Pauli–Rydberg–London Potential: An Accurate Pair Potential Function for Diatomic Systems

Jianing Colin Xie[1, †], Tapas Kar[1, ∗], and Rui-Hua Xie[2, ∗]

[1] *Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322, USA*
[2] *Department of Applied Physics, Xi'an Jiaotong University, Xi'an 710049, China;*
Department of Physics, Hubei University, Wuhan 430062 China

Based on a molecular-orbital theory for H_2^+, we have proposed and tested a pair potential function form for the diatomic systems. The new form has included the Pauli repulsive term, Rydberg potential, and London inverse-sixth-power energy, and is accurate at all relevant distances and simple enough for practical application in all-atom computer simulations. We find that an "approximate" universal reduced potential curve for strongly and weakly bound diatomic molecules may exist.

Keywords: Diatomic System, Pair-Potential, Pauli, Rydberg-London Potential, Nanocluster, Cluster, Coulomb Integral, Exchange Integral.

1. INTRODUCTION

The solution of the Schrödinger equation for a diatomic system[1, 2] under the Born-Oppenheimer approximation leads to families of R-dependent potential-energy functions $E(R)$, where R is the internuclear distance. Then, all properties of the system can be extensively explored with the complete basis set and information provided by the eigenfunctions of nuclear motion in the derived potentials.[1–5] In experiment, the interaction potentials of diatomic systems can be directly obtained by fully analyzing the spectroscopy data with the help of Rydberg–Klein–Rees (RKR) method, semi-empirical or empirical procedures.[4, 6] In theory, *ab initio* calculations[7] or quantum Monte Carlo simulations[8] may provide a direct numerical approach to achieving accurate potential curves for the diatomic systems, but they are quite prohibitively expensive ways for solving weakly bound systems[3] and/or many-electron systems.[4] Thus, attention has been paid to all kinds of empirical approaches. To date, there are many empirical functions that have been suggested to describe the diatomic potentials.[1–3, 5, 9–18] All of them can be summarized in two kinds of function forms. One is the well-known Dunham form,[19] which is expressed on the Taylor expansion of the potential $E(R)$ at the equilibrium internuclear distance R_e. The second one is based on exact analytical forms.[1, 2, 5, 13, 14]

The exact analytical form of the potential energy for a diatomic system is of interest, not only in molecular spectroscopy, but also in the prediction of clusters including nanostructures, in the atom–atom collision theory, and in the research of the analytical forms for the potential-energy hyper-surfaces for polyatomic molecules in the pair-interaction approximation, in particular as regards the thermodynamic and kinetic parameters of molecular liquids and gas. In this sense, it is of necessary to use analytical model potentials that adequately describe the regions at small and large internuclear distances R, as well as the region at the equilibrium distance R_e. Over the past 80 years, numerous attempts to analytically construct diatomic potentials have been reported.[2, 4–6, 9–18] The well-known potential functions include Morse, Rosen-Morse, modified Rosen-Morse, Rydberg, Born-Mayer, Linnett, Hulburt-Hirschfelder, Pöschl-Teller, Frost-Musulin, Varshni III, Lippincott, Lennard-Jones, Maitland-Smith, Tang-Toennies potentials[1, 2, 4–6, 11] as well as the recently proposed Morse-based potentials.[12, 16] These analytical potentials usually focus on describing either strongly or weakly bound, neutral or singly-charged diatomic molecules and often lose their quality for either small or relatively large internuclear distance. Long-term research effort has also been devoted to the construction of hybrid potentials, which use different functions for different interaction regions of R[4, 6, 15, 17, 18, 20] and thereby need more than four potential parameters. Well-known examples of hybrid potentials include the combined Morse-van der

∗Authors to whom correspondence should be addressed.
†Permanent address: 106 Walcourt Loop, College Station, Texas 77845.

Waals,[6] Cvetko,[15] general Buckingham-type $\exp(n, m)$,[6] Bellert-Breckenridge,[17] Rydberg–London potential,[18] and Morse-cubic spline-van der Waals (MSV)[20] potential.

In this work, following the molecular-orbital theory based approach,[13] we construct a very simple analytical potential function called Pauli–Rydberg–London Potential for diatomic systems. The potential function thus obtained has significant applicability insofar as it can describe diatomic molecules, ranging from weakly to strongly bound systems, with a favorite accuracy for all relevant internuclear distances. In particular, we find that an "approximate" universal reduced potential for bound diatomic systems may exist.

2. PAIR POTENTIAL MODEL
2.1. Analytical Potential Function Form

An analytical formula for the diatomic potential $E(R)$ is much easier to deal with than the energy values corresponding to a series of values of the internuclear distance R, such as are provided by *ab initio*, advanced quantum Monte Carlo calculation, or any other numerical approach.[1] For practical applications that require an analytical potential, it is of necessary to find an analytical functional form, which satisfies three basic criteria for a good diatomic potential:[1]

(i) Having a finite asymptotic value E_∞ at $R \to \infty$;
(ii) Allowing a global potential minimum $E_{\min}$ at the equilibrium distance R_e;
(iii) Approaching infinity as R goes to zero.

and is able to adequately describe short-, intermediate-, and large-R regions of the diatomic potential. As well as these characteristics, an additional characteristics (iv) is that the constructed potential form involves Coulomb and exchange interactions, but has only few parameters. To build such a potential model, the choice of the functional form is of great importance. Based on the molecular-orbital theory[21] for the simplest single-electron diatomic system H_2^+, we have recently found an analytical functional form[13] that is able to model the diatomic potentials. For convenience, we briefly summarize it here.

