Universal Reduced Potential Function for Diatomic Systems

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The potential energy functions of 200 diatomic systems, with dissociation energies D_e ranging from few eV to hundreds of μeV, are well described by a new three-parameter potential energy function. Identification of the evaluated values of a dimensionless quantity, $\xi_n = \frac{L_2}{L_n}$ [$L_n = (\frac{n!\mathrm{D}_e}{f_n})^{1/n}$, a scaled length parameter, and f_n, the nth force constant evaluated at the equilibrium internuclear distance R_e], is proposed as a reliable criterion to search for the universal scaling features of potentials and spectroscopic constants for bound diatomic systems. Our study suggests a useful approach to predicting future molecular spectroscopic constants.

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In the Born-Oppenheimer approximation for a diatomic system, the solution of the Schrödinger equation, as a function of the internuclear separation R, gives rise to families of diatomic potentials $E(R)$ [1–3]. The eigenfunctions for nuclear motion in these potentials then provide a complete basis set and information for describing all properties [1–3] (e.g., molecular spectroscopy) of the system. Also, modeling diatomic potentials is of fundamental importance to many other issues [1–3] such as molecular dynamics simulation. Thus, numerous approaches have been used to obtain "good" diatomic potentials [1–9]. The most widely used method is to represent the potential by a suitable analytical function. To date, many functions have been suggested, and they can be summarized in two types. The first is Dunham type [10] based on a Taylor expansion of $E(R)$ at the equilibrium internuclear distance R_e

$$E(R) = -\mathrm{D}_e + \sum_{n=2} \frac{f_n}{n!}(R - R_e)^n, \qquad (1)$$

where D_e and $f_n = \frac{d^n E(R)}{dR^n}|_{R=\mathrm{Re}}$ are the dissociation energy and the nth force constant, respectively. The second type is centered on closed-form expressions [1–9] containing adjustable parameters.

If a perfect scaling in molecular spectroscopy can be achieved, a universal diatomic potential will determine the energy and spectroscopic behavior of a universal bond [1–6,11–21], which can then be considered as the equivalent of "*the hydrogen atom in atom spectroscopy*" [6]. The search for a universal diatomic potential has also great interest for a number of practical chemical processes such as adhesion, cohesion, and chemisorption, where similar binding-energy relations were discovered [11,12,22–25]. Motivated by these aspects, considerable efforts have been made toward finding the universality of diatomic potentials for the past 80 years. Since the actual diatomic potentials span vibrational frequencies and dissociation energies [6] 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 [1–6,26]. Through the years, much work has been done on this issue [1,4,6,14–21]. However, various opinions persist whether or not a universal two- or three-parameter potential really exists [6]. The matter is certainly not yet solved [6]. Thus, the following two questions raised before [1,5,11,15,19] are still open: rigorously speaking, it could hardly be expected that an exact universal potential function would exist for all diatomic systems. Nevertheless, is it possible to have an "approximate" universal function for diatomic systems with similar linkage, i.e., those belonging to the same group, at least in the neighborhood of the minimum? And is it possible to find a simple globally accurate function for potential curves away from the vicinity of the minimum?

In this Letter, we wish to shed some light on the two questions and to suggest a reliable criterion to search for the universality of diatomic potentials and spectroscopic constants. Based on an accurate three-parameter potential function reported recently [9] and the suggested criterion, we demonstrate the existence of universal spectroscopic constant relations and a global universal reduced potential for bound ground-state diatomic systems with closed-shell and/or S-type valence-shell constituents. Our study provides a unified description for diatomic systems ranging from weakly to strongly bound neutral or ionic molecules, and suggests a useful approach to predicting future molecular spectroscopic constants.

To find the universality of the potentials for bound diatomic systems, we introduce a scaled length parameter, $L_n = (\frac{n!\mathrm{D}_e}{f_n})^{1/n}$ evaluated at R_e, and a dimensionless length, $R^* = \frac{R-R_e}{L_2}$ [note: $a^* = \sqrt{2}R^*$ in Ref. [24]], and also use the Puppi's definition [27] for a scaled dimensionless energy $\varepsilon = \frac{E(R)}{\mathrm{D}_e}$. First, we examine the universal scaling features of spectroscopic constants based on Eq. (1) which can be rewritten as

$$\varepsilon(R^*) = -1 + \sum_{n=2} (\xi_n R^*)^n, \tag{2}$$

where $\xi_n = \frac{L_2}{L_n}$ is a dimensionless quantity. Then, the five well-known dimensionless quantities [1,5], Δ [known as Sutherland parameter [28]], a_1^2, a_2, F, and G, which have been used to explore the universality of spectroscopic constants for the bound diatomic systems, can be expressed as

