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


Citation: J. Chem. Phys. 61, 911 (1974); doi: 10.1063/1.1682034

View online: http://dx.doi.org/10.1063/1.1682034

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


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(Received 29 January 1974)

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 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. Recent experimental and theoretical work has indicated that the nuclear motion for most of the alkali halides is governed by the diatomic 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 and its logical extension, the Rittner. 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. In a recent investigation, 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-Spencer curve via a cubic spline fit. Thus, although the Rittner potential is useful, it is not quantitative; it predicts the correct dissociation limit. The approximant formed from just a few pairs 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 assumed a potential energy of the form

\[ U = a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \cdots ) \]

where

\[ \xi = \frac{(R - R_e)}{R_e} \]  

Utilizing the WKB method of solving the Schrödinger equation, assuming the validity of the Born-Oppenheimer approximation, and employing the expression

\[ E(v_j) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} Y_{ij}(v + \frac{1}{2})[J(J+1)]^j \]

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 \( Y_{1j} \). 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\(^{2,3}\)-Klein\(^{2,3}\)-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 \( R \to \infty \). The only Padé approximants in the variable \( \xi \) that have the correct asymptotic behavior are the \( [2,2] \) approximants, i.e., those whose numerator and denominator are polynomials of the same degree in \( \xi \). The simplest of these is the \([2,2]\) approximant:

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

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

\[
[2,2] = a_2 \xi^2 / [1 - a_1 \xi^2 - (a_1^2 - a_2) \xi^2] .
\]

This equation has the correct behavior around the minimum of the curve and goes to a constant as \( R \to \infty \), giving an approximate value for the diabatic dissociation energy \( D_1 \)

\[
D_1 \equiv a_2 / (a_1^2 - a_2) .
\]

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 \( D_1 \) 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 \( a_2 \) and \( a_4 \) Dunham coefficients are also available the \([3,3]\) PA can be formed.

\[
[3,3] = d_1 \xi^3 [1 + e_1 \xi + e_2 \xi^2 + e_3 \xi^3] .
\]

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

\[
d_1 = a_2
\]

\[
d_2 = -2a_2a_1^2 + a_4^2 - a_6^2 - a_1^3 + 3a_2a_4
\]

\[
e_1 = a_4 - a_1a_2 + a_4^2 - a_6^2 - a_1a_2
\]

\[
e_2 = -a_4a_1^2 + a_4a_2 + a_1^2a_2 - a_1^3 - a_2a_2
\]

\[
e_3 = -a_4a_1^2 + a_4a_2 + a_1^2a_2 - 2a_1a_2a_3
\]

and the estimated dissociation energy is

\[
D_1 \equiv a_2 / [\frac{1}{2}a_4^2 - a_4^2 - a_6^2 - a_1^3 + 3a_2a_4 - a_1a_2 + a_4 + 2a_1a_2 - a_1^2 - 2a_1a_2a_3] .
\]

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 \( a_5, a_6, \ldots \).

In Table I we list the values of \( a_2, a_1, a_2, \) and \( a_3 \) 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 \( a_6 \) obtained from the \([2,2]\) PA. Expansion of the denominator of Eq. (4) enables one to obtain approximations to \( a_2, a_4, a_2, \ldots \) from \( a_1, a_2, a_2 \):

\[
a_2 \approx 2a_1a_2 - a_1^3
\]

\[
a_2 \approx 2a_1a_2 - a_1^3
\]

The \( a_2 \) '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:

\[
Y_{10} - \omega_e \quad Y_{20} - \omega_e x_e
\]

\[
Y_{01} - B_e \quad Y_{11} - \omega_e
\]

\[
Y_{00} - D_e \quad Y_{10} - \gamma_e
\]

\[
Y_{00} - H_e \quad Y_{10} - \beta_e
\]

Using

\[
Y_{21} \approx \frac{6B_e^2}{\omega_e^3} [5 + 10a_1 - 3a_2 + 5a_3 - 13a_1a_2 + \frac{1}{2} (a_1^2 + a_2^2)]
\]

and the approximation of Eq. (14) we find

\[
\gamma_e \approx \frac{6B_e^2}{\omega_e^3} [5 + 10a_1 - 3a_2 - 3a_1a_2 + \frac{25}{2} a_1 + \frac{49}{2} a_2] .
\]

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 \( a_4 \) are available), then the \( \gamma_e \)'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 \( \gamma_e \) 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: \( \alpha_e, 5.5%; \omega_e x_e, 4.9%; D_1, 2.9%; \gamma_e, 63.0%; \) and \( \beta_e, 138.0\% \).

