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# A new representation of potential energy curves for diatomic molecules

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We present a new method for constructing potential energy curves that allows one to incorporate available experimental information systematically. It consists of a variable transformation that properly takes into account the behavior of the vibrational potential when the nuclei are far apart. As a result, the Dunham power series are changed into a sequence with improved convergence properties. Potential energy curves obtained in this way are free from spurious maxima and unphysical singularities. The method predicts dissociation energies for both ionic and covalent molecules that are in much closer agreement with experiment than those obtained by other procedures that make use of the same input data. Results are given for 20 alkali halides and 3 covalent molecules.

## I. INTRODUCTION

The qualitative and quantitative understanding of molecular phenomena depends, to a large extent, on a knowledge of Born–Oppenheimer potential curves and surfaces. The most exact procedure to construct potential curves is the RKR<sup>1–3</sup> method. Unfortunately, experimental data is often not enough to perform this technique as in the case of ionic molecules and particularly of alkali halides. Due to this there is a great interest in obtaining accurate vibrational potentials from the scarce experimental information often available.

The first successful attempt to obtain structural properties of diatomic molecules from spectra is Dunham's work.<sup>4</sup> However, the convergence radius of the Dunham series

$$V(R) = a_0 x^2 (1 + a_1 x + a_2 x^2 + \dots), \quad x = (R - R_e)/R_e, \quad (1)$$

where  $R$  and  $R_e$  are the internuclear separation at a general point and at the potential minimum, respectively, is not larger than unity because the vibrational potential  $V(R)$  is singular at  $R = 0$ . Actually, the range of utility of the Dunham series is quite smaller than the convergence radius because only a few Dunham coefficients  $a_i$  are available even for the most widely studied molecules. The truncated Dunham series do not agree with the experimental RKR potential curves except in the vicinity of  $x = 0$  and tend to  $\pm \infty$  as  $R \rightarrow \infty$  depending on the sign of the last coefficient. These disadvantages of the Dunham series make it necessary to look for better descriptions of  $V(R)$ .

Several methods have been proposed to make use of the information about the interatomic potential contained in the Dunham coefficients.<sup>5–12</sup> The Padé approximants (PA)<sup>6</sup> and power series with improved convergence properties relative to the Dunham expansion<sup>7–12</sup> seem to be particularly promising. The latter are summarized in the following expression:

$$V(R) = v_0 f(x)^2 \{1 + v_1 f(x) + v_2 f(x)^2 + \dots\}, \quad (2)$$

where the function  $f(x)$  is chosen in order to obtain the largest possible convergence radius<sup>13,14</sup> and convergence rate. For example, when  $f_{\text{DUN}} = x$ ,  $f_{\text{SPF}} = x/(x+1)$ ,  $f_{\text{OT}} = x/(x+2)$ ,  $f_{\text{TH}} = \text{sgn}(p)\{1 - (1+x)^{-p}\}$ , we obtain the power series proposed by Dunham,<sup>4</sup> Simons *et al.*,<sup>7</sup> Ogilvie and Tipping,<sup>12</sup> and Thakkar,<sup>8</sup> respectively. Such series and the

PA's can be systematically improved as the experimental data becomes available. Besides, the former can be frequently given a firm quantum-mechanical basis.<sup>7,8</sup>

Both the power series and the PA's give quite realistic vibrational potential.<sup>6–12</sup> However, they have several disadvantages. Only low-order series and PA's can be constructed because a very few Dunham coefficients are often available and the experimental uncertainty increases with the order of the coefficient. Besides, the accuracy of some of the predicted molecular properties depends strongly on the accuracy of the Dunham coefficients. The convergence radii of the power series cannot be analytically calculated but only upper bounds to them determined by the real singularity at  $R = 0$ .<sup>7–14</sup> Due to this and to the small number of Dunham coefficients available in each case, the term range of utility seems to be more appropriate than radius of convergence.<sup>10</sup> Frequently, a method that leads to accurate potential energy curves for ionic (covalent) molecules fails in describing covalent (ionic) molecules. For example, the PA's<sup>6</sup> and the Thakkar's method<sup>8</sup> prove to be useful in studying only ionic and covalent molecules, respectively. The power series often exhibit spurious maxima and even negative dissociation energies<sup>7–10</sup> and the  $(N,N)$  PA's with  $N > 2$  show unphysical poles due to zeros of the denominator.<sup>6,9</sup>