$$\Delta = \frac{f_2}{2\mathrm{D}_e} R_e^2 = \left(\frac{R_e}{L_2}\right)^2; \tag{3}$$

$$a_1^2 = \left(\frac{f_3 R_e}{3 f_2}\right)^2 = \xi_3^6 \Delta; \tag{4}$$

$$a_2 = \frac{f_4 R_e^2}{12 f_2} = \xi_4^4 \Delta; \tag{5}$$

$$F = -1 - \frac{f_3 R_e}{3 f_2} = -1 - \xi_3^3 \sqrt{\Delta}; \tag{6}$$

$$G = \left(\frac{5 f_3^2}{3 f_2^2} - \frac{f_4}{f_2}\right) R_e^2 = (15 \xi_3^6 - 12 \xi_4^4)\Delta; \tag{7}$$

$$G = \left(15 - \frac{12 \xi_4^4}{\xi_3^6}\right)(F + 1)^2. \tag{8}$$

All of them are related to the spectroscopic constants, ω_e (vibrational frequency), I_e (moment of inertia), B_e (rotational constant), χ_e (anharmonicity constant), α_e (rotation-vibration interaction constant), and D (centrifugal distortion constant), for example, $\Delta = \frac{\omega_e}{4 B_e D_e}$ [see details in Appendix B of Ref. [29]]. Varshni [5] chose to represent a_1 as a function of Δ, rather than of $\sqrt{\Delta}$. As pointed out by Graves and Parr [13] and by our analysis, $\sqrt{\Delta}$ is the preferred parameter for a_1. Recently, three simple relations between F and G, $G = 6F^2 + 18F + 3$, $G = 5.8F^2 + 22.7F$, and $G = 27.4F^{4/3}$, have been suggested [20]. However, Eq. (8) shows an exact quadratic relation between G and F. If a universal potential $\varepsilon(R^*)$ does exist for all diatomic systems, the dimensionless quantity ξ_n for each diatomic system must have an identical or very similar value [29], i.e., $\xi_n^A \simeq \xi_n^B$ for diatomic systems A and B. As a result, F, G, a_1^2, and a_2 will surely satisfy the universal relations Eqs. (4)–(8) with respect to Δ. It should be emphasized that Graves-Parr scaling hypothesis [13] is still valid, but for diatomic systems having a same or close value of ξ_n. Hence, we propose the identification of the determined values of ξ_n for diatomic species as a criterion to test the universality of diatomic potentials.

Based on insufficiently good data of 23 bound diatomic systems, Goodisman [1] concluded that a universal three-parameter potential would seem to be ruled out, except as a rough approximation: $F \approx 0.36 + 0.11\Delta$, $G \approx 9 + 5\Delta$. This approximation is obviously not in the forms of Eqs. (6) and (7). Graves and Parr [13] devised a test of universality for 150 covalently or partially ionically bonded diatomic systems based on the highly accurate experimental values [30] of spectroscopic constants. They found that a_1^2 is not proportional to a_2 and thus concluded that the universal scaling features of potential curves for diatomic systems are less well satisfied with a completely universal function. Using the same data [13], Jhung *et al.* [16] found a nonlinear relation between $\beta_1^2 = \frac{a_1^2}{\Delta}$ and $\beta_2 = \frac{a_2}{\Delta}$. Particularly, they proved theoretically the existence of a universal three-parameter function but were unable to identify its analytical form [16]. [They suggested Morse potential [4] as the best candidate.] Moreover, Smith *et al.* [15] and Tellinghuisen *et al.* [17] pointed out that it was necessary to separate the molecules into two distinct classes, *covalent* and *partially ionic*, in testing the universality of diatomic potentials. Indeed, they showed that the parameters for the 88 covalently bonded molecules clearly demonstrated a universal behavior, while the remaining 62 partially ionic molecules are the largely scattering data points [15,16]. If the charge-transfer effect is included in the generalized universal equation, all 150 diatomic molecules exhibit a universal behavior [15]. Based on the scaling analysis of about 300 diatomic molecules [30], Hooydonk [6] pointed out that the Sutherland parameter Δ can never be a universal scaling factor. Other ever-continuing search [16,18–21] did not strongly support the universality. Stimulated by the well-known Badger rule and Herschbach-Laurie and Calder-Ruedenberg classifications [31] exploring the relations between f_n ($n = 2$, 3, 4) and R_e, we realize the importance of classification of diatomic types. Thus, we recheck the data of 13 types of molecules reported by Graves and Parr [13] and list the corresponding values of ξ_3 and ξ_4 in Table 1 of Ref. [29]. We find that the 13 types of molecules are distinguished from each other by the unique values of ξ_n. This supports our above-mentioned proposal. Thus, if the bound diatomic systems having identical or very similar values of ξ_n are put into a single group and sufficiently good data are available, a single reduced potential function could be found to describe all the group members. We are confirming this below.

