Simple Three-Parameter Model Potential for Diatomic Systems: From Weakly and Strongly Bound Molecules to Metastable Molecular Ions

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Based on a simplest molecular-orbital theory of H_2^+, a three-parameter model potential function is proposed to describe ground-state diatomic systems with closed-shell and/or *S*-type valence-shell constituents over a significantly wide range of internuclear distances. More than 200 weakly and strongly bound diatomics have been studied, including neutral and singly charged diatomics (e.g., H_2, Li_2, LiH, Cd_2, Na_2^+, and RbH^-), long-range bound diatomics (e.g., NaAr, CdNe, He_2, CaHe, SrHe, and BaHe), metastable molecular dications (e.g., BeH^{++}, AlH^{++}, Mg_2^{++}, and $LiBa^{++}$), and molecular trications (e.g., YHe^{+++} and $ScHe^{+++}$).

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Modeling the interaction potential of diatomic systems is of fundamental importance to many issues [1–8], including atom-atom collisions, molecular spectroscopy, prediction of cluster structures, molecular dynamics simulation, chemical reactivity, matter-wave interferometry, and transport properties for more complex systems. Also of great interest are the potential functions for long-lived metastable doubly or multiply charged ions [9] that are relevant to high-density energy storage materials and to characterization and analytical methods for biosystems.

Modern spectroscopy, diffraction, and scattering techniques [1,3] provide a direct experimental approach to studies of interaction potentials of diatomic systems. In particular, diatomic potentials can be inferred from the spectroscopy data by three general approaches [10]: (i) the Wentzel-Kramers-Brillouin (WKB) Rydberg-Klein-Rees (RKR) method, (ii) the WKB-based Dunham approach, and (iii) semiempirical or empirical procedures. On the theoretical side, a diatomic potential curve may be predicted directly by *ab initio* calculations [11] and quantum Monte Carlo simulations [12]. These theoretical methods can, in principle, be very accurate when sufficient electronic configurations are included in the calculations, but can be prohibitively expensive in weakly bound systems [2] and/or many-electron systems [3].

Numerous attempts to analytically model diatomic potentials have been made [3,5,10,13–16]. The well-known potential functions include Morse, Born-Mayer, Hulburt-Hirschfelder, Rosen-Morse, Rydberg, Pöschl-Teller, Linnett, Frost-Musulin, Varshni III, Lippincott, Lennard-Jones, and Maitland-Smith potentials [3,10], as well as the celebrated Tang-Toennies potential [5] and the recently proposed Morse-based potentials [13]. These potentials usually aim to describe either strongly or weakly bound, neutral or singly charged diatomics and often lose their validity for either small or relatively large internuclear distance (denoted R hereafter). Thus, recent effort has been devoted to the construction of hybrid potentials, which use different functions for different interaction regions of R [3,10,14–16] and thereby need more than four potential parameters. Well-known examples of hybrid potentials include the combined Morse–van der Waals [10], general Buckingham-type exp(n, m) [10], Cvetko [14], and Bellert-Breckenridge [15] potentials, as well as the most recently proposed Rydberg-London potential [16]. For metastable doubly or multiply charged molecules, none of the above-mentioned potential functions is able to describe their ground states. To date, only few theoretical models [17,18] that were specifically designed for metastable molecular dications [9] have been proposed.

The goal of this Letter is twofold. First, we propose a molecular-orbital theory based approach to obtain a very simple analytical potential of diatomic systems. The potential function thus obtained has significant applicability insofar as it can describe a wide variety of diatomic molecules with good accuracy for almost the whole range of R but excluding the large-R limit. Second, we show that this potential function can also describe metastable doubly charged diatomics as well as singly and tripl charged ones. Specifically, we advocate a very simple three-parameter ground-state potential function that is applicable to more than 200 diatomics with closed-shell and/or *S*-type valence-shell constituents (atoms or ions whose shells are closed or whose valence shells are *S* orbital). These include neutral and singly charged diatomics, long-range bound diatomics [19], metastable molecular dications [20], and molecular trications [21]. The details for these systems and the associated parameters of our model potential are given in Ref. [22].