In the present paper we propose a systematic procedure to construct a sequence of polynomials that approaches the potential energy curve of any diatomic molecule. Each term of the sequence is free from spurious maxima and unphysical singularities and takes into account both the Dunham series and the  $1/R$  asymptotic expansion. The method is quite general and useful in obtaining an approach to any unknown function obeying two known asymptotic expansions as is the case of the interatomic potentials for diatomic molecules. It is motivated in a resummation procedure that has been recently developed to deal with asymptotic divergent perturbation expansions usually encountered in quantum and field theory.<sup>15–19</sup>

The paper is organized as follows: The method is developed in Sec. II where the construction of vibrational potentials is illustrated by means of the Kratzer–Fues potential.<sup>20</sup> In Sec. III we calculate the dissociation energies of 20 alkali halides and construct the potential energy curve for the KI molecule using only a few Dunham coefficients. Results are

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compared with those obtained by other procedures that make use of the same input data. Covalent molecules are studied in Sec. IV and further applications of the method to molecular physics are discussed in Sec. V.

## II. THE METHOD

We have recently developed a method to deal with asymptotic divergent power series often encountered in quantum and field theory such as those for the eigenvalues of the anharmonic oscillator,<sup>15,17,18</sup> the Zeeman<sup>16,18</sup> and Stark<sup>19</sup> effects in hydrogen, a confining potential model,<sup>19</sup> and also for some integrals in statistical mechanics and field theory.<sup>15,18,19</sup> One of the most attractive advantages of this procedure is that quite accurate results are obtained by using a few terms of the series, even for the most strongly divergent ones. This suggests that the method may be useful in obtaining a satisfactory description of a diatomic vibrational potential from the corresponding Dunham series. If a large enough number of Dunham coefficients were available, this problem would be simpler than those mentioned before for the Dunham series has a finite convergence radius. In what follows we develop a modified version of the method.

Chemists and physicists are frequently faced with the problem of obtaining an approximate expression for a real function  $E(\lambda)$  ( $0 \leq \lambda < \infty$ ) about which they only know that it obeys two formal Taylor expansions

$$E(\lambda) = \sum_{i=0}^{\infty} E_i \lambda^i, \quad (3a)$$

$$E(\lambda) = \lambda^a \sum_{i=0}^{\infty} e_i \lambda^{bi}, \quad b < 0, \quad (3b)$$

about  $\lambda = 0$  and  $1/\lambda = 0$ , respectively. We suppose that the real numbers  $a$  and  $b$  that define the expansion (3b) are known and that the first  $N+1$  coefficients  $E_i$  are available. With this information at hand we will try and obtain an accurate description of  $E(\lambda)$ .

The basis of our approach is the transformation

$$\lambda^b = K\beta^b(1 - \beta), \quad K > 0 \quad (4)$$

that maps  $0 \leq \lambda < \infty$  onto  $0 \leq \beta < 1$ . Notice that  $\beta$  is a single-valued function of  $\lambda$  and can be expanded in powers of  $\lambda$  and  $\lambda^b$ :

$$\beta = \lambda/K^{1/b} + b^{-1}(\lambda/K^{1/b})^2 + \dots, \quad (5a)$$

$$\beta = 1 - \lambda^b/K - b(\lambda^b/K)^2 + \dots. \quad (5b)$$

The real, positive parameter  $K$  plays a key role in obtaining a sequence of polynomials that best approaches  $E(\lambda)$  as will be seen below.

Since

$$K^{a/b}(1 - \beta)^{a/b} = \lambda^a(1 + a\lambda^b/K + \dots), \quad (6)$$

then the function

$$S(K, \beta) = K^{-a/b}(1 - \beta)^{-a/b}E(\lambda(\beta)), \quad (7)$$

remains finite for all  $\lambda$  values and

$$\lim_{\lambda \rightarrow \infty} S(K, \beta) = S(K, 1) = \lim_{\lambda \rightarrow \infty} \lambda^{-a}E(\lambda) = e_0. \quad (8)$$

The coefficients of the Taylor expansion

$$S(K, \beta) = \sum_{i=0}^{\infty} \bar{E}_i(K) \beta^i, \quad (9)$$

are easily obtained in terms of the original ones  $E_i$ . A straightforward calculation using Eqs. (3a), (4), and (7) yields

$$\bar{E}_n(K) = \sum_{i=0}^n (-1)^n \binom{n-i}{n-i}^{a/b} E_i K^{i/b-a/b}, \quad (10)$$

where  $\binom{c}{i} = c(c-1)\dots(c-i+1)/i!$  and  $\binom{c}{0} = 1$ .

