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Use of Pade approximants in the construction of diabatic potential energy curves for ionic molecules*

K. D. Jordan, J. L. Kinsey, and R. Silbey

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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For most ionic molecules, sufficient experimental information is not available for the construction of an RKR potential curve; thus, model potentials have been employed which use some of the experimental information in their construction (e.g., Born–Mayer and Rittner potentials). In this paper, we present a simple method for constructing model potential curves which allows one to use all the available experimental information and to easily incorporate new information as it becomes available. This method, employing a Padé approximant technique, is capable of *predicting* the value of higher Dunham coefficients to within experimental accuracy from a knowledge of the lower ones. Consequently, it also predicts some spectroscopic properties from a knowledge of other data to much better accuracy than the Rittner or Born–Mayer models.

I. INTRODUCTION

The construction of potential energy curves from experimental data is an important problem in molecular chemistry. The most exact procedures to construct the curve is the RKR[1-3] method, but often the experimental data are insufficient to perform this technique. We are therefore forced to other, less reliable, procedures. Ionic molecules, and the alkali halides in particular, are unfortunate in this regard since there is not enough information for an RKR, and yet the curve crossing which occurs has made these molecules the object of a large number of experimental investigations.[4-8] Recent experimental and theoretical work[4,9,10] has indicated that the nuclear motion for most of the alkali halides is governed by the diabatic rather than the adiabatic potential curves. This is due to the large crossing points of the diabatic curves of the alkali halides. In such, nonadiabatic cases, the covalent and ionic configurations do not mix, and the dissociation products are the ions. Thus the most useful models have been the Born–Mayer[11] and its logical extension, the Rittner.[12] These potentials employ the knowledge of the asymptotic behavior for the diabatic curves, in addition to limited information about the minimum, in order to construct potential curves which are capable of reproducing the dissociation energy to about 5%, but which fail to give the spectroscopic constants correctly.[13,14] In a recent investigation,[6] it was found that the error in the Rittner and truncated Rittner is too large to enable the determination of the excited state potential of KI in chemiluminescence experiments. Hence a potential was synthesized by piecing together a truncated Rittner curve to a Hulbert–Hirshfelder curve via a cubic spline fit. Thus, although the Rittner potential is useful, it is not quantitative; it would be highly desirable to have a systematic procedure for developing these potential curves from experimental data as it becomes available. In a classic paper, Dunham[15] developed the Taylor series expansion for the potential of a diatomic molecule in powers of $(R - R_e)/R_e$, R_e being the equilibrium point of the potential. It is well known that this series cannot converge beyond $2R_e$ due to the presence of a pole at the origin.[16] However, in a recent paper, Simons, Parr, and Finlan[17] (SPF) accomplished an analytic continuation of the Dunham series outside its radius of convergence by rearranging the series, obtaining a new series with an extended radius of convergence. The SPF curves, while remaining finite as R goes to infinity, often extrapolate far from the correct dissociation limit. In some cases the SPF curves display a maximum for large R and in the $R \to \infty$ limit drop below the bottom of the potential well. A further difficulty noted by SPF is that the small R behavior may be unrealistic, tending to worsen as the correct large R asymptotic behavior is forced on the series.

In the present paper, we present a technique, using Padé approximants[18] (PA), to construct the potential energy curve for ionic molecules. This procedure is superior to the SPF procedure, and in fact contains it as a special case. However, the SPF change of variable is useful and allows our procedure greater flexibility. Our procedure is simple in conception and straightforward to apply: a rational function is formed as an approximation to the potential curve so as to reproduce the first few Dunham coefficients and (eventually) the dissociation limit. The approximant formed from just a few pieces of experimental data is capable of reproducing other experimental data (within their known accuracy).

In Sec. II, the theory is developed and compared to SPF in Sec. III. The two point approximants are introduced in Sec. IV. Comparison to experiment and other models are made throughout.

II. THEORY

Dunham[15] assumed a potential energy of the form

$$U = a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \cdots) , \tag{1}$$

where

$$\xi = (R - R_e)/R_e . \tag{2}$$

Utilizing the WKB[19] method of solving the Schrödinger equation, assuming the validity of the Born–Oppenheimer approximation,[20] and employing the expression

$$E(v, J) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} Y_{ij} (v + \tfrac{1}{2})^i [J(J+1)]^j \tag{3}$$

