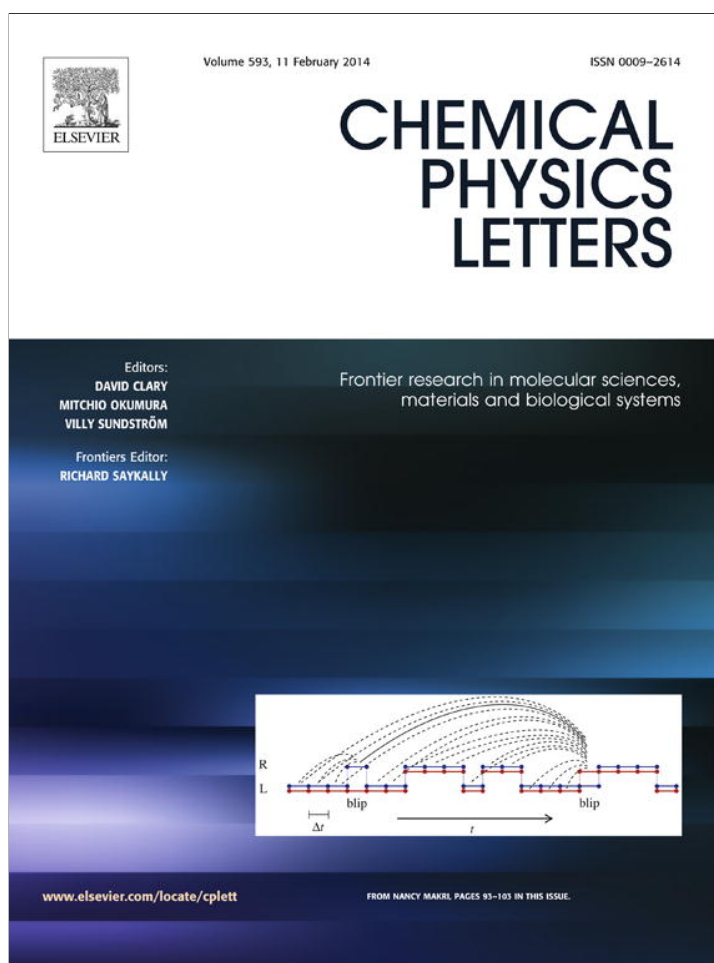


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Improved pair-potential function for diatomic systems

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ABSTRACT

A three-parameter pair-potential model recently constructed is improved in the short- and long-range interaction regions. We demonstrate that this improved potential function is able to accurately describe the entire potentials of the ground-state van der Waals systems such as rare-gas, triplet H₂, Alkali-helium, Alkaline-earth, and group 12 diatomic systems. All these systems show a single binding-energy relation in the attractive region. The improved function suggests a unique form for describing the potentials of diatomic systems ranging from strongly-bound to weakly-bound diatomic systems.

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1. Introduction

The interatomic potential is of fundamental importance for understanding the microscopic and thermodynamical properties of gases, liquids, and solids [1–25]. For practical applications [2,13,23] involving molecular dynamics simulation, prediction of cluster structures, atom–atom collisions, chemical reactivity, transport properties for more complex systems, and molecular spectroscopy, an analytical pair-potential form, in which few or more parameters are left to be evaluated (or fitted), could be very helpful and is required. Over the past 90 years, all kinds of analytical pair-potential function forms, either empirically or semi-empirically, have been reported (see review [1,2,6,13,14,25] and recent works [16,23,24,26]).

A good pair-potential function, $E(R)$ where R is the internuclear distance, is defined that it is able to adequately describe the relevant interaction regions [1–25] as well as to satisfy the basic criteria [1,2]:

- (i) Its asymptotic value $E(R \rightarrow \infty)$ for $R \rightarrow \infty$ is finite;
- (ii) A global potential minimum E_{\min} at the equilibrium distance R_e is allowed;
- (iii) It approaches infinity as $R \rightarrow 0$.

For general applications [2,13], it is also expected that the pair-potential function may show a desirable characteristics [1,2] that the

analytical formula is flexible enough to describe a unique function which has a maximum as well as a minimum. One of us has recently developed such a pair-potential function, i.e., a three-parameter model potential for diatomic systems (all equations and variables throughout this Letter are in atomic units) [23]

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

with

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

$$K_1(R, \alpha, \beta) = e^{-\alpha R} \left(\frac{1}{R} - \beta R \right), \quad (3)$$

$$S_0(R) = e^{-R} \left(1 + R + \frac{R^2}{3} \right), \quad (4)$$

known as the Coulomb, exchange, and overlap integrals, respectively, where α, β, γ are the adjusting parameters, and E_{∞} is the total energy of the system at the internuclear distance $R \rightarrow \infty$. This simple model potential satisfies the basic criteria (i), (ii), (iii) and the desirable characteristics addressed above, and is able to represent the potential curves of diatomic systems with closed-shell and/or S-type valence-shell constituents by a unique “approximate” reduced potential curve [27]. So far, this model potential has been successfully applied to describe more than 200 stable or meta-stable diatomic systems [23] over a significantly wide range of internuclear distances. Examples include strongly bound molecules (e.g., H₂⁺, H₂, and LiH), weakly bound van der Waals diatomic complexes (e.g., He₂, LiHe, Ca₂, Hg₂, CdNe, and NaAr), and meta-stable diatomic dications (e.g., BeH²⁺, AlH²⁺, and MgH²⁺) [23]. This three-parameter model potential plays a significant role on uniquely describing

