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Universal nature of diatomic potentials

Kyu Soo Jhung, In Ho Kim, Ki-Hwan Oh, and Ki Bok Hahn
Daejeon Machine Depot, Daejeon P.O. Box 35, Daejeon, Korea

Kwang Hwa Chung Jhung
Korea Standards Research Institute, Daedeog Science Town, P.O. Box 3, Daejeon, Korea

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A simple mathematical technique is introduced to establish the connection between the universality of diatomic potentials and correlation property of the Graves-Parr parameters β_1^2 $(=a_1^2/\Delta)$ and β_2 $(=a_2/\Delta)$ [Phys. Rev. A **31**, 1 (1985)]. On the basis of this universal feature of diatomic potentials, an accurate expression of the ground-state reduced potential valid for all diatomic molecules has been obtained.

I. INTRODUCTION

Recently we have reported[1] the existence of a universal potential valid for all diatomic molecules. The potential has been predicted on a theoretical basis and verified empirically in Ref. 1 (hereafter we will call it I). We present, in this paper, a full report on the subject based on a more refined mathematical technique and extensive experimental data.

Many simple analytic functions involving a few parameters have been empirically found[2–4] to represent the ground-state vibrational potential E accurately as a function of internuclear distance R for a certain group of diatomic molecules. Moreover, the parameters may be "scaled out" from the functions by introducing an appropriate reduced potential and scaled distance. This feature of diatomic potentials has led us to conjecture about the existence of a universal form of potential function for all diatomic molecules[5]

$$E = D_e F(z) . \tag{1}$$

Here D_e is the sum of dissociation energy and zero-point energy, z is the reduced internuclear distance which is supposed to be a function of R and it may contain various species-dependent parameters, and the reduced potential $F(z)$ is defined as a parameter-free function of z. Though the search for a universal potential $F(z)$ has persisted through the years, the question about the existence of the potential *per se* has never been answered.

In his reduced potential curve method,[6–10] Jenč has given an interesting procedure for obtaining the reduced distance and used it extensively for the comparative study of diatomic potentials. We expect to have a unique expression for z in an exact theory. However, in approximate theories, the functional form for z may depend largely on reduction schemes and the functional structure as well as the very existence of $F(z)$ would depend on the choice of z. It is well known[7] that Jenč potentials of various diatomic molecules do not coincide well, and it seems that a species-independent reduced potential valid for all diatomic molecules does not exist in this particular reduction scheme.

Recently Ferrante, Smith, and Rose[11] (FSR) have proposed a simple linearly scaled distance $z_1 = \kappa(R/R_e - 1)$, where κ is a scale factor and R_e is the equilibrium internuclear distance. Here we use the symbol z_1 for z to emphasize the fact that the reduced distance is linear in R. Such a possibility of universal scaling has stirred up a renewed interest in diatomic potentials and motivated Graves and Parr[12] (GP) to investigate the effect of the universal scaling on the predicted Dunham coefficients,[13] a_1 and a_2. The linear scaling concept[11] directly implies that the special combinations β_1^2 $(=a_1^2/\Delta)$ and β_2 $(=a_2/\Delta)$ (we will call them GP parameters) are some numbers independent of molecular species.[12] Here Δ is the Sutherland parameter.[3] However, Graves and Parr have found that experimental data for β_1^2 and β_2 of 150 diatomic molecules[12] obtained from measured diatomic spectra[14] vary by factors as much as 6 and 20, respectively. They also have observed that the sample data for β_1^2 and β_2 are highly correlated in the scatter diagram and argued that this is a good evidence for the need of a few more species-dependent parameters in $F(z)$, and the universal scaling is necessarily broken. Along this line, Smith and his co-workers[15] have modified their universal binding-energy relation[11] by adding a Coulomb term representing a net charge transfer between the two atoms of a molecule. At the price of the universal scaling they have an adjustable parameter, the net charge transfer, in β_1^2 and β_2 so that the predicted β_1^2 agrees exactly with the experimental value.

On the other hand, Tellinghuisen and his co-workers[16] have examined the scaling property of 35 cases of experimentally determined diatomic potentials. The result implies that many molecules particularly among chemically similar ones, e.g., alkali-metal dimers, share a nearly common reduced ground-state potential although the corresponding β_1^2 and β_2 still vary by factors of 2 to 3. Thus, the linear scaling seems to hold to a good approximation for a certain group of molecules while the result obtained by Graves and Parr indicates otherwise. This apparently contradicting situation needs an explanation.

The Dunham coefficients a_1 and a_2 are related to the second-, third-, and fourth-order derivatives of $F(z)$ with respect to R at R_e, and they depend on all the parameters contained in both $z_e^{(n)}$ $(=d^nz/dR^n|_{R_e})$ and $F^{(n)}(0)$ $(=d^nF(z)/dz^n|_{R_e})$ for $n=1$, 2, 3, and 4. In a universally scaled theory, all $F^{(n)}(0)$ are pure numbers and the parameter dependence of a_1 and a_2 arises solely from $z_e^{(n)}$. Here we recall that the scaled distance examined by Graves and Parr is linear in R (and so is z_1), and thus $R_ez_e^{(1)}$ $(=\Delta^{1/2})$ is the only species-dependent quantity in a_1 and a_2 for this particular choice of z. Moreover, a_1^2 and a_2 are both proportional to $(R_ez_e^{(1)})^2$, and consequently, the calculated β_1^2 and β_2 are independent of molecular species. On the other hand, if z should contain some additional parameters, then β_1^2 and β_2 would depend upon those parameters even if $F^{(n)}(0)$ are pure numbers. With this understanding, the disagreement between the predicted and observed values for β_1^2 and β_2 may be ascribed to the linear nature of $z_1=\Delta^{1/2}(R/R_e-1)$, and not to the universality of $F(z_1)$ *per se.*

Experiments indicate that we need species-dependent parameters in β_1 and β_2 (at least one) and here we have a choice for accomplishing this. We may either insist that we should have species-independent $F^{(n)}(0)$ and find a generalized reduced distance z to accommodate additional parameters, or keep the reduced distance linear (so that $z=z_1$) and find a way to give $F^{(n)}(0)$ the requisite parameter dependence to have a broken universality. Since our long-sought goal[5–12,15,16] is to find a species-independent universal potential, the choice is obvious. Thus, we want $F^{(n)}(0)$ to be species independent for all n $(=1,2,\ldots)$ and the reduced distance z should contain all the species-dependent parameters of the problem.