The Hamiltonian for H_2^+ is given, in atomic units, by

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \qquad (1)$$

where $r_A(r_B)$ is the distances between the single electron and nuclear $A(B)$. We are able to obtain an exact solution for the ground state H_2^+. In order to understand how the simplest version of the molecular-orbital theory may be improved and to see how the new model potential is constructed, we present the details of the exact solution here. Considering the S-type trial function of H_2^+, one can derive the energy of the bonding orbital[21]

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

where $E_\infty = -1/2$. The Coulomb integral $J_1(R)$ and exchange integral $K_1(R)$ are defined by[21]

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

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

respectively, where $|\phi_0\rangle = e^{-r}/\sqrt{\pi}$ is the 1s-orbital of H atom. The overlap integral $S_0(R)$ between the atomic orbital $|\phi_0^A\rangle$ and $|\phi_0^B\rangle$ is given by

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

It is found that the analytical potential function Eq. (2) of H_2^+ satisfies the pair potential requirements set above Ref. [13].

Figure 1 presents the resultant analytical curve of this function Eq. (2). It shows 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.[13] However, Eq. (2) should be constructively improved in comparison with the most accurate data available in the literature.[22] Advanced *ab initio* calculations have shown that if a much complicate trial function that involves *polarization* and even *diffuse* functions is considered, then the calculated potential curve will perform very well in all the regions of R.[13] We have demonstrated it in Figure 1 by using couple cluster method with single and double excitation (CCSD)[23] with 3-21G (2 sets of Gaussian functions in
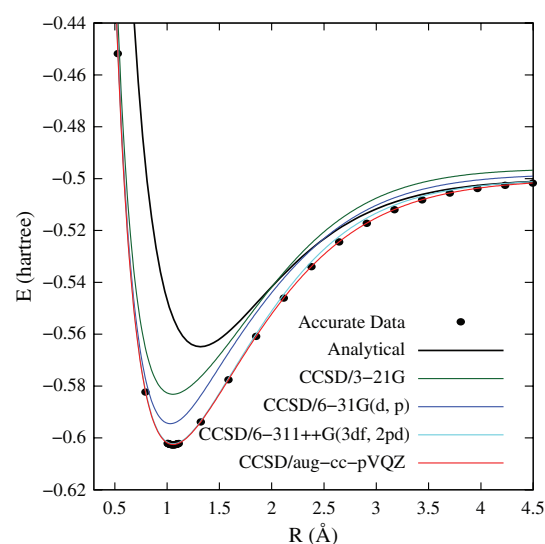

Figure 1. The potential energy curve of the ground state of simplest single-electron diatomic system, H_2^+: Analytical function Eq. (2) (black line), CCSD/3-21G (green line), CCSD/6-31G(d, p) (blue line,[13]), CCSD/6-311++G($3df$, $2pd$) (cyan line,[13]), and CCSD/aug-cc-pVQZ (red line). The filled dots are the most accurate data reported in the literature.[22]

the valence region), 6-31G(d, p) (including p and d polarization functions), 6-311++G($3df$, $2pd$) (including $2p$ and $1d$ polarization functions and diffuse functions), and aug-cc-pVQZ (including $4s$, $3p$, $2d$, $1f$ polarization functions and diffuse functions) Gaussian-type basis sets.[13] The numerical potential curve for the ground-state H_2^+ at the level of CCSD/aug-cc-pVQZ is in much excellent agreement with the most accurate literature data.[22]

2.2. Physics Insight

When we find an analytical functional form for constructing a model potential, we need to introduce parameters into the function. Before doing that, we expect to seek a physics insight into the division of constructed potentials into polarization and exchange, which can be traced back at least to the work of Kolos in the 1960s[24] and has a lot of literatures since then. Here we focus on reviewing the work of Tang and Toennies.[25, 26]

By using the theory of the permutation group and the unsymmetrical Rayleigh-Schrödinger perturbation theory (commonly known as the polarization approximation), Tang and Toennies[25, 26] developed a systematic and successful procedure to take account of exchange energies for the calculation of interatomic potentials for diatomic systems, for example, H_2^+, H_2, and multielectron diatomic systems. The ground-state energy of a diatomic system can be given by[25]

$$E = E_{\text{polar}} - \left(1 - \sum_{n=0}^{N-1} S_n\right)\epsilon_{\text{exch}} \quad (6)$$

where $E_{\text{polar}} = E_\infty + \sum_{n=1}^{N} \epsilon_n$ is the sum of the polarization energy series $\epsilon_n = \langle \phi_0 | V | \phi_{n-1}\rangle$ ($n = 1, 2, \ldots$), E_∞ is the zero-order energy, S_n is the nth-order overlap integral, ϵ_{exch} is the exchange energy, and V is the perturbed term in the Hamiltonian of the diatomic system.