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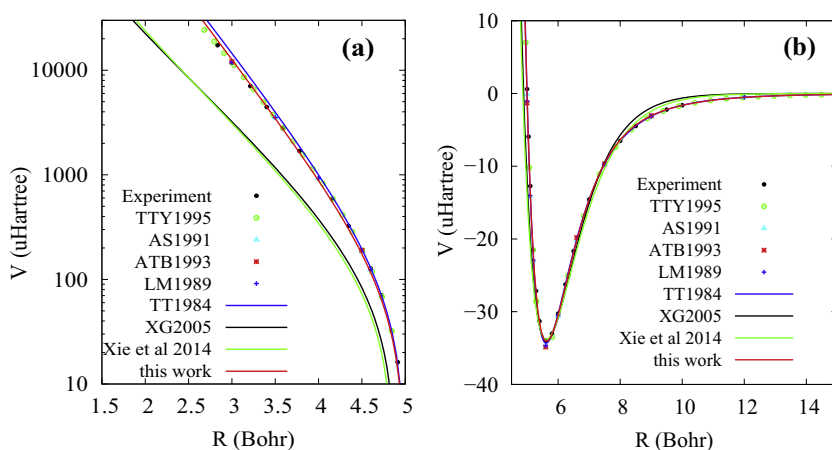


Figure 1. The comparison between the new model potential (red line, this work, $\alpha = 1.41, \beta = 0.05056, \gamma = 1.4, \eta = 62.6$, and $\zeta = 9$), three-parameter potential (XG2005) (dark line, $\alpha = 1.313, \beta = 0.04200863, \gamma = 1.4$, Ref.[23]), five-parameter potential (Xie et al. 2014) (green line, $\alpha = 1.185, \beta = 0.01391, \gamma = 1.75, n = 1.92$, and $\zeta = 1.408$, Ref.[28]), Tang-Toennies potential (TT1984) (blue line, $A = 41.96, b = 2.523$, Ref.[5,15]), quantum Monte Carlo calculation (ATB1993) (red star, Ref. [7]), LM2M2 potential (AS1991) (cyan triangle, Ref. [35]), variational LM2 (LM1989) (blue cross, Ref.[34]), Tang-Toennies-Yiu potential (TTY1995) (green open circle, $D = 7.449, \beta = 1.3443$, Ref. [8]), and experimental data (dark filled circles, Ref. [29]) for the weakly bound helium dimer. The potential energy $V(R) = E(R) - E_\infty$. The equilibrium distance R_e and minimum energy V_{\min} in new model potentials are fitted to 5.621 Bohr and $-34.0 \mu\text{Hartree}$, respectively, of Ref. [5,15]. (a) Repulsive region (Energy in log scale); (b) Attractive region. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

strongly or weakly bound systems, or meta-stable systems. Very recently, Xie *et al.*[28] have introduced 2 more parameters into Eq. (1) to improve the accuracy of this three-parameter model potential. Nevertheless, the overall accuracies in the repulsive and attractive regions of this model potential, as shown in Figure 1a and b for the ground-state He_2 in comparison with experiment [29], need to be further improved. It forms the purpose of this Letter.

2. New model potential

In the short-range (valence) region of the interaction, there is no difference between neutral and ion interaction [30]. At large separation of the fragments, however, there are important differences in the functional forms of the potential [2,4–6,14,24,30]. Neutral closed-shell fragments have a van der Waals interaction energy which is asymptotic to the multipolar dispersion expansion [2,5,30] with the dispersion terms as [5]: $-\sum_{n=3}^{\infty} C_{2n}/R^{2n}$. Accurate values of C_6, C_8 , and C_{10} are available in the literature, and the higher-order coefficients C_{2n} ($n \geq 6$) can be derived by $C_{2n} = (C_{2n-2}/C_{2n-4})^3 C_{2n-6}$ [5,8,15]. Two ions interact with an energy C_1/R [30]; an ion and a neutral (non-polar) closed shell fragment with $-C_4/R^4$ [30], etc. Under the large- R limit, the three-parameter model potential Eq. (1) [23] approaches E_∞ exponentially, a feature different from the mentioned forms.