The potential developed by Rittner has the following form:

J. Chem. Phys., Vol. 61, No. 3, 1 August 1974
TABLE I. Dunham coefficients.

<table>
<thead>
<tr>
<th>( a_0 ) (cm(^{-1}))</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( a_3 ) from [2, 2]PA</th>
<th>( d_R^8 )</th>
<th>( d_R^{10} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{7}\text{Li}^{19}\text{F} )</td>
<td>153 976 ± 74</td>
<td>-2.70062</td>
<td>5.101</td>
<td>-7.98</td>
<td>-7.756</td>
<td>-2.80946b</td>
</tr>
<tr>
<td>( ^{7}\text{Li}^{35}\text{Cl} )</td>
<td>146 437 ± 33</td>
<td>-2.72040</td>
<td>5.004</td>
<td>-7.30</td>
<td>-7.083</td>
<td>-2.51444</td>
</tr>
<tr>
<td>( ^{7}\text{Li}^{35}\text{Br} )</td>
<td>143 906 ± 552</td>
<td>-2.71712</td>
<td>4.567</td>
<td>-4.72</td>
<td>-4.759</td>
<td>-2.51364</td>
</tr>
<tr>
<td>( ^{7}\text{Li}^{127}\text{I} )</td>
<td>135 642 ± 781</td>
<td>-2.70194</td>
<td>4.509</td>
<td>-4.53</td>
<td>-4.659</td>
<td>-2.65615</td>
</tr>
<tr>
<td>( ^{23}\text{Na}^{35}\text{Cl} )</td>
<td>153 401 ± 82</td>
<td>-3.07637</td>
<td>6.473</td>
<td>-11.06</td>
<td>-10.709</td>
<td>-2.94100</td>
</tr>
<tr>
<td>( ^{23}\text{Na}^{35}\text{Br} )</td>
<td>147 261 ± 171</td>
<td>-3.04613</td>
<td>6.486</td>
<td>-11.62</td>
<td>-11.250</td>
<td>-2.94951</td>
</tr>
<tr>
<td>( ^{39}\text{K}^{19}\text{F} )</td>
<td>162 101 ± 159</td>
<td>-3.11535</td>
<td>6.347</td>
<td>-9.66</td>
<td>-9.304</td>
<td>-2.95026</td>
</tr>
<tr>
<td>( ^{39}\text{K}^{35}\text{Cl} )</td>
<td>142 568 ± 176</td>
<td>-3.01634</td>
<td>5.912</td>
<td>-8.30</td>
<td>-8.220</td>
<td>-2.95859</td>
</tr>
<tr>
<td>( ^{39}\text{K}^{35}\text{Br} )</td>
<td>152 116 ± 140</td>
<td>-3.24230</td>
<td>7.050</td>
<td>-12.33</td>
<td>-11.616</td>
<td>-3.16027</td>
</tr>
<tr>
<td>( ^{85}\text{Rb}^{19}\text{F} )</td>
<td>155 270 ± 105</td>
<td>-3.13473</td>
<td>6.678</td>
<td>-11.29</td>
<td>-10.441</td>
<td>-2.97350</td>
</tr>
<tr>
<td>( ^{85}\text{Rb}^{35}\text{Cl} )</td>
<td>151 050 ± 54</td>
<td>-3.32551</td>
<td>7.334</td>
<td>-12.75</td>
<td>-12.002</td>
<td>-3.19180</td>
</tr>
<tr>
<td>( ^{133}\text{Cs}^{19}\text{F} )</td>
<td>146 076 ± 73</td>
<td>-3.34403</td>
<td>7.180</td>
<td>-10.99</td>
<td>-10.627</td>
<td>-3.39641</td>
</tr>
<tr>
<td>( ^{133}\text{Cs}^{35}\text{Cl} )</td>
<td>168 551 ± 28</td>
<td>-3.03241</td>
<td>5.666</td>
<td>-7.29</td>
<td>-6.441</td>
<td>-3.12173</td>
</tr>
<tr>
<td>( ^{133}\text{Cs}^{35}\text{Br} )</td>
<td>159 133 ± 650</td>
<td>-3.31873</td>
<td>6.919</td>
<td>-10.11</td>
<td>-9.374</td>
<td>-3.35145</td>
</tr>
<tr>
<td>( ^{133}\text{Cs}^{127}\text{I} )</td>
<td>154 912 ± 14</td>
<td>-3.37682</td>
<td>7.597</td>
<td>-14.02</td>
<td>-12.803</td>
<td>-3.41098</td>
</tr>
</tbody>
</table>

