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Scaling properties of diatomic potentials

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The existence of a universal reduced potential valid for all diatomic molecules has been predicted on a theoretical basis and verified using Rydberg-Klein-Rees (RKR) potentials. The reduced RKR potentials for various molecules have been shown to coalesce into virtually a single curve when they are plotted against $z = z_1 + \frac{1}{2}(1-|\beta_1|)z_1^2 + \frac{1}{2}(\beta_2 - \frac{1}{4}\beta_1^2 - |\beta_1| + \frac{2}{3})z_1^3$, where $z_1 = \sqrt{\Delta}(R/R_e - 1)$ and $\beta_l = a_l/\Delta^{l/2}$. The Morse curve $[1-\exp(-z)]^2 - 1$ is found to represent the universal curve well. Here R is the internuclear distance, Δ is the Sutherland parameter, and a_l are the Dunham coefficients.

The concept of universal description of all diatomic potentials is irresistible, and it has led to conjecture[1,2] about the existence of a universal reduced potential $F(z) = E/D_e$ valid for all diatomic molecules. Here E is the ground-state vibrational potential energy, D_e is the sum of dissociation energy and zero-point energy, and the scaled distance z is a function of R. Although several approximate scaling procedures have been developed[1-3] and successfully used for comparative studies[4] of diatomic potentials, the very existence of the universal reduced potential has not been well established.[5-7] In this work we will predict a universal reduced potential on a theoretical basis and prove its validity using Rydberg-Klein-Rees[8-10] (RKR) potentials for various diatomic molecules.

We begin with the well-known Dunham expansion[11] of the potential function E which can be rewritten as

$$F = z_1^2\left[1 + \sum_{l=1}^{\infty} \beta_l z_1^l\right] - 1\,, \tag{1}$$

where $z_1 = \sqrt{\Delta}(R/R_e - 1)$ is the "linear" scaled distance[3,5,6] and $\beta_l = a_l/\Delta^{l/2}$ $(l = 1, 2, \ldots)$ are species-dependent combinations of spectroscopic constants. R_e is the equilibrium internuclear distance, Δ is the Sutherland parameter,[12] and a_l are the Dunham coefficients.[11] It is obvious from Eq. (1) as Graves and Parr[5] have found, F is not a universal function of z_1 unless all β's are pure numbers independent of molecular species. Suppose that there exists a scaled distance z so that F is a species-independent universal function of z. Then we may expand z into a power series of z_1,

$$z = z_1 + \sum_{l=2}^{\infty} b_l z_1^l\,, \tag{2}$$

for z_1 is an excellent choice for the scaled distance near the equilibrium point $z = 0$. Now the existence of the universal function $F(z)$ would depend on the answer to the question of whether it is possible to determine the coefficients b_l $(l = 2, 3, \ldots)$ so that F would reduce to a species-independent function of z. For this we solve Eq. (2) for z_1 in terms of z and b's, and substitute the resulting expression into Eq. (1). We then have

$$F = z^2\left[1 + \sum_{l=1}^{\infty} h_l z^l\right] - 1\,. \tag{3}$$

Here the coefficients h_l $(l = 1, 2, \ldots)$ are related to b's and β's through the following relations:

$$b_2 = \tfrac{1}{2}(\beta_1 - h_1)\,,$$

$$b_3 = \tfrac{1}{2}(\beta_2 - \tfrac{1}{4}\beta_1^2 - h_1\beta_1 + \tfrac{5}{4}h_1^2 - h_2)\,,$$

$$\vdots$$

$$b_l = \tfrac{1}{2}(\beta_{l-1} - f_{l-1})\,,$$

where f_{l-1} is a relation among $\beta_1, \ldots, \beta_{l-2}, h_1, \ldots, h_{l-1}$. Apparently, the reduced potential $F(z)$ [Eq. (3)] is a universal function of z, if and only if, the set of coefficients $\{h_l\}$ is independent of molecular species. From now on we assume that h's are pure numbers. In this case, the specific bonding characteristic of individual molecules would be involved only in the definition of the scaled distance z through the coefficients b's. Here we should notice that both z and $F(z)$ depend manifestly upon the still undetermined set of constants $\{h_l\}$, and the method of unequivocal determination of the constants is of vital importance in proving the uniqueness of the functions as well as in assessing the convergence criteria of the series Eqs. (2) and (3). But the question of how we find those constants corresponding to the true universal function should be answered not by mathematics but by experimental facts. Suppose that we truncate the series Eq. (2) by setting $b_l = 0$ for all $l \geq N+1$, then we have