Recently we have developed a simple mathematical technique and applied it to establish the connection between the universal potential and the correlation among GP parameters β_n $(n=1,2,\ldots)$. The result has already been reported briefly in I. The present paper is an extension and an outgrowth of I. The mathematical scheme we developed in I is refined further and its relation to the convergence property of the reduced distance z has been discussed in this paper.

II. UNIVERSAL REPRESENTATION

One of the central problems associated with diatomic bonding is the correct representation of the potential $E(R)$ $[=D_ef(R)]$ in terms of the internuclear distance R. The detailed functional form of the reduced potential $f(R)$ is expected to vary with the nature of individual molecules. In order to be free from model-dependent details of $f(R)$, we will base our discussion on the series representation of the reduced potential. A power-series expansion technique of potentials is one of the most powerful means of relating observed spectroscopic data to the structure of diatomic potentials.

The basis of our approach lies on the Dunham expansion[13] of $f(R)$ around the equilibrium point $R=R_e$ which can be cast into the form

$$f(z_1)=z_1^2\left[1+\sum_{n=1}^{\infty}\beta_nz_1^n\right]-1\ , \tag{2}$$

where $z_1=\Delta^{1/2}(R/R_e-1)$ is the linearly scaled distance used by FSR (Ref. 17) and others,[12,16]

$$\Delta=\tfrac{1}{2}R_e^2d^2f(R)/dR^2|_{R_e}$$

is the Sutherland parameter,[3] and $\beta_n=a_n/\Delta^{n/2}$ (for $n=1,2,\ldots$) are the parameters introduced by Graves and Parr.[12] Here the Dunham coefficients a_n are defined by

$$a_n=2\frac{R_e^n}{(n+2)!}\left.\frac{d^{n+2}f/dR^{n+2}}{d^2f/dR^2}\right|_{R_e} \tag{3}$$

for all $n=1,2,\ldots$. As found by Graves and Parr, β's calculated from experimental spectroscopic data[14] are species dependent and strongly correlated among themselves. Thus, $f(z_1)$ is manifestly species dependent and so is the graph $(z_1,f(z_1))$ [which is the plot of $f(z_1)$ against z_1].

Now we consider the variable transformation from the linearly scaled distance z_1 to a new variable $z(z_1)$ which can be approximated by a series expansion z_N,

$$z_N=\sum_{n=1}^{N}b_nz_1^n\ . \tag{4}$$

Then the reduced potential $f(z_1)$ can be rewritten as the function F of the new variable z through the definition $F(z)=f(z_1)$, and it can be expanded into the form

$$F(z)=z^2\left[1+\sum_{n=1}^{\infty}h_nz^n\right]-1\ , \tag{5}$$

where h's are the expansion coefficients yet to be specified. Because of the composite relation $f(z_1)=F(z)$ and $z=z(z_1)$, the coefficients b's are not independent but related to β's and h's. We can always recover the original function $f(z_1)$ from the composite relation regardless of the actual assigned values of h's. If we choose b's accordingly, it is always possible to assign species-independent numbers for the expansion coefficients h's in order to have a species-independent potential graph $(z,F(z))$ valid for all diatomic molecules. Here all the species-dependent parameters are embedded in the expression of z [Eq. (4)]. We should point out that the mapping $(z_1,f(z_1))\rightarrow(z,F(z))$ itself is arbitrary and devoid of physics unless we provide an unequivocal method for the unique determination of h's. The question of how we find the unique set of h's corresponding to the true universal function $F(z)$ should be answered based on some sound experimental properties of diatomic spectra.

As a first step to find such a method, we will obtain explicit expressions for b's in terms of β's and h's from the definition of a_n [Eq. (3)] and the relation $f(z_1)=F(z(z_1))$ by making use of the explicit expression[18] for the nth derivative of a composite function. After a little algebraic manipulation, we have the following expressions for b's $(b_1=1)$:

$$b_{n+1}=\tfrac{1}{2}(\tilde{\beta}_n-h_n)\ , \tag{6}$$

$$\tilde{\beta}_n=\beta_n-\sum_{m=1}^{n-1}\sum(m+2)!h_m b_1^{m_1}\cdots b_k^{m_k}/[m_1!\cdots m_k!]$$
$$-Q_n\quad(n>1)\ , \tag{7}$$

where the second sum is over all non-negative integer partitions

$$\{m_1,\ldots,m_k|\textstyle\sum m_k=m+2,\sum km_k=n+2\}\ .$$

Here $\tilde{\beta}_1=\beta_1$ and

$$Q_n=\begin{cases}2\sum_k b_k b_{n+2-k} & \text{for odd } n\ ,\\ (b_{n/2+1})^2+2\sum_k b_k b_{n+2-k} & \text{for even } n\ ,\end{cases} \tag{8}$$

where the sum is over k from 2 to $(n+1)/2$ for odd n and to $n/2$ for even n. Having explicit expressions of b's, we can examine the convergence property of the series z_N. Here we observe that the coefficient b_{n+1} is a function of $\beta_n,\beta_{n-1},\ldots,\beta_1$ and $h_n,h_{n-1},\ldots,h_1$:

$$b_{n+1}=b_{n+1}(\beta_n,\beta_{n-1},\ldots,\beta_1;h_n,h_{n-1},\ldots,h_1)\ . \tag{9}$$

For many diatomic molecules, GP parameters[12] β_1 and β_2 have been determined[1,12,15,16] from experimental spectroscopic constants[14] and in some cases even higher order β's are available. The expansion coefficients b's of the reduced distance z are dependent upon still undetermined numbers h's as well as on β's. We observe that the radius of convergence of the series [Eq. (4)] directly depends on the values of h's. Considering that the availability of reliable experimental data for β_n is rapidly diminishing with the increasing order n, the rapid convergence of the series is of vital importance in a practical realization of a universal potential. This aspect should be regarded as the most important single factor in the determination of h's. This has led us to determine h's so that they minimize the expansion coefficients b_n $(n=2,3,\ldots)$ simultaneously for all diatomic molecules in the sense of the least-squares principle.