If the asymptotic multipolar expansion is added to a near-Hartree-Fock potential, the resulting potential is quite accurate in the van der Waals attractive region [31]. Tang, Toennies, and their teams have shown that the addition of a Born-Mayer repulsive potential to the above-mentioned dispersion terms is able to give a good description of rare-gas [5,8], alkali-helium [10,11], alkaline-earth-helium [12], alkaline-earth dimers [17–20], and group 12 dimers [22] potentials. A similar scheme with Morse potentials has been successfully used to derive rare-gas potentials from bulk properties [32]. The pair-potential proposed by Korona *et al.* [9] is also a good representation of the potentials of all homo- and hetero-nuclear dimers of He, Ne, Ar and Kr. Very recently, with the asymptotic multipolar expansion added to the constructed potential, Patkowski, Spirko, and Szalewicz [24] have reproduced the observed spectra of the ground-state Beryllium dimer. Several other promising models with the inclusion of the asymptotic expansion

were reviewed in a recent work [25]. In the light of these successes, we examine in this Letter a modified form of the three-parameter potential Eq. (1) by adding the asymptotic terms, i.e.,

$$E(R, \alpha, \beta, \gamma, \eta, \zeta) = E_\infty + \frac{J_1(R, \gamma, \eta) + K_1(R, \alpha, \beta)}{1 + S_0(R)} - F(R/R_e) \left(1 - e^{-(R/\zeta)^5}\right) \sum_n \frac{C_n}{R^n} \quad (5)$$

with

$$J_1(R, \gamma, \eta) = e^{-2\gamma R} \left(\frac{1}{R} + \eta\right), \quad (6)$$

where $F(R/R_e)$ is a sign function defined as: (i) $F(R/R_e) = +1$ for $R/R_e \geq 10^{-3}$ and (ii) $F(R/R_e) = -1$ for $R/R_e < 10^{-3}$. The number n in the third term of Eq. (5) is defined by specifically studied cases, for example, $n = 6, 8, 10, \dots$ for neutral closed-shell atoms. The asymptotic $-C_n/R^n$ term has an improper behavior in that it goes to $-\infty$ as R approaches to 0. This is due to the asymptotic nature of the dispersion expansion, which is only valid for the internuclear distances where charge distributions do not overlap. To eliminate the unrealistic behavior, a damping term [3], $1 - \exp[-(R/\zeta)^5]$ with a damping parameter ζ and a sign function $F(R/R_e)$, is put in the sum of the C_n/R^n terms. To account for the accuracies in the repulsive wall, a new parameter η , as shown in Eq. (6), is introduced into the Coulomb integral Eq. (2), i.e., $J_1(R, \gamma, \eta)$ shown in Eq. (6).

3. Applications

Another purpose in this Letter is trying to provide a few-parameter analytical function form to uniformly describe the potential energy of diatomic systems. The potential parameters $\alpha, \beta, \gamma, \eta$, and ζ can be determined by using the Nonlinear Least-Squares Fitting Fortran program (see Appendix A) developed by one of us. The most accurate coefficients C_6, C_8 and C_{10} for the systems are available from the literature. Table 1 list the potential parameters and multipolar dispersion coefficients of the diatomic systems studied in this Letter. Here we only report the results of $\text{He}_2, \text{H}_2, \text{Ca}_2, \text{Hg}_2$ and LiHe . All the other cases are summarized in the supporting material (see Appendix A).

Table 1

Potential Parameters $\alpha, \beta, \gamma, \eta$ and ζ , the minimum energies $V_{\min} = E_{\min} - E_{\infty}$ (in units of $\mu\text{Hartree}$), the equilibrium distance R_e , and the dimensionless length L_2 determined for van der Waals diatomic systems. Multipolar dispersion coefficients C_6, C_8 and C_{10} for LiHe [11], NaHe [11], KHe [11], RbHe [11], CsHe [11], He₂ [5], Ar₂ [15], Kr₂ [15], H₂ (triplet) [5], Ca₂ [17], Mg₂ [18], Sr₂ [19], Ba₂ [20], Hg₂ [21], Cd₂ [22], and Zn₂ [22] are listed. All in atomic units, and $N_{\max} = 5$.

