Lett. 74 (1995) 1546.
[5] J. Koperski, Phys. Rep. 369 (2002) 177.
[6] J. Koperski, Van der Waals Complexes in Supersonic Beams, Wiley-VCH, Weinheim, 2003.
[7] Y.P. Varshni, Chem. Phys. 342 (2007) 297.
[8] G.D. Zhang, J.Y. Liu, L.H. Zhang, W. Zhou, C.S. Jia, Phys. Rev. A. 86 (2012) 062510.
[9] K. Cahill, V.A. Parsegian, J. Chem. Phys. 121 (2004) 10839.
[10] R.H. Xie, J.B. Gong, Phys. Rev. Lett. 95 (2005) 263202.
[11] R.H. Xie, P.S. Hsu, Phys. Rev. Lett. 96 (2006) 243201.
[12] D.A. McQuarrie, Quantum Chemistry, University Science Books, Mill Valley, CA, 1983.
[13] J.M. Peek, J. Chem. Phys. 43 (1965) 3004.
[14] J. Patel, J. Chem. Phys. 47 (1967) 770.
[15] A. Ruzsinszky, J.P. Perdew, G.I. Csonka, J. Phys. Chem. A 109 (2005) 11006.
[16] M.J. Frisch et al., GAUSSIAN 09, Revision D.01, Gaussian Inc., Wallingford, CT, 2009.
[17] K.T. Tang, J.P. Toennies, J. Chem. Phys. 95 (1991) 5918.
[18] G.L. Guo, K.T. Tang, J.P. Toennies, C.L. Yiu, J. Chem. Phys. 98 (1996) 8777.
[19] K.T. Tang, J.P. Toennies, C.L. Yiu, Int. Rev. Phys. Chem. 17 (1998) 363.
[20] J. Cizek, J. Chem. Phys. 45 (1966) 4256.
[21] W. Kolos, J. Rychlewski, J. Chem. Phys. 98 (1993) 3960.
[22] I. Tobias, J.T. Vanderslice, J. Chem. Phys. 35 (1961) 1852.
[23] Y.C. Chan, D.R. Harding, W.C. Stwalley, C.R. Vidal, J. Chem. Phys. 85 (1986) 2436.
[24] R. Feltgen, H. Kirst, K.A. Köhler, H. Pauly, F. Torello, J. Chem. Phys. 76 (1982) 2360.
[25] R.E. Grisenti, W. Schöllkopf, J.P. Toennies, G.C. Hegerfeldt, T. Köhler, M. Stoll, Phys. Rev. Lett. 85 (2000) 2284.
[26] D. Mathur, Phys. Rep. 225 (1993) 193.
[27] C.A. Nicolaides, M. Chrysos, P. Valtazanos, J. Phys. B 23 (1990) 791.

[28] H. Hogreve, Chem. Phys. Lett. 394 (2004) 32.
[29] C.A. Nicolaides, M. Chrysos, P. Valtazanos, J. Phys. B 23 (1990) 791.
[30] K. Franzreb, R.C. Sobers Jr., J. Lörincik, P. Williams, Phys. Rev. A 71 (2005) 024701.
[31] K. Franzreb, R.C. Sobers Jr., J. Lörincik, P. Williams, Appl. Surf. Sci. 231 (2004) 82.
[32] P.M.W. Gill, L. Radom, J. Am. Chem. Soc. 110 (1988) 5311.
[33] P.M.W. Gill, L. Radom, Chem. Phys. Lett. 147 (1988) 213.
[34] R.G. Gordon, Y.S. Kim, J. Chem. Phys. 56 (1972) 3122.
[35] E.L. Duman, B.M. Smirnov, Opt. Spectrosc. (USSR) 29 (1970) 229.
[36] J.N. Bardsley, T. Holstein, B.R. Junker, S. Sinha, Phys. Rev. A 11 (1975) 1911.
[37] B.M. Smirnov, M.I. Chibisov, Soviet Phys. JETP 21 (1965) 624.
[38] U. Kleinekathöfer, K.T. Tang, J.P. Toennies, C.L. Yiu, Chem. Phys. Lett. 249 (1996) 257.
[39] J.E. Lennard-Jones, Proc. Phys. Soc. 43 (1931) 461.
[40] B.L. Blaney, G.E. Ewing, Ann. Rev. Phys. Chem. 27 (1976) 553.