For one-electron H_2^+, 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. Therefore, the "*exchange*" refers to the exchange of two protons. If the first-order exchange energy $\epsilon_{\text{exch}}^{(1)}$ is used, the ground state energy of H_2^+ is given by Ref. [26]:

$$E \approx E_{\text{polar}} - \left(1 - \sum_{n=0}^{N-1} S_n\right)\epsilon_{\text{exch}}^{(1)} \quad (7)$$

where N is the perturbation order. As shown in Table I, the potential energies at $R = 1.0, 2.0, 3.0$ Bohr are getting closer to the exact values as the perturbation order N is increased from $N = 1$ to $N = 3$.

For the first-order polarization approximation, the energy Eq. (7) of the ground-state H_2^+ can be written in the following form[25, 26]

$$E(R) = E_{\text{polar}} - (1 - S_0)\epsilon_{\text{exch}}^{(1)} \quad (8)$$

where $E_{\text{polar}} = E_\infty + J_1(R)$ and $\epsilon_{\text{exch}}^{(1)} = [S_0 J_1(R) - K_1(R)]/(1 - S_0^2)$. It can be shown that Eq. (8) is equivalent to Eq. (2).

For two-electron H_2, the exchange can be interpreted as a result of an exchange of the two electrons. The potential energy function for the ground-state H_2 is then also given by Eq. (8).[25, 26] 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.

For neutral multi-electron diatomic systems, there is a fundamental approximation that the exchange interactions between two multi-electron atoms is dominated by the exchange of a single pair of electrons at any time.[27] Taking the coupling of orbital and spin angular momenta of all equivalent electrons into account, Tang, Toennies and Yu[26] concluded that "*the 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 κ*" (see Eq. (164) in Ref. [26]). Although the constant κ is the result of a rather complicated angular momentum coupling, all of them are identical to the results of a simple counting procedure. Thus, the constant κ is equal to the number of possible exchanges between valence electrons with the same spin in the two atoms.[26] Based on the polarization approximation,[25, 26] the ground-state potential energy of neutral multi-electron diatomics is also describable by Eq. (8).

2.3. New Potential Model

Stimulated by the *ab initio* CCSD calculation 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[13] for diatomic systems based on the analytical form Eq. (2), i.e.,

$$E(R, \alpha, \beta, \gamma) = E_\infty + \frac{J_1(R, \gamma) + K_1(R, \alpha, \beta)}{1 + S_0(R)} \quad (9)$$

with

$$J_1(R, \gamma) = e^{-2\gamma R}\left(1 + \frac{1}{R}\right) \quad (10)$$

$$K_1(R, \alpha, \beta) = e^{-\alpha R}\left(\frac{1}{R} - \beta R\right) \quad (11)$$

and $S_0(R)$ is given in Eq. (5). As shown in Table I, this 3-parameter model potential for H_2^+ agrees well with the most accurate data for a set of parameters (α, β, γ).[13] It shows that the three parameters can be properly adjusted so that contributions of both the polarization and exchanging energies can be accounted for in an efficient way, thereby achieving in effect the same goal as that of using larger basis sets (e.g., 6-311++G($3df$,

Table I. Comparison of the potential energies (Hartree) derived by using polarization approximation approach, and 3-parameter potential model[13] for H_2^+ at the nuclear-nuclear distance R (bohr). Perturbation results are adapted from Ref. [25], accurate results are from Ref. [22], and δ is the relative error between theoretical and accurate results.

	Perturbation theory[25]			3-Parameter model[13]	Accurate[22]
R	$E(N=1)$ (δ)	$E(N=2)$ (δ)	$E(N=3)$ (δ)	E_{model} (δ)	$E_{accurate}$
1.0	-0.2884 (36.17%)	-0.4406 (2.48%)	-0.4403 (2.55%)	-0.4724 (4.36%)	-0.4518
2.0	-0.5538 (8.10%)	-0.5876 (2.49%)	-0.5994 (0.53%)	-0.60263(0.01%)	-0.6026
4.0	-0.5369 (1.68%)	-0.5427 (0.62%)	-0.5445 (0.29%)	-0.5429 (0.59%)	-0.5461

$2pd$), aug-cc-pVQZ) in the trial wavefunction.[13] This 3-parameter model has been successfully applied to over 200 diatomic systems[13] (including weakly bound diatomics) with closed-shell and/or S-type valence-shell constituents over a significantly wide of internuclear distance. Nevertheless, its overall accuracy needs to be further improved, in particular of the large-R portion of the potential.

