Chapter 3 Energy Levels of a Diatomic near Dissociation

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1 Introduction

2 A User's Guide to the Theory of Long-range Intermolecular Forces
   - General
   - Inverse-power Contributions to the Long-range Potential
   - Validity of the Inverse-power Expansion

3 Distribution of Vibrational Levels near Dissociation
   - Background: Birge–Sponer Plots
   - Derivation and Analysis of the Method
   - For a General \( R^{-n} \) Tailed Potential, ignoring Rotation (\( J = 0 \))
   - Rotation-dependent (\( J \neq 0 \)) Level Density for \( R^{-4} \) Potentials
   - Utilization of the Method
   - Distribution of Levels of Simple Model Potentials
   - For Spectroscopic Analyses: Methodology
   - Results of Spectroscopic Analyses

4 Behaviour of the Rotational Constant \( B_r \) for Levels near Dissociation
   - Background
   - Derivation and Analysis of the \( B_r \) Functionality
   - Utilization of the \( B_r \) Expressions
   - Spectroscopic Applications: Predictions of Unobserved \( B_r \) Values
   - Distribution of Vibrational–Rotational Levels near \( D \)

5 Rotational Predissociation and Long-range Potentials
   - Background: The Limiting Curve of Dissociation (LCD)
   - Bernstein's 'Locus of Barrier Maxima' (LBM):
   - Derivation and Analysis
   - Applications of the LBM Expression: Results and Non-results

6 Analysis of Long-range RKR Turning Points
   - Background: Calculating RKR Potentials near Dissociation
   - Graphical Methods
   - Results of RKR Analyses

7 Concluding Remarks
molecular spectroscopy has been its explanation of the motion of the nuclei in diatomic molecules. In 1926, immediately after the publication of Schrödinger’s differential equation formulation of the quantum theory, Fues derived expressions for the energy levels of a diatomic which had the correct dependence on positive powers of \((v+\frac{1}{2})\) and \(J(J+1)\), where \(v\) and \(J\) are, respectively, the (non-negative integer) vibrational and rotational quantum numbers. The following year Born and Oppenheimer showed how to separate the motions of the electrons and nuclei in Schrödinger’s equation, yielding a formal basis for that most ubiquitous concept, the internuclear potential-energy function. From this point on, much of molecular spectroscopy has been concerned with the rationalization of experimentally observed frequencies and intensities as rigorously calculable manifestations of such potential curves. For a long time the intensities resisted analytic treatment and were either discussed qualitatively in terms of the Franck-Condon principle, or examined using exact numerically calculated wavefunctions. However, expressions for matrix elements coupling different vibrational-rotational levels in the lower part of a potential well have recently been obtained as explicit functions of the potential parameters.

The frequencies of transitions involving the lower vibrational-rotational levels have long been understood as quantitative reflections of the nature of the potential near its minimum. From the late 1920s until fairly recently, the determination of an internuclear potential from an energy-level spectrum often involved the use of simple 3- or 5-parameter model potentials for which analytic expressions relate the level energies to the parameters. For a few cases, such as the harmonic oscillator and Morse functions, these expressions give the exact eigenvalues. More often though, they involve approximations which limit their accuracy except near the potential minimum (e.g. for the Lennard-Jones, Hulbert-Hirschfelder, and exponential—6 functions). For a wide selection of such forms, comparisons have been made of both

\[ V(R) = a_0 \left( \frac{R-R_s}{R_c} \right)^2 \left[ 1 + a_1 \left( \frac{R-R_s}{R_c} \right) + a_2 \left( \frac{R-R_s}{R_c} \right)^2 + \cdots \right] \]

the second-order WKB approximation gives the eigenvalues

\[ G(v,J) = \sum_{\ell,m} Y_{\ell m} (v+\frac{1}{2}) \left[ J(J+1) \right]^{\ell \mu} \]

where the \(Y_{\ell m}\) coefficients are explicitly related to the potential constants \(a_i\). However, expression (1) diverges at large \(R\) values instead of asymptotically approaching a dissociation limit, and hence this approach is not acceptable near the top of the potential well.

Another WKB-based procedure, one which is accurate over the whole attractive potential well, is the RKR method. Utilizations of this approach for levels near the dissociation limit will be discussed in Section 6.

Considerable attention has been paid recently to the more limited objective of predicting merely the total number of levels bound by a potential, and its dependence on the rotational quantum number \(J\) and \(R\). Obvious applications

\[ \text{J. L. Dunham, Phys. Rev., 1932, 41, 713, 721; J. E. Kirkpatrick, J. Chem. Phys., 1959, 30, 801, later showed that Dunham’s eigenvalue expansion equation (2) could be obtained by treating the potential of equation (1) as a perturbed harmonic oscillator.} \]


\[ \text{H. Harrison and R. B. Bernstein, J. Chem. Phys., 1963, 38, 2135, erratum 1967, 47, 1884; the corrected tables described in the latter were used here.} \]

\[ \text{F. Calogero and G. Cosenza, Nuovo Cimento, 1966, A45, 867.} \]
of such results are in estimating the equilibrium constant for dimer formation or the bound-state contribution to the second virial coefficient, since at temperatures which are large relative to the molecular binding energy the internal partition function for the dimer is simply the total number of bound levels. Although such results are less general than those sought below, they will yield useful points of comparison with some of the present methods.

In the following, the question of the nature of the distribution of vibrational-rotational levels near dissociation and its dependence on the long-range interaction potential is examined from four points of view. All make use of the asymptotic theoretical inverse-power expansion for interatomic potentials, and hence this material is briefly reviewed in Section 2. Although three of the four methods are based on the semi-classical WKB approximation, each is uniquely characterized by the type and extent of the experimental information required for its application. Hence, their order of presentation is based on the increasing sophistication of the requisite data.

2 A Users' Guide to the Theory of Long-range Intermolecular Forces

General.—Although much of the present theory of long-range intermolecular forces was developed during the early days of quantum mechanics, the past few years have seen a resurgence of activity in this field. The present section will summarize those parts of the current conventional wisdom which bear on the discussion in the rest of the chapter.

It has long been known that if two atoms are sufficiently far apart that their electron clouds overlap negligibly, their interaction energy may be expanded as (ignoring electronic degeneracy and fine-structure effects):

\[ V(R) = D - \sum_{n=4}^{\infty} C_n/R^n \]

where \( D \) is the dissociation limit, the powers \( m \) have positive integer values, and perturbation theory yields formal expressions for the constants \( C_n \).

The nature of the atoms to which a given molecular state dissociates determines which terms contribute to equation (3), and also sometimes defines their sign. Only the first- and second-order perturbation energies are considered here; the former can yield terms with \( m > 1 \), and the latter even-power terms with \( m > 2 \). The contributions from third- and higher-order perturbations correspond to \( m > n + 2 \), and hence they would tend to represent a large fraction of \( V(R) \) only at small distances where equation (3) is no longer valid (see discussion on p. 119).

If the leading terms in equation (3) all have the same sign, the interaction potential in any subinterval of the long-range region may be accurately approximated by

\[ V(R) \approx D - C_n/R^n \]

where \( n \) is some weighted average (in general non-integer) of the powers of the locally important terms. Asymptotically this \( n = \bar{n} \), the (integer) power of the leading term in equation (3); then as \( R \) decreases, i.e. the magnitude of \( V(R) \) increases, this 'local' \( n \) will gradually increase owing to the growing relative strength of terms with \( m > \bar{n} \). It will be seen that a theoretical knowledge of the asymptotic power \( \bar{n} \) greatly facilitates utilization of the methods of Sections 3–6. Unless explicitly stated otherwise, the discussion here will always assume that all significant contributions to equation (3) are attractive, and hence that \( n \) behaves as described above.

Inverse-power Contributions to the Long-range Potential.—The coulombic \( m = 1 \) term in equation (3) will be present only if both atoms are charged. For this case the coefficient \( C_1 = -Z_A Z_B e^2 \), where \( Z_A e \) and \( Z_B e \) are the charges on atoms A and B, respectively.

The \( m = 2 \) term would arise classically in the interaction between a dipole moment and an ion. Although no atom has a permanent dipole moment, an electronically excited one-electron atom (e.g. excited H, He+, or Li++) perturbed by the presence of another particle will sometimes behave as if it does. This can occur when eigenstates with different orbital angular momentum quantum numbers but the same principal quantum number are degenerate. The presence of the perturber can then cause a mixing of these states of different symmetry to yield a hybrid atomic orbital which is effectively dipolar. This resulting state will then interact as if it had a permanent dipole, and if its interacting partner is an ion, it will give rise to an \( m = 2 \) contribution to equation (3).

The \( m = 3 \) term in equation (3) classically corresponds to the interaction between a pair of dipoles. Thus, as discussed above, it would arise in the interaction between a pair of electronically excited one-electron atoms,
each of which is in a hybrid dipolar state. On the other hand, this \( m = 3 \) term can also arise as a 'resonance' interaction between a pair of atoms of the same species which are in electronic states between which electric dipole transitions are allowed. In practice this means that the total angular momenta of the atomic states must differ by one (S and P, P and D, ... etc.). In this case the sign of the \( C_4 \) coefficient is determined by the symmetry properties of the particular molecular state; for the interactions between an \( S \)- and a \( P \)-state atom, results are given in ref. 29.

The \( m = 4 \) term in equation (3) mainly arises as the second-order charge induced-dipole interaction between an ion and a neutral charge distribution. In this case \( C_4 = (Z \varepsilon \alpha a_0/2) \) where \( Z \varepsilon \) is the ionic charge and \( \alpha \) the polarizability of the neutral atom. Another situation which may also give an \( m = 4 \) contribution to \( V(R) \) is the first-order interaction between an atom with a dipole moment (e.g. electronically excited hydrogen, see above) and one with a permanent quadrupole moment (e.g. ground-state B, Al, Ga, C, Si, O, S, F, Cl, Br, or I).