for the energy levels of a diatomic molecule, Dunham was able to obtain expressions for fifteen of the most important rotational and vibrational energy constants in terms of the a_i. He then expressed the a_i in terms of the Y_{ij}. The potential curve generated via the Dunham procedure is expected to reproduce the correct curve very accurately in the vicinity of the equilibrium point. In fact Jarmain[21] has shown the equivalence of the inverted Dunham series and the Rydberg[1]–Klein[2]–Rees[3] results. As mentioned above, the Dunham expansion converges only for $0<R<2R_e$. Depending upon the number of terms retained in Eq. (1), the potential will diverge to either plus or minus infinity as $R\rightarrow\infty$. The only Padé approximants in the variable ξ that have the correct asymptotic behavior are the $[N,N]$ approximants, i.e., those whose numerator and denominator are polynomials of the same degree in ξ. The simplest of these is the $[2,2]$ approximant:

$$[2,2]=d_1\xi^2(1+e_1\xi+e_2\xi^2)^{-1}\ . \tag{4}$$

The coefficients d_1, e_1, and e_2 are determined by requiring the expansion of (3) to reproduce the first three terms of the series (1) giving

$$[2,2]=a_0\xi^2/[1-a_1\xi+(a_1^2-a_2)\xi^2]\ . \tag{5}$$

This equation has the correct behavior around the minimum of the curve and goes to a constant as $R\rightarrow\infty$, giving an approximate value for the diabatic dissociation energy D_i

$$D_i\cong a_0/(a_1^2-a_2)\ . \tag{6}$$

This simple approximation works extremely well for the diabatic potential curves of the alkali halides. In this paper we are ignoring the ubiquitous curve crossing problem and are considering dissociation into ions. Use of the $[2,2]$ PA for extrapolation to D_i is much less reliable in the case of covalently bonded molecules.[22] This is not surprising since the curves for covalently bonded molecules, which display a $1/R^6$ asymptotic behavior rise much more steeply than those for ionic molecules which asymptotically interact coulombically.

If the a_3 and a_4 Dunham coefficients are also available the $[3,3]$ PA can be formed.

$$[3,3]=\frac{d_1[1+d_2\xi]\xi^2}{1+e_1\xi+e_2\xi^2+e_3\xi^3}\ . \tag{7}$$

Expansion of the denominator of Eq. (7) and comparison with Eq. (1) yield

$$d_1=a_0 \tag{8}$$

$$d_2=\frac{-2a_3a_1+a_4-a_2^2-a_1^4+3a_1^2a_2}{-a_3+2a_1a_2-a_1^3} \tag{9}$$

$$e_1=\frac{a_4-a_1a_3-a_2^2+a_1^2a_2}{-a_3+2a_1a_2-a_1^3} \tag{10}$$

$$e_2=\frac{-a_1a_4+a_2a_3+a_1^2a_3-a_1a_2^2}{-a_3+2a_1a_2-a_1^3} \tag{11}$$

$$e_3=\frac{-a_2a_4+a_3^2+a_1^2a_4+a_2^3-2a_1a_2a_3}{-a_3+2a_1a_2-a_1^3} \tag{12}$$

and the estimated dissociation energy is

$$D_i\cong\frac{a_0(-2a_3a_1+a_4-a_2^2-a_1^4+3a_1^2a_2)}{-a_2a_4+a_3^2+a_1^2a_4+a_2^3-2a_1a_2a_3}\ . \tag{13}$$

One could form higher order Padé approximants utilizing additional Dunham coefficients, but as discussed by Cashion,[23] it is not possible to obtain accurate values of a_5, a_6, ...

In Table I we list the values of a_0, a_1, a_2, and a_3[24] for the alkali halides as determined from the millimeter wave molecular beam spectroscopy experiments of Gordy and co-workers.[25] Table I also contains approximate values of a_3 obtained from the $[2,2]$ PA. Expansion of the denominator of Eq. (4) enables one to obtain approximations to a_3, a_4, a_5, ... from a_1 and a_2:

$$a_3\cong 2a_1a_2-a_1^3 \tag{14}$$

$$a_4\cong a_2^2+a_1^2a_2-a_1^4\ . \tag{15}$$

The a_3's obtained from Eq. (14) agree *quite well* with the experimentally determined ones (to within experimental error in all but six cases). As shown in Ref. 22, Eqs. (14) and (15) are poorer approximations for covalently bonded molecules. Thus, not only does the $[2,2]$ PA provide a substantial improvement over the Dunham expansion utilizing the same data [as evidenced by the success of Eqs. (6) and (14)], but it also provides a means of estimating additional spectroscopic constants from those which are known accurately.[26]

To the first order, the following approximations are valid:

$$\begin{array}{ll} Y_{10}\sim\omega_e & Y_{20}\sim-\omega_e x_e \\ Y_{01}\sim B_e & Y_{11}\sim-\alpha_e \\ Y_{02}\sim-D_e & Y_{21}\sim\gamma_e \\ Y_{03}\sim H_e & Y_{12}\sim-\beta_e\ . \end{array} \tag{16}$$