On the other hand, as discussed before, polarization and diffusion play an important role in a good description of the potential. Thus, the nth-order overlap integral S_n should be taken into account in the construction of model potential functions. Mathematically, the constructed 3-parameter potential function is not simple enough for practical application. Meanwhile, in general, more parameters introduced in a potential function imply greater flexibility and the great possibility of a closer representation of the true potential $E(R)$. Therefore, based on the analytical form Eq. (2) and the 3-parameter potential model Eq. (9), we re-construct a new pair potential form for diatomic systems as follows:

$$E(R, \alpha, \beta, \gamma, \zeta, C_6, \eta)$$
$$= E_\infty + \eta[J_1(R, \alpha, \gamma) + K_1(R, \alpha, \beta, \gamma)]$$
$$- \frac{C_6}{R^6 + \zeta R^{-6}} \tag{12}$$

with

$$J_1(R, \alpha, \gamma) = e^{-2\gamma R}\left(e^{-(\alpha - 2\gamma)R} + \frac{1}{R}\right) \tag{13}$$

$$K_1(R, \alpha, \beta, \gamma) = e^{-\alpha R}\left(\frac{1}{R}e^{-(2\gamma - \alpha)R} - \beta R\right) \tag{14}$$

$$\eta = \frac{1}{1 + S_0(R)} \tag{15}$$

Above form satisfies the basic criteria (i) and (ii) for being a good potential function. To satisfy the basic criterium (iii), we examine Eqs. (3) and (4) and consider replacing the **1/R** and **1** terms in exchange and Coulomb integrals on purpose by $\mathbf{e^{-(2\gamma - \alpha)R}/R}$ and $\mathbf{e^{-(\alpha - 2\gamma)R}}$, respectively, to achieve a pure Pauli-type repulsive form $\mathbf{e^{-2\gamma R}/R}$ (Note: there are two Pauli-type terms in the 3-parameter model,[13]) and a pure Born-Mayer "exponential" form $\mathbf{e^{-\alpha R}}$. This is different from Tang-Toennis,[5] and Rydberg–London[18] potentials, whereas only the Born-Mayer form appears as the repulsion terms.

Different from the 3-parameter model potential,[13] to satisfy the basic condition (iv), both Coulomb and exchange integrals are described by adding one more parameter to account for the effect of polarization and diffusion functions. In the Coulomb integral $J_1(\alpha, \gamma, R)$, we introduce two parameters, α and γ and replace **1** on purpose with an exponent term $e^{-(\alpha - 2\gamma)R}$. In the exchange integral $K_1(\alpha, \beta, \gamma, R)$, we introduce three parameters, α, β, and γ and replace **1/R** on purpose with $e^{-(2\gamma - \alpha)R}/R$.

To account for the effect of the sum (i.e., $\sum_{n=0}^{N-1} S_n(R)$) of the N-order overlap integral $S_n(R)$ and to make the function mathematically simple, we introduce a unitless parameter η to replace the term containing the zero-order overlap integral $S_0(R)$.

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 3-parameter model potential[13] approaches E_∞ exponentially, a feature different from that suggested by the multipolar dispersion expansion. Motivated by the work of Cahill and Parsegian,[18] we combine the London inverse-sixth-power energy into above proposed function.

Re-organizing the function (12), we have found that the new potential model can be re-written in a simple form

$$E(R, \alpha, \beta, \gamma, \eta, \zeta, C_6) = E_\infty + \frac{2\eta e^{-2\gamma R}}{R} + \eta e^{-\alpha R}(1 - \beta R)$$
$$- \frac{C_6}{R^6 + \zeta R^{-6}} \tag{16}$$

This new potential function constructed above includes one pure Pauli-like term, $2\eta e^{(-2\gamma R)}/R$, and one pure Born-Mayer-like term, $\eta e^{-\alpha R}$. In particular, the new potential contains a term, $\eta e^{-\alpha R}(1 - \beta R)$ (note: here η has a unit of energy and β has a unit of of the inverse of the distance, different from the parameters η and β in Pauli-Rydberg-London potential Eq. (16)), which is actually the Rydberg potential proposed by Rydberg[28] to incorporate spectroscopic data, and was largely ignored until recently.[18, 29, 30] In this sense, our newly constructed potential function is actually a hybrid form of Pauli repulsive term, Rydberg potential, and London inverse-sixth-power energy. We call this potential form Pauli–Rydberg–London potential.

Table II. The potential parameters of 11 pairs of neutral atoms. The values of α, β, η, ζ, and C_6 are directly adapted from Refs. [18, 31]. The values of γ are determined in this work. Dissociation energy D_e and internuclear equilibrium distance R_e,[31] and the scaled length quantities L_2 calculated by using Pauli–Rydberg–London potential are listed.

	D_e (eV)	R_e (Å)	α (Å^{-1})	β (eV Å^{-1})	γ (Å^{-1})	η	ζ (Å^{12})	C_6 (eV Å^6)	L_2 (Å)
H_2	4.7467	0.7417	2.99	2.453	9.90	53.8	47.6	3.884	0.4738
Ar_2	0.01234	3.757	2.6920	0.2631	2.55	1720	177588	37.943	0.5890
Kr_2	0.01735	4.017	2.5249	0.2466	2.25	2499	199064	78.214	0.6423
O_2	5.2136	1.2075	4.48	1.06	5.50	3610	58.4	16.08	0.3911
N_2	9.8995	1.09768	4.3533	1.1777	12.5	3752.6	34.8	14.382	0.3719
I_2	1.5571	2.668	2.8013	0.4351	4.10	14361	208000	230.05	0.5384
NO	6.609	1.1590	4.4196	1.0943	8.20	3809.5	47.0	11.245	0.3644
OH	4.624	0.9707	3.6909	1.4668	7.30	377.8	32.5	6.854	0.4355
Li_2	1.0559	2.6730	1.62	0.5101	3.00	199.48	2850000	829.33	1.1574
Na_2	0.74664	3.0786	1.5311	0.4292	3.50	231.9	9400000	929.76	1.1811
K_2	0.55183	3.9243	1.3409	0.3269	1.80	325.05	99400000	2328.6	1.3441