It is our purpose to find an appropriate  $K$  value so that the sequence  $SE_N(K, \beta)$  ( $N = 0, 1, 2, \dots$ ):

$$SE_N(K, \beta) = K^{a/b}(1 - \beta)^{a/b}S_N(K, \beta), \quad (11)$$

is a close enough approximation to  $E(\lambda)$  for all  $\lambda$  values. The most unfavorable case is obviously  $\lambda \rightarrow \infty$  (or  $\beta = 1$ ). Since  $S_N(K, 1)$  should become  $K$  independent as  $N \rightarrow \infty$ , it seems to be reasonable to choose the  $K$  value that belongs to the flat-test part of the curve  $S_N(K, 1)$  vs  $K$ . To this end, we look for the stationary point  $K_N^S$ ,  $(\partial S_N / \partial K)(K_N^S, 1) = 0$ , with the smallest absolute value of the second derivative or the inflexion point  $K_N^I$ ,  $(\partial^2 S_N / \partial K^2)(K_N^I, 1) = 0$ , with the smallest absolute value of the first derivative. When neither stationary nor inflexion points are real we choose the real part of  $K_N^S$ . Notice that in either case  $K$  depends on  $N$  and our sequence of polynomials should be written as  $SE_N(K_N, \beta)$ , ( $N = 0, 1, 2, \dots$ ). Therefore, Eq. (4) is an order-dependent mapping as those studied by Seznec and Zinn-Justin<sup>21</sup> in connection with a divergent power series.

From a practical viewpoint  $SE_N$  must have a larger range of utility than the corresponding truncated  $\lambda$ -power expansion. Not only does  $SE_N$  yield the first  $N+1$  terms of the power series (3a) but also obeys an expansion about  $1/\lambda = 0$  which resembles that in Eq. (3b):

$$SE_N(K, \beta) = \lambda^a \{ S_N(K, 1) + \sum_{i=1}^{\infty} T_{Ni}(K) \lambda^{bi} \}. \quad (12)$$

The form of the coefficients  $T_{Ni}$  is irrelevant to our aims.

In order to show that our sequence of polynomials offers an acceptable description of a diatomic potential energy curve, we will consider the Kratzer-Fues model<sup>20</sup> as an illustrative example. We find it convenient to write this potential in the following way:

$$V_{KF}(R) = D \{ (R_e/R)^2 - 2R_e/R + 1 \} = Dx^2/(1+x)^2, \quad (13)$$

where  $D$  is the dissociation energy of the molecule. We have chosen such an oversimplified model because it enables us to carry out the calculation analytically. Furthermore, the two  $R$ -dependent terms in Eq. (13) resemble the centrifugal and Coulomb terms, respectively, that also appear in actual vibrational potentials being the cause of their pole at  $R = 0$ .

The function  $E(x) = D^{-1}x^{-2}V_{KF}(R) = (1+x)^{-2}$  obeys the following Taylor expansions:

$$E(x) = \sum_{i=0}^{\infty} E_i x^i, \quad E_i = (-1)^i(i+1), \quad (14a)$$

$$E(x) = x^{-2} \sum_{i=0}^{\infty} e_i x^{-i}, \quad e_i = E_i, \quad (14b)$$

that are particular cases of those in Eq. (3) with  $a = -2$  and  $b = -1$ . Clearly, Eq. (14a) is closely related to the Dunham series [ $a_0 = D$ ,  $a_i = (-1)^i(i+1)$ ] and it is the starting point to construct the sequence  $SE_N$ .

According to Eq. (4) the proper mapping is

$$x = \beta/K(1 - \beta), \quad \beta = Kx/(1 + Kx), \quad (15)$$

that equals the Euler transformation<sup>22</sup> when  $K = 1$ . From the discussion above it follows that our method is suitable for describing  $V(R)$  only when  $x > 0$  ( $R > R_e$ ). In fact,  $S_N(K, \beta)$  has an unphysical pole of order  $N$  at  $x = -1/K$  due to the singularity of  $\beta(x)$  at that point. This is not a drawback of our method for the region  $R > R_e$  strongly controls the vibrational eigenvalue spectrum and it is the more important for most purposes. Besides, there are actually several acceptable approaches to  $V(R)$  for  $R < R_e$ .<sup>10</sup>