Using

$$Y_{21}=\frac{6B_e^3}{\omega_e^2}\left[5+10a_1-3a_2+5a_3-13a_1a_2+\tfrac{15}{2}(a_1^2+a_1^3)\right] \tag{17}$$

and the approximation of Eq. (14) we find

$$\gamma_e\cong\frac{6B_e^3}{\omega_e^2}\left[5+10a_1-3a_2-3a_1a_2+\tfrac{25}{2}a_1^3+\tfrac{15}{2}a_1^2\right]\ . \tag{18}$$

Since we have shown that the approximation to a_3 manifested in the $[2,2]$ PA is good to a few percent (providing accurate values for a_1 and a_2 are available), then the γ_e's given by Eq. (18) will also be determined quite accurately, probably to within an average error of about 3%. This amounts to a vast improvement over the situation with estimation of γ_e from the Rittner potential,[13,14,25,27,28] where the results are in error by as much as a factor of 10. The recent paper of Brumer and Karplus[14] considers the 17 alkali halides for which the dipole moment is known and finds that the average percentage errors for various spectroscopic constants as determined from the Rittner potential to be: α_e, 5.5%; $\omega_e x_e$, 4.9%; D_i, 2.9%, γ_e, 63.0%, and β_e, 138.0%.

The potential developed by Rittner has the following form:

TABLE I. Dunham coefficients.

	a_0(cm^{-1})	a_1	a_2	a_3	a_3 from [2, 2]PA	$a_1^{R\,\mathrm{a}}$	$a_2^{R\,\mathrm{a}}$
^{7}Li^{19}F	153 976 ± 74	−2.70062 ±0.00049	5.101 ±0.018	−7.98 ±0.15	−7.756	−2.80946[b]	4.89563[b]
^{7}Li^{35}Cl	146 437 ± 33	−2.72040 ±0.00023	5.004 ±0.017	−7.30 ±0.13	−7.093	−2.51444	3.74648
^{7}Li^{79}Br	142 906 ± 552	−2.71712 ±0.00413	4.567 ±0.204	−4.72 ±1.88	−4.759	−2.51364	3.73444
^{7}Li^{127}I	135 642 ± 781	−2.70194 ±0.00629	4.509 ±0.244	−4.53 ±2.36	−4.639	−2.65615	4.23202
^{23}Na^{19}F	164 454 ± 212	−3.13311 ±0.00160	6.431 ±0.226	−9.23 ±2.12	−9.540	−2.78856	4.81700
^{23}Na^{35}Cl	152 401 ± 82	−3.07637 ±0.00094	6.473 ±0.083	−11.06 ±0.90	−10.709	−2.94100	5.36829
^{23}Na^{79}Br	147 261 ± 171	−3.04613 ±0.00146	6.486 ±0.113	−11.82 ±1.10	−11.250	−2.94951	5.38755
^{23}Na^{127}I	142 568 ± 176	−3.01634 ±0.00178	5.912 ±0.154	−8.30 ±1.50	−8.220	−2.99589	5.43850
^{39}K^{19}F	162 100 ± 179	−3.11568 ±0.00141	6.347 ±0.232	−9.66 ±2.13	−9.304	−2.95026	5.35780
^{39}K^{35}Cl	152 166 ± 140	−3.24320 ±0.00225	7.050 ±0.039	−12.33 ±0.69	−11.616	−3.16027	6.21677
^{39}K^{79}Br	147 850 ± 38	−3.24151 ±0.00047	6.912 ±0.040	−11.01 ±0.50	−10.754	−3.19180	6.35007
^{39}K^{127}I	142 889 ± 60	−3.24629 ±0.00087	6.884 ±0.067	−10.98 ±0.74	−10.483	−3.25495	6.6268
^{85}Rb^{19}F	165 356 ± 82	−3.13473 ±0.00072	6.678 ±0.098	−11.29 ±0.93	−10.441	−2.97350	5.42045
^{85}Rb^{35}Cl	155 270 ± 105	−3.29643 ±0.00145	7.078 ±0.074	−11.50 ±0.88	−10.844	−3.37775	7.24700
^{85}Rb^{79}Br	151 050 ± 54	−3.32551 ±0.00092	7.334 ±0.108	−12.75 ±1.17	−12.002	−3.31983	6.90893
^{85}Rb^{12}I	146 076 ± 73	−3.34403 ±0.00180	7.180 ±0.145	−10.99 ±1.64	−10.627	−3.39041	7.23051
^{123}Cs^{19}F	168 551 ± 28	−3.03241 ±0.00028	5.660 ±0.055	−7.29 ±0.51	−6.441	−3.12173	5.96026
^{133}Cs^{35}Cl	159 133 ± 650	−3.31873 ±0.00520	6.919 ±0.103	−10.11 ±1.64	−9.374	−3.35145	7.00037
^{133}Cs^{79}Br	154 912 ± 14	−3.37682 ±0.00036	7.597 ±0.018	−14.02 ±0.22	−12.803	−3.41098	7.27648
^{133}Cs^{127}I	150 327 ± 34	−3.42908 ±0.00095	7.608 ±0.066	−12.79 ±0.81	−11.859	−3.50774	7.73625