We require a few-parameter potential function to satisfy the following basic conditions: (i) its asymptotic value E_∞ 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 $R \to 0$. (iv) One local potential maximum $E_{\max}$ at $R_{\max}$ is allowed to describe metastable systems. (v) Both Coulomb and exchange interactions can be described by using only few parameters. To seek such a potential function we revisit the molecular-orbital theory [23] as applied to H_2^+, the simplest single-electron diatomic system, with the associated Hamiltonian $H = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$ (in atomic units), where r_A and r_B denote electron-nucleus distances. This case can be solved exactly, but here it is used as a reference system to understand how the simplest version of the molecular-orbital theory may be improved. To that end consider the S-type trial function of H_2^+: $\Psi = c_1|\phi_0^A\rangle + c_2|\phi_0^B\rangle$, where $|\phi_0\rangle = \frac{e^{-r}}{\sqrt{\pi}}$ (the 1s orbital of H atom). The energy of the bonding orbital is then given by

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

where $E_\infty = -\frac{1}{2}$, $J_1(R) = e^{-2R}(1 + \frac{1}{R})$, $K_1(R) = e^{-R}(\frac{1}{R} - \frac{2}{3}R)$, and $S_0(R) = e^{-R}(1 + R + \frac{1}{3}R^2)$ [22,23]. In the literature [5,23], J_1 and K_1 are called the Coulomb and exchange integrals, respectively, and S_0 is the overlap integral between the orbitals $|\phi_0^A\rangle$ and $|\phi_0^B\rangle$. Figure 1(a) shows the resultant potential curve of H_2^+. The minimum energy $E_{\min}$ is -0.56483 hartree, located at $R_e = 2.500$ bohr. This should be compared with the most accurate data [24]: $E_{\min} = -0.60263$ hartree, at $R_e = 1.999$ bohr. Clearly then, while the analytical potential function of H_2^+ derived above satisfies most of the general pair potential requirements set above, quantitatively it should be improved. Indeed, if *polarization* and even *diffuse* functions are included in the trial function, then the potential curve in the bonding region has a much better performance. As illustrated in Fig. 1(b), by using couple cluster method with single and double excitation (CCSD) [25] with STO-3G (1s orbital only), 6–31 G(d, p) (including polarization function), and 6–311 ++ G($3df, 3pd$) (including diffuse functions) Gaussian-type basis sets, one obtains $E_{\min} = -0.58270, -0.59449, -0.602201$ hartree at $R_e = 2.0043$, 1.9482, 1.9999 bohr, respectively.

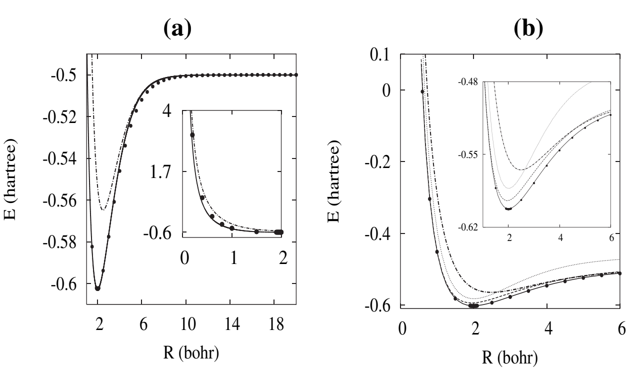

FIG. 1. The potential energy curve of the ground state of H_2^+: (a) Eq. (1) (dot-dashed line) and Eq. (2) (solid line, $\alpha = 1.051\,110\,6$, $\beta = 0.917\,034\,242$, $\gamma = 2.25$); (b) Eq. (1) (dot-dashed line), CCD/STO-3G (dotted line), CCSD/6–31 G(d, p) (dashed line), and CCSD/6–311 + +G($3df, 3pd$) (solid line). The filled dots in (a) and (b) are the most accurate data reported Ref. [24]. The inset in (a) is for the short-range region.