Except for particular cases in which the \( C_4 \) coefficient is precisely zero for reasons of symmetry, the \( m = 5 \) term will contribute to the long-range potential whenever neither of the atoms is in an \( S \) electronic state. It arises from the first-order quadrupole–quadrupole interaction, and accurate general expressions for it have long been known. In 1938 Knipp showed that a \( C_4 \) coefficient could be separated into an angular factor which depends only on the symmetry properties of the molecular electronic state formed by atoms A and B, times the product \( \langle r_x^2 \rangle \langle r_y^2 \rangle \), where \( \langle r_x^2 \rangle \) is the expectation value of the square of the electronic radius of the unoccupied valence shell of atom X. Knipp reported values of these angular factors for a number of cases, and Chang extended his tables considerably. Furthermore, relativistic Hartree–Fock–Slater calculations of the expectation values \( \langle r_x^2 \rangle \) have recently been reported for all orbitals of all ground-state atoms with nuclear charge between 2 and 126. Therefore, fairly reliable \( C_4 \) constants may be calculated for virtually all molecular states formed from ground-state atoms. On the other hand, the reported \( C_4 \) values of \( \langle r_x^2 \rangle \) will be lower bounds to those for excited states, so that \( C_4 \) values thus calculated for states formed from excited atoms will tend to be lower bounds to the true values.

The \( m = 5 \) term described above can contribute to all interactions between non-\( S \)-state atoms. If the atoms are uncharged and have \((np)^\alpha \) valence configurations (i.e. \( \mu \) electrons in an unoccupied \( p \) shell), this is the only non-vanishing non-resonant contribution to the first-order interaction. For atoms with \((nd)^\alpha \) configurations there will be in addition \( m = 7 \) and 9 contributions, while \((nf)^\alpha \) configurations will cause the appearance of yet higher-power terms in \( R^{-1} \).

Validit of the Inverse-power Expansion.—At very long range, where \( R \) is of the order of wavelengths characteristic of the allowed transitions of the interacting atoms, the form of a number of the terms in equation (3) begins to change owing to 'retardation' effects. For example, in this limit the \( R^{-4} \) dispersion terms begin to die off more quickly, asymptotically tending to \( R^{-5} \) dependence. However, such effects are in general negligible for \( R \leq 100 \text{ Å} \), and beyond this range the interaction potential is sufficiently weak that it has no significant effect on the level distribution.

At small \( R \) the increasing overlap of the electron clouds of the two atoms leads both to the addition of 'exchange' terms to the potential, and to the
increasing inappropriateness of equation (3) for describing the coulombic interaction. The exchange terms increase exponentially with decreasing $R$, and are attractive or repulsive depending on whether or not the state in question is chemically bound. In addition, the simple inverse-power terms in equation (3) are accurate only at moderate-to-long range, while they overestimate the 'true' coulombic interaction energies by increasingly large amounts at small $R$. This breakdown has been studied in detail for a number of hydrogen and helium systems.\textsuperscript{39–42} One fact clearly demonstrated was the asymptotic nature of expansion (3), which means that although the first terms may yield a fairly good estimate of $V(R)$, the sum to $m = \infty$ will always diverge. The results of refs. 39–42 also suggest that the term of inverse-power $m$ is no longer valid for $R \leq (2C_m)/C_n$.\textsuperscript{39–42}

It seems reasonable to associate the growth of the exchange term and the breakdown of equation (3) with the radii of the valence electron shells on atoms A and B,\textsuperscript{39} since both effects are due to electronic overlap. For the cases considered in refs. 39–42, the approximation of representing $V(R)$ by the sum of the first few terms in equation (3) breaks down unless

$$R > 2\left[ \langle r_A^2 \rangle + \langle r_B^2 \rangle \right]^\frac{1}{2}$$

(5)

This seems a reasonable rule for yielding a lower bound to the region of validity of equation (3). From analogous considerations, Stwalley\textsuperscript{43} suggested the less flexible (and often somewhat more severe) rule that equation (3) should not be used for $R < 5 \text{Å}$.

Another type of situation in which equation (3) becomes inappropriate is when there are interactions between different molecular states of the same symmetry. This can give rise to avoided curve crossings which manifest themselves as maxima or abrupt changes in the shape of a potential curve. There is no known form of a potential in a region where such interactions arise, and hence methods based on equations (3) and (4) must be used very circumspectly in cases where these effects can occur. Unless stated otherwise, it is assumed that this difficulty does not arise in any of the problems considered below.

3 Distribution of Vibrational Levels near Dissociation

Background: Birge–Sponer Plots.—For almost half a century the Birge–Sponer extrapolation procedure has been essentially the only method used for determining diatomic dissociation limits from experimental vibrational energies.\textsuperscript{44–47} It is based on the observation that the spacings between successively higher vibrational levels usually decrease monotonically as the levels approach the dissociation limit. Since level energies $G(v)$ are rarely observed all the way to dissociation, an extrapolation of some sort is required. Birge and Sponer\textsuperscript{44} suggested the use of a plot of the level spacing $\Delta G_{v+1} = [G(v+1) - G(v)]$ versus the vibrational quantum number $v$, such as that shown in Figure 1. The dissociation energy is then obtained by adding the

![Figure 1: Birge–Sponer plot of Brown's experimental vibrational spacing for $I_2 (B^3 \Xi_{v_0}^+)$](image)

energy of the highest observed level ($v_0$) to the area under the extrapolated curve between $v_0$ and the intercept. In practice this extrapolation has often been performed linearly, largely because of the lack of a more plausible alternative, but perhaps also because the vibrational spacings of the familiar Morse potential are precisely linear in $v$. Uncertainty as to the nature of the 'correct' extrapolation is reflected in the area under the extrapolated curve, as is illustrated by the shaded area in Figure 1. The lower limit there corresponds to a straight line through the last few points, the solid line to the intuitive extrapolation by the experimenter who made the measurement,\textsuperscript{48} and the upper limit to the 'true' extrapolation (see below).

In spite of its ambiguous nature, the Birge–Sponer procedure has undergone no real change in the past four and a half decades. Alternative extrapolation methods were suggested by Birge\textsuperscript{49} and Rydberg,\textsuperscript{19} but they were never widely used. Studies have also been made of the ways in which a linear Birge–Sponer approach breaks down for different classes of diatomics.\textsuperscript{44–46}

\begin{itemize}
  \item G. Herzberg, 'Spectra of Diatomic Molecules' Van Nostrand, Toronto, 1950.
  \item W. G. Brown, Phys. Rev. 1931, 38, 709.
\end{itemize}
but they were usually impaired by a lack of knowledge of the ‘natural’ functionality of the distribution of levels near dissociation. This deficiency is removed by the results described below.

Note that throughout this chapter the rotationless vibrational energy \( G(v, J = 0) \) is written as \( G(v) \), and the turning points (see Figure 2) as \( R_1(v) \equiv R_1(v, J = 0) \) and \( R_2(v) \equiv R_2(v, J = 0) \).

![Figure 2: Lower: eigenvalues and turning points for levels of a model LJ(12,6) potential; the dashed curve is the long-range attractive part of the potential. The bars (e.g., \( \bar{R} \)) indicate that energies and lengths are scaled relative to the well depth \( D \) and equilibrium distance \( R_e \), respectively. Upper: exact integrand of equation (7) for the four indicated vibrational eigenvalues; the dashed curve is the approximate \( v = 20 \) integrand obtained on replacing the exact \( V(R) \) by the long-range part. (Reproduced by permission from (J. Chem. Phys., 1970, 52, 3869))](image)

**Derivation and Analysis of the Method.**—For a General \( R^{-n} \) Tailed Potential, ignoring Rotation \((J = 0)\). The following presentation is largely based on the work of Le Roy and Bernstein.\(^{30,41}\) An alternate derivation of their fundamental result was later reported by Stwalley,\(^{42}\) but although his approach yields the correct functionality, it is less accurate than that described here. For the particular case of an \( R^{-4} \) long-range potential, Tani and Inokuti\(^{42}\) obtained a more general result which includes the dependence of the level density on the rotational quantum number \( J \); this is described later (p. 128).

Like Dunham’s method,\(^{41}\) the present approach is semi-classical in origin, being based on the first-order WKB quantum condition for the eigenvalues of a potential \( V(R) \):

\[
\nu + \frac{1}{2} = \frac{(2\mu)^{1/2}}{\pi \hbar} \int_{R_1(v)}^{R_2(v)} \frac{[G(v) - V(R)]^{1/2}}{R} \, dR
\]

where \( \mu \) is the nuclear reduced mass, and \( R_1(v) \) and \( R_2(v) \) are the classical turning points (see Figure 2) at which \( G(v) = V(R) \). The allowed eigenvalues are the energies \( G(v) \) corresponding to integer values of \( \nu \). Since we are concerned with the distribution of eigenvalues, it seems natural to differentiate equation (6) with respect to \( G(v) \) to obtain the density of levels:

\[
\frac{d\nu}{dG(v)} = \frac{(\mu/2)^{1/2}}{\pi \hbar} \int_{R_1(v)}^{R_2(v)} \frac{[G(v) - V(R)]^{-1/2}}{R} \, dR
\]

Figure 2 shows the integrand of equation (7) for four levels of a model Lennard-Jones \((12,6)\) potential.*\(^{43}\) \( V_{12}(R) = D[(R/R_e)^{12} - 2(R/R_e)^{6}] \). It is immediately clear that for the upper levels the dominant contributions to the integral in equation (7) come from the regions near the turning points where the integrand becomes singular. Furthermore, the anharmonicity of the potential makes the neighbourhood of the outer turning point by far the more important, and this weighting becomes increasingly pronounced as the levels approach dissociation. This suggests the fundamental approximation of replacing the actual potential \( V(R) \) with an expression which is accurate at the outer turning points and only approximate elsewhere. Our knowledge of the theoretical inverse power form of long-range potentials suggests the use of equation (4): \( V(R) = D - C/R^n \). For the \( v = 20 \) level of our \((n - 6)\) chosen LJ\((12,6)\) potential, the effect of replacing the actual \( V_{12}(R) \) by its attractive long-range part \( D[1 - 2(R/R_e)^{6}] \) is shown by the dashed curve in the lower half of Figure 2. In this case the substitution clearly has a negligible effect on the value of the integral in equation (7). A minor additional approximation is setting \( R_n(0) = 0 \); its main effect will be to cancel part of the error introduced by ignoring the \( R_n(0) \) singularity in the exact integrand of equation (7).

\* In the notation of Harrison and Bernstein\(^{47}\) the parameters of the chosen 24-level model potential correspond to \( D = 2\mu DR_e^2/\hbar^2 = 10000 \). The eigenvalues were calculated numerically\(^{48}\) and are accurate to \( 10^{-6} D \).