*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.

\[
U_R(R) = A \exp(-R/p) - C R^6 - e^2 R^{-1} - e^2(\alpha + \alpha_0)/(2R) - 2e^2(\alpha_0, \alpha_0) R^{-2},
\]

where the successive terms represent, respectively, the short-range repulsion \((A, p)\), the van der Waals interaction; the Coulombic interaction; the ion-induced dipole interaction \((\alpha_0, \alpha_0)\) are the ion polarizabilities), and the induced dipole-induced dipole interaction. \( A \) and \( p \) are determined from

\[
(d^2U_R/dR^2)_{R_e} = \text{force constant}.
\]

(21)

Honig, Mandel, Sticht, and Townes expanded \( U_R(R) \) in powers of \( \xi \) and found expressions for the Dunham coefficients \( a_1 \). 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 mak-
The results in the min, max columns show the spread in the extrapolated $D_j$ values. We have calculated percentage errors are about 3 and 10%, respectively, due to the errors in the rotational–vibrational coupling constant $\alpha_2$ and the anharmonicity constant $\omega_4 e_4$.

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 $D_j$ (average error of 5.9%). We have also expanded the [2, 2] PA in powers of $R^{-1}$ and calculated the coefficient $c_i$ of this expansion. The correct value of $c_i$ is $e_i^c$ (118.140 for energies in cm$^{-1}$, distances in Å). Again, considering only the three leading coefficients from the expansion about the equilibrium point are used, the fact that the average error in $c_i$ is 12 percent (see Table II) is impressive.

It would be highly advantageous to study the [3, 3] PA utilizing $a_2$ and $a_4$. Our experience with PA's on series expansions on analytic model potentials, 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 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 $a_2$'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 $a_2$ coefficient in a PA we found that even a 1% uncertainty in $a_2$ could result in a PA whose extrapolation to infinite internuclear separation would give a less reliable $D_j$ than the simpler [2, 2] PA. In fact another order of accuracy in the $a_2$ values would greatly facilit-