3. RESULTS

Based on the polarization approximation,[5] the ground-state potentials $E(E_p, \epsilon_{ex})$ of H_2 and other multi-electron diatomic systems, when expressed in terms of the polarization and exchange energies, can take a similar form Eq. (8) to that of H_2^+, despite that their origins of the exchange energy are totally different. Motivated by these known theoretical results, we have carried out extensive studies of many other diatomic systems, for which experimental or *ab initio* data are available. The model potential curves thus determined for these diatomic systems agree with the available experimental or theoretical data. Table II lists the parameters for 11 diatomic molecules, in which the five parameters α, β, η, ζ, C_6 have already been determined by using Rydberg–London potential.[18, 31]

3.1. Fitting the Potential Parameters

For practical application, we explain one important step about how to get the parameters used in this new model potential:

- First, the five parameters α, β, ζ, η and C_6 are obtained directly by using Rydberg–London potential,

$\eta e^{-\alpha R}(1 - \beta R) - C_6/(R^6 + \zeta R^{-6})$ and following the procedures developed in the recent work of Cahill.[31]

- Then, the sixth parameter γ is achieved by fitting the bound and large-R regions of the Rydberg–London potential, and by fitting the short-R region if the most accurate data of the system is available in the literature.

Since the formulation of quantum mechanics, the hydrogen molecule has been one of the most favorite systems used for testing quantum theory and for testing theoretical methods or calculations. Therefore, we study H_2, the simplest multi-electron system.

First, we show in Figure 2 how we adjust the additional parameter γ to improve the potential in comparison with Rydberg–London potential[18] and the most accurate data.[7] First, we apply a a trial value of $\gamma = 1.5$ Å. We find that the fitting potential curve, as shown in Figure 2, is far away from the desired potential curve. Then, we decrease the value of γ from $\gamma = 1.5$ Å, and notice that the fitting curve is getting worse. Then, we turn to increase the value of γ. As shown in Figure 2, the fitting curve is getting better and better as γ is increased gradually from $\gamma = 1.5$ Å, to 3.5 Å,

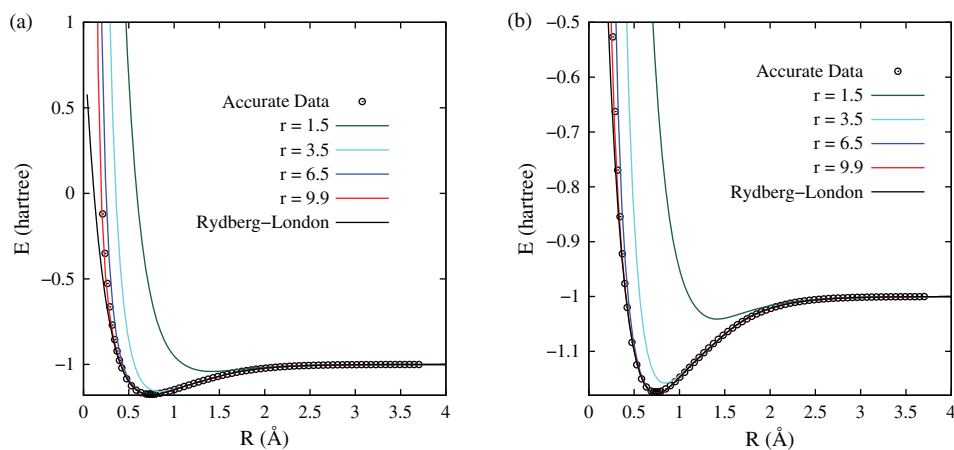**Figure 2.** Fitting the sixth parameter γ in the Pauli–Rydberg–London potential (this work, $\alpha = 2.99$ Å^{-1}, $\beta = 2.453$ eV Å^{-1}, $\eta = 53.8$, $\zeta = 47.6$ Å^{12}, $C_6 = 3.884$ eV Å^6) for the ground-state H_2. The Rydberg–London potential (black line, $\alpha = 2.99$ Å^{-1}, $\beta = 2.453$ Å^{-1}, $\eta = 53.8$ eV, $\zeta = 47.6$ Å^{12}, $C_6 = 3.884$ eV Å^{6},[18]) and accurate data (black open circles,[7]) are presented for fitting. Two energy scales are displayed: (a) $E = -1.18 \sim 1$ hartree and (b) $E = -1.18 \sim -0.5$ hartree. The fitting values of γ are 1.5 (dark green line), 3.5 (cyan line), 6.5 (blue line), 9.9 (red line) Å^{-1}.
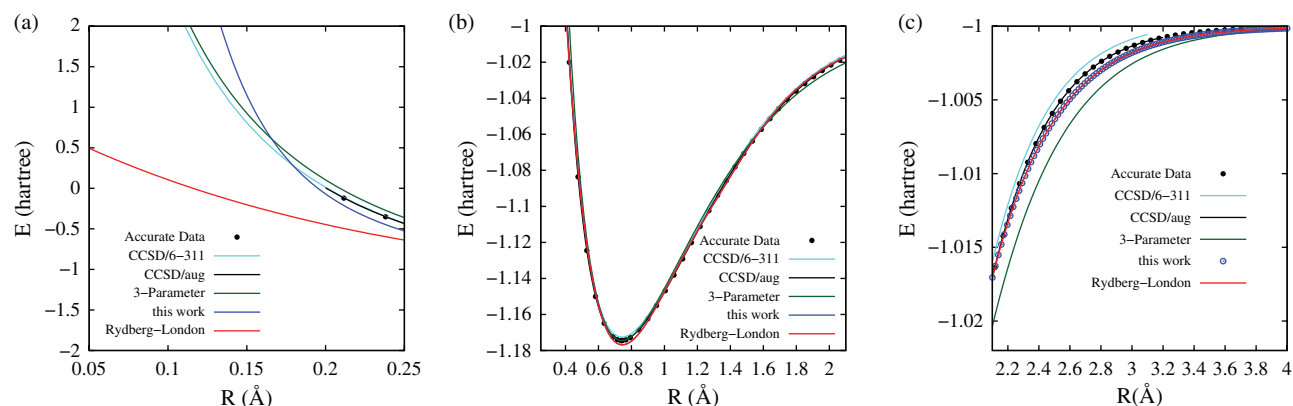
Figure 3. The comparison between Pauli–Rydberg–London potential (this work) (blue), Rydberg–London potential (red,[18]), 3-parameter model potential (dark-green,[13]), CCSD/6-311++G($3df$, $2pd$) (cyan), CCSD/aug-cc-pV5Z (black line), and the most accurate data (filled black circles,[7]) for hydrogen molecule H_2 at (a) $R = 0.05 \sim 0.25$ Å; (b) $R = 0.25 \sim 2.1$ Å; $R = 2.1 \sim 4.0$ Å.