Beginning with $n=2$, we successively minimize $\Lambda_n=\sum b_n^2$ for all n $(n\geq 2)$, where the sum extends over all available sample values for the relevant β's. By utilizing the expression [Eq. (6)] for b_n, we have the variation

$$\delta\Lambda_n=-\frac{1}{2}\left[\sum(\tilde{\beta}_{n-1}-h_{n-1})\right]\delta h_{n-1}\ .$$

Here the condition $\delta\Lambda_n=0$ $(n\geq 2)$ should be satisfied for an arbitrary variation δh_{n-1}. Then we obtain

$$h_{n-1}=\sum\tilde{\beta}_{n-1}/N_s\ , \tag{10}$$

where N_s is the number of sample points in the sum and the sum is over all samples. For notational convenience we introduce the symbol $\langle\tilde{\beta}_{n-1}\rangle$ to represent the algebraic average in Eq. (10), and we have

$$h_n=\langle\tilde{\beta}_n\rangle\ . \tag{11}$$

The expansion coefficients of the reduced distance z are uniquely determined by

$$b_{n+1}=\tfrac{1}{2}(\tilde{\beta}_n-\langle\tilde{\beta}_n\rangle)\ . \tag{12}$$

We also note that $\tilde{\beta}_n$ contains $h_{n-1},\ldots,h_2$, and h_1 which are already determined by $\langle\tilde{\beta}_{n-1}\rangle,\ldots,\langle\tilde{\beta}_2\rangle$, and $\langle\tilde{\beta}_1\rangle$, respectively. There is only one set of $\{h_n\}$ for all diatomic molecules. The reduced distance truncated at Nth order is obtained by setting $b_n=0$ $(n\geq N+1)$:

$$z_N=z_1+\sum_{n=2}^{N}\tfrac{1}{2}(\tilde{\beta}_{n-1}-\langle\tilde{\beta}_{n-1}\rangle)z_1^n\ . \tag{13}$$

Equations (5), (11), and (13) uniquely define a hierarchy of universal potentials for diatomic molecules, z_N and $F(z_N)$ for $N=1,2,\ldots$.

Now we examine the condition of the Nth-order truncation $b_{N+1}=0$. Because of Eq. (12) the condition can be rewritten as

$$\tilde{\beta}_N=h_N\ , \tag{14}$$

which represents a relation among $\beta_1,\beta_2,\ldots,\beta_N$ and there exist similar relations for higher order β_n $(n>N+1)$. The relation [Eq. (14)] is the condition imposed on spectroscopic constants when we truncate the series at an Nth-order term. Since we have minimized all $\sum b_n^2$ $(n\geq 2)$ for the determination of h's, the magnitude of b_n should decrease rapidly as n increases, and the truncated series z_N [Eq. (13)] is expected to approximate the reduced distance z very accurately even for values of N as small as 2–3. Thus, we should expect to have a strong correlation between β_1 and β_2 if the graph $(z_3,F(z_3))$ is a good approximation to the universal curve $(z,F(z))$. Therefore, it is essential to show that β's of real diatomic molecules actually satisfy the correlation governed by $\tilde{\beta}_2=h_2$ $(=\langle\tilde{\beta}_2\rangle)$ for the proof of the existence of the universal graph $(z,F(z))$. Here we should note that[12] the existence of the universal potential $F(z)$ does not mean that the bonding structure is identical to all diatomic molecules. The potential form necessary to solve various physical problems is ordinarily required to be given as a function of R, $D_ef(R)$, and this is different from one molecule to another as it should be, although there is only one $F(z)$ for all diatomic molecules.

III. CORRELATION AMONG SPECTROSCOPIC CONSTANTS

It has long been known that there exist some regular features among spectroscopic constants D_e, R_e, and ω_e. Morse[19] proposed in 1929 that the product of R_e^3 and the harmonic frequency ω_e is approximately constant for some class of diatomic molecules, especially for those in which the masses of two atoms are approximately equal. Subsequently, the Morse relation had been modified by Clark[20] and Badger[21] to have better descriptions for a wide group of molecules. Later Frost and Musulin[5] proposed still another expression relating k_e $(=d^2E/dR^2|_{R_e})$, D_e, and R_e. The fact that so many expressions give reasonable agreement indicates that each is only an approximation to a certain accurate rule.

In order to study possible relations among higher-order derivatives of $E(R)$ at equilibrium, Varshni[3] has examined two quantities H [Ref. 22] and G involving ω_e, the vibrational anharmonicity $\omega_e x_e$, the rotational constant B_e, and the vibrational-rotational coupling constant α_e:

$$H = \alpha_e \omega_e / 6B_e^2 ,$$

$$G = 8\omega_e x_e / B_e .$$

Those are related to the third- and fourth-order derivatives of the potential function with respect to R at equilibrium. Varshni has shown that both H and G are functions of the Sutherland parameter $\Delta = k_e R_e^2 / 2D_e$ only for various potential functions attributed to Morse,[19] Rydberg,[23] Rosen-Morse,[24] Pöschl-Teller,[25] Frost-Musulin,[26] and other potential models studied by Varshni. This has led Varshni to plot an experimental variation of H and G against Δ for 27 diatomic molecules,[3] and he found that the sample points are scattered around the straight lines $H = 0.11\Delta + 0.36$ and $G = 5\Delta + 9$. However, when we plot H and G against Δ by utilizing experimental data for 265 diatomic molecules,[14,27–51] we can hardly recognize any correlations in the scatter diagrams, Figs. 1 and 2. Here it is interesting to observe that the data points are rather well correlated in the H-G plot (Fig. 3) than in H-Δ or G-Δ plot.

Calder and Rudenberg[52] also have examined 160 diatomic molecules in order to determine whether or not there exist consistent relationships among spectroscopic constants. On the basis of the Dunham expansion[13] of the potential, they proposed that the Dunham coefficients a_1 and a_2 are identical for almost all the molecules they examined. The average values of a_1 and a_2 they determined are -3.22 ± 0.09 and 6.44 ± 0.75, respectively. But those values are somewhat misleading, since hydrides and lithides, for which the values of a's deviate most from the averages, were not included in the averaging process. In fact, it has turned out that a_1 and a_2 are far from being constant.

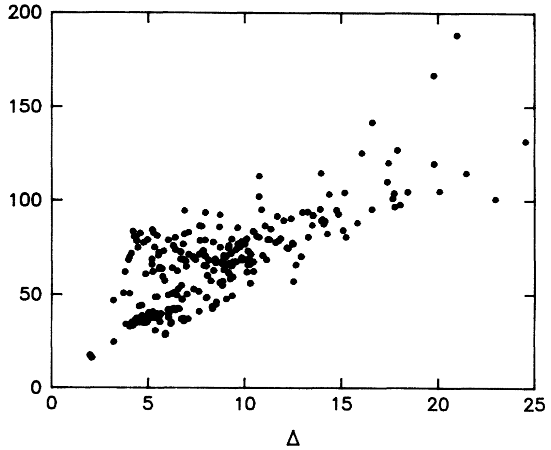

FIG. 2. Experimental values of G plotted against Δ for 265 molecules.