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Molecular Spectroscopy

Substituting equation (4) into equation (7), making a change of variables, and setting \( R(t) = 0 \) yields the desired result:⁶⁹

\[
\frac{dG(v)}{dv} = K_n[D - G(v)]^{m+2/2n} \tag{8}
\]

where the factor

\[
K_n = \frac{\overline{K}_n}{\mu^4(C_n)^{1/n}} = \frac{(2\pi)^{1/2}}{\mu^4(C_n)^{1/n}} \left[ \frac{n \Gamma \left(1 + \frac{1}{n}\right)}{\Gamma \left(\frac{3}{2} + \frac{1}{n}\right)} \right]^{1/2}
\]

and \( \Gamma(x) \) is the familiar gamma function.⁶² It is often more convenient to use the integrated form of equation (8), which for \( n \neq 2 \) is

\[
G(v) = D - [(v_{p} - v)H_n]^{2n/(n-2)} \tag{9}
\]

where \( H_n = ((n-2)/2m)K_n = \overline{H}_n/\mu^4(C_n)^{1/n} \), and \( v_{p} \) is an integration constant. For various values of \( n \), the numerical constants \( \overline{K}_n \) and \( \overline{H}_n \) are given in Table 1, together with values of analogous factors which arise in Sections 4 and 5.

### Table 1: Numerical factors from equations (8), (9), (32), (33), and (42) for various \( n \), assuming units of energy, length, and mass to be cm\(^{-1}\), Å, and amu, respectively

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \overline{K}_n )</th>
<th>( \overline{H}_n )</th>
<th>( \overline{P}_n )</th>
<th>( \overline{Q}_n )</th>
<th>( \overline{S}_n )</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>16.4234</td>
<td>-8.21171</td>
<td>( a )</td>
<td>( a )</td>
<td>( a )</td>
</tr>
<tr>
<td>2</td>
<td>25.7978</td>
<td>0.0</td>
<td>( a )</td>
<td>( a )</td>
<td>( a )</td>
</tr>
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<td>3</td>
<td>34.5429</td>
<td>5.75715</td>
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<td>60225.244</td>
<td>709.7684</td>
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<td>22.3544</td>
<td>136.330</td>
<td>18.2749</td>
</tr>
</tbody>
</table>

* These constants do not exist for \( n < 2 \).

For \( n > 2 \), \( v_{p} \) takes on physical significance as the effective (in general non-integer) vibrational index at the dissociation limit. On the other hand, for \( n < 2 \), \( v_{p} \) must be smaller than the index \( v \) of any of the allowed levels, and hence is negative. For the special case \( n = 2 \), integration of equation (8) yields

\[
D - G(v) = [D - G(v_{p})] \exp[-n\hbar(v - v_{p})/2\mu C_n] \tag{10}
\]

where \( v_{p} \) is an arbitrarily chosen reference level. Expression (10) is identical to the exact quantal result for a pure \( R^{-2} \) potential,⁶⁴ except for a small additive correction to the apparent \( C_n \) constant.⁶⁵ Results analogous to equations (8)—(10) have also been obtained⁶⁹ for exponential-tailed potentials, \( V(R) = D - Ae^{-\alpha R} \); however, this case is of less physical interest and is not discussed here.

A couple of useful expressions obtained from the derivatives of equation (9) are:

\[
\frac{dG(v)}{dv} = \left[ \left(\frac{2n}{n-2}\right)\left(\frac{\bar{H}_n}{(n-2)}\right)^{2n/(n-2)} \right] [v_{p} - v]^{2n/(n-2)} \tag{11}
\]

and⁷

\[
\frac{dG(v)}{dv} \bigg| \frac{d^2G(v)}{dv^2} = -(v_{p} - v) \left(\frac{n-2}{n+2}\right), \quad n \neq 2 \tag{12}
\]

Together with equation (8), equations (11) and (12) suggest that simple plots using derivatives obtained by interpolating over a set of energy levels should yield values of the physically interesting parameters \( n, v_{p}, \) and \( C_n \). Figure 3 shows the plot suggested by equation (12) for levels of the model \( \text{LJ}(12,6) \) potential discussed above; the highest bound levels clearly exhibit the expected \( n = 6 \) behaviour.

Equations (8) and (11) imply that Birge–Sponer plots of level spacings for the special case of \( n = 2 \), the right-hand side of equation (12) becomes \(-\mu C_n/2\hbar\)².

* For the special case of \( n = 2 \), the right-hand side of equation (12) becomes \(-\mu C_n/2\hbar\)².

same \( C_n \), and the same \( \mu \) was assumed in obtaining their vibrational spacings\(^*.\)

The reference curve A was obtained by substituting this \( C_n \) and \( \mu \) into equation (11), together with \( n = 6 \); it is the exact semi-classical result for the potential of equation (4) with \( n = 6 \). The convergence of the other curves to A for levels approaching \( \nu_n \) demonstrates the essential validity of expressions (8)—(10).

A more quantitative test of the present results can be made by fitting exact calculated eigenvalues of a chosen model potential to equation (9), and then comparing the resulting potential parameters with their known values. This has been done for both Lj(12,6)\(^{10}\) and Lj(12,3)\(^{12}\) potentials, for which \( n = 6 \) and 3, respectively. In both cases, least-squares fits of equation (9) to the levels lying closest to D yielded highly accurate results, whereas the addition of more deeply bound levels gradually increased the errors.

An important qualitative implication of equations (8)—(10) is their prediction of positive curvature for Birge–Sponer plots in the region near the dissociation limit where the outer branch of the potential is accurately described by equations (3) or (4). This result should be as universal as the inverse-power form of the attractive long-range potential. Apparent exceptions will occur for molecules with small reduced mass \( \mu \) whose level density is so low that no eigenvalues lie in the immediate neighbourhood of dissociation. For example, the outer turning points of the two highest vibrational levels of ground-state \( \text{He}_2 \) are 3.3 and 2.7 Å, distances much too small for the inverse-power expansion (3) to be appropriate. Thus, equations (8) and (9) are not valid for these levels, and it is not surprising that their Birge–Sponer plot shows increasingly negative curvature at D.\(^{16}\)

Although the region of validity of equations (8)—(12) necessarily reflects itself in positive curvature on a Birge–Sponer plot, observation of such curvature does not necessarily imply that use of these expressions is appropriate. A sufficient condition for the latter is that the outer turning points of the levels considered must lie in the long-range region where the attractive potential is accurately described by equation (3). This criterion appears somewhat nebulous since one is generally dealing only with experimental vibrational energies, and initially has no knowledge of the turning points. However, the parameters obtained on fitting equation (9) to experimental data yield an effective potential of the form of equation (4), and it may be examined retrospectively to determine whether use of this 'near-dissociation' method was justified.

For model potentials consisting of a repulsive part plus a single inverse-power attractive term, errors in equations (8) and (9) arise from approximations to the integral in equation (7) in the neighbourhood of \( R_0(\alpha) \) (see

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\* More generally, a mass-reduced version of Figure 4 which would be independent of the choice of \( \mu \) would plot \( \mu^{-\frac{1}{2}} \Delta G(\alpha) \) versus \( (2\nu_n - 3) \mu^{1/2} \). The \( \Delta G(\alpha) \) results for the \( \exp(\alpha,6) \) potentials were calculated\(^{14}\) from the semi-classical results of ref. 17, while the \( \Lambda(12,6) \) \( \Delta G(\alpha) \) curve (labelled D) was obtained from exact calculated \( \Delta G_{\text{exact}}(\alpha) \) values.

Energy Levels of a Diatomic near Dissociation

Note that the outer turning point $R_0(\nu, J)$ appearing in equation (13) and in the definition of $\Lambda$ is given by:

$$R_0(\nu, J) = \frac{\left[4C_1(D - G(\nu, J)) + [J(J+1)\hbar^2/(2\mu)]^4 - J(J+1)\hbar^2/2\mu \right]^{1/2}}{[2(D - G(\nu, J))]^{1/4}}$$

Equation (13) in general allows the hard core radius $R_1$ to be non-zero. However, an increase in $\eta$ from four to infinity [i.e., $R_1$ decreases from $R_0(\nu)/4$ to zero] affects values of $T(\eta, \Lambda)$ by less than $1\%$. Furthermore, the error introduced by setting $\eta = \infty$ ($R_1 = 0$) is in the opposite direction to, and for the $R^4$ model potentials of Figure 4 it is also smaller than, the error due to neglect of the singularity at $R_0(\nu)$ in the exact integrand of equation (7). Hence it is unlikely that setting $\eta = \infty$ will significantly weaken equation (13). The main effect will be to simplify $T(\eta, \Lambda)$, since $\eta = \infty$ implies $\varphi = \pi/2$, for which case the two incomplete elliptic integrals become the slightly more tractable complete elliptic integrals of the first and second kind.

It is very interesting to note that equation (13) is also valid at energies above the dissociation limit, but below the top of the centrifugal potential barrier. The elliptic integrals are continuous over this change from positive to negative $\Lambda$, and the $(-1)^J$ in the factor $(D - G(\nu, J))^J$ is cancelled by one in $(2 + \Lambda)^J$ as long as $\Lambda < -2$. This latter criterion points out the fact that $\Lambda = -2$ corresponds to the maximum of the centrifugal potential barrier for $J \neq 0$.

Equation (13) is clearly a generalization of equation (8) for $n = 4$ to cases where $J \neq 0$, and it is readily shown that the two expressions are identical in the limit $\eta = \infty$ and $J = 0$. Unfortunately, it does not appear to be possible to integrate equation (13) to obtain an expression for $G(\nu, J)$ as the corresponding analogue of equation (9). This fact, coupled with its relative complexity, effectively precludes the application of equation (13) to the type of spectroscopic analysis for which equations (8) and (9) are used below. However, in chemical applications of a knowledge of the density of levels, its explicit $J$-dependence makes equations (13) potentially much more useful than equations (8)–(10).

A generalization of equation (13) to the case of any inverse-power potential $C_1/R^3$ is obtained by a rather different route in Section 4. The discussion there shows that the principal source of error in both results arises from the neglect of all but the asymptotic term (here $R^4$) in the actual long-range potential of equation (3).

Utilization of the Method.——Distribution of Levels of Simple Model Potentials.