We now introduce a simple analytical potential function to improve the above potential for H_2^+. That is,

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

where parameter γ is introduced in the Coulomb integral J_1, i.e., $J_1(R, \gamma) = e^{-2\gamma R}(1 + \frac{1}{R})$, and two parameters α and β are introduced in the exchange integral K_1, i.e., $K_1(R, \alpha, \beta) = e^{-\alpha R}(\frac{1}{R} - \beta R)$. Below we briefly discuss the meanings of the three parameters in the light of the polarization approximation [5]. A detailed discussion of this issue is presented in Ref. [22]. In the first-order polarization approximation, Eq. (2) can be rewritten as $E(R, \alpha, \beta, \gamma) = E(E_p, \epsilon_{\rm ex}) = E_p - [1 - S_0(R)]\epsilon_{\rm ex}$, where $E_p = E_\infty + J_1(R, \gamma)$ and $\epsilon_{\rm ex} = \frac{1}{1 - S_0(R)^2}[S_0(R)J_1(R, \gamma) - K_1(R, \alpha, \beta)]$ are the polarization and exchange energies, respectively. [For one-electron H_2^+, the *exchange energy* can be interpreted as resulting from the electron hopping back and forth across the median plane between two protons [5], therefore referring to the exchange of two protons.] Clearly, parameter γ directly adjusts $J_1(R, \gamma)$ and hence the polarization energy E_p. Because $\epsilon_{\rm ex}$ also depends on $J_1(R, \gamma)$, the introduction of γ also affects the dispersion (positive) part of $\epsilon_{\rm ex}$. Through the term $K_1(R, \alpha, \beta)$, parameters α and β are used to account for the R dependence of $\epsilon_{\rm ex}$ that is already affected by γ. In particular, the *induction* part (the negative term) of $\epsilon_{\rm ex}$ is adjusted only by parameter α, and parameter β further adjusts the dispersion part of $\epsilon_{\rm ex}$ through the negative term of $K_1(R, \alpha, \beta)$. Certainly there are alternative approaches for realizing these adjustments, but the new potential function constructed above includes both the Pauli repulsive term $\frac{e^{-bR}}{R}$ and the well-known Born-Mayer "exponential" form Ae^{-bR}. This is different from Tang-Toennis [5], Cvetko [14], and Rydberg-London [16] potentials, whereas only the Born-Mayer form appears as their repulsion terms. It should also be stressed that although $E(R, \alpha, \beta, \gamma)$ now has three adjusting parameters, it is still analogous to Eq. (1) in many aspects (e.g., satisfying all the pair potential requirements set above). Based on this three-parameter potential function, we find that the potential curve for H_2^+, as shown in Fig. 1(a), would agree very well with the most accurate data available in Ref. [24] if we choose $\alpha = 1.051\,110\,6$, $\beta = 0.917\,034\,242$, and $\gamma = 2.25$. This confirms that α, β, γ can be properly adjusted such that contributions of both the polarization and exchange energies can be accounted for in an efficient way, thereby achieving, in effect, the same goal as that of using larger basis sets in the trial wave functions.