Graves and Parr[12] have shown that a_1^2 and a_2 vary by large factors over the sample data and they exhibit a certain tendency towards data correlation. This directly reflects the correlation feature revealed in the H-G plot (Fig. 3) since a_1 and a_2 are related to H and G through the relations

$$a_1 = -1 - H ,$$

$$a_2 = 5(1+H)^2/4 - G/12 .$$

In the same work, Graves and Parr have shown that the correlation feature of a_1^2 and a_2 is further enhanced in the scatter diagram of β_1^2 and β_2. In terms of experimental spectroscopic constants, β_1^2 and β_2 are obtained from their definition a_1^2/Δ and a_2/Δ, respectively. Here the parameters a_1 and a_2 are, to a very good approximation,[3,4,13,16,53]

$$\Delta = \omega_e^2 / 4B_e D_e , \tag{15}$$

$$a_1 = -1 - \omega_e \alpha_e / 6B_e^2 , \tag{16}$$

$$a_2 = 5a_1^2/4 - 2\omega_e x_e / 3B_e . \tag{17}$$

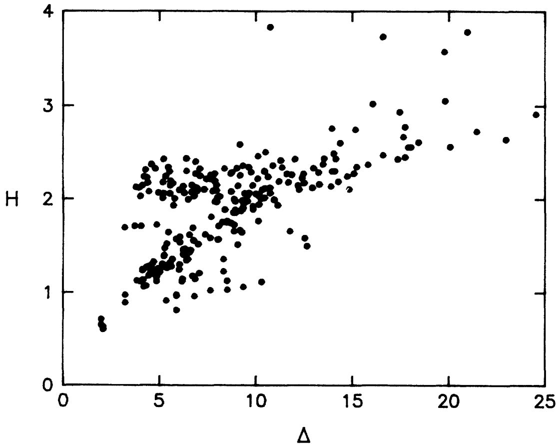

FIG. 1. Experimental values of H plotted against Δ for 265 molecules.

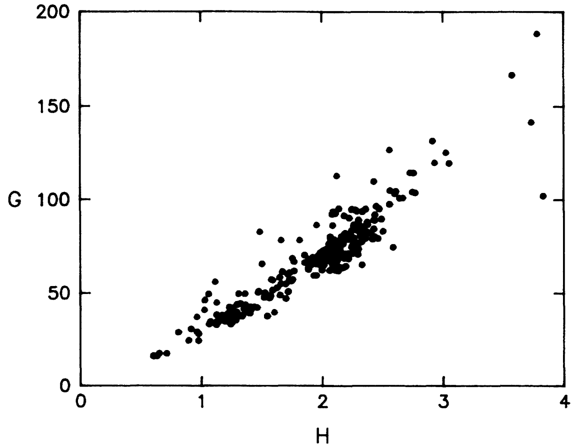

FIG. 3. Experimental values of G plotted against H for 265 molecules.

The GP parameters β_1 and β_2 are especially interesting because they are just the first two expansion coefficients of the series expansion of $E(R)/D_e$ in terms of z_1 [Eq. (2)], and the property of the reduced potential is directly determined by the values of those constants. If the scaling hypothesis like that of FSR (Ref. 11) should hold true for all diatomic molecules, β_1 and β_2 (and all β's for that matter) would be independent of molecular species. We have plotted β_1 against β_2 in Fig. 4 for 265 diatomic molecules for which all of R_e, D_e, ω_e, $\omega_e x_e$, B_e, and α_e are known.[14,27–51] As we see from Fig. 4, β_1 and β_2 vary by large factors over the samples. This has an important implication that the universal scaling hypothesis[11] should fail and $f(z_1)$ [Eq. (2)] cannot be a species-independent universal function of z_1.[1,12].

Graves and Parr have shown that the regression line of the scatter diagram (Fig. 2 in Ref. 12) can be approximated by

$$\beta_1^2=(1.378\pm0.023)\beta_2+(0.166\pm0.019)\ . \tag{18}$$

The existence of a correlation between β_1 and β_2 apparently necessitates more parameters (at least one more) in addition to the ones already existing in the linearly scaled theory.[12]

Smith and co-workers[15] have introduced such an extra parameter into their universal binding-energy relation through a net charge-transfer term. They have defined the net charge transfer so that the predicted value of β_1^2 agrees exactly with the experimental value; however, the universal scaling is necessarily broken in this approach. A similar method has already been considered by Graves and Parr.[12] They have introduced a generalized Morse function to have one more parameter on which β_1^2 and β_2 depend, but this is not particularly successful. These methods have two drawbacks. The resulting reduced potentials are manifestly species dependent and the way of introducing requisite parameters is not unique.

Recently we have introduced a new method[1] of understanding the observed correlation between β_1 and β_2. In I we obtained the relation

$$\beta_2=f_2(\beta_1;h_1,h_2)\ , \tag{19}$$

where $f_2=\frac{1}{4}\beta_1^2+h_1\beta_1-5h_1^2/4+h_2$, as a condition of the existence of a universal reduced potential valid for all diatomic molecules. Here the constants h_1 and h_2 can be determined by requiring them to minimize $\sum(\beta_2-f_2)^2$, where the sum extends over all samples. In I, we had $h_1=-1.073\pm0.028$ and $h_2=0.744\pm0.046$ based on the data of 150 diatomic molecules.[12] However, we obtain $h_1=-1.061\pm0.028$ and $h_2=0.719\pm0.044$, instead, by utilizing the spectroscopic data for 265 molecules[14,27–51] and we have found that most data points fall very close to the correlation line

$$\beta_2=\frac{1}{4}\beta_1^2-1.061\beta_1-0.688\ , \tag{20}$$

which is represented by the dotted line in Fig. 4.

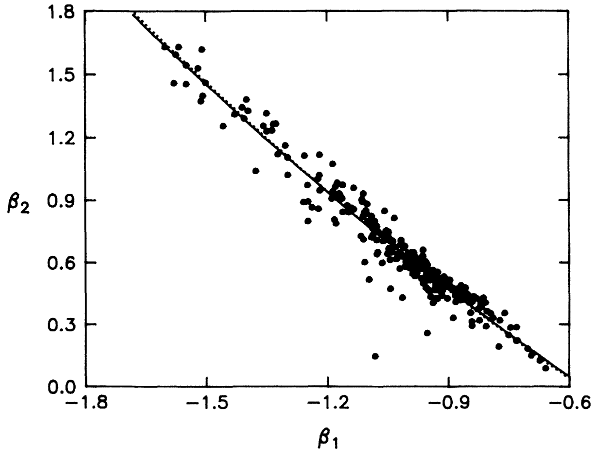

FIG. 4. Experimental data distribution for β_1 and β_2 of 265 molecules. The solid curve represents the line determined by Eq. (23) with the values $h_1=-1.036$ and $h_2=0.679$ and the dotted line represents the correlation line [Eq. (20)].