The following discussion is concerned with the distribution of vibrational levels in simple model potentials consisting of a repulsive part plus a single inverse-power attractive term. Those explicitly considered are the generalized $J_n(\alpha n)$ functions,

$$V_{1,2}(R) = \epsilon \left( \frac{n}{\alpha - n} \left( \frac{R_0}{R} \right)^n - \frac{\alpha}{\alpha - n} \left( \frac{R_0}{R} \right)^{\alpha} \right)$$

---

**Footnotes:**

1. Throughout, the $J$-dependence of the centrifugal potential, level energies, etc., is written in terms of $(J + 1)$ rather than the $(J + 1)^4$ which Langer showed was appropriate for semi-classical analyses using equation (6). For realistic systems, effects associated with the Langer correction are small and, in any case, results obtained herein may be corrected by simply replacing $(J + 1)^4$ by $(J + 1)$.

the analogous \( \exp(a,n) \) potentials,
\[
V_{\exp}(R) = \varepsilon \left( \frac{n}{a-n} \right) \exp \left[ -a \left( \frac{R - R_e}{R_e} \right) \right] - \left( \frac{a}{a-n} \right) \left( \frac{R_e}{R} \right)^n
\]  \( \quad (15) \)
and the Sutherland potential which arises from both equations (14) and (15) in the limit \( \alpha \to \infty \),
\[
V_s(R) = -\varepsilon (R_s/R) \quad \text{for } R > R_s,
\]
\[
= \infty \quad \text{for } R < R_s
\]  \( \quad (16) \)
In each of the above, \( \varepsilon \) is the well depth, \( R_e \) the equilibrium distance, and \( a \) and \( \alpha \) are constants (in general non-integer) such that \( \alpha > n > 0 \). For all three types of functions, the long-range potential coefficient is given by the same expression:
\[
C_n = \alpha(R_s)^n[a/(a-n)]
\]  \( \quad (17) \)
and hence within the context of equation (9) these potentials are precisely equivalent.

Figure 4 shows that equation (9) accurately describes the distribution of levels near the dissociation limits of model Lj(12,6) and \( \exp(a,n) \) potentials, although it becomes an increasingly poor approximation with increasing binding energy and decreasing \( \alpha \). These observations are readily understood in terms of the two types of error inherent in the derivation of equation (9) for these simple potentials. On the one hand, the approximation of replacing the actual \( V(R) \) by equation (4) tends to underestimate the integral in equation (7) by ignoring the area under the singularity at \( R_0(\alpha) \) (see Figure 2); on the other, replacing \( R_0(\alpha) \) by zero tends to overestimate this integral by spuriously adding the area under the approximate integrand between \( R_0(\alpha) \) and zero.* The fact that the exact model-potential results in Figure 4 all lie below the reference curve A obtained from equation (11) shows that in these examples the first type of error is dominant. However, in the \( \alpha \to \infty \) limit where equations (14) and (15) become equation (16), the first kind of error completely disappears and the actual \( D\alpha(\phi) \) curve will tend to lie above that calculated from equation (9). These observations are in agreement with the upward trend with \( \alpha \) of the \( D\alpha(\phi) \) curves for \( \exp(a,n) \) potentials, seen in Figure 4. Furthermore, they imply that for both equations (14) and (15) there will exist some intermediate \( \alpha(n) \) values for which the two types of errors roughly cancel. For these cases, equation (9) should describe the overall vibrational spacings with fairly good accuracy.

A more convenient model-potential form of equation (9) is obtained if we introduce Harrison and Bernstein's 17 dimensionless parameter
\[
\mathcal{B} = 2\mu\varepsilon(R_s)^2/\hbar^2
\]  \( \quad (18) \)
* Of course, for real molecules several terms contribute to the attractive part of the potential, and the types of errors discussed here are negligible relative to the effect of the higher-power terms in equation (3) in the region near \( R_s(\alpha) \).

**Energy Levels of a Diatomic near Dissociation**

to characterize the potential. Substituting it and expression (17) into equation (9) yields:
\[
D - G(\phi) = \varepsilon((\nu_0 - \nu)/\mathcal{B}^2 a_{\lambda}(a,n))^m(\nu - \nu_0)
\]  \( \quad (19) \)
where
\[
a_{\lambda}(a,n) = [a/(a-n)]^{1/n}[\Gamma(\frac{1}{2} + \frac{1}{n})/\Gamma(\frac{1}{2} + \frac{1}{n})]f[2(n-2)\pi]^1.
\]
Since equation (19) is known to be accurate near \( D \) (see Figure 4), one can test its utility over the rest of the potential well by seeing whether it correctly predicts the total number of levels supported (i.e. the number lying within \( \varepsilon \) of \( D \)).

According to the WKB eigenvalue criterion equation (6), a (hypothetical) vibrational level lying at the potential minimum corresponds to \( \phi = \frac{\pi}{2} \), and hence \( [D - G(\phi)] = \varepsilon \). Substituting this relation into equation (19) then yields
\[
\nu_0 + \frac{1}{2} = a_{\lambda}(a,n)\mathcal{B}^2
\]  \( \quad (20) \)
as the present method's estimate of the number of levels lying between dissociation and the potential minimum. For \( Lj(a,n) \) potentials, an exact semi-classical analysis 81 yields an expression identical to equation (20), but with \( a_{\lambda}(a,n) \) replaced by
\[
a_{\lambda,\phi}(a,n) = \mu/\varepsilon(a+n)^2[\Gamma(\frac{1}{2} - \frac{1}{n})/\Gamma(\frac{1}{2} + \frac{1}{n})]f[2\pi(\alpha + n)]
\]
where \( \lambda \equiv (\alpha-2)/(\alpha-n) \). Thus equation (20) will predict the correct number of vibrational levels for those \( Lj(a,n) \) potentials for which \( a_{\lambda}(a,n) = a_{\lambda,\phi}(a,n) \), and equation (19) should yield a good description of the overall level spectra for these cases. For \( n = 3, 4, 5, \) and 6, respectively, \( a_{\lambda}(a,n)/a_{\lambda,\phi}(a,n) \) grows smoothly from 0.980, 0.961, 0.945, and 0.931 for \( a = n + 1 \), to 1.120, 1.198, 1.253, and 1.294 for \( \alpha = \infty \) and equals one at \( a = 8.580, 10.570, 12.563, \) and 14.557. Thus, equation (19) (or equation (9)) should provide a fairly good description of all the vibrational levels of \( Lj(8.580,3), Lj(10.570,4), Lj(12.563,5), \) and \( Lj(14.557,6) \) potentials. Similarly, Harrison and Bernstein's 17 numerical WKB results for \( \exp(a,n) \) potentials show that equation (19) will be most accurate for \( \exp(15,6,2) \) functions. It is also intriguing to note the similarity between the eigenvalue expression obtained for these cases by substituting equation (20) into equation (19):
\[
D - G(\phi) = \varepsilon((\nu_0 - \nu)/\mathcal{B}^2 + \frac{1}{2})^m(\nu - \nu_0)
\]  \( \quad (19a) \)
and the exact quantal eigenvalue expression for a Morse potential, 47
\[
D - G(\phi) = \varepsilon((\nu_0 - \nu)/\mathcal{B}^2 + \frac{1}{2})^m
\]
* Versions of this result for the special cases of \( Lj(12,6) \) and \( Lj(a,n) \) potentials had been reported earlier. 14-20 For \( Lj(14,6) \) potentials Mahan 42 also obtained a semi-classical analogue of equation (20) which is valid for all \( J \). At the appropriate \( a_{\lambda}(a,n) \) is identical to the coefficient of \( a^{10} \) in the exact quantum analogues of equation (20) for \( Lj(2n-2,4) \) and Sutherland potentials. 16, 17, 21
Of course in the latter, \( (v_0 + \frac{1}{2}) \equiv \beta \gamma R_n \), where \( \beta \) is the usual Morse exponential parameter.

Despite the disparaging comments in Section 1, it is often desirable to use simple two-term model potential functions such as equations (14)—(16) in test calculations of physical properties. In this context, equation (19) (or equation (19a)) may prove quite useful as an eigenvalue predictor in the numerical solution of the radial Schrödinger equation to determine exact vibrational eigenvalues and eigenfunctions. This application of the Le Roy–Bernstein expressions may proceed in a number of ways. The simplest approach is to simply substitute equation (20) into equation (19) to obtain

\[
D - G(\varepsilon) = e^1{(1 + (v + \frac{1}{2})/\gamma \alpha /2)} \gamma n_{\alpha}^2(n_{\alpha} - 1)
\]

and use the result equation (21) directly. However, this expression will be adequate for all vibrational levels only if equation (20) is fairly accurate in its own right, i.e. for potentials such as the Lj(14, 557, 6) and exp(15.6, 6) functions discussed above. On the other hand, Figure 4 demonstrates that equation (19) will almost always yield a fairly accurate estimate of the vibrational spacings. Thus, if one substitutes the exact calculated eigenvalue of any particular level \( G(v') \) into equation (19) to first obtain an effective local \( v_0 \) value, \( v_0(v') \), then the use of this constant in equation (19) should yield very accurate predictions of the relative energies of levels near \( v' \). This local \( v_0(v') \) may clearly be continuously adjusted as one moves up or down in the well.

For the particular case of an Lj(12, 6) potential, Cashion \(^{57}\) discussed the properties of eigenvalue predictors in some detail. He defined four criteria for an ideal scheme, all of which are reasonably well satisfied by the present approach. Cashion's \(^{57}\) Dunham expression for Lj(12, 6) potentials is certainly much more accurate than the present results, and it has the additional advantage of also being valid for \( J \neq 0 \). However, equations (19)—(21) may be applied to any potential with an inverse-power outer branch, while the restriction to \( J = 0 \) is not a serious problem since the spacing between levels \( \psi_J \) and \( \psi_{J+1} \) is virtually always accurately given by \( (J+1)(J)G(\psi_J) - G(\psi_{J+1}) \).

For Spectroscopic Analyses: Methodology. The present section will describe a few of the ways in which equation (8) and its corollaries may be used to rationalize experimental energy levels and to obtain values of \( D, n, C_n \), and \( v_0 \). Equations (8)—(10) describe the distribution of those vibrational levels lying sufficiently near dissociation that the potential at their outer turning points has the long-range inverse-power form of equation (4). In utilizing these expressions for spectroscopic analyses, one must know the energies and relative vibrational numbering of a few such levels. Nothing need be known about the number or distribution of any deeper levels, nor of the rotational properties of the levels under consideration. The latter fact allows the use of the unresolved band head measurements which are often the only data available for levels near dissociation, while errors in the absolute vibrational numbering will simply result in an integral shift of the parameter \( v_0 \).