Recently, a molecular-orbital theory-based approach has been proposed to arrive at accurate few-parameter potential functions for diatomic groups based on the classification of the valence-shell types of constituents [9]. For example, an accurate three-parameter potential function is found to describe 200 bound diatomic systems with closed-shell and/or S-type valence-shell constituents [9],

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

where α, β, and γ are adjustable parameters and J_1, K_1, and S_0 are given in detail in Ref. [9]. The advantage of this diatomic group is the inclusion of a number of weakly or strongly bound, neutral or ionic diatomic systems (e.g., CdNe, H_2, $\mathrm{He}^{+}{}_{2}$, Li_2^-, AlHe^{2+}, YHe^{3+}), and the reliable accuracy of their potential functions given by Eq. (9). [For example, our vibrational level calculations reported in Table 2–7 in the supplementary material of Ref [9] showed that the relative errors between theory and experiment are within only few percent, such as 0.1% to 2.2% for Li_2, 0.5% for SrHe, 0.6% for BaHe, and 0.1% for CaHe. And as shown in Table 2 of Ref. [29], we fit D_e exactly, and R_e with an average relative error of 0.021% and a root mean square error of 0.017% to the accurate literature data.] Thus, it is a good example to test and confirm the universal criterion discussed above. Based on Eq. (9), we have derived the values of L_n at R_e for 200 diatomic systems and report their relations in Fig. 1. [The detailed values of L_2, ξ_3, and ξ_4 for diatomic systems are listed in Tables 2 and 3 of Ref. [29]. It should be noted that R_e and D_e are functions of α, β, and γ and they are determined by fitting accurate experimental or theoretical data and are specifically listed in Refs. [9,29].] We find that there exist good linear scale relations between L_n ($n = 2$, 3, 4), which give approximate universal constants ξ_n ($n = 3$, 4), i.e., $\xi_3 \approx -0.972\,354$ and $\xi_4 \approx 0.836\,198$ for the 200 systems. Thus, we obtain from Eqs. (4)–(8) the universal relations: $a_1^2 = 0.850\Delta$, $a_2 = 0.493\Delta$, $F = -1 + 0.922\sqrt{\Delta}$, $G = 0.0682\Delta$ (G in units of 10^2), $a_1^2 = 1.722 a_2$, and $G = 0.0804(F + 1)^2$. On the other hand, the five dimensionless quantities, Δ, a_1^2, a_2, F, and G, are derived directly from Eq. (9). [The detailed values are listed in Table 3 of Ref. [29].] As expected, universal relations between these dimensionless quantities are well satisfied (see Fig. 2). The fitting results given in Fig. 2 agree well with those evaluated by using the approximate universal constants ξ_3 and ξ_4 obtained from Fig. 1. We emphasize that our dimensionless scaling for the 200 systems has given a unified description of both weakly and strongly bound, both neutral and ionic diatomic systems with closed-shell and/or S-type valence-shell constituents, and contrary to the statement of Ref. [6], the Sutherland parameter Δ is still valid as a universal scaling factor. Finally, three remarks are in order. First, our derived spectroscopic constants for 35 diatomic systems are compared with the actual experimental values [30] in Table 5 of Ref. [29]. This quantitative assessment shows the reliability of our potential energy function. Second, given ω_e, D_e, and R_e, either from experiments or modern *ab initio* methods, spectroscopic constants for this class of diatomic systems can be predicted by using the above-derived universal relations [see Table 6 in Ref. [29]]. For example, our predicted spectroscopic constants (e.g., $\chi_e = 0.00287$, $\alpha_e = 0.00136\ \mathrm{cm}^{-1}$) for a new diatomic ion, $Th^{3+}O^{2-}$, are in good agreement with a recent experiment [32]. Last, the universality for diatomic systems with other-type valence-shell constituents may also be found if sufficiently good data are available [see Fig. A and B in Ref. [29]].

The above tests of universality probed the relationship only in the vicinity of R_e. This is a severe test since predictions of third and fourth derivatives were involved. Is it possible to find a simple globally accurate function for potential curves away from the vicinity of R_e? To answer this question, we test the global universality of the closed-form expression Eq. (9) for the 200 systems investigated above. Figure 3(a) presents the results for H_2, H_2^+, and He_2 based on two scaling schemes: the usual one [33] with a dimensionless length $R_s = \frac{R-R_e}{R_e}$ and Kratzer's one [34] with $\lambda = \frac{R-R_e}{R}$. The weakly bound He_2 is distinguished from the strongly bound H_2 and H_2^+. Thus, the two schemes show that there is no single binding-energy relation for weakly and strongly bound diatomic systems although both H_2 and H_2^+, as shown in Fig. 3(a) and in Ref. [5], may have a reduced curve for the usual scheme [33]. However, using the dimensionless length R^*, we find that 172 diatomic systems out of the 200 systems, as shown in Fig. 3(b) and in Fig. C of Ref. [29], can have a universal reduced potential curve (similar to that of H_2^+) away from the vicinity of R_e. The remaining 28 diatomic systems show some deviations from the reduced curve at $R^* > 2$. Thus, while the values D_e and L_2 vary from system to system, the reduced curve $\varepsilon(R^*)$ for the 172 seemingly