### Table II. Dissociation energies $c_i$.

<table>
<thead>
<tr>
<th>Experimental</th>
<th>$D_j$(cm$^{-1}$)</th>
<th>$[2, 2]$ PA Est. of $D_j$(cm$^{-1}$)</th>
<th>$C_i^e$ estimated from [2, 2] PA (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>64 070 (±1100)</td>
<td>64 492</td>
<td>135 299</td>
</tr>
<tr>
<td>LiCl</td>
<td>53 990 (±1200)</td>
<td>52 531</td>
<td>140 150</td>
</tr>
<tr>
<td>LiBr</td>
<td>51 680 (±1150)</td>
<td>49 393</td>
<td>106 302</td>
</tr>
<tr>
<td>Li</td>
<td>48 250 (±570)</td>
<td>45 641</td>
<td>112 446</td>
</tr>
<tr>
<td>NaF</td>
<td>55 020 (±650)</td>
<td>53 619</td>
<td>86 572</td>
</tr>
<tr>
<td>NaCl</td>
<td>46 510 (±400)</td>
<td>45 291</td>
<td>123 692</td>
</tr>
<tr>
<td>NaBr</td>
<td>44 750 (±500)</td>
<td>43 053</td>
<td>143 286</td>
</tr>
<tr>
<td>NaI</td>
<td>41 510 (±600)</td>
<td>40 255</td>
<td>115 975</td>
</tr>
<tr>
<td>KF</td>
<td>48 360 (±700)</td>
<td>46 334</td>
<td>99 120</td>
</tr>
<tr>
<td>KCl</td>
<td>42 250 (±250)</td>
<td>40 430</td>
<td>109 402</td>
</tr>
<tr>
<td>KBr</td>
<td>39 060 (±500)</td>
<td>38 436</td>
<td>104 607</td>
</tr>
<tr>
<td>KI</td>
<td>37 200 (±400)</td>
<td>35 953</td>
<td>105 748</td>
</tr>
<tr>
<td>RbF</td>
<td>46 840 (±1250)</td>
<td>44 830</td>
<td>111 559</td>
</tr>
<tr>
<td>RbCl</td>
<td>40 220 (±770)</td>
<td>38 996</td>
<td>99 359</td>
</tr>
<tr>
<td>RbBr</td>
<td>38 470 (±800)</td>
<td>38 550</td>
<td>106 601</td>
</tr>
<tr>
<td>Rbl</td>
<td>36 360 (±700)</td>
<td>36 496</td>
<td>96 878</td>
</tr>
<tr>
<td>CsF</td>
<td>46 020 (±900)</td>
<td>46 056</td>
<td>95 813</td>
</tr>
<tr>
<td>CsCl</td>
<td>39 020 (±800)</td>
<td>38 842</td>
<td>92 912</td>
</tr>
<tr>
<td>CsBr</td>
<td>38 160 (±900)</td>
<td>38 070</td>
<td>110 959</td>
</tr>
<tr>
<td>CsI</td>
<td>35 020 (±980)</td>
<td>33 540</td>
<td>97 712</td>
</tr>
</tbody>
</table>


*b Results of Bruner and Karplus, Ref. 6. These truncated Rittner $D_j$'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 $D_j$ due to the uncertainties in $a_0$, $a_1$, $a_2$, $a_4$ uncertainties causing most of the spread.

+d Correct value of $e_i^c = e_1^c + 116 141$ cm$^{-1}$ Å.

The average error in the $D_j$'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 $D_j$ is 2.9 and 3.5%, respectively.  

J. Chem. Phys., Vol. 61, No. 3, 1 August 1974

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TABLE III. Percent uncertainties in Dunham coefficients.

<table>
<thead>
<tr>
<th></th>
<th>a₀</th>
<th>a₁</th>
<th>a₂</th>
<th>a₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>0.05</td>
<td>0.02</td>
<td>0.35</td>
<td>1.97</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.02</td>
<td>0.01</td>
<td>0.40</td>
<td>1.78</td>
</tr>
<tr>
<td>KF</td>
<td>0.11</td>
<td>0.04</td>
<td>3.65</td>
<td>22.04</td>
</tr>
<tr>
<td>KCl</td>
<td>0.09</td>
<td>0.07</td>
<td>0.54</td>
<td>5.60</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.12</td>
<td>0.05</td>
<td>1.74</td>
<td>9.33</td>
</tr>
<tr>
<td>RbI</td>
<td>0.05</td>
<td>0.05</td>
<td>2.01</td>
<td>14.96</td>
</tr>
</tbody>
</table>

The precision was obtained from the same spectroscopic data and to see that the [2, 2] PA gives a Dᵣ 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 Dᵣ only 9% too high. However due to the much greater uncertainty in most of the aᵢ than in the a₀, a₁, a₂, a₃, this approximation may not always lead to an improved curve for large R. For example the [2, 2] PA for KCl gave a Dᵣ 6.4% too high while Eq. (27) gave a result 11.9% too low.

IV. TWO POINT PADING APPROXIMANTS

Two point PA's 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:

$$U(R)=D_{1} \sum_{\pi} C_{\pi} R^{-\pi}$$  \hspace{1cm} (28)

Where c₁ = e², c₂ = c₃ = 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] PA can be obtained with no spectroscopic constants except a₀ and a₁. If a₁, a₂, a₃, and D₁ are accurately known, determination of the coefficients of Eq. (7) gives

$$d_0 = a_0$$  \hspace{1cm} (29)

$$d_1 = (a_2 + a_3^2 - 2a_1 a_2)/(a_1^2 - a_2 - a_3 D_1^{-1})$$  \hspace{1cm} (30)

Unlike the Dunham expansion the Uₘₚ series extrapolates to a constant. However the PA is in general, as discussed by Baker, 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 Nth order) behave properly as R → ∞, since y → 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 y 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 Uₘₚ potential is

$$Uₘₚ = (142889.4) y^2 [1 - 1.24629 y + 0.14499 y^2 + 1.0795 y^3 + ⋯]$$  \hspace{1cm} (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 a₀, a₁, and a₂. It is seen that the [2, 2] PA affords considerable improvement.