[a] Obtained from data of Varshni and Shukla (Ref. 10). The magnitude of the errors in a_1 and a_2 is nearly the same in the truncated Rittner model (of Ref. 6) as for the above listed Rittner results.

[b] a_1^R and a_2^R values for LiF are obtained using the recent values of ω_e and B_e of Pearson and Gordy.

$$U_R(R)=A\exp(-R/\rho)-CR^{-6}-e^2R^{-1}$$
$$-e^2(\alpha_+ + \alpha_-)/(2R^4)-2(e^2\alpha_+\alpha_-)R^{-7}\,, \qquad (19)$$

where the successive terms represent, respectively, the short-range repulsion (A, ρ), the van der Waals interaction; the Coulombic attraction; the ion-induced dipole interaction (α_+ and α_- are the ion polarizabilities), and the induced dipole-induced dipole interaction. A and ρ are determined from

$$(dU_R/dR)_{R_e}=0 \qquad (20)$$

$$(d^2U_R/dR^2)_{R_e}=\text{force constant}\,. \qquad (21)$$

Honig, Mandel, Stitch, and Townes[27] expanded $U_R(R)$ in powers of ξ and found expressions for the Dunham coefficients a_i. Due to the constraint imposed by Eq. (21), the series expansion of the Rittner potential has the correct harmonic component. As shown in Refs. 21 and 24 the a_1 and a_2 values predicted by the Rittner model differ from the experimental values due to deviation of the alkali halides from the completely ionic model. Using the experimental values tabulated in Ref. 6 and making use of the formulas,[15]

$$a_1 = (Y_{11}Y_{10})/(6Y_{01}^2) - 1 \tag{22}$$

$$a_2 = Y_{12}\,\omega_e^2/(48B_e^4) + \tfrac{19}{8} + (\tfrac{9}{4})a_1 + (\tfrac{9}{8})a_1^2 \tag{23}$$

we have calculated a_1^R, a_2^R from the Rittner model and have also listed these values in Table I. The average percentage errors are about 3 and 10%, respectively, due to the errors in the rotational–vibrational coupling constant α_e and the anharmonicity constant $\omega_e x_e$.

In Table II we compare the dissociation energies predicted by the Rittner model and the [2, 2] PA with the experimental values. The Rittner model, as expected, gives generally good results (an average error of 2.9%). In view of the fact that the [2, 2] PA employs *only* the spectroscopic constants a_0, a_1, and a_2, it is rather surprising that it also gives reasonable estimates of D_i (average error of 5.9%). We have also expanded the [2, 2] PA in powers of R^{-1} and calculated the coefficient c_1 of this expansion. The correct value of c_1 is e^2 (116 140 for energies in cm^{-1}, distances in Å). Again, considering that only the three leading coefficients from the expansion about the equilibrium point are used, the fact that the average error in c_1 is 12 percent (see Table II) is impressive.

It would be highly advantageous to study the [3, 3] PA utilizing a_3 and a_4. Our experience with PA's on series expansions on analytic model potentials,[22] leads us to believe that the [3, 3] PA is superior to the [2, 2] in the lower half of the potential curve, but the dissociation energies obtained from it may be poorer than those from the [2, 2] PA. In principle one could hope to learn something about the curve-crossing problem[4] from a Padé analysis of the series expansions. However we expect that this would require many more Dunham coefficients than can be generated from existing experimental data. Further they would have to be determined with more precision than is now possible. In fact, the uncertainties in many of the a_3's are so large that it is questionable whether they should be employed at all in analytic continuation. Table III lists the uncertainties in the coefficients of KCl, NaBr, RbI, KF, LiF, and LiCl. In our study of various ways of utilizing the a_3 coefficient in a PA we found that even a 1% uncertainty in a_3 could result in a PA whose extrapolation to infinite internuclear separation would give a less reliable D_i than the simpler [2, 2] PA. In fact another order of accuracy in the a_2 values would greatly facili-

TABLE II. Dissociation energies c_1.