System	α	β	γ	η	ζ	C_6	C_8	C_{10}	V_{\min}	R_e	L_2
H ₂ (³ Σ_u)	1.046	0.02618	0.874	5.8	11.58	6.499	124.4	3286	-20.4547	7.796	1.3574456
He ₂	1.40826	0.050783	1.39	60.5	9.0	1.461	14.11	183.5	-34.134	5.628	0.9852352
Ar ₂	1.41971509	13.4773495	0.704291784	80.9966379	10.2	64.30	1623.0	49060	-454.281	7.124	1.1456531
Kr ₂	1.35607455	8.7269567	0.765828689	206.380386	10.3	129.6	4187.0	155500.0	-643.25	7.583	1.1867907
LiHe	0.721	0.01011	0.64	4.33	19.0	22.507	1083.2	72602.1	-7.0385	11.723	1.8812927
NaHe	0.6949	0.00874	0.69	8.1	19.3	23.768	1307.6	94563.2	-5.9492	12.171	1.9976355
KHe	0.645	0.007177	0.55	3.2	19.95	34.038	2525.2	237538	-4.0831	13.794	2.1917189
RbHe	0.6158	0.00644	0.55	3.01	22.0	36.289	2979.0	300406	-3.7076	14.285	2.2614580
CsHe	0.5885	0.005643	0.546	3.25	23.0	41.417	3903.4	453443	-3.1432	15.044	2.3915291
Mg ₂	1.05795181	3.67097693	0.499242836	17.4184595	10.7	627	41500	2757000	-1968	7.326	1.8321816
Ca ₂	0.78884	3.1899	0.369987	15.8	15.15	2121	223000	21320000	-50102	8.119	1.9118386
Sr ₂	0.785467116	3.10926315	0.399101564	26.5914016	16.0	3103	379200	42150000	-4929	8.828	1.9348461
Ba ₂	0.685979692	0.960619083	0.475823144	83.3087266	17.0	5160	772000	101400000	-5453.35	9.776	1.9743901
Zn ₂	1.04950583	0.89490001	0.56756431	10.5555675	10.6	359	13500	640000	-1105.5	7.298	1.6983069
Cd ₂	1.02411942	1.77266453	0.526618617	15.7820342	11.0	686	28900	1537000	-1494.0	7.722	1.7874285
Hg ₂	0.983398619	3.86501339	0.436746668	12.0345448	10.0	392.0	12920.0	537000	-1788.4	6.956	1.5889788

3.1. Rare-gas systems

The interatomic potentials between members of the rare gas family of atoms provide the largest class of chemically identical atoms which interact via van der Waals potentials [15]. He₂ is probably the atom–atom system which has been studied most extensively theoretically as well as experimentally. Two very accurate refined potentials based on the combined evaluation of both bulk and molecular beam scattering data were proposed by Aziz and co-workers [33] and Feltgen and co-workers [29]. Having only four electrons in closed shells, He₂ is ideally suited for a theoretical study. Here we apply the new model to describe the ground state of He₂ (the results for Ar₂ and Kr₂ are reported in the supporting material, see Appendix A). The results are reported in Figure 1 and compared with literature data. Details are summarized in Table 2. We find that the new potential curve in the short- and large-R regions has been greatly improved in comparison with

the three-parameter potential curve (XG2005) [23] and the recently constructed five-parameter potential curve [28]. In the whole interaction regions, the new potential curve is in good agreement with experiment [29] and perturbation calculations of Tang-Toennies-Yiu (TTY1995) [8], variational LM-2 (LM1989) [34], and LM2-M2(AS1991) [35] potentials, and quantum Monte Carlo (ATB1993) [7]. To be noted, for $R < 4.5$ Bohr, Tang-Toennies potential (TT1984) [5] is slightly harder than the others.

3.2. H₂ triplet state

This is the only system for which an exact *ab initio* potential [36] is available within the Born–Oppenheimer approximation. In Figure 2, we report the new potential curve for the triplet state (³ Σ_u) of H₂. It is compared with the exact *ab initio* results of Kolos and Wolniewicz [36,37], Tang-Toennies potential (TT1984) [5], Tang-Toennies-Yiu perturbation calculation (TTY1994) [37], and

Table 2

Comparison of He₂ potential energies $V(R) = E(R) - E_{\infty}$ (in units of $\mu\text{Hartree}$): New model potential (this work, $\alpha = 1.40826, \beta = 0.050783, \gamma = 1.39, \eta = 60.5$, and $\zeta = 9$), three-parameter potential (XG2005) ($\alpha = 1.313, \beta = 0.04200863, \gamma = 1.4$, Ref.[23]), Tang-Toennies potential (TT1984)(Ref.[5,15]), quantum Monte Carlo calculation (ATB1993)(Ref. [7]), LM2M2 potential (AS1991) (Ref. [35]), variational LM2 (LM1989) (Ref.[34]), Tang-Toennies-Yiu potential (TTY1995) (Ref. [8]), and experimental data (Ref. [29]). The value in the parenthesis is the relative error, Error% = |Theory – Experiment| * 100/Experiment, compared to experiment. R in atomic units.