There are a number of other, often readily available, facts about the system which can greatly facilitate a spectroscopic analysis based on equations (8)—(10). The simplest of these is the nature of the atoms which the given molecular state yields on dissociation. The discussion of Section 2 shows that this information will yield \( \tilde{n} \), the (lower bound) limiting value of the effective power \( n \) occurring in equations (4), (8), and (9). It also helps if the given molecular state is properly identified, since this information is usually a pre-requisite to the use of any theoretical knowledge of the \( C_n \) constant and sometimes also has a bearing on the value of \( \tilde{n} \). For example, although states formed from ground-state halogen atoms in general have \( \tilde{n} = 5 \), the \( C_n \) coefficient for the ground \( X^1 \Sigma^+ \) state happens to be precisely zero and hence in this particular case \( \tilde{n} = 6 \).\(^{59, 61}\) It will be seen below that a prior knowledge of \( D \) or \( C_n \) can further simplify the application of equations (8) and (9).

The most general way of applying the above results to real systems is simply to fit a set of experimental energies to equation (9) by least-squares to obtain values of the four parameters \( D, n, C_n \) and \( v_0 \).\(^{50, 61}\) If the levels considered lie sufficiently near dissociation, this fitted \( n \) will be very close to its (usually known) asymptotic value \( n \). In this case, fixing \( n \) exactly equal to \( \tilde{n} \) and repeating the fit while successively omitting the deepest observed levels from consideration should yield optimal values of \( D, C_n \), and \( v_0 \). The constants thus obtained may then be substituted into equation (9) and used to predict the energies of all bound levels lying above the highest one observed.

Figure 5 illustrates the dependence of such least-squares parameter values on the number of data used in the fit.\(^{48}\) The \( n \) values shown there were obtained from fits to equation (9) with all four parameters varying freely. In spite of the indicated statistical uncertainties, the effective local \( n \) for the uppermost \( S \)—\( 7 \) levels had clearly converged to its known asymptotic value \( n = 5 \). Therefore the fits were repeated with \( n \) fixed at 5 and only three free parameters, yielding the \( D, C_n \), and \( v_0 \) values shown in the lower part of Figure 5. Although the standard error of the fit decreases when fewer data are used (i.e. as \( v_n \rightarrow v_0 \)), the statistical confidence intervals on the parameters eventually begin to diverge. Thus, although the assumptions on which equations (8) and (9) are based are most accurate if only the four highest levels are considered, the parameter values for this case, corresponding to \( v_n = 28 \) in Figure 5, are probably less reliable than those corresponding to \( v_n = 25 \). \( ^{-27} \)

If the local \( n \) for the levels considered is not effectively equal to its asymptotic value, the fitted \( n \) and \( C_n \) will correspond only to an approximate local potential with the \( C_n \) having no theoretical significance. Similarly, the

---


parameter $v_p$ loses its physical significance and becomes merely an integration constant depending on $n$. However, the value obtained for $D$ should still be quite accurate. This assertion was tested for the same sample problem considered above [Cl$_2$ ($B^3Π_u^o$)]. The experimental energies were repeatedly fitted to equation (9) eight adjacent levels at a time, while the highest observed levels were successively omitted from consideration. Figure 6 shows the ‘local’ $D$ values so obtained, plotted vs. the energy of the highest vibrational level included in a given fit, $G(v_n)$. It is striking to note that even if no levels had been observed above $v = 20$, which lies some 244 cm$^{-1}$ below $D$, the fitted dissociation limit would have been a mere 5.5 cm$^{-1}$ in error! In contrast, a linear Birge-Sponer extrapolation from $v = 20$ yields an estimate of $D$ which is some 70 cm$^{-1}$ too low.

The general least-squares fitting approach discussed above is probably the best way of determining the parameters $D$, $C_4$, and $v_p$. However, simple graphical methods can often yield virtually indistinguishable results. Such methods presume a knowledge of the asymptotic power $n$ for the state in question, and also that some of the observed levels lie in the asymptotic $R^{-n}$ region. Furthermore, as long as it does not introduce significant error, considerable practical simplification is achieved by approximating derivatives by differences:  

$$dG(v+1)/dv \approx \Delta G_{v+1} = [G(v+1) - G(v)]$$  

$$dG(v)/dv \approx \Delta G_v = \{\Delta G_{v+1} + \Delta G_{v-1}\} = \{G(v+1) - G(v-1)\}$$  

Of course, the ensuing expressions become identical to equations (8) and (11) if derivatives obtained by numerical interpolations are used in place of these differences.

Substituting equation (23) into equation (8) and replacing $n$ with $\bar{n}$ yields  

$$(\Delta G_v)^{(\bar{n}/(\bar{n}+2)} = [D - G(v)](K_4)^{(\bar{n}/(\bar{n}+2)}$$  

An example of the type of plot suggested by equation (24) is shown in Figure 7; it is based on the same experimental data which yielded the Birge-Sponer plot in Figure 1 (for which case $\bar{n} = 5$). The straightforwardness
of the brief linear extrapolation here is a marked contrast to the uncertainty in Figure 1, the correct result in the latter corresponding to the upper edge of the shaded region. Substituting the D and C values obtained in this way into equation (9) together with experimental G(ν) values (and n = 4) will then yield the remaining parameter, υD.

The present method’s analogue of the Birge–Sponer plot is defined by the expression obtained on substituting equation (22) into equation (11) (with n = 4):

\[(ΔG_{ν+4})^{(4-3)/4} = (\nu_D - \nu - 1)\left(\frac{2\nu}{n-2}\right)(H_A)^{3/4}(Δ-3/4)^{(n-4)/4}
\]

(25)

For the same problem considered in Figures 1 and 7 [I_2 (B+Π^0_0+), for which n = 4], the plot suggested by equation (25) is shown in Figure 8. As in

Figure 8  Plot suggested by equation (25) for the highest observed levels of I_2 (B+Π^0_0+), for which n = 5; energies are in cm^{-1}. This is the Le Roy–Bernstein method’s analogue of the Birge–Sponer plot of Figure 1

Figure 7  Plot suggested by equation (24) for the highest observed levels of I_2 (B+Π^0_0+), for which n = 5; energies are in cm^{-1}. (Reproduced by permission from J. Mol. Spectroscopy, 1971, 37, 109)

Figure 9  Plot suggested by equation (26) for the highest observed levels of Cl_2 (B+Π^0_0+), for which n = 5; energies are in cm^{-1}. The value of D was taken from Table 2. (Reproduced by permission from J. Mol. Spectroscopy, 1971, 37, 109)

Another type of problem is one in which n and C_A (and hence H_A) are known, but D and υD are not. This is the case for the ground (X+Σ^+0) state of Ar_4 for which n = 6 and an accurate theoretical C_A has been calculated. Figure 10 shows (triangular points, right ordinate scale) the plot suggested by equation (25) with the true extrapolation (line T) being defined as a straight line through the highest point having a slope [3(H_A)^{3/4}] calculated from the known C_A. It differs markedly from the experimenters’ linear extrapolation (line E) of a Birge–Sponer plot (round points, left ordinate scale) based on the same data; curve C is the corrected Birge–Sponer extrapolation corresponding to line T. The binding energy of the highest observed level may then be determined by substituting the υD obtained as

\[D - G(ν)^{3/4} - \frac{3}{2}H_A = (υD - ν)H_A
\]

(26)

where, as in equations (24) and (25), the parameters occurring on the left-hand side are known. An example of the type of plot suggested by this expression is shown in Figure 9.


the intercept of line T into equation (9) together with the known \( n = 6 \) and \( C_8 \).

An alternative approach to a somewhat similar situation was that, applied by Stwalley to the \( B(\Sigma^+)^+ \) state of \( \text{H}_2 \), for which \( \tilde{n} = 3 \) and an accurate theoretical \( C_8 \) is known. In this case, the last few vibrational levels converged much too abruptly for equations (22) or (23) to be accurate, and hence equations (24) and (25) cannot be used. Instead Stwalley made plots based on equation (26) using several trial values of \( D \), the optimum value being that for which the limiting slope corresponded to the \( C_8 \) calculated from the known \( C_8 \). As is shown in Figure 11, this approach is also capable of yielding very precise values of \( D \) and \( v_0 \).

**Figure 11** \( \text{H}_2 (B \Sigma^+)^+ \) energy levels plotted according to equation (26), using three trial \( D \) values: points \( \bullet \) correspond to \( D = 118337.7 \), points \( \nabla \) to 118338.1, and points \( \triangle \) to 118337.3 cm\(^{-1}\). The slope \( C_8 \) of the solid line is calculated from the theoretically known \( C_8 \); energies are in cm\(^{-1}\).

(Reproduced by permission from *Chem. Phys. Letters*, 1970, 6, 241)
Results of Spectroscopic Analyses. At the present time the techniques described above have been applied to only a few systems; the results thus obtained are summarized in Table 2. In all of these cases the highest observed levels lie close enough to dissociation to depend on the theoretically-known asymptotic power \( \tilde{n} \), and hence physically significant values of \( C_n \) and \( \nu_0 \) were obtained together with accurate values of \( D \). This also allowed reliable predictions to be made for the energies of the \((\nu_0 - \nu)\) unobserved vibrational levels adjacent to \( D \), where \( \nu_0 \) is the integer obtained on truncating \( \nu_0 \); the number of such levels ranged from 3, for Ar\(_2\) and Cl\(_2\), to 15, for I\(_2\). Combining the accurate \( D \) values in Table 2 with known atomic energy level differences \(^{59}\) yields the improved ground-state dissociation energies \( D_0 \) given in Table 3. Equally good \( D \) values are similarly obtainable for all other electronic states of these species.