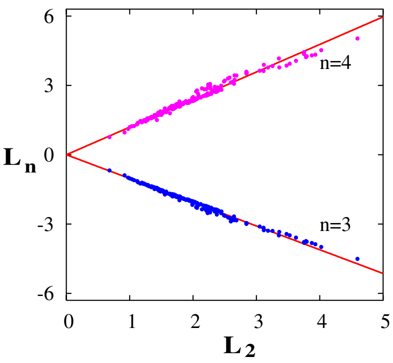

FIG. 1 (color online). Relations between L_n ($n = 2$, 3, 4) for 200 bound diatomic systems [9]. Solid lines are the fitting results: $L_2 = (-0.972\,354 \pm 0.002\,059)L_3$, $L_2 = (0.836\,198 \pm 0.002\,829)L_4$.

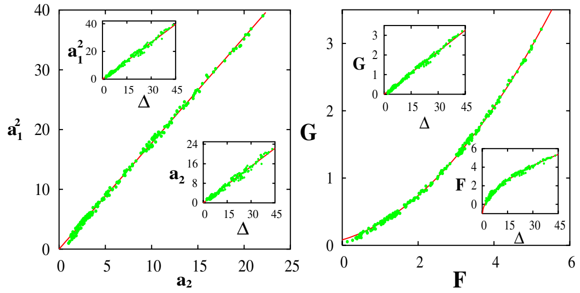

FIG. 2 (color online). Relations between a_1^2, a_2, G (in units of 10^2), F, and Δ for 200 bound diatomic systems [9]. Solid lines are the fitting results: $F = (-1.21052 \pm 0.03304) + (0.98078 \pm 0.008\,532)\sqrt{\Delta}$, $G = (0.072\,422 \pm 0.000\,303\,7)\Delta$, $a_2 = (0.496\,257 \pm 0.00297)\Delta$, $a_1^2 = (0.879\,818 \pm 0.004\,258)\Delta$, $a_1^2 = (1.77023 \pm 0.003\,009)a_2$, $G = (0.082\,251\,1 \pm 0.000\,115\,2) \times (F + 1)^2$.

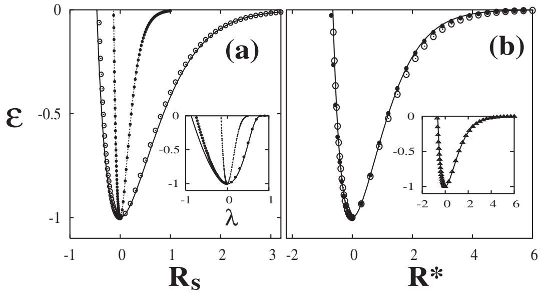

FIG. 3. Reduced potential curves ε for H_2^+ (solid line), He_2 (filled circles), and H_2 (open circles) in dimensionless scaling schemes: (a) $R_s = \frac{R-R_e}{R_e}$ (inset: Kratzer length $\lambda = \frac{R-R_e}{R}$); (b) $R^* = \frac{R-R_e}{L_2}$ [inset: the comparison between our result and that (triangles) of Refs. [11,14,24] for H_2^+].

diverse systems does not. As for the remaining 28 diatomic systems, this expression is inadequate at $R^* > 2$. It may be due to insufficiently good data available in the literature, or the asymptotic exponential behavior [9] of Eq. (9) in the large-R limit. Note that our reduced potential curve for H_2^+ agrees well with that [11,14,24] obtained from Rydberg function, $\varepsilon = -(1 + \sqrt{2}R^*)e^{-\sqrt{2}R^*}$ [see the inset in Fig. 3(b)], which was found to be a good representation of the potential curves of covalently bonded materials and has been used in a wide range of situations such as diatomic-molecule energetics, chemisorption, bimetallic adhesion, cohesion in solids, and even interactions in nuclear matter [11,12,15,19,25]. In this sense, our universal reduced potential energy function may find possible applications in these fields.

In conclusion, we have proposed a reliable criterion to search for the universality of diatomic potentials and spectroscopic constants. Our study has provided a unified description of both weakly and strongly bound diatomic systems ranging from neutral to ionic molecules, and suggests a useful empirical approach to predict the spectroscopic constants of new diatomic molecules.

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