A straightforward algebraic manipulation of Eq. (10) yields the following expression for the coefficients of the sequence:

$$\bar{E}_n(K) = K^{-2}y^n(n+1), \quad (16)$$

where  $y = 1 - K^{-1}$ . The Taylor expansion for  $S(K, \beta)$  about  $\beta = 0$  converges when  $|\beta| < |1/y|$ . Therefore, if  $K \gg 1$  the series will converge for all  $0 \leq \beta \leq 1$  and, thereby,  $SE_N(K, \beta)(N \rightarrow \infty) = E(x)$  for all  $0 \leq x < \infty$ . Particularly, when  $K = 1$  the convergence radius becomes infinite and  $SE_N(1, \beta) = E(x)$  for all  $N$  because  $\bar{E}_i(K) = 0$  if  $i > 0$ . This fortunate situation is due to the simplicity of the model and is not to be expected in a general case. In the next section we will show that the Euler transformation<sup>22</sup> is not the proper one to deal with an actual Dunham series and that more reasonable results are obtained when  $K$  is order dependent ( $K = K_N^S, K_N^I$ ).

All the stationary and inflection points of  $S_N(K, 1)$  are easily obtained in the case of the Kratzer–Fues potential because the sum can be performed analytically:

$$S_N(K, 1) = \sum_{i=0}^N \bar{E}_i(K) = (N+1)y^{N+2} - (N+2)y^{N+1} + 1. \quad (17)$$

A simple and direct calculation yields

$$K_N^S = 1, \quad K_{N,1}^I = 1, \quad K_{N,2}^I = N/3 + 1. \quad (18)$$

The inflection point  $K_{N,2}^I$  leads to an  $N$ -dependent mapping and to a wrong result  $S_N(K_{N,2}^I, 1)(N \rightarrow \infty) = 1 - 4e^{-3}$ . However, according to our prescription,  $K_{N,2}^I$  must be discarded because it is not related to the smallest absolute value of the first derivative. On the other hand,  $K_N^S$  and  $K_{N,1}^I$  make null both first and second derivatives and lead to the exact result.

Recent calculations using a different version of the present method and a careful investigation of the order dependence of  $K_N^S$  and  $K_N^I$  suggest that linear- $N$  dependencies always give rise to sequences converging to wrong limits.<sup>23</sup> This conclusion is supported by the study of the strongly divergent series originated in the perturbation expansions for a simple integral and for the eigenvalues of the anharmonic oscillator and the linear confining potential model.<sup>23</sup>

Though the Kratzer–Fues potential is an oversimplified model for an actual potential energy curve, the success of our method in dealing with it makes our assumptions and

prescriptions reasonable. They will be checked in the following sections where we make use of the Dunham series for a large number of diatomic molecules to obtain accurate descriptions of their interatomic potentials and estimates of their dissociation energies that closely agree with experiment. The conclusions of our previous discussion may be a valuable guide when applying the procedure because we are not at present able to prove rigorously whether the sequence of polynomials constructed from the Dunham series converges to the actual vibrational potential.

### III. IONIC MOLECULES

The method developed in the preceding section applies to the vibrational potential of any diatomic molecule because  $V(R)$  can be expanded in Taylor series about  $R = R_e$  and  $1/R = 0$ . In addition to the Dunham series (1) the expansion

$$V(R) = D - C/R + O(R^{-2}) = D - CR_e^{-1}/x + O(x^{-2}), \quad C > 0, \quad (19)$$

where  $D$  and  $-C/R$  are the dissociation energy and Coulomb interaction, respectively, is known to hold for ionic molecules.<sup>24</sup> In this paper we ignore level crossing and consider dissociation into ions. Therefore our potential curve is supposed to be a good enough interpolation between the ionic branches of the two adiabatic potentials as discussed, e.g., in Ref. 25 with regard to the Rittner potential.<sup>24</sup> Information about avoided crossing and long range behavior is in principle contained in the Dunham coefficients. However, since a very few of them are available we have to introduce such information explicitly into the approximate potential curve.

In order to apply our method, we find it convenient to define the function

$$E(x) = V(R)/a_0x^2, \quad (20)$$

that obeys expansions like those in Eq. (3) with  $a = -2$  and  $b = -1$ . We are thus led to the transformation (15) that differs from those used previously.<sup>6–12</sup> When  $K = 1$  we obtain the Euler transformation<sup>22</sup> and the SPF series<sup>7</sup> that can be given a rigorous quantum mechanical basis.