Certainly our real motivation is to extend this simple and successful procedure from H_2^+ to other multielectron diatomic systems. A number of established results about the electronic structures of diatomic systems suggest that this is possible for ground-state diatomics with closed-shell and/or S-type constituents [22]. In the zeroth-order approximation, the outermost electrons in a multielectron system move in the Hartree-Fock self-consistent field or the effective potential of all the core electrons and the positive nucleus, and the asymptotic exchange energy of a multielectron system can arise primarily from the outermost electrons. The exchange interactions between two multielectron atoms, which play a crucial role in chemical bonding, are dominated by the exchange of a single pair of electrons, and the associated exchange energy is given by that of a single-electron pair multiplied by a constant. Based on the polarization approximation [5], the ground-state potentials $E(E_p, \epsilon_{\rm ex})$ of H_2 and other multielectron diatomic systems, when expressed in terms of the polarization and exchange energies, can take a similar form [22] 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 more than 200 diatomic systems for which experimental or *ab initio* data are available. We find that, indeed, the above three-parameter potential can be proposed as a widely applicable potential function for ground-state diatomics with closed-shell and/or S-type constituents.

To determine the three parameters of the proposed potential function we suggest several numerical approaches in the Appendix C of our supplementary material [22]. The model potential curves thus determined for more than 200 weakly and strongly bound 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 [see Table 1 and Fig. A in Ref. [22]]. Below we discuss some sample results. In particular, Fig. 2 shows that the potential curve for H_2 is in good agreement with the recent 14-parameter model potential [26] and the most accurate data [11], thereby giving a better performance than the Morse function [3] and the most recent hybrid Rydberg-London potential [16]. Even more significantly, our potential function is applicable to metastable S-type molecular dications [20] (e.g., He_2^{++}, Be_2^{++}, BeH^{++}, Mg_2^{++}, MgH^{++}, BH^{++}, AlH^{++}, $LiBa^{++}$, KBa^{++}, $NaBa^{++}$, and Ba_2^{++}), and molecular trications [21] (e.g., YHe^{+++}, $ScHe^{+++}$) as well as neutral and singly charged diatomic systems. The potential curves for BeH^{++} and AlH^{++} using our potential function are shown in Fig. 3, where the potential barriers agree well with Ref. [20]. Figure 4 displays the calculated rotationless vibrational levels for ^{7}LiH, H_2, CdNe, and Na^{40}Ar [see Ref. [22] for results of isotopes], reaching good accuracy as compared with experiments [27–30]. Quite unexpectedly, even for very weakly long-range bound diatomics [2] such as $^4He_2$, ^{40}Ca^{4}He, ^{86}Sr^{4}He, and ^{137}Ba^{4}He, we are able to find a set of potential parameters that predict a single vibrational level at -0.107, -67.099, -59.875, and -48.560 μeV [22], consistent with the recent literature data, -0.0999, -67.161, -59.573, and -48.279 μeV, respectively [1,31].

For the metastable dications He_2^{++}, Be_2^{++}, BeH^{++}, and Mg_2^{++}, we found that they can support 5, 18, 8, and 20 vibrational levels that again agree with Refs. [20,32]. Furthermore, with the new potential function we predict that the metastable dication AlH^{++} can support 12 vibrational levels. The estimated lifetimes for the lowest four vibrational states of BeH^{++} are $\tau = 4.9 \times 10^{10}$, 3.3×10^7, 4.8×10^4, and 130 μs, and those for the lowest six vibrational states of AlH^{++} are $\tau = 2.8 \times 10^{16}$, 1.8×10^{13}, 2.0×10^{10}, 3.3×10^7, 8.3×10^4, and 288 μs [see Table 8 in Ref. [22]]. Note that BeH^{++} and AlH^{++} have been recently observed to survive flight times of about 4 and 7 μs, respectively [33], thus supporting our calculations.

Before concluding we make one final remark. 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 $\sum_{n=3}^{\infty} C_{2n}/R^{2n}$ [3,5,34]. In this limit our model potential approaches E_∞ exponentially, a feature different