Table 3  Diatomic ground \((X^{1}\Sigma^+_g)\) state dissociation energies \( D_0 \) (in cm\(^{-1}\)) obtained from the results in Table 2

<table>
<thead>
<tr>
<th>Species</th>
<th>Le Roy–Bernstein method</th>
<th>Best previous value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>36118.6(±0.5)</td>
<td>36117.3(±1.0)(^*)</td>
</tr>
<tr>
<td>Ar(_2)</td>
<td>84.0(±3.5)</td>
<td>76.9(±1.9)</td>
</tr>
<tr>
<td>^8(^{19})Cl</td>
<td>19997.1(±0.14)</td>
<td>19999(±2)</td>
</tr>
<tr>
<td>^7(^{19})Br(^{19})Br</td>
<td>15894.5(±0.4)</td>
<td>15892.2(±0.5)</td>
</tr>
<tr>
<td>^8(^{18})Br(^{18})Br</td>
<td>15896.6(±0.5)</td>
<td>15893.9(±0.5)</td>
</tr>
<tr>
<td>^1(^{12})FI</td>
<td>12440.9(±1.2)</td>
<td>12432.5(±1.5)</td>
</tr>
</tbody>
</table>

\(^*\) Herzberg's best estimate was his upper bound, 36118.3 cm\(^{-1}\). \(^{64}\)

The impact of the present approach on the determination of dissociation limits is perhaps best illustrated by an examination of its effect on the apparent binding energy of the highest observed level, \( \nu_0 \). Table 4 compares the present values of \([D-G(\nu_0)]\) for the species in Table 2 with the estimates of the experimenters who originally measured the levels. Although neglect of the influence of the long-range potential can evidently lead to large relative errors, the magnitudes of the improvements shown in Table 4 are not very large on a chemical scale. However, Figures 6–9 show that the results obtained in some of these cases would not have been seriously affected if the highest 5–10 reported levels had in fact not been observed. Considerably greater error would almost certainly have arisen in analyses which ignored the characteristic near-dissociation behaviour represented by equations (8) and (9).

The experimental data for H\(_2\) \((B^{1}\Sigma^+_u)\) were analysed using the graphical approach discussed above and illustrated in Figure 11.\(^{64}\) The improved ground-state dissociation energy thus obtained (see Table 3) is particularly interesting in view of the conflict which had existed between experiment \(^{62}\) and the value of \( D_0 \) calculated from the accurate \textit{ab initio} potential of Kolos and Wolniewicz.\(^{80,81}\) Although Herzberg's new measurements \(^{64}\) of the photo-dissociation threshold resolved this discrepancy in favour of the theoretical value, Stwalley's analysis \(^{62}\) yielded a much more precise estimate of \( D \). Unfortunately his improved accuracy was partly compromised by experimental uncertainty in the absolute frequency, as is indicated by the difference between the uncertainty in Table 4 and those in Tables 2 and 3. An additional noteworthy point about the H\(_2\) analysis was the way in which the functionality of equation (9) or equation (25) was exploited in identifying and reassessing lines in the complex experimental spectrum.\(^{64}\) Similar techniques for making vibrational reassessments were also applied in ref. 51.

* Unless specified otherwise, the energy of a dissociation limit \( D \) is always expressed relative to the \( \nu = 0, J = 0 \) level of the ground electronic state of the particular isotopic species.

Table 4  Binding energy \([D-G(\nu_0)]\) (in cm\(^{-1}\)) of the highest observed level \( \nu_0 \) of each of the species considered in Table 2

<table>
<thead>
<tr>
<th>Species</th>
<th>( \nu_0 )</th>
<th>Obtained using Le Roy–Bernstein equations (8) and (9) Previous estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>1.3(±0.10)</td>
<td>a</td>
</tr>
<tr>
<td>Ar(_2)</td>
<td>12.1(±1.7)</td>
<td>5.4</td>
</tr>
<tr>
<td>^8(^{19})Cl</td>
<td>2.74(±0.14)</td>
<td>3.1(±2)</td>
</tr>
<tr>
<td>^7(^{19})Br(^{19})Br</td>
<td>5.24(±0.2)</td>
<td>2.7(±0.5)</td>
</tr>
<tr>
<td>^8(^{18})Br(^{18})Br</td>
<td>6.96(±0.3)</td>
<td>4.1(±0.5)</td>
</tr>
<tr>
<td>^1(^{12})FI</td>
<td>19.6(±1.2)</td>
<td>12.6</td>
</tr>
</tbody>
</table>

\(^*\) Comparison not appropriate; see ref. 52.

potential for this species \(^{47}\) and the 99.04 cm\(^{-1}\) obtained on correcting the vibrational amplitude of an earlier bulk property potential.\(^{48}\) These values are also in reasonable accord with the 102.2±2.0, 100.4, and 97.81 cm\(^{-1}\) obtained from molecular beam scattering measurements.\(^{49, 70}\)

For the last four cases in Table 2, the desired parameter values were obtained from least-squares fits of experimental energies to equation (9), with \(n\) held fixed at the known asymptotic value of \(\bar{n} = 5.50, 51\) Although \(C_4\) constants for the \(B\)-state halogens may be calculated quite readily, such values were not believed to be sufficiently reliable\(^{52}\) and hence these coefficients were treated as parameters to be fitted. The resulting experimental \(C_4\) values are seen in Table 2 to be in reasonable agreement with the corresponding theoretical estimates, but any significant remaining differences are attributed to the latter.

The results presented here for \(B(\Pi_{u}^\pi)\)-state \(Cl_2\) are slightly different from those given in refs. 50 and 51. The original analysis selected the optimum parameter values as those associated with \(v_B = 28\) in Figure 5, since this minimized the influence of deeply bound levels. However, it appears equally desirable to minimize the large statistical uncertainties associated with least-squares fits which have very few degrees of freedom. The results associated with \(v_B = 26\) in Figure 5 seem a likely compromise, and they are used in Tables 2–4. The concomitant changes in the predicted binding energies of the three unobserved levels are quite small, the new values being 1.00 (±0.09), 0.23 (±0.03), and 0.016 (±0.004) cm\(^{-1}\) for \(v = 32, 33,\) and 34, respectively.

Within the Born–Oppenheimer approximation,\(^{5} the internuclear potential energy of a given electronic state is precisely the same for all isotopic forms of a particular chemical species. Furthermore, although there are distinct \(D\) and \(v_B\) values for each isotope, the former merely differ by the differences in the ground-state zero-point energies, whereas the latter are (semiclassically) related through their respective reduced masses:

\[ m_B(i)^{\frac{1}{2}}(v_B(j)^{\frac{1}{2}} + 1) = [m(i)\mu(j)]^{\frac{1}{2}} \]

As a result, data for different isotopes in the same electronic state may be treated concurrently, rather than separately possibility since it reduces the number of free parameters. This feature was partially exploited in the analysis of experimental data for the \(^{18}\)Br\(^{18}\)Br and \(^{34}\)Br\(^{34}\)Br isotopes of \(B(\Pi_{u}^\pi)\) Br\(_2\).\(^{51}\)


As in the preceding case (Cl\(_2\)), the levels considered lay close enough to \(D\) that the effective \(n\) could be held fixed at \(\bar{n} = 5.5\). Barrow and Coxon\(^{71}\) recently found that the assumed vibrational numbering of the Br\(_2\) levels used in the analysis of ref. 51 should be reduced by one. Fortunately, the main effect on the published results is an integer decrease in the fitted \(v_B\) values (yielding those shown in Table 2), and a corresponding change in the numbering of the unobserved levels whose energies were predicted in Table 2 of ref. 51. Le Roy and Bernstein\(^{51}\) chose to rely on neither equation (27) nor the known\(^{76, 79}\) ground-state zero-point energy differences, but fitted the data utilizing five independent parameters (\(C_6\), two \(D\) values, and two \(v_B\) values) rather than three. Consequently, the statistical uncertainties for their Br\(_2\) results (in Tables 2–4)\(^{51}\) are considerably larger than the probable errors. This conclusion is attested to both by the very small discrepancy found on substituting the fitted \(v_B\) values into equation (27), and by the agreement between the predicted zero-point isotope shift of 2.05 (±0.12) cm\(^{-1}\) and the experimental value of 2.03 (±0.02) cm\(^{-1}\).\(^{78}\) It is further confirmed by the excellent agreement between the predicted energies of the \(v = 54–57\) levels of \(^{18}\)Br\(^{18}\)Br of ref. 51 and subsequent measurements of Barrow and Coxon,\(^{51}\) the ±0.01 cm\(^{-1}\) discrepancies being more than an order of magnitude smaller than the statistical uncertainties in the former.

The analysis of \(B\)-state \(I_2\) yielded\(^{61, 74}\) a new value for the ground-state dissociation energy which differed significantly (see Table 3) from that reported by Verma some years earlier.\(^{74}\) As Figure 7 indicates, a 12 cm\(^{-1}\) error in the present value is exceedingly unlikely. In addition, the present method points out an anomaly in the previous analysis which offers a good illustration of the often very compelling qualitative implications of equations (8) and (9). Verma’s\(^{59}\) value of \(D_0\) was based on the well-defined convergence of eighteen vibrational levels lying near the ground-state dissociation limit. Their vibrational spacings \(\Delta G_{v+1}\) were almost perfectly linear in \(v\), having a maximum possible curvature of ≤0.001 cm\(^{-1}\). On the other hand, substituting the known ground-state \(\bar{n} = 6\) and a plausible \(C_6 = 3 \times 10^6\) cm\(^{-1}\) \(\AA^6\) into equation (9) yields a limiting Birge–Sponer curvature of 6(\(H_2\))\(^2\) = 0.054 cm\(^{-1}\) for this case. This conflict, together with the above noted discrepancy in \(D_0\) values, led to a proposed reassignment of these eighteen levels to an excited \(O_2^+\) state correlating with the same dissociation limit as the ground state, but having a potential maximum at large \(R\).\(^{74}\) Although this reassessment is still debated,\(^{78}\) it is evident that the qualitative implications of equation (9) with regard to the shape of Birge–Sponer plots near dissociation also have a useful role to play in spectroscopic analyses.

Results such as those listed in Table 2 were also reported for ground-state
Molecular Spectroscopy

Energy Levels of a Diatomic near Dissociation

144

(\chi^1\Sigma^+_u) Cl\textsubscript{2}, for which \bar{n} = 6,\textsuperscript{41} however, they are now believed to be erroneous. In the first place, the fitted \(C_A\) predicts outer turning points of 3.1 and 2.5 \texttext{Å} for the two highest observed levels (bound by 92 and 287 cm\textsuperscript{-1}, respectively). These values are significantly larger than the minimum distance 4.1 \texttext{Å} corresponding to criterion (5), which implies that the use of equations (8) and (9) was invalid. In addition, this 'experimental' \(C_A\) is an order of magnitude smaller than one which Cummings\textsuperscript{37} calculated for this species. These results also cast doubt on the vibrational reassignment for this state proposed in ref. 51, and the reassignment labelled \((\textcal{A}, \textcal{A}')\) now appears more reasonable than the \((\textcal{B}, \textcal{B}')\) assignment adopted there. However, firm conclusions on this point should really await the observation of more levels in the near-dissociation region.