to 6.5 Å. As $\gamma = 9.9$ Å, we find that the new potential curve almost fits the accurate potential curve and all the bound region of the Rydberg–London potential. Thus, the value of the sixth parameter γ is determined.

In Figures 3(a)–(c), we compare the new model potential with other model potentials and the most accurate data for the ground-state hydrogen molecule H_2 in the short-, intermediate-, and large-R regions. In the short-R region (Fig. 3(a)), Rydberg–London potential[18] has large difference from *ab initio* CCSD calculations, the three-parameter model potential,[13] and the Pauli–Rydberg–London potential. In the intermediate-R region (Fig. 3(b)), we find that all of them have quite identical performance.

In the large-R region (Fig. 3(c)), CCSD/aug-cc-pV5Z calculations are in excellent agreement with the accurate literature data.[7] Both Pauli–Rydberg–London and

Rydberg–London potentials overlap well, have a slight difference from the accurate data,[7] and give a better performance than the recent three-parameter model potential.[13]

Using the Pauli–Rydberg–London potential, we calculate the rotationless vibrational levels for the ground-state molecule H_2. As observed in experiment,[32] we have obtained in total fifteen vibrational levels. The calculated vibrational energies are listed in Table III and compared with the results obtained by using the 3-parameter model potential. For Pauli–Rydberg–London potential, we find that calculated vibrational energies from $\nu = 0$ to 12 reach a relative error of less than 1.5% from experiment,[32] while the energies for $\nu = 13$ and 14 have a relative error of 9.1% and 51.72%, respectively. The large error of $\nu = 13$, 14 is due to the unfavorite performance of the potential in the

Table III. The calculated vibrational energies for H_2 using three-parameter model,[13] and Pauli–Rydberg–London (this work) potentials. The value in the parenthesis is the relative error of the calculation from experiment.[32]