R	TT1984 Ref. [5,15]	TTY1995 Ref. [8]	LM1989 Ref.[34]	AS1991 Ref.[35]	ATB1993 Ref.[7]	XG2005 Ref.[23]	This work	Experiment Ref.[29]
3.0	14489 (23.78)	11860 (1.32)	11930 (1.92)	12010 (2.61)	12070 (3.12)	3215	12615 (7.77)	11705
3.212	8425 (19.78)	7201 (2.37)	–	–	–	2112	7312 (3.95)	7034
3.401	5155 (16.42)	4553 (2.82)	–	–	–	1437	4473 (1.02)	4428
3.5	3971	3561	3520	3531	–	1169	3448	–
3.591	3115 (13.23)	2829 (2.84)	–	–	–	963	2708 (1.82)	2751
3.780	1861 (10.64)	1730 (2.85)	–	–	–	633	1625 (3.39)	1682
4.0	996	947.5	928.3	927.7	–	375	877	–
4.157	622 (6.33)	600 (2.74)	–	–	–	249	551 (5.65)	584
4.5	194	191.4	–	185.2	190.0	83	175	–
4.6	129 (2.32)	128 (0.81)	124 (2.34)	123.4 (2.81)	–	54	117 (7.85)	126.97
5.0	-0.105	-0.0408	-1.06	-0.1225	-1.3±2.6	-11.99	-1.12	–
5.1	-13.34 (4.79)	-13.39 (5.18)	-14.03 (10.29)	-14.16 (11.23)	–	-19.90	-13.58 (6.68)	-12.73
5.2	-22.39 (3.95)	-22.55 (4.69)	-22.91 (6.36)	-23.03 (6.92)	–	-25.60	-22.21 (3.11)	-21.54
5.6	-34.32 (0.94)	-34.77 (2.26)	-34.65 (1.91)	-34.74 (2.18)	-34.87 (2.56)	-33.99	-34.10 (0.29)	-34.00
6.0	-30.32 (0.166)	-30.75 (1.59)	-30.54 (0.89)	-30.63 (1.19)	–	-30.85	-30.48 (0.69)	-30.27
6.6	-20.05	-20.28	–	-20.14	-19.8	-21.03	-20.25	–
7.5	-9.71 (0.00)	-9.763 (0.55)	-9.68 (0.31)	-9.689 (0.22)	-9.66 (0.51)	-9.47	-9.60 (1.13)	-9.71
9.0	-3.14 (0.32)	-3.138 (0.26)	-3.12(0.32)	-3.128 (0.01)	-3.04 (2.88)	-1.96	-3.06 (2.24)	-3.13
9.5	-2.24 (0.43)	-2.237 (0.31)	–	–	–	-1.12	-2.22 (0.45)	-2.23
10.0	-1.62 (0.00)	-1.624 (0.25)	-1.62 (0.00)	–	–	-0.63	-1.64 (1.23)	-1.62
12.0	-0.53 (1.92)	-0.5255 (1.06)	-0.52 (0.00)	-0.5251 (0.98)	–	-0.06	-0.542 (4.23)	-0.52
15.0	-0.1341	-0.1341	–	-0.1341	-0.12	-0.0016	-0.1346	–

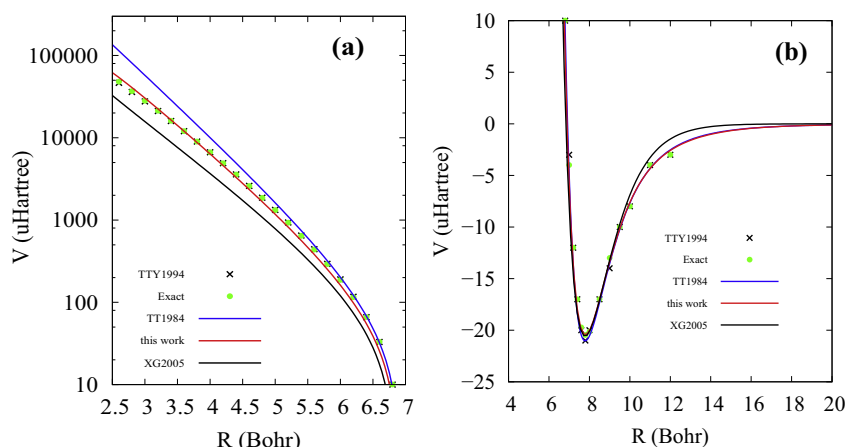


Figure 2. The comparison between the new model potential (red line, this work, $\alpha = 1.046$, $\beta = 0.02618$, $\gamma = 0.874$, $\eta = 5.8$, and $\zeta = 11.58$), three-parameter potential (XG2005) (dark line, $\alpha = 0.978$, $\beta = 0.02228$, $\gamma = 0.874$), Tang-Toennies-Yiu perturbation calculation (TTY1994) (dark cross, Ref. [37]), Tang-Toennies potential (TT1984) (blue line, $A = 9.30$, $b = 1.664$, Ref. [5]), and exact data (green filled circles, Ref. [37,36]) for the triplet $H_2(\Sigma_u^+)$ state. The potential energy $V(R) = E(R) - E_\infty$. The equilibrium distance R_e and minimum energy V_{\min} in the new model potentials are fitted to 7.80 Bohr and $-20.5 \mu\text{Hartree}$, respectively, of Ref. [5]. (a) Repulsive region (Energy in log scale); (b) Attractive region. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