Now we will examine the data correlation problem in the scatter diagram (Fig. 4) based on the formalism developed in this work which is a natural extension of I. In this section we introduce a method that determines the set of expansion coefficients h's of $F(z)$ by making use of the least-squares principle. The coefficients are chosen so that they minimize $\sum b_2^2, \sum b_3^2, \ldots, \sum b_n^2, \ldots$, simultaneously. In the Nth-order truncated approximation $z=z_N$, we have the relation among $\beta_1, \beta_2, \ldots, \beta_N$: Eq. (14), or

$$\tilde{\beta}_N=\langle\tilde{\beta}_N\rangle\ . \tag{21}$$

In order that z_N be a good approximation to z for real diatomic molecules, Eq. (21) has to be satisfied accurately by experimental β's. Even though the overall accuracy in Eqs. (13) and (21) is expected to increase as N increases, the $N=2$ case should be a reasonable approximation in due consideration of the work of FSR. For $N=2$, we have $b_3=0$, or

$$\tilde{\beta}_2=h_2\ , \tag{22}$$

where $\tilde{\beta}_2=\beta_2-\frac{1}{4}\beta_1^2-h_1\beta_1+5h_1^2/4$. Equation (22) can be rewritten as

$$\beta_2=\frac{1}{4}\beta_1^2+h_1\beta_1-5h_1^2/4+h_2\ . \tag{23}$$

Here Eqs. (19) and (23) are identical except the values of h's. In Eq. (23) h_1 and h_2 are given by $\langle\beta_1\rangle$ and $\langle\tilde{\beta}_2\rangle$, respectively. We obtain $h_1=-1.036\pm0.012$ and $h_2=0.679\pm0.005$ from the arithmetic averages over 265 diatomic molecules.[14,27–51] The curve [Eq. (23)] thus obtained has been plotted in Fig. 4 as the solid line. We notice that the values of h's in Eqs. (19) and (23) are not much different, and the corresponding curves are almost indiscernible. This is not surprising because the method of determining h's in this work is a natural generalization of that developed in I. Considering that the functional form of Eq. (23) is predetermined by the requirement of the existence of a universal reduced potential, it is remarkable that all data points in Fig. 4 fall very closely to the curve [Eq. (23)]. The fact that the conformation of experimental data to the correlation curve demonstrates that there exists an intimate relation between the existence of the universal potential and the observed correlation between β_1 and β_2. This point will be discussed in more detail in the next section.

IV. DIATOMIC POTENTIALS

A knowledge of accurate ground-state diatomic potentials is of great importance in molecular theory. Thus, it is imperative to have a self-consistent method of constructing potential curves from experimental data. We will first show that experimental reduced potentials $E(R)/D_e$, obtained by making use of the method of Rydberg, Klein, and Rees (RKR),[23,54–57] fall on a single curve $F_e(z)$ almost in the entire experimental range when they are plotted against z. Then the experimental curve $F_e(z)$ may be identified with $F(z)$ [Eq. (5)] which is the universal potential we have sought for. It is very convenient, in practice, if we have a suitable analytic function $F_a(z_N)$ to fit the experimental curve $F_e(z)$ accurately. Then from the expression of $F_a(z_N)$ we can construct a very accurate potential-distance relation for each diatomic molecule from its experimental Dunham coefficients, Δ, $a_1, a_2, \ldots$, by substituting the expression [Eq. (13)] for z_N in $F_a(z_N)$.

Here we have tacitly assumed that the truncated series z_N would converge rapidly to the true value as N increases, and, in a certain sense, it is designed to be so. But this and other results must be verified in experiments. With these verifications in our minds, we will closely examine the first several cases of truncation approximation by taking $N=1$, 2, and 3 in succession.

If we retain only the first term in Eq. (13), then we recover the scaling procedure developed by FSR.[11,15] In this case, the calculated spectroscopic data are then found to satisfy unrealistic relations $\beta_m = \text{const}$ for all $m \geq 1$. On the other hand, when we truncate the series [Eq. (13)] at second term we have $z = z_2$, where

$$z_2 = z_1 + b_2 z_1^2 \,, \qquad b_2 = \tfrac{1}{2}(\beta_1 - h_1) \,. \tag{24}$$

Here h_1 is given by the arithmetic average of β_1 over 265 diatomic molecules. In this approximation β_1 is directly determined by the experimental data of individual molecules; however, the value of β_2 is related to β_1 through Eq. (23). Thus, the experimental data for β_2 of individual molecules cannot be exactly reproduced; instead they are represented by the points on the solid curve in Fig. 4. However, as we pointed out before, experimental points lie very close to the solid curve, and this is a drastic improvement over that $\beta_m = \text{const}$.

Now we will examine the next order approximation by setting $b_n = 0$ for all $n \geq 4$. Then we have $z = z_3$ and

$$z_3 = z_1 + b_2 z_1^2 + b_3 z_1^3 \,, \qquad b_3 = \tfrac{1}{2}(\tilde{\beta}_2 - h_2) \,. \tag{25}$$

We still use the same h_1 determined in the previous approximation and $h_2 = \langle \tilde{\beta}_2 \rangle$. Here β_1 and β_2 are experimental values although β_m ($m \geq 3$) are related to β_1 and β_2. If higher-order Dunham coefficients $a_3, a_4, \ldots$ were known accurately for a sufficient number of molecules, we could systematically determine $h_3, h_4, \ldots$ by means of the least-squares principle [Eqs. (7), (8), and (11)] and find accurate expressions for z and $F(z)$ by summing up the series, at least, in principle.

In due consideration of the successful application of Morse or Rydberg functions[3,11,58] using the scaled distance $z = z_1$, the series [Eq. (13)] is expected to converge very rapidly. We have examined the ground-state experimental potentials of 29 molecules listed in Tables I and II. We have chosen those molecules because of the availability of their experimental potentials, spectroscopic constants (used for constructing these potentials), and D_e. If our approach to the universality is correct, then all the reduced experimental curves plotted against z_1, z_2, and z_3 should converge rapidly towards a single curve $F_e(z)$, which may be identified with $F(z)$, as the order of truncation increases.

For the demonstration of this property of experimental potential curves, we will examine 29 cases[27–51] of the ground-state RKR or inverted perturbation approach[59,60]

TABLE I. Experimental values of R_e, D_e, $\sqrt{\Delta}$, β_1, and β_2 and calculated values of b_2 and b_3 for 13 molecules. Here we note that $|b_2| \gg |b_3|$.