Using Eq. (10) (with  $a = -2$ ,  $b = -1$ ,  $E_0 = 1$ , and  $E_i = a_i$ ) and the Dunham coefficients tabulated in Ref. 6, we calculate the first four coefficients  $\bar{E}_i(K)$ ,

$$\begin{aligned} \bar{E}_0(K) &= K^{-2}, \quad \bar{E}_1(K) = a_1K^{-3} + 2K^{-2}, \\ \bar{E}_2(K) &= a_2K^{-4} + 3a_1K^{-3} + 3K^{-2}, \\ \bar{E}_3(K) &= a_3K^{-5} + 4a_2K^{-4} + 6a_1K^{-3} + 4K^{-2}, \end{aligned} \quad (21)$$

of the sequence of polynomials

$$SE_N(K, \beta) = K^2(1 - \beta)^2 S_N(K, \beta), \quad S_N(K, \beta) = \sum_{i=0}^N \bar{E}_i(K)\beta^i. \quad (22)$$

It immediately follows from Eqs. (12), (19), and (20) that

$$D_N = a_0 S_N(K, 1) \quad (23)$$

is our estimate of the dissociation energy. We hope that  $D_N$  approaches  $D$  as  $N$  increases, a fact that will be checked later on. The importance of the parameter  $K$  is made evident by the fact that, whereas the SPF series ( $K = 1$ ) yields unphysical dissociation energies,<sup>7</sup> the sequence (23) (with  $K = K_N^S$ ,

TABLE I. Percent absolute deviations of predicted dissociation energies for 20 alkali halides calculated as  $d_N = 100|1 - D_N/D_{\text{exp}}|$  using  $a_0$ - $a_N$ .

Molecule	$K_3^I$	$d_3$	$K_2^I$	$d_2$
LiF	3.0300	6.3	2.4388	1.9
LiCl	3.1778	0.9	2.5271	5.2
LiBr	3.3993	7.6	2.6740	0.5
LiI	3.3773	4.9	2.6613	2.2
NaF	3.7161	17.3	2.9776	12.8
NaCl	3.5566	5.1	2.8320	0.6
NaBr	3.4643	0.7	2.7523	5.4
NaI	3.6375	2.9	2.8822	3.7
KF	3.7591	12.0	2.9650	4.0
KCl	3.8509	7.0	3.0329	0.2
KBr	3.8791	7.0	3.0720	0.0
KI	3.9268	6.1	3.0912	1.3
RbF	3.6345	2.0	2.9006	3.7
RbCl	4.0069	8.7	3.1449	1.5
RbBr	3.9853	7.0	3.1339	0.0
RbI	4.0916	8.5	3.2199	1.6
CsF	3.8713	4.1	2.9924	5.5
CsCl	4.1548	8.4	3.2378	0.4
CsBr	4.0606	7.0	3.1718	0.7
CsI	4.2036	7.1	3.2857	0.6

$K_N^I$ ) gives us very acceptable results as will be seen below.

When  $N = 2$  there are two stationary and two inflection points for each of the 20 alkali halides studied. We choose the largest inflection point because the flattest part of the curve  $S_2(K, 1)$  vs  $K$  appears in its neighborhood. The same choice is found to be appropriate when  $N = 3$ .

Using the Dunham coefficients tabulated in Ref. 6, we have calculated the percent absolute deviation  $d_N$  of our predicted dissociation energies  $D_N(N = 2, 3)$  from the experimental values.<sup>6</sup> Results are shown in Table I together with the corresponding  $K$  value. Since  $d_N$  (NaF) is much larger than any other one, which may be probably due to very large errors in the Dunham coefficients for NaF, we will exclude its value from the discussion below.

The average percent absolute deviation (Av) is larger when  $N = 3$  (Av = 6.0%) than when  $N = 2$  (Av = 2.1%). This is due to a larger experimental uncertainty in  $a_3$  than in  $a_2$ . The order-increasing inaccuracy in the Dunham coefficients is perhaps the main drawback of the procedures that require such an input data.<sup>6,8</sup>

Our series  $SE_2$  compares favorably with the (2,2) PA<sup>6</sup> (Av = 5.9%) that requires an equal number of Dunham coefficients and even with the empiric model developed by Rittner<sup>24</sup> (Av = 2.9%) that is frequently used in fitting RKR curves. If we take into account that the experimental dissociation energies have an error of about 1% we will conclude that our  $D_2$  is an acceptable approach to  $D$ .