$$\beta_N = f_N(\beta_1, \ldots, \beta_{N-1}; h_1, \ldots, h_N)\,, \tag{4}$$

and similar relations for β_l $(l \geq N+1)$ in terms of $\beta_1, \ldots, \beta_{N-1}, h_1, \ldots, h_l$. The expression Eq. (4) represents a functional relationship among the specific combinations of spectroscopic data $\beta_1, \ldots, \beta_N$. Thus it seems quite natural to use Eq. (4) for finding $h_1, \ldots, h_N$ by the principle of least squares. $\{h_l, \ldots, h_N\}$ will be chosen to minimize $\sum(\beta_N - f_N)^2$, where the sum extends over all samples values for $\{\beta_1, \ldots, \beta_N\}$ of diatomic molecules, and z and b's will be determined in terms of h's thus obtained. Here we have tacitly assumed that the truncated series for z and the corresponding (infinite) series for F would converge to the true functions in the limit of large N. We also remark that we may accelerate the convergence of the truncated series by choosing $b_{N+1} = \frac{1}{2}(\beta_N - \bar{\beta}_N)$, where $\bar{\beta}_N$ represents the least-squares fitted expression for β_N. In this approximation scheme, β_N for an individual molecule is exactly reproduced. However, all those predictions must be verified in experiments. With experimental verifications in mind, we will examine the first several cases of truncation approximation.

If we retain only the first term in Eq. (2), then we recover the scaling procedure attributed to Ferrante, Smith, and Rose[3] and the spectroscopic data should satisfy the unrealistic relations $\beta_m = \text{const}$ for all $m \geq 1$ as Graves and Parr have found for $z = z_1$. On the other hand, when we make a truncation at the second term, we have $z = z_2$, where $z_2 = z_1 + b_2 z_1^2$,

$$\beta_2 = \tfrac{1}{4}\beta_1^2 - h_1|\beta_1| - \tfrac{5}{4}h_1^2 + h_2 , \tag{5}$$

and $b_2 = \frac{1}{2}(\beta_1 - h_1)$. Since $\beta_1 < 0$, we used $-|\beta_1|$ for β_1 in Eq. (5). Equation (5) represents a relation between β_1^2 and β_2 involving two unknown numerical constants h_1 and h_2. We have calculated β_1^2 and β_2, as Graves and Parr[5] have done, from the spectroscopic data[13] for 150 diatomic molecules for which D_e, the harmonic frequency ω_e, the vibrational anharmonicity $\omega_e x_e$, the rotational constant B_e, and the vibrational-rotational coupling constant α_e were all available. From the scatter diagram in Fig. 1 we see that the data points lie very close to a single curve, and it is most natural to make a least-squares fit of the expression Eq. (5) to the experimental data. The solid line in Fig. 1 represents the fitted curve,

$$\bar{\beta}_2 = \tfrac{1}{4}\beta_1^2 - h_1|\beta_1| - \tfrac{5}{4}h_1^2 + h_2 , \tag{6}$$

where $h_1 = -1.0731 \pm 0.0281$ and $h_2 = 0.7438 \pm 0.0458$. Here it is gratifying to observe that the predetermined functional form [Eq. (6)] is consistent with the observed correlation between β_1^2 and β_2 of real diatomic molecules. In this approximation, the experimental data for β_2 of diatomic molecules cannot be reproduced; instead they are represented by the points on the line in Eq. (6). However, as we pointed out before, we should be able to reproduce experimental data for β_1^2 and β_2 by choosing $b_3 = \frac{1}{2}(\beta_2 - \bar{\beta}_2)$. Then we have an improved approximation $z = z_3$, where

$$z_3 = z_1 + b_2 z_1^2 + b_3 z_1^3 . \tag{7}$$

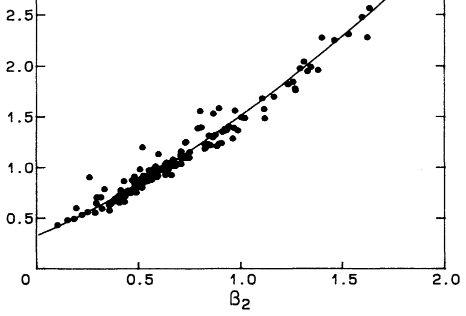

FIG. 1. Experimental data distribution of β_1^2 and β_2 for 150 diatomic molecules. The solid line represents the fitted curve, Eq. (6).