Experimental[a] D_i(cm^{-1})		Truncated[b] Rittner D_i(cm^{-1})	[2, 2] PA Est. of D_i (cm^{-1}) average[e]	Min[c]	Max[c]	C_1[d] estimated from [2, 2]PA (cm^{-1})
LiF	64 070 (±1100)	64 492	70 233	69 545	70 935	135 299
LiCl	53 990 (±1200)	52 531	61 102	60 627	61 585	140 150
LiBr	51 680 (±1150)	49 383	50 754	46 789	55 413	106 302
LiI	48 250 (±870)	45 641	48 580	43 938	54 259	112 446
NaF	53 520 (±650)	53 615	48 572	44 238	52 289	86 572
NaCl	46 510 (±400)	45 291	50 946	50 253	52 539	123 692
NaBr	44 790 (±500)	43 053	52 728	49 109	56 904	143 286
NaI	41 810 (±600)	40 255	44 741	42 482	47 246	115 975
KF	48 360 (±700)	48 334	48 236	44 962	52 014	99 120
KCl	41 250 (±250)	40 430	43 872	41 611	46 375	109 402
KBr	39 660 (±400)	38 436	41 128	40 634	41 635	104 607
KI	37 200 (±400)	35 953	39 099	38 317	39 838	105 748
RbF	46 840 (±1250)	46 830	50 910	49 345	52 606	111 559
RbCl	40 220 (±770)	38 996	40 986	40 075	41 938	99 389
RbBr	38 470 (±800)	···	40 550	39 328	41 863	106 601
RbI	36 360 (±700)	···	36 498	35 103	38 006	96 878
CsF	46 020 (±900)	46 096	47 671	46 906	48 461	95 813
CsCl	39 020 (±800)	37 842	38 863	37 443	40 380	92 912
CsBr	38 160 (±900)	···	40 705	40 478	40 935	110 959
CsI	35 020 (±980)	33 540	36 223	35 591	36 877	97 712

[a] These values were obtained by averaging the D_0 values from the following sources, giving each source a weight proportional to the inverse of its stated limits of error: L. Brewer and E. Brackett, Chem. Rev. **61**, 425 (1961); *JANAF Thermochemical Tables* (Dow Chemical Co., Midland, MI, 1971), 2nd ed.; A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall, Ltd., London, 1968), 3rd ed.; B. deB. Darwent, Natl. Bur. Stand. Ref. Data Ser., Nat. Bur. Stand. (U. S.), 31 (1970). These values agree quite well with those of Brumer and Karplus, Ref. 6.

[b] Results of Brumer and Karplus, Ref. 6. These truncated Rittner D_i's are slightly better than those of the regular Rittner model. See Ref. 10.

[c] The results in the min, max columns show the spread in the extrapolated D_i due to the uncertainties in a_0, a_1, a_2; a_2 uncertainties causing most of the spread.

[d] Correct value of $e_1 \equiv e^2 = 116141$ cm^{-1} Å.

[e] The average error in the D_i's determined from the [2, 2] PA is 5.9%. Omission of NaBr from the averaging lowers this to 5.2%. If only the Cs, K, and Rb salts are considered the average error is 4.1%. The average errors in the Rittner and truncated Rittner models for D_i is 2.9 and 2.5%, respectively.

TABLE III. Percent uncertainties in Dunham coefficients.

	a_0	a_1	a_2	a_3
LiF	0.05	0.02	0.35	1.87
LiCl	0.02	0.01	0.40	1.78
KF	0.11	0.04	3.65	22.04
KCl	0.09	0.07	0.54	5.60
NaBr	0.12	0.05	1.74	9.33
RbI	0.05	0.05	2.01	14.96

tate the analysis of the power of the [2, 2] PA.

This sensitivity of the PA's to the accuracy of the a_i, allows them to be used in determination of possible error in experimental results. For example, when we employed the data of Veazey and Gordy for LiF, the [2, 2] PA gave a D_i with an error of 300%, clearly out of line with all the other alkali halides. The new, much more accurately determined data of Pearson and Gordy gave a D_i only 9% too high. The rather large errors in the D_i's of NaBr and LiCl may also indicate error in their experimentally determined Dunham coefficients.