Though Thakkar's method<sup>8</sup> predicts reasonable dissociation energies for covalent molecules, it yields poor results (Av = 25%) when applied to the alkali halides studied here. More accurate estimates are obtained via the (2,3) PA built from the SPF series<sup>7</sup> (Av = 8.5%). The importance of this PA that behaves properly when  $R \rightarrow \infty$  seems to have been misjudged.<sup>8</sup>

Figure 1 shows the vibrational potential (in units of  $a_0$ ) for KI obtained using  $a_0$ - $a_2$  and different approximate meth-

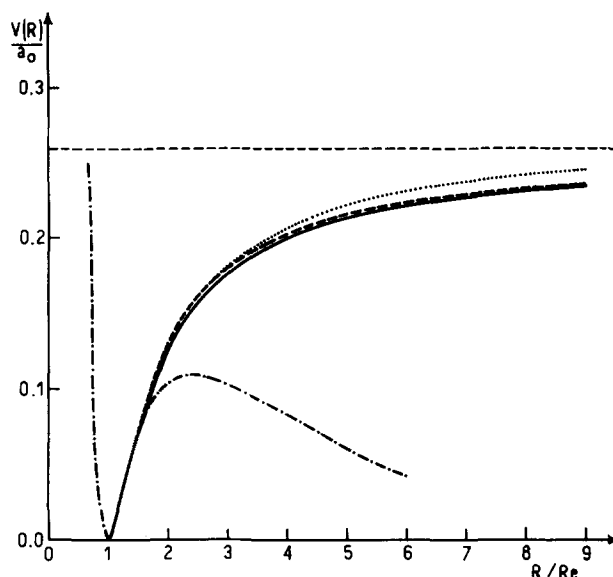


FIG. 1. Potential energy curve for KI constructed from  $a_0$ - $a_2$ . — Present:  $x^2SE_2(K_2^I, \beta)$ ; --- present:  $SE_2(K_4^I, \beta) + D/a_0$ ; ... (2,2) Padé approximant; - · - · - SPF series:  $x^2SE_2(1, \beta)$ .

ods. The present approach [ $x^2SE_2(K_2^I, \beta)$ ] and the (2,2) PA<sup>6</sup> give reasonable curves for all  $R > R_e$  and agree with the SPF series [ $x^2SE_2(1, \beta)$ ] for  $R_e < R < 1.5R_e$ . In this region the SPF series is known to be a close approximation to the RKR curves of covalent molecules.<sup>7</sup> The behavior of the SPF series is clearly unphysical for  $R > 2R_e$  showing a spurious maximum about  $2.5R_e$ . A comparison between our approximate curve and the SPF one reveals the relevant role of the parameter  $K$ . In fact, whereas  $x^2SE_2(K, \beta)$  is an unphysical curve when  $K = 1$ , it is quite a reasonable one when  $K = K_2^I \approx 3.1$  (see Table I).

One of the advantages of our method is that it allows one to take into account the experimental data systematically as it becomes available. For example, if the experimental dissociation energy is known in addition to the Dunham coefficients, we can obtain a closer approach to the vibrational potential as follows: We define

$$E^D(x) = \{V(R) - D\}/a_0, \quad (24)$$

that obeys

$$E^D(x) = -D/a_0 + x^2(1 + a_1x + a_2x^2 + \dots) \quad (25a)$$

and

$$E^D(x) = x^{-1}\{-C/a_0R_e + O(x^{-1})\}. \quad (25b)$$

Therefore, the method of Sec. II applies to this new problem ( $a = b = -1$ ) leading to the same transformation [Eq. (15)] discussed above. The sequence

$$SE_N^D(K, \beta) = K(1 - \beta)S_N^D(K, \beta), \quad S_N^D(K, \beta) = \sum_{i=0}^N \bar{E}_i^D(K)\beta^i \quad (26)$$

is supposed to be a satisfactory approximation to  $E^D(x)$  provided the coefficients  $\bar{E}_i^D$  obey Eq. (10), where  $\bar{E}_i$  and  $E_i$  must be replaced by  $\bar{E}_i^D$  and  $E_i^D$ , respectively, and  $E_0^D = -D/a_0$ ,  $E_1^D = 0$ ,  $E_2^D = 1$ ,  $E_i^D = a_{i-2}$  ( $i > 2$ ).

Using the Dunham coefficients  $a_0$ - $a_2$  and the dissocia-

tion energies tabulated in Ref. 6 we construct  $SE_4(K, \beta) + D/a_0$  that must be an adequate description of the actual  $V(R)/a_0$  for the alkali halides in Table I. The potential energy curve for KI ( $K_4^I = 4.890$ ) is shown in Fig. 1. Notice that this new approximation closely agrees with the (2,2) PA for  $R_e \leq R \leq 3R_e$  and does not differ too much from our previous one.