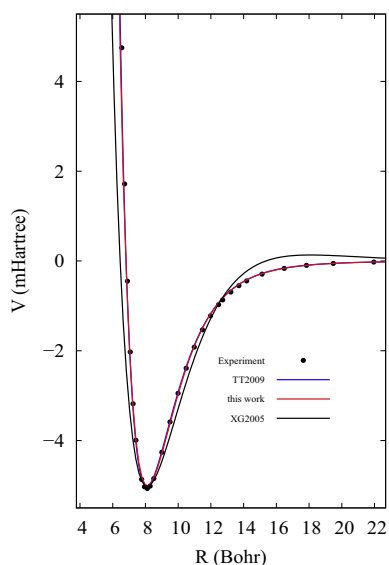


Figure 3. The comparison between the new model potential Eq. (2) (Red line, this work, $\alpha = 0.78884$, $\beta = 3.1899$, $\gamma = 0.369987$, $\eta = 15.8$, and $\zeta = 15.15$), three-parameter potential (XG2005) Eq. (1) (dark line, $\alpha = 0.49231$, $\beta = 0.39345895$, $\gamma = 0.19$, Ref. [23]), Tang-Toennies (TT2009) potential (blue line, $A = 28.23$, $b = 0.9987$, Ref. [17]), and experiment data (dark dots, Ref. [38,39]) for the weakly-bound ground-state Ca_2 . The potential energy $V(R) = E(R) - E_\infty$, in units of *milli*Hartree (mHartree). The equilibrium distance R_e and minimum energy V_{\min} in the new model potentials are fitted to 8.081 Bohr and $-5.021 \mu\text{Hartree}$, respectively, of Ref. [17]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the three-parameter model potential (XG2005) [23]. The new potential curve is in good agreement with the exact *ab initio* results and TTY1994 perturbation calculation. The differences between the new potential energies and exact potential energies in the well region are smaller than 2%, while those at the repulsive region are less than 10%. At $R < 6$ Bohr, we found that the TT1984 potential [5] is much harder than the exact curve, TTY1994 perturbation calculation, and the new potential curve, and its difference from *ab initio* point is more than 10% and increases greatly when R decreases. Compared to the three-parameter model potential [23], the new

Table 3

Comparison of the calcium dimer potential between the experiment of Allard et al. [38,39], the Tang-Toennies model (TT-2009) [17], and the new model potential. The value in the parenthesis is the relative error, $Error\% = |Theory - Experiment| * 100 / Experiment$, compared to experiment. All energies are in units of cm^{-1} and R in units of Å.

R	TT-2009 (Error %)	This work (Error %)	Experiment
3.463960	795.3 (22.94)	712.1 (31.01)	1032.1575
3.555705	248.3 (33.46)	203.0 (45.59)	373.1825
3.647450	-169.6 (73.84)	-191.5 (96.30)	-97.557
3.739195	-499.1 (13.26)	-491.7 (11.59)	-440.6477
3.830940	-724.7 (4.81)	-714.7 (3.37)	-691.4483
3.922685	-884.6 (1.91)	-875.0 (0.80)	-868.0599
4.106174	-1061. (0.33)	-1053.6 (0.36)	-1057.5163
4.197920	-1094. (0.06)	-1090.5 (0.26)	-1093.3715
4.289664	-1102. (0.01)	-1102.2 (0.03)	-1101.884
4.381409	-1090. (0.01)	-1094.4 (0.40)	-1090.1029
4.500000	-1056. (0.24)	-1063.2 (0.92)	-1053.4653
4.761905	-930.4 (0.44)	-943.97 (1.90)	-926.3289
5.023859	-785.3 (0.73)	-797.93 (2.34)	-779.6277
5.285714	-642.5 (0.29)	-654.41 (2.14)	-640.6405
5.547619	-519. (0.01)	-526.48 (1.42)	-519.073
5.809524	-413. (0.98)	-418.57 (0.35)	-417.1011
6.071429	-328.3 (1.55)	-330.59 (0.86)	-333.4624
6.333333	-259. (2.56)	-260.42 (2.03)	-265.8181
6.595238	-205.2 (3.02)	-205.24 (2.99)	-211.5934
6.726191	-182.3 (3.43)	-182.39 (3.37)	-188.7677
6.988095	-144.1 (4.12)	-144.49 (3.85)	-150.2882
7.250000	-114.8 (4.21)	-115.08 (3.96)	-119.8441
7.500000	-92.67 (4.28)	-93.17 (3.75)	-96.8103
8.000000	-61.15 (4.05)	-62.20 (2.39)	-63.7338
8.717949	-34.68 (3.67)	-36.21 (0.57)	-36.0021
9.435897	-20.5 (3.13)	-21.78 (2.93)	-21.1638
10.30342	-11.47 (2.47)	-12.15 (3.32)	-11.761
11.61111	-5.263 (2.04)	-5.41 (0.74)	-5.373

potential curve is greatly improved in the short- R range and in the large- R region.