III. COMPARISON WITH THE METHOD OF SIMONS, PARR, AND FINLAN (SPF)

In this section we compare the PA procedure with the Euler transformation[29] method of Simons, Parr, and Finlan (SPF) to rearrange the Dunham expansion of Eq. (1), expanding in $(R-R_e)/R \equiv y$ instead of $(R-R_e)/R_e \equiv \xi$, obtaining

$$U_{SPF}(R) = b_0 y^2 [1 + b_1 y + b_2 y^2 + b_3 y^3 + \cdots] \tag{24}$$

where the coefficients b_j are given in terms of the Dunham coefficients a_i as

$$\begin{aligned} b_0 &= a_0 \\ b_1 &= a_1 + 2 \\ b_2 &= a_2 + 3b_1 - 3 \\ b_3 &= a_3 + 4b_2 - 6b_1 + 4 . \end{aligned} \tag{25}$$

Unlike the Dunham expansion the U_{SPF} series extrapolates to a constant. However the PA is in general, as discussed by Baker,[18,30] a more powerful means of analytic continuation. In terms of the variable y arbitrary $[N, M]$ PA's (i.e., rational fractions whose numerators are Nth order polynomials and whose denominators in polynomials of Mth order) behave properly as $R \to \infty$, since $y \to 1$, in that limit. Moreover, the $[N, N]$ PA's are invariant under Euler transformations, so that the asymptotically well-behaved $[N, N]$ PA's in ξ all have equivalent $[N, N]$ PA forms in terms of y. Hence the SPF variable y appears to be more generally useful for analytic continuation by PA's since a wider variety of functional forms can be used. For the KI the U_{SPF} potential is

$$U_{SPF} = (142\,889.4) y^2 [1 - 1.24629 y + 0.14499 y^2 + 1.07959 y^3 + \cdots] . \tag{26}$$

In Fig. 1 this function is compared to the Dunham function obtained from the same spectroscopic data and to the simple [2, 2] PA employing a_0, a_1, and a_2. It is seen that the [2, 2] PA affords considerable improvement.

In those cases in which a_1 through a_3 are accurately known but no reliable value for a_4 is available one may now proceed via the [3, 2] PA on the U_{SPF} series.

$$[3, 2] = a_0 y^2 / [1 - b_1 y + (b_1^2 - b_2) y^2 + (2b_1 b_2 - b_1^3 - b_3) y^3] . \tag{27}$$

The [3, 2] PA on the Dunham series would tend to zero as $R \to \infty$. In the case of LiF the $R \to \infty$ $(y \to 1)$ limit of Eq. (27) gives a dissociation energy only 3.2% too high (the [2, 2] PA result was 9.1% too high). However due to the much greater uncertainty in most of the a_3 than in the a_0, a_1, a_2, this approximation may not always lead to an improved curve for large R. For example the [2, 2] PA for KCl gave a D_i 6.4% too high while Eq. (27) gave a result 11.9% too low.

IV. TWO POINT PADÉ APPROXIMANTS

Two point PA's[30-32] have recently been introduced in treatment of physical problems in which one has expansions about two points. The construction of potential curves via two point PA's seems highly desirable for ionic molecules where one knows the *exact* values of the first three coefficients in the R^{-1} expansion of the potential at large R in addition to any spectroscopic data:

$$U(R) \sim D_i - \sum_n C_n R^{-n} \tag{28}$$

$c_1 = e^2$, $c_2 = c_3 = 0$. The coefficients of the PA can now be determined with input from both Eqs. (1) and (28). If the dissociation energy is known, it can be used to determine one of the coefficients of the PA. In this case a $[2, 2]_{D_i}$ PA can be obtained with no spectroscopic constants except a_0 and a_1. If a_1, a_2, a_3, and D_i are accurately known, determination of the coefficients of Eq. (7) gives

$$d_0 = a_0 \tag{29}$$

$$d_1 = (a_3 + a_1^3 - 2a_1 a_2) / (a_1^2 - a_2 - a_0 D_i^{-1}) \tag{30}$$

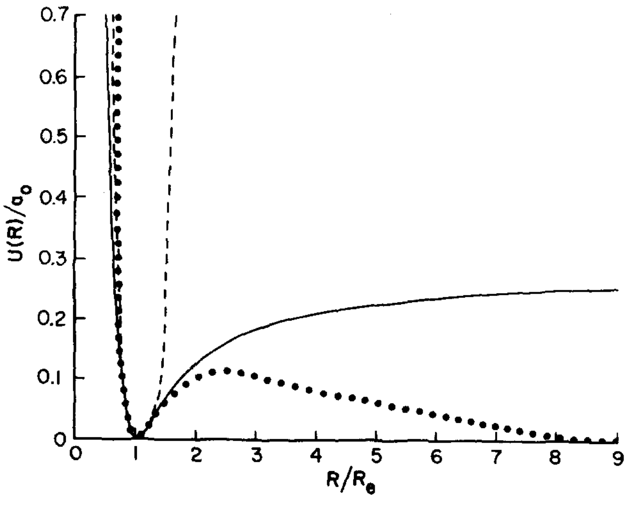

FIG. 1. Curves constructed from a_0, a_1, a_2 for KI. Solid line, [2, 2] PA; dashed line $a_0\xi^2[1 + a_1\xi + a_2\xi^2]$; dotted lines U_{SPF}.