In conclusion, our method appears to be successful in obtaining accurate enough dissociation energies and acceptable vibrational potentials for ionic molecules. The fact that our sequences, the (2,2) PA and the SPF series all agree in the vicinity of  $R_e$  strongly suggests that they are close approximations to the actual interatomic potential in such a region. This is very important because RKR curves do not exist for alkali halides due to lack of sufficient experimental information. The accuracy in the estimated dissociation energies (Table I) indicates that  $a_0 x^2 SE_2(K_2^I, \beta)$  may be a close approach to the actual  $V(R)$  in the large- $R$  regime.

#### IV. COVALENT MOLECULES

The  $1/R$  expansions for the vibrational potentials of ionic and covalent molecules differ markedly. This is the main reason why most of the methods developed to construct potential energy curves from the Dunham series are successful in dealing with only one class of molecules. Engelke<sup>10</sup> has suggested that it is necessary to take into account the large- $R$  expansion properly in order to have an adequate description of  $V(R)$  and an accurate enough dissociation energy. One of the advantages of our procedure is that the sequence  $SE_N(K, \beta)$  can be easily given the desired expansion about  $1/R = 0$ .

A typical expansion for covalent molecules when the nuclei are far apart is

$$V(R) = D + C'/R^6 + \dots, \quad (27)$$

where the  $R^{-6}$  term comes from the van der Waals interaction. As in the previous section we define the function  $E(x)$  [Eq. (20)] that obeys

$$E(x) = x^{-2}(D/a_0 + C'R_e^{-6}/x^6 + \dots), \quad (28)$$

in addition to the Taylor expansion about  $x = 0$ . Though the series between brackets in Eq. (28) is not an  $x^{-6}$ -power expansion, we apply our method with  $a = -2$  and  $b = -6$  in order to take into account the first two terms. This choice leads to the following transformation:

$$x^{-6} = K\beta^{-6}(1 - \beta). \quad (29)$$

Notice that the singularity of  $V(R)$  at  $R = 0$  is mapped into the interval  $0 < \beta < 1$ . Therefore, if  $K$  were  $N$  independent the convergence radius of the  $\beta$ -power series would be smaller than or equal to  $\beta(x = -1)$ . However, since the stationary and inflection points of  $S_N(K, 1)$  prove to be order dependent, we will assume that the range of utility of the sequence

$$SE_N(K, \beta) = K^{1/3}(1 - \beta)^{1/3}S_N(K, \beta),$$

$$S_N(K, \beta) = \sum_{i=0}^N \bar{E}_i(K) \beta^i, \quad (30)$$

is larger than that of the Dunham series when the coefficients  $\bar{E}_i(K)$  obey Eq. (10), where  $a = -2$ ,  $b = -6$ ,  $E_0 = 1$ ,

TABLE II. Percent deviations of predicted dissociation energies for CO, HF, and HCl calculated as  $\delta_N = 100(1 - D_N/D_{\text{exp}})$  using  $a_0$ - $a_N$ .

N	K	CO			
		$\delta_N^a$	$\delta_N^b$	$\delta_N^c$	$\delta_N^d$
1	781.9	67.4	...	-133.0	-103.0
2	689.0 <sup>c</sup>	46.4	-143.0	-82.0	290.0
3	116.8	40.9	...	-36.0	342.0
4	85.8 <sup>c</sup>	23.0	182.0	-3.6	229.0
HF					
1	265.6	71.4	...	-164.0	-210.0
2	433.9 <sup>c</sup>	56.9	-161.0	-126.0	-96.0
3	51.5	47.3	...	-104.0	-68.0
4	29.9 <sup>c</sup>	26.4	-182.0	-46.0	117.0
5	33.6	25.9	...	7.1	264.0
HCl					
1	353.3	64.3	...	-205.2	-261.1
2	435.9 <sup>c</sup>	43.8	-194.7	-141.9	-17.5
3	71.1	36.9	...	-75.9	145.4
4	56.0 <sup>c</sup>	16.3	-1931.0	-5.5	327.6
5	21.5	16.9	...	-63.2	484.0
6	7.2	8.9	...	143.4	796.1

<sup>a</sup> Present.

<sup>b</sup>  $(N/2 + 1, N/2 + 1)$ PA (Refs. 6 and 8).

<sup>c</sup> Thakkar's method (Ref. 8).