Discussion and Prognosis.—The methods described above provide a hierarchy of different ways of applying equation (8), the basic result of Le Roy and Bernstein,\textsuperscript{36} to experimental data. The approach most appropriate in any particular case depends on the nature of the data and our prior knowledge of the system under consideration. The greatest practical distinction is between the general least-squares fitting techniques and the linear graphical methods. The latter may only be used if the distribution of the levels in question effectively depends on the known limiting asymptotic power \(n = \bar{n}\). Where \(D\) is also known (as well as \(\bar{n}\)), one may readily determine the remaining parameters \(C_n\) and \(n_p\) using the type of plot suggested by equation (26) (e.g. see Figures 9 and 11). If \(D\) is not known, but the difference approximations [equations (22) and (23)] for the derivatives \(\frac{dG(\bar{n})}{\text{d}u}\) are known fairly accurately (and again, the effective \(n = \bar{n}\)), one may use plots of the type suggested by equations (24) and (25) (e.g. see Figures 7, 8, and 10) to obtain \(C_n\) and \(D\) or \(n_p\), respectively. If the approximations of equations (22) and (23) are not accurate, one could still utilize the latter types of plots after first determining derivatives \(\frac{dG(\bar{n})}{\text{d}u}\) by interpolating numerically over the observed energies. However, if numerical methods are to be introduced, one might as well turn to the general least-squares fitting techniques. Of course, if the parameter \(C_n\) is also known, it defines the slope in all these types of plots and greatly simplifies the determination of the intercept (e.g. see the discussion of Figures 10 and 11).

When the effective power \(n\) for the levels in question is not known or is not equal to \(\bar{n}\), the data are best treated by fitting them by least squares to equation (9). This approach may also be applied in any of the cases considered above and it will always yield the optimum results, since it does not make use of approximations such as equations (22) or (23).

These methods clearly provide accurate new ways of determining molecular dissociation energies and long-range potentials. In cases to which they have so far been applied, they appear to yield results as good as or better than any obtainable by other means.\textsuperscript{39–52, 40} In addition, the use of equation (9) to predict the number and energies of unobserved levels near \(D\) obviates the laborious procedure of repeatedly solving the Schrödinger equation to determine their eigenvalues. Another result which may be obtained from equation (9) if \(\bar{n}\) and \(C_n\) (and hence \(H_\bar{n}\)) are known is an upper bound \((H_\bar{n})^\text{max} = \bar{n} + 2\) for the binding energy of the highest bound level. This limit may prove very useful in cases where a lack of data precludes a determination of \(\text{VP}\).

A necessary step in the utilization of the present techniques is an examination of the question of whether or not equation (3) is valid at the outer turning points of the levels under consideration. If it is, one must further determine whether or not the local value of \(n\) for these levels is effectively equal to its asymptotic value \(\bar{n}\) for the given state. A test of the latter point for the \(\text{B}(\text{P}_4\text{A}_2)\) halogens\textsuperscript{77–79} uncovered a paradox which underlines the importance of an impending sequel to the present results.

The long-range internuclear potential for \(B\)-state \(\text{Cl}_2\), \(\text{Br}_2\), and \(I_2\) has the form

\[
\mathcal{V}(R) = D - C_4/R^6 - C_6/R^8 - C_8/R^{10} - \cdots
\]  

(28)

where the constants \(C_4\), \(C_6\), and \(C_8\) are all attractive (positive).\textsuperscript{77} The Table 2 parameter values for these species were obtained from least-squares fits of experimental data to equation (9) with \(n\) held fixed at its asymptotic value \(\bar{n} = 5\). For the highest observed levels of \(\text{Cl}_2\) and \(I_2\), least-squares fits to equation (9) verified this \(n = \bar{n} = 5\) behaviour, and the extrapolation of this result to \(\text{Br}_2\) is very soundly based on the chemical similarity of these molecules and the relative binding energies of the levels concerned.\textsuperscript{78, 81} On the other hand, analyses of the RKR potentials for these species (see Section 6) showed that the \(R^{-4}\) term in equation (28) also makes a substantial contribution to the potential at the outer turning points of these levels.\textsuperscript{77–79}

This apparent contradiction raises questions about the significance of the basic results equations (8) and (9). However, the validity of these expressions is attested to by the results of the model-potential analyses (e.g. see Figures 3 and 4), by the agreement between the theoretical and experimental \(C_n\) values in Table 2, and by the linearity seen in the plots of Figures 7–9. Further evidence in their favour is the virtually exact agreement between the new data\textsuperscript{77} for \(\text{Br}_2\) and the energy levels predicted in ref. 51, a result which certainly confirms the accuracy of the present \(D\) value for this molecule.

The apparent contradiction is evidently due to a cancellation of errors associated with the influence of equations (8) and (9) of higher-power terms in equation (3) with \(m = \bar{n}\). It has been found that the lowest-order correction to equation (9) arising from inverse-power contributions to equation (3) with \(m = n\) is precisely zero for \(m = n + 1\).\textsuperscript{89} In this case therefore, equations (8) and (9) with \(n = \bar{n}\) will be 'anomalously accurate' in that they will be valid far into the region where the \(R^{-(n+1)}\) term in the potential becomes significant.

79 R. J. Le Roy and F. E. Cummings, unpublished work.
81 R. J. Le Roy, to be published.
Thus, a conclusion that \( n \) in equations (8) and (9) 'is effectively equal to \( \tilde{n} \) does not necessarily carry over to the potential of equation (4) at the outer turning points of the levels considered. At the same time, this result does not affect the accuracy of the parameters \( D, C_n \), and \( \tilde{v} \) obtained in such a situation.\(^{81}\)

Except for the special case of \( n = 4 \) considered above (p. 128), the results described in this section were restricted to the rotationless \( J = 0 \) case. As a result, virtually all present applications of equations (8)—(10) have been concerned with spectroscopic analyses and predictions, and the determination of long-range potentials. In contrast, chemical applications of a knowledge of the density of states usually require it to be known for all \( J \). Although equation (13) provides an accurate result for the important case of \( R^{-4} \) tailed potentials, its analytic complexity will tend to inhibit its use. A slightly less accurate, but much more useful result, will be obtained below on combining equation (9) with an expression for the \( v \)-dependence of the rotational constant \( B_v \) near dissociation.

### 4 Behaviour of the Rotational Constant \( B_v \) for Levels near Dissociation

**Background.**—Understanding the nature of the rotational constant \( B_v \) for highly excited vibrational levels was long an unresolved problem in diatomic spectroscopy. For the lower vibrational levels, \( B_v \) values may clearly be expressed as

\[
B_v = \sum_{l \geq 0} Y_l \langle v + l | 0 \rangle \langle v | R^{-2} | 0 \rangle
\]

where the Dunham coefficients \( Y_l \) are defined in terms of the properties of the potential at its minimum.\(^{11}\) Furthermore, for all vibrational levels \( B_v \) depends on the expectation value of \( R^{-2} \).\(^{47, 81}\)

\[
B_v = \langle \hbar/4\pi c \rangle \langle \tilde{v}, 0 | R^{-2} | v, 0 \rangle
\]

(29)

However, until recently, no 'natural' behaviour was known for the region near the dissociation limit, other than the generally accepted conclusion that \( B_v \to 0 \) as \( G(0) \to D \).

Stwalley considered this question qualitatively in his analysis of the \( B \to \Lambda \) spectrum of \( H_2 \).\(^{48}\) He noted that for levels very near dissociation it is reasonable to associate the expectation value in equation (29) with \([R_2(\tilde{v})]^{-2}\), where \( R_2(\tilde{v}) \) is the classical outer turning point of level \((v,J = 0)\). Interpreting this conclusion in terms of the \( H_2 \) \((B \to \Lambda) \) long-range potential \((D - C_\Lambda/R^3)\) yield the functionality \( B_v \propto [D - G(0)]^{-3/2} \) for this \((n = 3)\) case.\(^{49}\) Extending Stwalley's approach to the general case of an \( R^{-n} \) tailed potential clearly yields:

actual $V(R)$ is replaced by an expression for its long-range part: $D = C_d/R^n$, and $R_k(v)$ is set equal to zero. For $n > 2$ this yields:

$$B_n = P_n(D - G(v))^{1/n}$$ (32)

where the constant

$$P_n = \frac{\hbar}{4\pi\alpha\mu_n} \left[ \frac{\Gamma\left(1 + \frac{1}{n}\right)}{\Gamma\left(\frac{1}{2} + \frac{1}{n}\right)} \right]^{1/n} (C_n)^{1/n}$$

Combining equation (32) with the vibrational energy expression equation (9) then yields the more useful formula

$$B_n = Q_n[(\nu_v - \nu)\nu_v^{(n-2)}]$$ (33)

where $Q_n = \overline{P}_n[\mu^2(C_n)^{1/n}V^{(n-2)}] = \overline{P}_n(H_{n-2})$, and $\nu_v$ and $H_n$ are as defined earlier (p. 124). The constants $P_n$ and $Q_n$ appearing above are collections of numerical factors, and values of them are given in Table 1.

Figure 12: Integrands of integrals in equation (31) for three levels of a model 24-level $LJ(12,6)$ potential; $k = 0$ corresponds to the integral in the numerator and $k = 2$ to that in the denominator. The dot-dash curve is the approximate $k = 0$, $s = 20$ integrand obtained on ignoring the repulsive $R^{-13}$ contribution to the potential. (Reproduced by permission from *Canad. J. Phys.*, 1972, 50, 953)

Expressions (32) and (33) are not valid for $n < 2$ because in this case the integral in the numerator of equation (31) diverges when $R_k(v)$ is replaced by zero. Although the more primitive result equation (30) would appear to be unaffected by this difficulty, it too becomes invalid for $n < 2$. The physical reason for the breakdown in both cases is that, for $n < 2$, the expectation value $\langle 0 | R^{n-1} | 0 \rangle$ is no longer dominated by contributions from the neighbourhood of the outer turning point. Note that the gamma-function factor in equation (32) which was absent in equation (30) is fairly large, its values ranging from 3.25 to 1.63 as $n$ increases from 3 to 6.

Figure 13: $B_n$ plots for the diverse model potentials considered in Figure 4; the reference curve, $A$, was calculated from equation (33).