3.3. Alkaline-earth diatomic systems

The interaction potentials of alkaline-earth dimers have been the subject of many investigations. They are excimer species and are therefore of interest in laser applications. In recent years, investigations in these systems intensified mainly because of cold

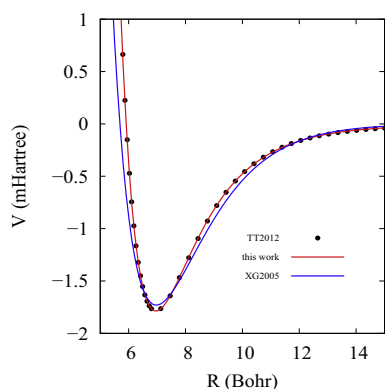


Figure 4. The comparison between the new model potential (red line, this work, $\alpha = 0.983398619$, $\beta = 3.86501339$, $\gamma = 0.436746668$, $\eta = 12.0345448$, and $\zeta = 10.0$), three-parameter potential (XG2005) (blue line, $\alpha = 0.7621$, $\beta = 0.3249866$, $\gamma = 0.35$, Ref.[23]) and Tang-Toennies (TT2012)) potential (dark filled circles, $A = 17.96$, $b = 1.2669$, Ref.[21]) for the ground-state Hg_2 . The potential energy $V(R) = E(R) - E_\infty$. The equilibrium distance R_e and minimum energy V_{\min} in the new model potentials are fitted to 6.955 Bohr and -1.786 mHartree, respectively, of Ref. [21]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

atom physics. Among them, Mg_2 is the first van der Waals molecule for which the electronic ground state potential was constructed from spectroscopic measurements. As such, it became a benchmark system. In the supporting materials, we report the results for Mg_2 , Sr_2 and Ba_2 (see Appendix A). Here we only present the results of Ca_2 .

The ground state potential energy curve of Ca_2 calculated from Eq. (5) is shown in Figure 3. To compare with Tang-Toennies potential (TT2009) [17] and experiment [38,39], some numerical data are listed in Table 3. The shape of the present potential is in good agreement with the experimentally determined potential [38,39]. As seen in Table 2, in the entire attractive part of the potential, the largest difference between the present model and the experiment is only 3.96% at 7.25 Å. Both TT2009 potential [17] and the new potential model have almost identical potential shape except small differences at 4.5 to 5.5 Å and 3.4 to 3.7 Å as shown in Table 3. The new potential curve in the repulsive and large-R regions has been greatly improved in comparison with the three-parameter potential (XG2005) curve [23].

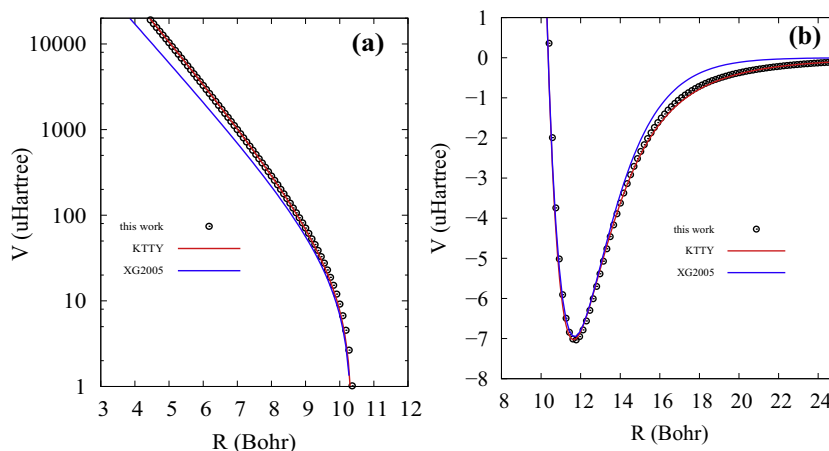


Figure 5. The comparison between the new model potential (dark circles, this work, $\alpha = 0.721$, $\beta = 0.01011$, $\gamma = 0.64$, $\eta = 4.33$, and $\zeta = 19.0$), three-parameter potential (XG2005) (blue line, $\alpha = 0.701$, $\beta = 0.00958$, $\gamma = 0.64$, Ref.[23]) and Kleinekathöfer-Tang-Toennies-Yiu ((KTTY)) potential (red line, $A = 2.430857$, $b_1 = 1.04911$, $b_2 = 0.00381298$, Ref.[11]) for the weakly bound LiHe . The potential energy $V(R) = E(R) - E_\infty$. The equilibrium distance R_e and minimum energy V_{\min} in the new model potentials are fitted to 11.645 Bohr and -7.02 $\mu\text{Hartree}$, respectively, of Ref. [11]. (a) Repulsive region (Energy in log scale); (b) Attractive region. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.4. Group 12 diatomic systems

The group 12 dimers (Zn_2 , Cd_2 , Hg_2) have been investigated for a long time. These dimers are of interest for a variety of reasons as listed in the report of Koperski [13]. Experimentally, Hg_2 potential is probably the most extensively studied among these three dimers. Because much higher temperature is required to vaporize cadmium and zinc, Cd_2 and Zn_2 are less extensively studied than Hg_2 . The progress in theoretical calculations is so rapid that accurate potential energy curves calculated with advanced *ab initio* methods are available.