| ν	Exp. [eV]	3-Parameter model [eV]	Pauli–Rydberg–London [eV]
0	−4.4774	−4.4628 (0.33%)	−4.5247 (1.06%)
1	−3.9615	−3.9218 (1.00%)	−3.9779 (0.41%)
2	−3.4747	−3.4166 (1.67%)	−3.4729 (0.05%)
3	−3.0166	−2.9465 (2.32%)	−3.0101 (0.22%)
4	−2.5866	−2.5111 (2.92%)	−2.5856 (0.04%)
5	−2.1847	−2.1099 (3.42%)	−2.1899 (0.24%)
6	−1.8110	−1.7427 (3.77%)	−1.8169 (0.33%)
7	−1.4661	−1.4093 (3.87%)	−1.4673 (0.08%)
8	−1.1508	−1.1097 (3.57%)	−1.1459 (0.43%)
9	−0.8665	−0.8439 (2.61%)	−0.8578 (1.00%)
10	−0.6153	−0.6123 (0.49%)	−0.6068 (1.38%)
11	−0.4000	−0.4155 (3.88%)	−0.3957 (1.08%)
12	-0.2245	−0.2543 (13.27%)	−0.2271 (1.16%)
13	−0.0945	−0.1301 (37.67%)	−0.1031 (9.10%)
14	−0.0174	−0.0452 (159.77%)	−0.0264 (51.72%)
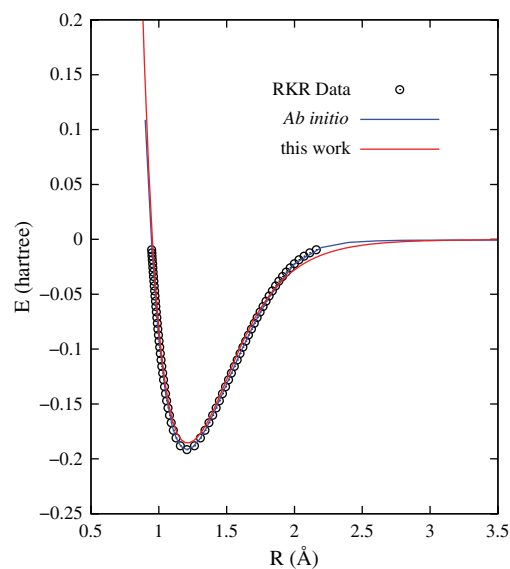
Figure 4. The comparison between Pauli–Rydberg–London potential (Red line, this work), accurate *ab initio* calculation (Blue line,[34]), and RKR data (Open circles,[33]) for the ground-state oxygen molecule O_2.

Table IV. The calculated vibrational energies for $^{16}O_2$ using Pauli–Rydberg–London potential (this work). The value in the parenthesis is the relative error of the calculation from recent RKR data.[33]

ν	RKR data [eV]	This work [eV]	ν	RKR data [eV]	This work [eV]
0	−5.117	−5.150 (0.64%)	17	−2.224	−2.226 (0.09%)
1	−4.924	−4.962 (0.77%)	18	−2.080	−2.038 (2.06%)
2	−4.734	−4.775 (0.86%)	19	−1.938	−1.909 (1.52%)
3	−4.546	−4.590 (0.96%)	20	−1.799	−1.831 (1.75%)
4	−4.362	−4.406 (0.99%)	21	−1.664	−1.646 (1.09%)
5	−4.181	−4.224 (1.02%)	22	−1.532	−1.464 (4.64%)
6	−4.002	−4.043 (1.01%)	23	−1.403	−1.291 (8.68%)
7	−3.826	−3.864 (0.98%)	24	−1.277	−1.129 (13.11%)
8	−3.654	−3.687 (0.89%)	25	−1.155	−1.044 (10.63%)
9	−3.484	−3.513 (0.83%)	26	−1.037	−0.978 (5.69%)
10	−3.316	−3.340 (0.72%)	27	−0.922	−0.840 (8.89%)
11	−3.152	−3.171 (0.60%)	28	−0.811	−0.714 (11.96%)
12	−2.990	−3.005 (0.50%)	29	−0.705	−0.600 (14.89%)
13	−2.831	−2.841 (0.35%)	30	−0.604	−0.498 (17.55%)
14	−2.675	−2.675 (0.00%)	31	−0.507	−0.407 (19.72%)
15	−2.522	−2.522 (0.00%)	32	−0.417	−0.327 (21.58%)
16	−2.372	−2.391 (0.79%)	33	−0.333	−0.257 (22.82%)

large-R region up to the dissociation limit. Overall, the accuracies obtained by using this Pauli–Rydberg–London potential are much better than those[13] by using the three-parameter potential model, in particular, in the large-R region.

3.2. Diatomic Molecule O_2

Oxygen is of great significance in biological, combustion, and atmospheric chemistry as well as in many other processes. The ground state of O_2 is a triplet. Very recently, Hajigeorgiou[33] has determined the potential energy function of the ground electronic state of the oxygen molecule $^{16}O_2$ by fitting a simple analytical model to a set of vibrational-rotational term values calculated from available Dunham coefficients. The potential energy function is accurate up to $\nu = 31$ (or up to an energy that is 90% of the dissociation limit) and is the most extensive and dependable function reported in the literature for the oxygen molecule to date, although there are indications

that the function may be trustworthy up to an energy of 99% of the dissociation limit.

In Figure 4, we present the Pauli–Rydberg–London potential for the ground-state O_2 (to be noted, the parameter β is re-fitted to be 1.06, instead of 1.05 reported in the literature).[18] The curve is compated with accurate *ab initio* calculation[34] and recent RKR data points.[33] We find that the Pauli–Rydberg–London potential curve for O_2 except the large-R region ($R > 2$ Å) agrees well with literature data.[33, 34]

Using the Pauli–Rydberg–London potential determined above, we calculate the rotationless vibrational levels for the ground-state molecule O_2. The results are summarized in Table IV and compared with the recent RKR data.[33] The calculated vibrational energies from $\nu = 0$ to 21 reach a relative error of less than 2%, while those from $\nu = 22$ to 33 reach a relative error of 5% to 23%.