$$e_1 = (a_3 + a_1^3 - 2a_1a_2)/(a_1^2 - a_2 - a_0 D_i^{-1}) - d_1 \tag{31}$$

$$e_2 = -a_1(a_3 + a_1^3 - 2a_1a_2)/(a_1^2 - a_2 - a_0 D_i^{-1}) + a_1^2 - a_2 \tag{32}$$

$$e_3 = [(a_3 + a_1^3 - 2a_1a_2)/(a_1^2 - a_2 - a_0 D_i^{-1})]D_i^{-1}a_0 \,. \tag{33}$$

This is expected to provide a very good representation of the potential curve.[22] Higher-order PA's may also be constructed.[33] For example we have considered the [4, 4] PA utilizing a_0, a_1, a_2, D_i, c_1, and which sets c_2 and $c_3 = 0$. It should be noted that the poles of the [2, 2] PA's all occur for complex R with the real part of R negative. The [3, 3] PA's defined by Eq. (8)–(12) had no poles for ξ real and positive. However, some of the two point [3, 3] PA's have a spurious pole for $\xi > 0$.[22]

In Fig. 2 we plot for KI the Rittner, the [2, 2] PA and the $[2, 2]_{D_i}$ PA. Examination of Table I reveals that the a_1 and a_2 values obtained from the Rittner model are in relatively good agreement with the experimentally determined values—the respective errors being 0.4 and 3.7%. For most of the other alkali halides the discrepancy between the PA and Rittner curves will be even more serious. We believe that part of the disagreement between the [2, 2] PA and the Rittner curve is due to the fact that the Rittner model inadequately treats the overlap region. We plan to compare the spectra calculated for the various model potentials and compare the results with the experimental ones in order to resolve this problem.

We have also studied Sandeman's[34] inversion of the Dunham series

$$\xi = \pm (U/a_0)^{1/2}[1 \pm h_1(U/a_0)^{1/2} + h_2(U/a_0) \pm h_3(U/a_0)^{3/2} + \cdots] \tag{34}$$

where the first few conversion formulas between the a_i and h_i are

$$a_1 = -2h_1 \tag{35}$$

$$a_2 = -2h_2 + 5h_1^2 \tag{36}$$

$$a_3 = -2h_3 + 12h_1h_2 - 14h_3 \tag{37}$$

$$a_4 = -2h_4 + 7(2h_1h_3 + h_2^2) - 56h_1^2h_2 + 42h_1^4 \,. \tag{38}$$

Equation (34), unlike the Dunham series, is not limited to convergence only near $\xi = 0$.[16] In fact, Jarmain[21] has examined the RKR expressions in Sandeman's form and has shown that term by term the RKR is equivalent to Sandeman's approach. Davis and Vanderslice[35] and Hurley[36] proved the equivalence up to the dissociation limit. If Eq. (34) is truncated at the $U^{3/2}$ term, the following approximation to ξ is obtained

$$\xi = \pm (U/a_0)^{1/2}[1 \pm h_1(U/a_0)^{1/2} + h_2(U/a_0)] \,. \tag{39}$$

In Fig. 3 we compare the potential curve generated from Eq. (39) and compare it with the quartic Dunham and the [2, 2] PA results for KI. As depicted in the figure, the Sandeman expression has a larger region of usefulness than does the Dunham expansion. However for $R > 1.3R_e$ and for $R < 0.8R_e$ the [2, 2] Padé seems to provide a much more reasonable potential curve. Inspection of Eq. (40) reveals that $U \to \infty$ as $R \to \infty$. The inability of the inverted Dunham expansion of Sandeman to accurately continue the results vary far beyond the region in which spectroscopic data is utilized is also the case in RKR.[33] We expect that PA's will also prove very useful in extending the RKR method especially in the estimation of accurate dissociation energies and long range behavior when the energy levels are known except near the dissociation limit.[37,38]