Molecules	R_e (Å)	D_e (cm^{-1})	$\sqrt{\Delta}$	β_1	β_2	b_2	b_3
Br-Br	2.2811	16 058.0	4.480	−0.795	0.355	0.120	0.017
Br-F	1.7590	20 884.8	3.885	−0.844	0.424	0.096	0.017
Cl-Cl	1.9877	20 276.5	3.978	−0.848	0.434	0.094	0.019
Cs-Cs	4.6480	3 649.5	3.210	−0.659	0.087	0.188	−0.021
I-Cl	2.3209	17 557.6	4.292	−0.842	0.412	0.097	0.012
K-K	3.9243	4 447.0	2.923	−0.694	0.150	0.171	−0.014
Li-Li	2.6733	8 541.0	2.319	−0.826	0.376	0.105	0.006
Na-Na	3.0786	5 988.0	2.614	−0.751	0.249	0.143	−0.004
Na-Cs	3.8500	4 950.0	2.918	−0.729	0.223	0.154	−0.001
Na-K	3.4968	5 274.9	2.767	−0.732	0.222	0.152	−0.004
Na-Li	2.8850	7 068.0	2.490	−0.863	0.459	0.086	0.020
Rb-Rb	4.2099	3 980.9	3.059	−0.673	0.125	0.181	−0.012
Zn-D	1.5937	7 654.3	3.539	−0.731	0.288	0.152	0.029

TABLE II. Experimental values of R_e, D_e, $\sqrt{\Delta}$, β_1, and β_2 and calculated values of b_2 and b_3 for 16 molecules. Here we note that $|b_2| \simeq 0$.

Molecules	R_e (Å)	D_e (cm^{-1})	$\sqrt{\Delta}$	β_1	β_2	b_2	b_3
Al-O	1.6178	42 993.0	2.949	−1.110	0.714	−0.037	−0.041
B-O	1.2047	67 722.0	2.714	−0.968	0.572	0.034	−0.002
Ca-Ca	4.2769	1 095.0	4.578	−1.044	0.613	−0.004	−0.040
C-O	1.1283	90 543.9	2.594	−1.040	0.669	−0.002	−0.008
H-H	0.7411	38 288.8	1.441	−1.134	0.961	−0.049	0.063
K-H	2.2400	17 030.0	2.043	−1.048	0.667	−0.006	−0.016
Li-H	1.5956	20 286.0	1.800	−1.053	0.755	−0.009	0.024
Mg-Mg	3.8900	424.1	4.073	−1.161	0.974	−0.063	0.048
N-N	1.0977	79 889.7	2.951	−0.930	0.540	0.053	0.011
Na-H	1.8890	16 300.0	2.083	−0.996	0.573	0.020	−0.022
Na-D	1.8890	16 700.0	2.054	−1.005	0.605	0.015	−0.014
Na-K*	5.4385	209.1	4.007	−1.004	0.609	0.016	−0.011
O-O$^+$	1.1170	54 689.2	3.135	−1.004	0.597	0.016	−0.017
Si-H	1.5201	25 012.0	2.357	−0.986	0.648	0.025	0.022
Si-H$^+$	1.4990	27 004.8	2.371	−0.963	0.630	0.036	0.031
Sr-Sr	4.4460	1 060.0	4.446	−1.028	0.617	0.004	−0.025

(IPA) potentials. Rather accurate potential curves and spectroscopic constants D_e, R_e, Δ, β_1, and β_2 are available for those 29 molecules.

The spectral constants corresponding to the following 21 molecules of the 257 molecules presented in Ref. 14 are replaced by the values[27–46] consistent with the potentials: Al-O (Ref. 27), B-O (Ref. 28), Br-Br (Ref. 29), Br-F (Ref. 30), Ca-Ca (Ref. 31), Cl-Cl (Ref. 32), C-O (Ref. 33), Cs-Cs (Ref. 34), H-H (Ref. 35), I-Cl (Ref. 36), K-K (Ref. 37), Li-Li (Ref. 38), Li-H (Ref. 39), Mg-Mg (Ref. 40), Na-Na (Ref. 41), Na-K (Ref. 42), N-N (Ref. 43), O-O$^+$ (Ref. 44), K-H (Ref. 45), Na-H (Ref. 45), and Si-H (Ref. 46). Besides those 257 molecules, we also have taken into account 8 more molecules: Na-Cs (Ref. 47), Na-D (Ref. 45), Na-K*($a\ ^3\Sigma^+$) (Ref. 42), Na-Li (Ref. 48), Rb-Rb (Ref. 49), Si-H$^+$ (Ref. 46), Sr-Sr (Ref. 50), and Zn-D (Ref. 51).

Thus, we have 265 points in the scatter diagram in Fig. 4 and used those sample points to calculate h's. Then we have $h_1 = -1.036 \pm 0.012$ and $h_2 = 0.679 \pm 0.005$. Those values of h's are used, in turn, to evaluate b_2 and b_3 for the 29 molecules for which accurate experimental potential curves are available. The experimental constants as well as b's are listed in Tables I and II.

We have plotted 29 reduced experimental potentials[27–51] against the linearly scaled distance z_1 in Fig. 5. The spread among the curves is excessively high in both of the repulsive and attractive branches. Here it is interesting to observe that the 29 potential curves in Fig. 5 can be divided into two groups of molecules. The one group is composed of 13 molecules listed in Table I and the other group consists of 16 molecules given in Table II. The first group of potential curves is marked by a circle in Fig. 5 and the curves belonging to this group seem to lie very close to each other. In order to clarify this point further we have plotted these 13 potentials in Fig. 6, and we recognize that all the curves fall very near to a single line in the attractive branch, although the spread is somewhat large in the repulsive branch. This feature of the graph $(z_1, F(z_1))$ for a certain group of diatomic molecules has already been recognized by Tellinghuisen and co-workers.[16] Those authors have shown that the reduced potentials of analogous electronic states in chemically similar molecules are nearly congruent over the full range of the bound well, yet the corresponding GP parameters are not constant as would be required for the graph $(z_1, f(z_1))$ to be universal. The seemingly contradicting features of these potentials can be understood by examining the values of β_1 and β_2 of these molecules given in Table I. Although the values of β_1 and β_2 are species-dependent, they vary in such a way that the series approximation to $f(z_1)$, $z_1^2(1+\beta_1 z_1+\beta_2 z_1^2)$, especially its [1,1] Padé summant[61]

$$f(z_1) \simeq z_1^2[1+z_1(\beta_1-\beta_2/\beta_1)]/(1-z_1\beta_2/\beta_1) ,$$

behaves like a species-independent function of z_1 for those 13 molecules in a wide range of z_1, $-0.3 \lesssim z_1 \lesssim 1.0$.