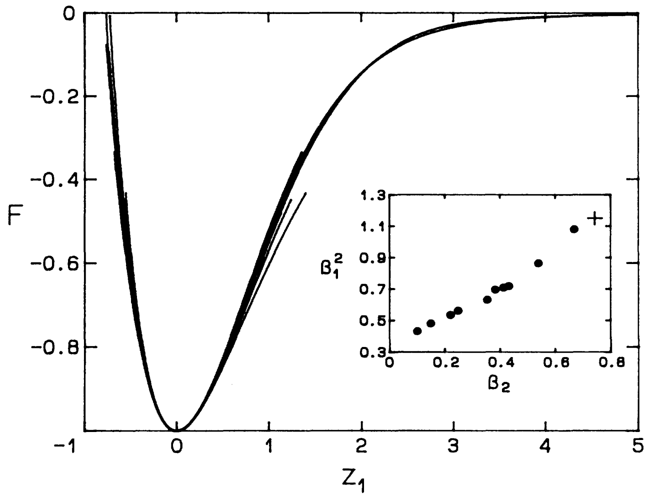

FIG. 2. Ten reduced RKR potentials vs z_1. The dots in the inset represent experimental values of β_1^2 and β_2 for 10 molecules and the sign + represents the predicted value.

We still use the same h_1 and h_2 determined in the previous approximation. If higher-order Dunham coefficients $a_3, a_4, \ldots$ were known, then we could systematically determine $h_3, h_4, \ldots$ by means of least-squares fitting. However, the availability of reliable data for Dunham coefficients is rapidly diminishing with the increasing order l, and the approximation $z = z_3$ may set the practical limit on the truncation approximation. Thus the proof of the rapid convergence of the series, Eq. (2), is essential. In due consideration of successful applications of Morse or Rydberg functions[3,12] based on $z = z_1$, the series is expected to converge very rapidly, but it still remains to be

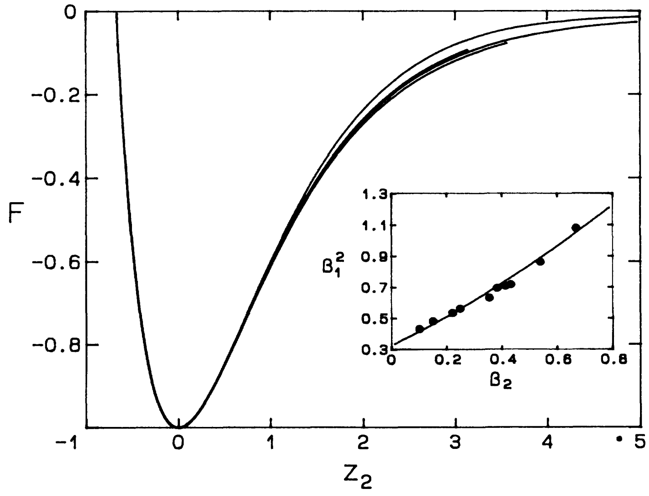

FIG. 3. Ten reduced RKR potentials vs z_2. The solid line in the inset is the predicted curve, Eq. (6).

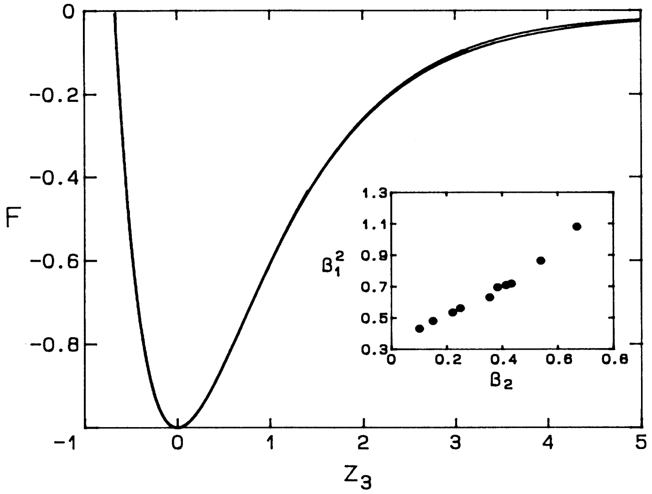

FIG. 4. Ten reduced RKR potentials vs z_3. β_1^2 and β_2 for each individual molecule is exactly reproduced.