V. SUMMARY AND DISCUSSION

In this paper we have introduced a new class of approximations to potential curves of ionic molecules. Since RKR curves do not exist for alkali halides due to lack of sufficient experimental information, approximate potential curves which reproduce the known experiments are of importance. These have the highly desirable property of providing a systematic means of utilizing available information describing the molecule near the bottom of the well in addition to the asymptotic behavior. We are currently studying the spectrum calculated from the various PA potentials developed here. This should provide a stringent test of the utility of these models. These results will be compared with those of the Rittner model, various spline-fitted curves as well as the available experimental vibrational and rotational transitions. We are also investigating various means of circumventing the Dunham expansion, which in principle should be an excellent procedure, but computationally does not allow for accurate evaluation of the higher Dunham coefficients.[23] One possible procedure involves a direct least-squares fit of a rational function to the experimental data. We expect that the PA type potential curves especially when combined with an analogous analytic continuation treatment of the dipole moment[33] will prove useful in the study of thermal and photochemical reactions where the alkali halide products are often excited to $v \sim 100$ or higher.[39]

Earlier we mentioned that due to the R^{-6} asymptotic behavior of covalently bonded molecules, the [2, 2] PA will not provide as useful a description of covalent mole-

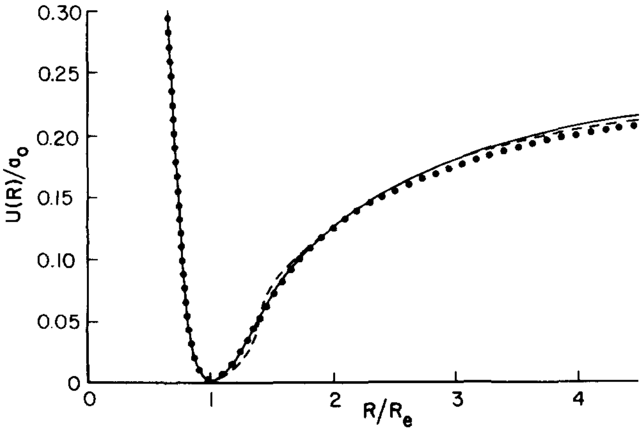

FIG. 2. Comparison of Rittner model with [2, 2], $[2, 2]_{D_i}$ PA Solid line, [2, 2] PA; dotted line $[2, 2]_{D_i}$ PA; dashed line Rittner curve using data of Ref. 1. For large R the $[2, 2]_{D_i}$ curve crosses the Rittner curve since the $[2, 2]_{D_i}$ goes to the correct dissociation energy and the Rittner curve extrapolates to a result 3.1% too low. On the scale used here, the three curves are essentially superimposable for $R < R_e$. We have shifted the Rittner curve by adding the dissociation energy.

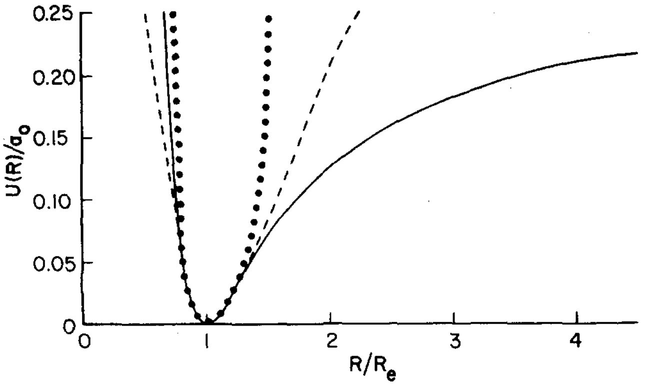

FIG. 3. Comparison of Sandeman, Dunham and [2, 2] PA's for KI. Solid line [2, 2] PA; dotted line quartic Dunham; dashed line Sandeman expression utilizing e_1, e_2 coefficients.

cules as for the diabatic ground state curves of ionic molecules. In fact, it is necessary to employ a [6, 6] or higher order PA to obtain the R^{-6} asymptotic behavior. The more complicated nature of the interaction in covalent molecules at intermediate distances[40] also requires more information than that contained in a_0, a_1, and a_2 if it is to be reproduced by a PA. Molecular quantum mechanical calculations demonstrate that the alkali halides can be reasonably described, even appreciably far from R_e by just the Hartree–Fock ground state wavefunction.[40] However in the case of covalent molecules one must consider the mixing of various excited determinantal wavefunctions with the Hartree–Fock ground state.

The recent pseudopotential calculations on various alkali halides by Redmon and Micha[41] also indicate that for $R < R_c$ (the crossing point of the diabatic curves) a single configuration (the ionic valence bond structure) is necessary to describe the potential curve. Although only results on the alkali halides are reported in this paper, the methods described here should be useful in studying other ionic compounds. Calculations on several other classes of halides including those of copper, indium, silver, aluminum, thallium, and gallium also have been performed and the results are promising.[22] Preliminary studies have also indicated the utility of PA's in the study of metallic hydrides and oxides.

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