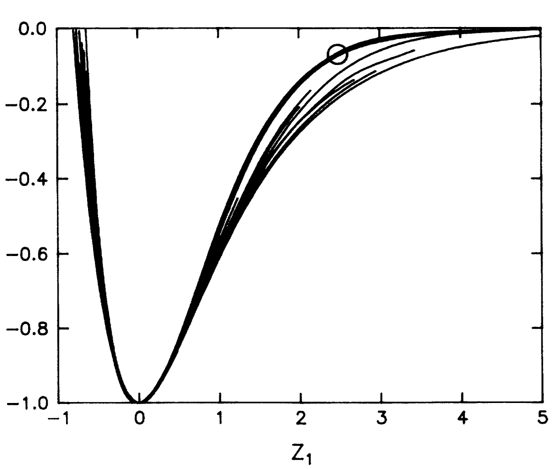

FIG. 5. Experimental reduced potential F plotted against z_1 for 29 molecules. The curves marked by an open circle are experimental potentials for the 13 molecules specified in Table I.

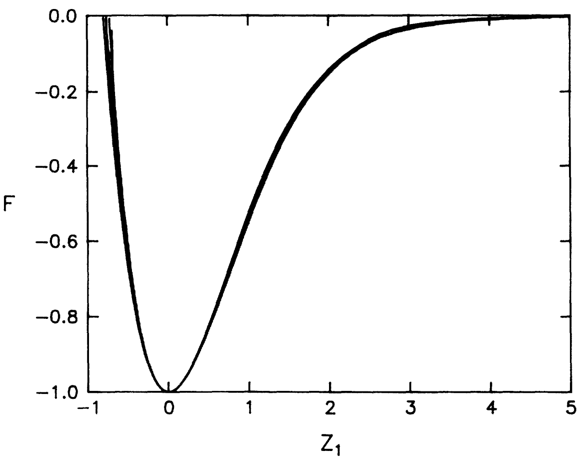

FIG. 6. Experimental reduced potentials of 13 molecules marked by a circle in Fig. 5. The spread of the curves is still large in the repulsive range.

This property of experimental β's is directly reflected in the plot of experimental potentials in Fig. 6. Therefore, we see that reduced potentials may coincide to a certain degree of approximation without having the same β's.

Now we examine the other group consisting of 16 molecules of which potential curves are lying consistently below those of the group of 13 molecules in Fig. 5. Here we notice that the curves are widely spread, especially in the attractive range. We recognize in Table II that the values of β_1 for those 16 molecules are very close to the average value of β_1 over 265 molecules, which is h_1. Those molecules are shown inside a rectangular symbol in Fig. 7. The expansion coefficient b_2 [Eq. (24)] of those molecules are expected to be very small. As we notice from Table II, the magnitude of b_2 of those molecules is one order smaller than that of 13 molecules given in Table I. This clearly indicates that the series for z_N converges much more rapidly in this case. The interesting point is that this "supposed to be fast convergent group" of 16 molecules includes four van der Waals molecules: Mg-Mg, Sr-Sr, Na-K*, and Ca-Ca. Here it is important to note that the order of magnitude of b_2 for these 16 molecules is the same as that of errors associated with the evaluation of h_1, and it is hardly expected that z_2 and z_3 would greatly improve the situation over that of z_1. However, due to the smallness of b_2, the linearly scaled distance z_1 should be a good approximation to z, at least for those 16 molecules, and the graphs $(z_1,f(z_1))$ for those molecules should lie close to a supposedly accurate graph $(z_3,f(z_3))$. For elucidating this point, we have superimposed the graphs $(z,f(z))$ of all 29 molecules in Fig. 8 by taking $z=z_1$ for the group of 16 molecules (the dotted lines) and $z=z_3$ for the group of 13 molecules (the solid lines) for which higher-order corrections arising from b_2 and b_3 are significant. As expected, the potential curves of 16 molecules are centered around the collapsed curves of 13 molecules. The spread of the dotted lines is caused partly by the lack of higher-order corrections and partly by the inaccurate values of available spectroscopic constants (especially D_e), among other things. Here we note that the graphs $(z_1,f(z_1))$ and $(z_3,f(z_3))$ for the 13 molecules are quite different when they are superimposed, in contrast to the case of 16 molecules aforementioned, since higher-order corrections are important in these cases, especially b_2 corrections are significant. This indicates that $z=z_1$ is a good approximation to z only for a molecule of which β_1 is close to the average value $\langle\beta_1\rangle$.

For the determination of an analytic function $F_a(z)$, we have plotted reduced potentials for 20 molecules (7 molecules from Table II and 13 molecules from Table I) against z_3 in Fig. 9. The 7 molecules are Al-O, B-O, C-O, N-N, O-O$^+$, Si-H, and Si-H$^+$. All those 20 experimental potential graphs nearly fall on a single curve in Fig. 9, and such a representative curve can be analytically ap-

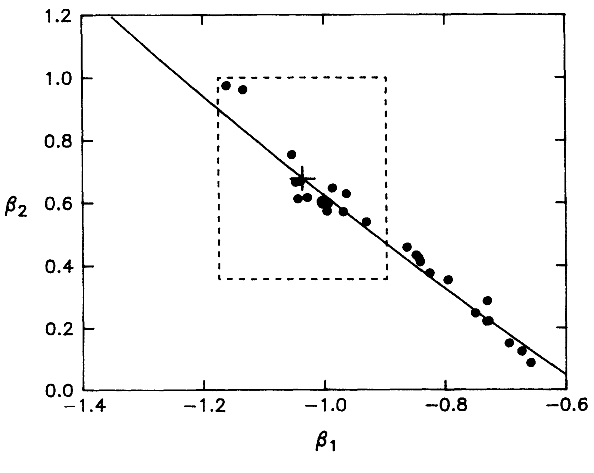

FIG. 7. Experimental values for β_1 and β_2 of 29 molecules given in Tables I and II. The symbol + marks the point (h_1,h_2) and the enclosed in the rectangular symbol are the points representing 16 molecules in Table II.