<sup>d</sup> Equation (22) of Ref. 7.

<sup>e</sup> Real part of  $K_N^S$ .

$E_i = a_i$  ( $i > 0$ ). This assumption will be checked below by numerical calculation of the dissociation energy which is the most unfavorable case ( $\beta = 1$  or  $1/R = 0$ ).

It is very easy to show that Eq. (23) is an approach to the dissociation energy provided  $K$  is properly chosen. Due to the fact that  $b = -6$  we find that neither the stationary nor the inflection points are real for some  $N$  values. In such cases we choose  $K$  to be the real part of the stationary point that gives rise to the smallest absolute value of the second derivative. There is not any particular reason for this choice and it may be easily verified that the use of the real part of the appropriate inflection point leads to a similar result.

Using the Dunham coefficients tabulated in Refs. 6, 24, and 26 for CO, HF, and HCl, we have calculated the dissociation energy in each case by way of different approximate techniques and the percent deviation from the experimental value<sup>6,24,26</sup> is shown in Table II. Only Thakkar's method and the present one seem to yield acceptable results. However,

TABLE III. Predicted dissociation energy for HCl using covalent ( $a$ ) and ionic ( $b$ ) parameters.

N	$D_N^a/a_0$	$D_N^b/a_0$
1	0.062 871	0.604 240
2	0.099 036	0.498 981
3	0.111 204	0.454 131
4	0.147 554	0.428 698
5	0.146 513	0.412 272
6	0.162 115	0.400 771
Experimental $D/a_0$	0.176 29	

<sup>a</sup>  $a = -2$ ,  $b = -6$ .

<sup>b</sup>  $a = -2$ ,  $b = -1$ .

Thakkar's series seem to be divergent (all their coefficients are similar in magnitude) and they produce large deviations when adding a large enough number of Dunham coefficients. A similar conclusion was previously obtained by Engelke.<sup>10</sup> On the other hand, our sequences  $D_N$  approach the experimental dissociation energies from below and seem to be more reliable. A larger number of Dunham coefficients is required in order to verify whether our sequences actually converge towards the corresponding dissociation energies.

Engelke<sup>10</sup> has suggested the importance of taking into account the large- $R$  expansion for  $V(R)$  when calculating the dissociation energy. To check this proposal we have calculated  $D(\text{HCl})$  using covalent ( $a = -2$ ,  $b = -6$ ) and ionic ( $a = -2$ ,  $b = -1$ ) parameters. Results are shown in Table III. Though  $0 < \beta(R=0) < 1$  for the covalent sequence, it approaches the dissociation energy more quickly than the ionic sequence for which  $\beta(R=0) > 1$  is easily attained. Therefore, when calculating dissociation energies by means of potential energy curves constructed from Dunham coefficients, it appears to be fruitful to take into account the appropriate expansions about  $1/R = 0$ .

## V. FURTHER COMMENTS

The method proposed in this paper seems to be very promising in constructing potential energy curves from spectra. Only the shape of  $V(R)$  in the vicinity of  $R = R_e$  and qualitative knowledge of its large- $R$  behavior is required in order to obtain an acceptable approach to it for all  $R > R_e$  and even an accurate enough estimation of the dissociation energy. The procedure is particularly useful in those cases where RKR curves do not exist due to lack of sufficient experimental information. The approximate vibrational potential can be systematically improved as the experimental data becomes available.

It would be highly desirable to find precisely the conditions under which the sequence  $SE_N(K_N, \beta)$  converges to the exact result. However, a rigorous mathematical proof is too difficult and a numerical investigation impossible due to the lack of a large enough number of Dunham coefficients. This drawback is also present in the PA technique<sup>6</sup> and in all the power-series approaches.<sup>7,12</sup> Application of the present technique to a large number of divergent perturbation expansions<sup>15-19,23</sup> suggests that the sequences are always convergent though they converge to wrong limits when  $K_N$  depends

linearly on  $N$ .<sup>23</sup> The prescriptions of Sec. II for determining  $K_N$  seem to overcome this difficulty leading to the correct answer.

The procedure developed in Sec. II is quite general and allows one to study other problems in molecular spectroscopy. For example, prediction of level crossing<sup>5</sup> and dependence of dipole moments and Einstein coefficients on the internuclear separation distance<sup>27-29</sup> are at present under study in our laboratory. The latter problem is particularly suitable for applying our method because both the large- and small- $x$  expansions for the dipole moments and Einstein coefficients are frequently available.

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