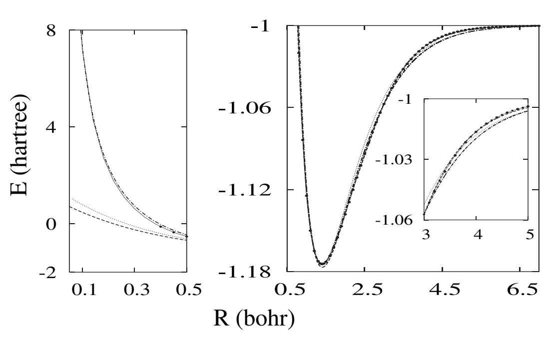

FIG. 2. The comparison between the new potential (dot-dashed line, $\alpha = 1.5065756$, $\beta = 2.48475652$, $\gamma = 1.45$), 14-parameter-fit model potential [solid line, Ref. [26]], hybrid Rydberg-London potential [dashed line, Ref. [16])], Morse potential (dotted line), and the most accurate *ab initio* data [filled circles, Ref. [11]] for hydrogen molecule H_2. Inset in the rightmost figure is the enlarged part between 3.0 and 5.0 bohr.

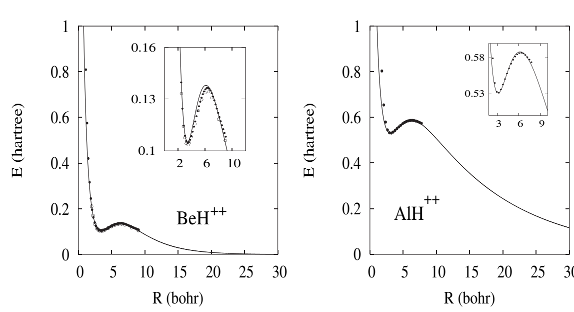

FIG. 3. The potential energy curve of the ground state of BeH^{++} ($\alpha = 0.687$, $\beta = 1.43632004$, and $\gamma = 0.1185$) and AlH^{++} ($\alpha = 0.585984$, $\beta = 0.796691521$, and $\gamma = 0.0365$). The filled/open circles denote the previous data from Ref. [20].

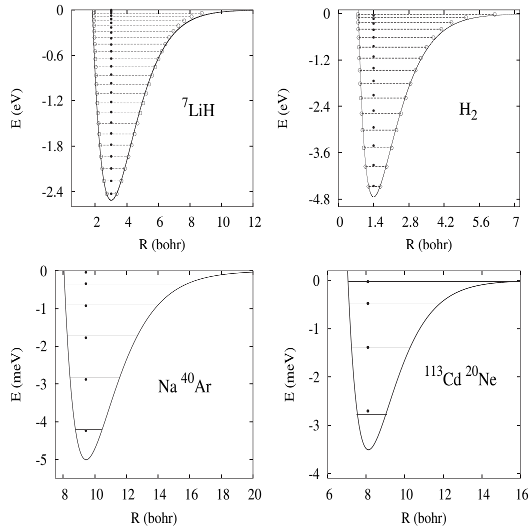

FIG. 4. The computed vibrational levels (filled circles) of ^{7}LiH ($\alpha = 0.888\,559\,1$, $\beta = 1.514\,790\,03$, $\gamma = 0.345$), H_2, Na^{40}Ar ($\alpha = 0.6365$, $\beta = 0.022\,970\,141\,4$, $\gamma = 0.50$), and ^{113}Cd^{20}Ne ($\alpha = 0.89314$, $\beta = 0.332\,438\,39$, $\gamma = 0.40$). The solid horizontal lines denote the measured vibrational levels for Na^{40}Ar [28] and CdNe [27]. The open circles (dashed lines) are RKR potential points (measured vibrational levels) for H_2 [30] and ^{7}LiH [29].

from that suggested by the multipolar dispersion expansion. Nevertheless, because the proposed potential is applicable for internuclear distances far beyond the equilibrium position (e.g., see Figs. 1 and 2), its asymptotic exponential behavior should not present an issue except for some extreme cases such as ultracold collisions.

In conclusion, we have proposed an analytical three-parameter potential function for more than 200 weakly and strongly bound ground-state diatomics, including metastable molecular dications, with good accuracy over a significantly wide range of internuclear distances.

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