In those cases in which a₁ through a₃ are accurately known but no reliable value for a₄ is available one may now proceed via the [3, 2] PA on the Uₘₚ series.

$$[3, 2] = a_1 y^2 [1 - b_1 y + (b_1^2 - b_2) y^2 + (2b_3 - b_1^2 - b_1 y^2)]$$  \hspace{1cm} (27)

The [3, 2] PA on the Dunham series would tend to zero as R → ∞. In the case of LiF the R → ∞ (y → 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 aᵢ than in the a₀, a₁, a₂, a₃, this approximation may not always lead to an improved curve for large R. For example the [2, 2] PA for KCl gave a Dᵣ 6.4% too high while Eq. (27) gave a result 11.9% too low.

FIG. 1. Curves constructed from a₀, a₁, a₂ for KI. Solid line, [2, 2] PA; dashed line a₀ y² [1 + a₁ y + a₂ y²], dotted lines Uₘₚ.
This is expected to provide a very good representation of the potential curve. Higher-order PA's may also be constructed. For example we have considered the [4, 4] PA utilizing \( a_0, a_1, a_2, D_1, c_1 \), 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 \( \xi \) real and positive. However, some of the point \([3, 3]\) PA's have a spurious pole for \( \xi > 0 \).

In Fig. 2 we plot for KI the Rittner, the \([2, 2]\) PA and the \([2, 2]Dl\) 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 \([2, 2]\) 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 inversion of the Dunham series

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

where the first few conversion formulas between the \( a_i \) and \( h_i \) are

\[ a_1 = -2h_1 \] (35)

\[ a_2 = -2h_2 + 5h_1^2 \] (36)

\[ a_3 = -2h_3 + 12h_2h_1 - 14h_3 \] (37)

\[ a_4 = -2h_4 + 7(2h_3h_2 + h_3^2) - 56h_2^2h_1 + 42h_4 \] (38)

Equation (34), unlike the Dunham series, is not limited to convergence only near \( \xi = 0 \). In fact, Jarmain 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 and Hurley proved the equivalence up to the dissociation limit. If Eq. (34) is truncated at the \( U^{3/2} \) term, the following approximation to \( \xi \) is obtained

\[ \xi = (U/a_0)^{1/2} [1 \pm h_1(U/a_0)^{1/3}] + h_2(U/a_0) \] (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 \([2, 2]\) PA seems to provide a much more reasonable potential curve. Inspection of Eq. (40) reveals that \( U \rightarrow \infty \) as \( R \rightarrow \infty \). 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. 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.

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 and comparing the results with the experimental ones in order to resolve this problem.

Earlier we mentioned that due to the \( R^{5/2} \) asymptotic behavior of covalently bonded molecules, the \([2, 2]\) PA will not provide as useful a description of covalent mole-

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*J. Chem. Phys., Vol. 61, No. 3, 1 August 1974*
ultrafor the diabatic ground state curves of ionic
coulomb molecules as for the diabatic ground state curves of ionic
quantum mechanical calculations demonstrate that the
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molecules. In fact,
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molecules one must consider the mixing of various ex­
cited determinational wavefunctions with the Hartree--Fock
ground state.

The recent pseudopotential calculations on various
alkali halides by Redmon and Micha also indicate that
for R < R_e (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 sev­
eral other classes of halides including those of copper,
indium, silver, aluminum, thallium, and gallium also
have been performed and the results are promising. Preliminary studies have also indicated the utility of
PA's in the study of metallic hydrides and oxides.

ACKNOWLEDGMENT

The authors are grateful to Professor J. Gole for
helpful discussions.

*Work supported in part by grants from the National Science
Foundation.

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