3.3. Reduced Potential Energy Curve

The search for a universal diatomic potential has great interest for a number of practical chemical processes such as chemisorption, adhesion, and cohesion, where similar binding-energy relations were discovered.[35–37] In history, the tests of the universality[6, 11, 14] of diatomic potentials probed the relationship only in the vicinity of the equilibrium internuclear distance R_e. This is a severe test since predictions of third and fourth derivatives were involved.[11] Since the actual diatomic potentials span vibrational frequencies and dissociation energies, which range over several orders of magnitude, the search for the universal potential turns into a quest for a suitable scaling scheme that is able to bring the scattering data-points down to almost a single smooth line.[13, 38] Through the years, much work has been done on this issue.[14, 36, 37] However, various opinions persist whether or not a universal few-parameter potential really exists.[13] Rigorously speaking, it could hardly be expected that an exact universal potential function would exist for all diatomics. Is it possible to find a simple, but "approximate" and accurate function form for potential curves away from the vicinity of the minimum?
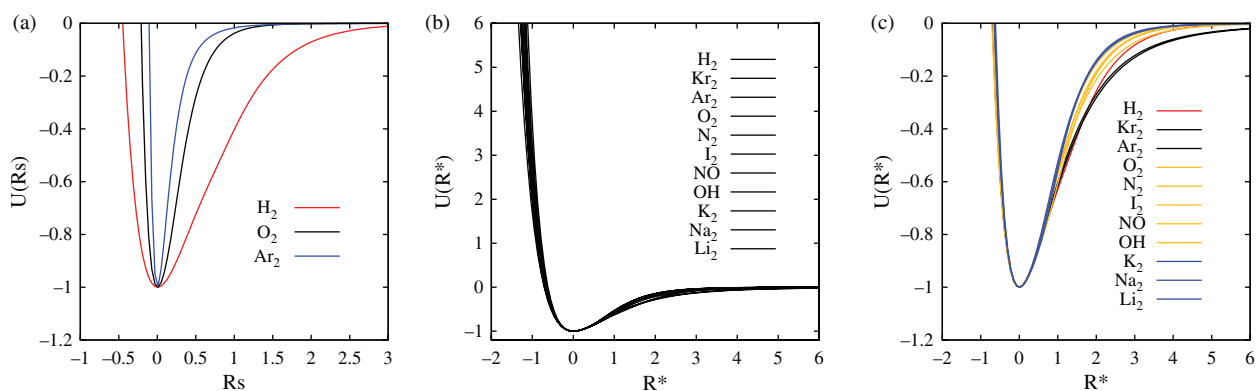

Figure 5. Reduced potential curves U for diatomics in dimensionless scaling schemes: (a) $R_s = (R - R_e)/R_e$; (b), (c) $R^* = (R - R_e)/L_2$.

To answer above question, we test the global universality of the Pauli–Rydberg–London potential form for strongly bound and weakly bound diatomics. Here we use two scaling schemes.[14] One is the usual one with a dimensionless length defined by $R_s = ((R - R_e)/R_e)$. Another scaling scheme[14] uses a dimensionless length $R^* = ((R - R_e)/L_2)$ with the scaled length parameter $L_n = (n!D_e/f_n)^{(1/n)} (n = 2)$ evaluated at R_e, where $f_n = d^n E(R)/dR^n|_{R=R_e}$ is the nth force constant. Both schemes define a scaled dimensionless energy as $U = (E(R)/D_e)$, where D_e is the dissociation energy.

As shown in Figure 5(a), strongly or weakly bound diatomics are distinguished from each other in the R_s scheme. This scheme shows that there is no single binding-energy relation for weakly and strongly bound diatomics.

Then, using the R^*-scheme, as shown in Figures 5(b)(c), we find that the 11 ground-state diatomic molecules can have an "approximate" universal reduced potential curve away from the vicinity of R_e. Thus, while the values of D_e and L_2 vary from system to system (see Table II), the reduced curve $U(R^*)$ for these seemingly diverse systems does not. Moreover, as shown in Figure 5(c), we find that there are some deviations from the reduced curve. The determined values of L_2 listed in Table II seem to show that if one restricts oneself to a certain group of diatomic molecules which have similar linkages (similar L_2 value), an universal potential curve exists for this group. To demonstrate this point, we are collecting more and more accurate data and expect to report it in the future.

4. CONCLUSION

The foregoing results clearly show that the molecular orbital theory-based approach is able to develop an alternative family of few-parameter analytical potential functions, which satisfy the four conditions set in Section 2, to describe the diatomic systems including weakly bound diatomics. The calculated vibrational energies for the ground-state diatomic molecule H_2 and O_2 by using the Pauli–Rydberg–London model potential are in agreement with experiment reaching a favorite accuracy applicable for a widely internuclear distances. Thus, we anticipate that the Pauli–Rydberg–London model potential form may provide a useful guide towards supplementing the potential curves obtained from the RKR, Dunham and other methods. To date, there are many commercial molecular-modeling softwares. They use pair potentials more for speed than for accuracy (for example, harmonic potential for covalently bonded pair of neutral atoms, and the Lennard-Jones potential for unbonded pairs).[18] The constructed Pauli–Rydberg–London potential is nearly as fast and accurate. We expect a possible application of this new model potential in all-atom computer simulations.

We have shown that an "approximate" universal reduced potential function may exist for both weakly and strongly bound diatomic systems. This needs to be demonstrated by collecting more and more accurate data.

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