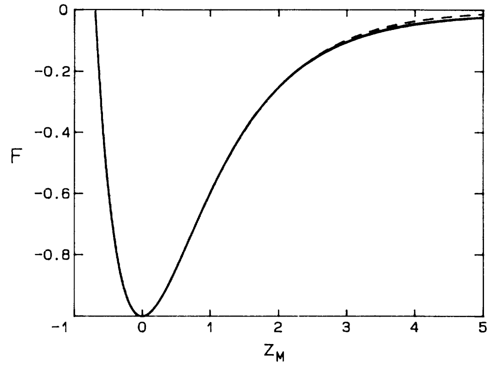

FIG. 5. Ten reduced RKR potentials vs z_M. The dashed line represents the Morse curve.

verified in experiments. For this purpose, we have examined the ground-state RKR potentials of the following ten molecules: Br_2 (Ref. 14), Cl_2 (Ref. 15), ICl (Ref. 16), CO (Ref. 17), N_2 (Ref. 18), Cs_2 (Ref. 19), K_2 (Ref. 20), Li_2 (Ref. 21), Na_2 (Ref. 22), NaK (Ref. 23). The selection criterion of those molecules is the availability of RKR potentials, spectroscopic constants used for constructing RKR potentials, and D_e. If our scaling law characterized by Eqs. (2) and (3) is true, then all the reduced RKR curves plotted against z_1, z_2, and z_3 must converge rapidly toward a single universal curve $F(z)$ as the order of truncation increases. We have plotted ten reduced RKR potentials versus z_1, z_2, and z_3 in Figs. 2, 3, and 4, respectively. The inset in each figure depicts the values for β_1^2 and β_2 for the molecules in each approximation. Figure 2 is the plot of the reduced RKR potentials against the linear scaled distance z_1. Although those curves seem to lie around a single curve, the spread among the curves is excessively high both in the repulsive and attractive branches, and β_1 and β_2 are independent of molecular species. This exemplifies the limitation of the linear scaling as pointed out by Graves and Parr,[5] and Tellinghuisen *et al.*[6] On the other hand, Fig. 3 shows a much improved overall picture especially in the repulsive branch. Finally, all ten curves nearly coalesce into a single curve when they are plotted against z_3, as we see in Fig. 4. Thus a single curve $F(z)$ is found capable of representing all ten RKR curves to a good approximation, and this clearly implies that our scaling procedure has been indeed well founded. We notice that the present scaling is given by the series representation [Eq. (3)] whose accuracy should be understood in a perturbative sense. This effect is well reflected by the increase in the difference between the universal curve and the RKR potentials for large $|z|$. We also notice that the relation $1 \gg b_2 \gg b_3$ holds for all cases, and the convergence of the series for z is found sufficiently fast so that we may regard z_3 as an exact representation of z for all practical purposes. Though we have shown that reduced RKR potentials coalesce into a single curve, the functional form of the curve $F(z)$ is still undetermined. In conjunction with the determination of analytic expression for F, it is worth noting that the reduced curves in Fig. 4 almost coincide with the Morse function $[1-\exp(-z_3)]^2-1$. This near congruity is not a fortuitous accident. We should be able to understand this by observing that the least-squares fitted h_1 and h_2 are not much different from those of the Morse function, namely, $h_1=-1$ and $h_2=\frac{7}{12}$. Moreover, the effects due to small differences in h's also have been partly taken into account in the definition of b_3 so that Δ, a_1, and a_2 are the same in both cases. In the absence of reliable higher-order Dunham coefficients for most diatomic molecules, constructing a higher-order truncation approximation becomes unrealistic. Thus it is more reasonable to choose the Morse function for $F(z)$ and construct corresponding z_3 (which we will denote by z_M hereafter) using $h_1=-1$ and $h_2=\frac{7}{12}$ to have analytic approximations to F and z. It has been shown in Fig. 5 that all ten curves plotted against z_M coalesce into a single curve virtually identical to the Morse curve, and we have

$$F_M=[1-\exp(-z_M)]^2-1\,,$$

$$z_M=z_1+\tfrac{1}{2}(1-|\beta_1|)z_1^2+\tfrac{1}{2}(\beta_2-\tfrac{1}{4}\beta_1^2-|\beta_1|+\tfrac{2}{3})z_1^3\,.$$

These expressions can be used most conveniently to construct an accurate ground-state potential-energy E for a diatomic molecule from its spectroscopic data. Note that the possible inaccuracy at large $|z|$, which may be significant for the van der Waals molecules, can, in principle, be refined by including higher-order terms in z_M, since $1/R^6$ can also be approximated by the above expressions.

In this work, a self-consistent scaling procedure has been developed to show the existence of a universal reduced potential valid for all diatomic molecules. Further applications of this work will be presented in forthcoming publications.

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