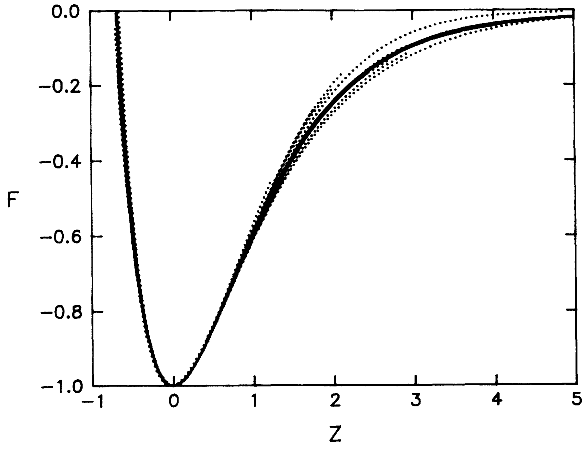

FIG. 8. The solid curves are experimental potentials of 13 molecules (Table I) plotted against z_3 ($=z$) and dotted lines are experimental potentials of 16 molecules (Table II) plotted against z_1 ($=z$). Here we notice that the solid curves fall in the middle of the dotted curves.

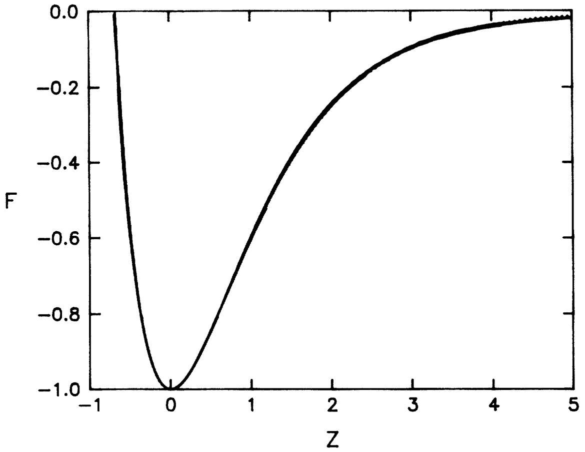

FIG. 9. The plots of experimental reduced potentials of 20 molecules (solid curves) and Hulburt-Hirschfelder function (dotted curve) against z_3. They are almost indiscernible.

proximated by a function $F_a(z_3)$. In I we have shown that RKR curves for 10 molecules would coalesce into a single curve when they are plotted against z_3 and $F_a(z)$ has been approximated by Morse function. The values of h_1 and h_2 of Morse function are -1 and 0.583, respectively, which are rather close to experimental values -1.036 and 0.679. Although the differences are small, these should be corrected for a better approximation. We examine the modified Morse function introduced by Hulburt and Hirschfelder;[53]

$$F_a(z)=[1-\exp(-z)]^2+cz^3\exp(-az)-1\ , \tag{26}$$

where $c=1+h_1$ and $a=(7/12-h_2)/c$. This function has correct values for h_1 and h_2 as required. The first term on the right-hand side of Eq. (26) is the usual Morse function and the second term is a modification to the function to have the h values corrected. This function has been plotted (for $h_1=-1.036$ and $h_2=0.679$) in Fig. 9 as a dotted curve which almost coincides with the 20 other potential curves in the entire range of experiments. Here it is interesting to observe that the correction term in Eq. (26) is so small in the attractive range that Morse function itself may represent $F(z)$ quite accurately, but the correction term is important in the repulsive range where simple Morse function lies consistently below the experimental curves. However, the Hulburt-Hirschfelder function [Eq. (26)] reproduces the reduced experimental potential curve $F_e(z)$ very accurately including the repulsive branch. Thus, analytic expressions [Eqs. (13) and (26)] can be used, in practice, to obtain an accurate approximation to the reduced potential of a real diatomic molecule as a function of internuclear separation distance by utilizing the composite relation $f(R)=F_a(z_3(z_1))$.

V. DISCUSSION

For finding the reduced potential $f(R)$ from a knowledge of experimental spectroscopic constants, it has been customary[3,4,53] to assume a mathematical form for $f(R)$ which contains a number of parameters. These species-dependent parameters are then adjusted to give the best fit to the experimental spectroscopic constants of each molecule. Numerous attempts to find suitable functional forms have been made. In these approaches the problems of finding a functional form for $f(R)$ and understanding correlation properties among experimental spectroscopic constants have been treated as separate problems while it should be regarded as a single problem for internal consistency.

Since combinations of spectroscopic constants, e.g., the Dunham coefficients a's [Eq. (3)] or the GP parameters β's, are related to higher-order derivatives of the potential function $f(R)$ at equilibrium, those constants should also depend on the parameters contained in $f(R)$. Thus, if the potential $f(R)$ contains only a finite number of species-dependent parameters, then there should exist internal relationships among spectroscopic constants. Here we note that the number of independent parameters in $f(R)$ dictates how many GP parameters should be involved in the relation among themselves. If $f(R)$ contains N independent parameters, then there exists a relation among $\beta_1,\beta_2,\ldots\beta_{N-2}$. On the other hand, the functional form of $f(R)$ determines the form of mathematical expression of the internal relation which should be satisfied by GP parameters and vice versa. Thus, in any self-consistent attempt to construct the reduced potential $f(R)$ valid for all diatomic molecules, it is essential to know the detailed mathematical expression of the internal relation among experimental GP parameters. Although we may need an infinite number of parameters in $f(R)$ in an exact theory, the number of parameters in the function should be restricted as small as possible in any attempt of practical realization of $f(R)$. Furthermore, it is important to show that the effect of any additional parameters should be small compared with that of the parameters already taken into account. Here we note that the relationship among β's cannot be exact in algebraic sense in a theory involving only a finite number of parameters. Rather it should be understood as a correlation property in the scatter diagram of β's. Figure 4 exemplified this clearly.

Motivated by this reasoning, we have developed a simple mathematical scheme in order to unravel the interrelationship between the functional structure of $f(R)$ and correlation among β's. We have assumed that the expansion coefficients b_n of the reduced distance z_N [Eq. (4)] should be minimized for all n (>1) in the sense of the least-squares principle to make the series converge rapidly. This assumption, in fact, completely determines the correlation among β's [Eq. (21)] and the expansion coefficients b's [Eq. (12)]. The correlation property as well as the universality of the graph $(z_N,F(z_N))$ have been tested against experimental data. The predicted relation between β_1 and β_2 [Eq. (23)] well conforms to the data distribution in the scatter diagram, Fig. 4. We have shown that the universal potential $F(z)$ can be represented by $F_a(z_3)$ [Eq. (26)] to a very good approximation. Here we mention that the same universal feature has also been found for various bounded potential systems including excited states of diatomic molecules, surface adsorptions, and metallic cohesions. The result is to be published elsewhere.[62]

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