The ground state Hg_2 potential predicted by the Tang-Toennies model (TT2012) is possibly the most accurate to date [21]. The excellent results for the entire potential curves [22] obtained for the ground states of Cd_2 and Zn_2 demonstrate again the ability of the Tang-Toennies potential model to mimic the van der Waals potentials in cases where the bonding is not purely dispersive. Thus, in Figure 4, we compare the new potentials for the ground states of Hg_2 (those for Cd_2 and Zn_2 are presented in the supporting material) with the TT2012 [22]. It reaches an excellent agreement between the new potential curve and TT2012. In comparison with the three-parameter model (XG2005), the new model leads to much better results, not only in the repulsive region, but also in the attractive region.

3.5. Heteronuclear diatomic systems

Alkali metals have been known for a long time to have very weak interactions with helium with typical well depths of $0.5 \sim 1.5 \text{ cm}^{-1}$ at pair separations of $6 \sim 8 \text{ \AA}$. Mainly the repulsive branches of these potentials have been characterized with experimental methods while the low collision energies needed to gain information on the well region are not easily accessible. The shallowness of the wells has led to the widespread belief that they do not support bound states.

Of the diatomic van der Waals molecules, those containing helium, the most chemically inert of the noble gases, are the most weakly bound. There is much theoretical interest in the study of diatomic molecules involving helium, including questions over their existence. To date, the only ground-state helium diatomic molecule that has been directly detected in the gas phase is He_2 . Kleinekathöfer et al. [11] predicted that for all alkali-helium diatomic molecules, there exists a single bound rovibrational state

in the $X^2 \Sigma$ ground electronic state. Very recently, weakly bound van der Waals molecule LiHe has been detected spectroscopically [40]. In Figure 5, we report the new potential for the ground-state LiHe by fitting the Kleinekathofer-Tang-Toennies-Yiu (KTTY) potential (KTTY) (The root-mean-square (RMS) is 0.04). In the repulsive part, the three-parameter (XG2005) curve is softer than KTTY and the new one. In the large-R region, XG2005 shows a large difference from the KTTY and XG2005 curves. In the supporting material (see Appendix A), we also report the results for NaHe, KHe, RbHe and CsHe, which are in good agreement with the results of Kleinekathöfer et al. [11].

3.6. Reduced potential curves

The improvement over the three-parameter model Eq. (1) leads us to re-examine the scaling scheme of the potential energy curves of diatomic systems. Is it possible to find a simple globally accurate function for potential curves away from the vicinity of the equilibrium distance R_e for van der Waals diatomic systems? To answer this question, we test the global universality of the closed form expression Eq. (5) for the systems investigated above. In Fig. S8 of the supporting material (see Appendix A), we present the results for the scaling scheme of $U(R_s) = V(R)/D_e$ with a dimensionless length $R_s = (R - R_e)/R_e$ [27], where $D_e = |E_{\min} - E_{\infty}|$. It shows that Rare-gas, Alkali-Rare gas, Alkaline-earth, or group 12 diatomic systems seem to present their own single binding energy relation. However, All these systems do not support a single binding-energy relation. This finding agrees with the conclusion demonstrated in Ref. [27] and by Tang and colleagues [19].

For the scaling scheme of $U(R^*) = V(R)/D_e$ with the dimensionless length $R^* = (R - R_e)/L_2$ [27], where $L_2 = \sqrt{2D_e/f_2}$, and f_2 the second-order force constant of Eq. (5) at the equilibrium distance R_e , we report the results in Figs. S9–S23 (see the supporting material). For a better view, all are referenced to the reduced potential curve of the ground-state He₂. It is found that all the systems reported in this Letter show a single binding-energy relation in the attractive region. This may be due to the fact that these systems all have a closed outer electronic s^2 shell. Especially, we find that for $-1 < R^* < 2$, all reduced potential curves overlap well with the reduced curve obtained from Rydberg function, $U(R^*) = -(1 + \sqrt{2}R^*)e^{-\sqrt{2}R^*}$ [27], which was found to be an approximate representation of all strongly-bound and weakly-bound diatomic systems [27] (Actually, this reduced Rydberg function is also a good representation of the potential curves of covalently bonded materials, where $U(a^*) = -(1 + a^*)e^{-a^*}$ [41]). In the short-R range, however, there is no single binding-energy relation, i.e., all systems are well distinguished from each other. The present results for the single-binding energy relation in the attractive region provide only a conjecture. Further evidence to the conjecture is expected.

4. Conclusion

We have demonstrated that the modified pair-potential function form Eq. (5) is able to accurately describe the entire potential curves of weakly bound diatomic systems that we have reported in this Letter, performing much better than the three-parameter

model potential Eq. (1). This new function suggests a unique form for describing the potentials of diatomic systems ranging from strongly-bound molecules to weakly-bound diatomic complexes.

Appendix A. Supplementary data

In this supporting material, we provide a Nonlinear Least Squares Fortran (Fortran 90) program and as an example, an input file and an output for He₂ as well as Figs. S1–S23 and a section about how to determine potential parameters of Eq. (5). All the supplementary data and info associated with this article can be found in the online version. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2013.12.072>.

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