Expressions (32) and (33) imply that for levels lying near dissociation where the approximation of replacing $V(R)$ by equation (4) $(D - C_d/R^n)$ is fairly good, $B_n$ values should depend only on the long-range part of the potential. In Figure 13 this is shown to be the case for $LJ(12,6)$ and $exp(\alpha,6)$ potentials with different well depths and equilibrium distances, but the same long-range tail. These model potentials are the same ones examined in Figure 4. The ‘true’ $B_n$ values in Figure 13 were obtained by interpolating over Harrison and Dernstein’s 17 numerical WKB integrals and substituting the results into equation (31), while the reference curve (A) was obtained from equation (33).

Figure 12 shows that the integrand in the immediate neighbourhood of $R_k(v)$ plays a somewhat less dominant role in the $k = 0$ integral in the numerator of equation (31) than it does in the $k = 2$ integral in the denominator of equation (31) and in equation (7). As a result, errors introduced by the approximations fundamental to the derivation of equations (8), (9), (32), and (33) should be relatively more serious for the latter. A comparison of Figures 4 and 13 demonstrates this fact; the divergence from the theoretical curve A with increasing $(\nu_v - \nu)$ is much more rapid in the $B_n$ plot. Of course the source of the error in these examples is quite different from that in real physical problems. As discussed earlier (p. 130), for simple two-term model...
potentials the error is associated with approximations to the integrands of equation (31) in the neighbourhood of $R_b (0)$. On the other hand, for real systems most of the error is due to the influence of the higher-power terms in the long-range potential (just as in the vibrational problem).

In applications to real molecules the consequence of the relatively lower accuracy of the $B_v$ expressions is that a value of $P_a$ or $Q_a$ calculated from a known $C_a$ will tend to be too large, or in other words, a $C_a$ obtained by fitting experimental $B_v$ values to equations (32) or (33) will be somewhat high. These effects are illustrated by the data for Cl$_2$ ($B ~ ^3Π_{0+}$) shown in Figure 14. According to equations (25) and (33), both plots are expected to be linear for levels near $D$. Although this is the case for the vibrational plot (upper half), it is clearly not true for $B_v$ data (lower half).

The fact that an empirical $P_a$ or $Q_a$ will tend to yield an upper bound to the true $C_a$ is demonstrated by the different slopes of the solid and dot-dashed lines in Figure 14 and is qualitatively demonstrated by the results in Table 5. The numbers in the last two columns of the latter were obtained by substituting the experimental $B_v$ for level $v$ into equations (32) or (33), respectively, together with $G(v')$ or $v'$ and the appropriate intercept $D$ or $v_D$ taken from Table 2. The differences among the various estimates of $C_a$ in Table 5 may be explained in terms of their dependence on the factor $P_a$, which effectively contains all the error in the $B_v$ expressions. It is readily seen that $C_a$ (32) [i.e., the estimate of $C_a$ obtained using equation (32)] varies as $(P_a)^{1/2}$, while $C_a(33)$ depends on $(P_a)^{1/2}$, and $C_a(8-9)$ has no $P_a$ dependence at all. This leads us to expect the observed ordering:

$$C_a(32) > C_a(33) > C_a(8-9) \approx C_a(true)$$

**Utilization of the $B_v$ Expressions.**—*Spectroscopic Applications: Prediction of Unobserved $B_v$ Values.* The preceding discussion has shown that parameter values $n$, $C_a$, $D$, and $v_D$ obtained by fitting experimental data to equations (32) and (33) will be less accurate than those obtainable from a vibrational analysis [based on equations (8) and (9)] of the same levels. Fortunately, whenever experimental $B_v$ values are available for levels near $D$ the corresponding vibrational energies $G(v,J = 0)$ will also be known, and hence the desired parameters may be extracted from the latter. As a result, the main spectroscopic role of equations (32) and (33) presently appears to lie in predicting $B_v$ values for levels near $D$ for which they have not been observed.

The expected limiting linearity of plots of $(B_v)^{1/2}$ versus $v$ has not been observed for any of the species considered in Section 3 (see Table 2). However, the foregoing discussion indicates that the achievement of this behaviour is probably an excessively exclusive criterion for the applicability of equation (33). The less restrictive requirement adopted here is that the vibrational energies of the highest observed level(s) must be accurately described by equation (9) with $n = n$. In other words, reliable values of $D$, $n$, $C_a$, and $v_D$ must be known for the state in question; this criterion is satisfied for all the species mentioned in Table 2.

Upper bounds to $B_v$ for levels near $D$ may be obtained from equation (33) using the known $n$ and $v_D$, and a $Q_a$ (theory) calculated from the known $C_a$. For B-state Cl$_n$, these upper bounds correspond to points at integer $v$ on the
Molecular Spectroscopy

For $n = 4$ and $J = 0$, it is readily shown that both equation (35) and its first derivative with respect to $\{J(J+1)\}$ are identical to the analogous quantities obtained from the Tani–Inokuti expression [equation (13)] (with $n = \infty$). This equivalence is expected since both were derived from the initial expression (6) using essentially the same approximations. In fact the only real difference between the exact semi-classical result [equation (13)] and the more approximate expression [equation (35)] is that the latter only takes account of a linear term in $J(J+1)$, whereas the former implicitly includes the exact $J$-dependence. On the other hand, equation (35) has advantages over equation (13) in that it is valid for all $n$ (rather than just $n = 4$), and because its analytic simplicity makes it much easier to use. In addition, there is no integrated form of equation (13) analogous to the simple eigenvalue expression [equation (34)].

For pure $R^\infty$ potentials, the main deficiency of the present results [equations (34) and (35)] is associated with the fact that they only take account of a linear term in $J(J+1)$ (see also footnote on p. 130). The effect of this approximation will now be examined by comparing expressions for the $J$-dependence of the total number of bound and quasi-bound levels obtained from equations (34) and (35), with corresponding exact quantal or semi-classical results.\(^{18-21}\)

Substituting $G(v,J) = D$ into equation (34) and using the definition of $Q_n$ and $H_n$ one obtains

$$G(v,J) = D = (J(J+1))^{1/2} = \left( \frac{P_n}{\sqrt[2]{n^2}} \right) \left( \frac{H_n}{\sqrt[2]{n^2}} \right)$$

where $v$ is the vibrational index (in general non-integral) of the level which lies at $D$ when the molecule has a rotational energy specified by $J$. The total number of bound levels is therefore

$$N(J) = N(0) - [J(J+1)]^{1/2}$$

where $N(0) = v_n + 1$ is the number of bound levels for $J = 0$. Values of $(P_n)/\sqrt[2]{n^2}$ are presented in Table 7, where they are seen to be in reasonable agreement with the analogous coefficients $(n-2)^{-1}$ which occur in both the exact quantal $N(J)$ expressions for $LJ(2n-2,n)$ potentials and in the exact semi-classical $N(J)$ for Sutherland potentials [equation (10)].\(^{11}\) The discrepancies range from 22% for $n = 3$ down to 3% for $n = 8$. Although additional terms in the Sutherland potential result\(^{21}\) reflect the present neglect of all but linear $[J(J+1)]$ contributions to equations (34) and (35), it is interesting to note that the linear term $[J(J+1)]^{1/2}(n-2)$ represents the total $J$-dependence of the exact quantal $LJ(2n-2,n)$ version of equation (36).\(^{10,11,21}\)

As with the Tani–Inokuti result [equation (13)],\(^{22}\) the present expressions [equations (34) and (35)] may also be used to describe the quasi-bound levels lying above the dissociation limit. The centrifugal barrier maximum is associated with the zero of $dG(v,J)/dv$. Hence equation (35) suggests that

<table>
<thead>
<tr>
<th>Species</th>
<th>$\tilde{n}$</th>
<th>$v_n^a$</th>
<th>$v^a$</th>
<th>$Q_n(v^a)^a$</th>
<th>$Q_n(\text{theory})^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ ($\Sigma^+\Sigma^+$)</td>
<td>3</td>
<td>43.26</td>
<td>37</td>
<td>$2.84 \times 10^{-4}$</td>
<td>$3.62 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ar$_2$ ($\Xi^\pm\Xi^\pm$)</td>
<td>6</td>
<td>8.27</td>
<td>e</td>
<td>$1.07 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>$^{35}$Cl$^{35}$Cl ($\Pi^\pm\Pi^\pm$)</td>
<td>5</td>
<td>34.82</td>
<td>31</td>
<td>$3.01 \times 10^{-3}$</td>
<td>$4.06 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{35}$Br$^{35}$Br ($\Pi^\pm\Pi^\pm$)</td>
<td>5</td>
<td>59.51</td>
<td>52</td>
<td>$5.71 \times 10^{-4}$</td>
<td>$8.12 \times 10^{-4}$</td>
</tr>
<tr>
<td>$^{81}$Br$^{35}$Br ($\Pi^\pm\Pi^\pm$)</td>
<td>5</td>
<td>60.28</td>
<td>52</td>
<td>$5.43 \times 10^{-4}$</td>
<td>$7.78 \times 10^{-4}$</td>
</tr>
<tr>
<td>$^{129}$I$^{129}$I ($\Pi^\pm\Pi^\pm$)</td>
<td>5</td>
<td>87.74</td>
<td>62</td>
<td>$1.41 \times 10^{-4}$</td>
<td>$2.55 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

* From vibrational analyses—see Table 2; \(^a\) highest level for which an experimental $B_n$ value is available; \(^b\) obtained on substituting $\tilde{v}_n^a$, $v^a$ and the experimental $B_n$ into equation (33); \(^d\) calculated from the $C_n$ values given in Table 2; \(^*\) no experimental values of $B_n$ are available for this case.

The dot-dash line in the lower half of Figure 14. In addition, if an experimental $B_n$ value is known for the highly excited level $v'$, it may be substituted into equation (33) to yield an empirical $Q_n(v')$ which will in turn yield lower bounds to $B_n$ values for levels $\tilde{v} = v'$ and upper bounds to those for $v < v'$. This case corresponds to points on the solid line in the lower part of Figure 14. For the species listed in Table 2, these upper- and lower-bound values of $Q_n$ are given in Table 6. Although the two limits differ by between 25 and 45% of the larger value, the true $B_n$ values will clearly be closer to the lower bound for $v$ near $v'$, but will converge on the upper bound as $v \rightarrow v_n$. Hence a reasonable interpolation between the two limits should yield predicted $B_n$ values with errors considerably smaller than the uncertainties suggested by the difference between the bounds.

Distribution of Vibrational–Rotational Levels near $D$. One of the more interesting features of the present results [equations (32) and (33)] is that they allow a generalization of the vibrational energy expressions [equations (8) and (9)] to the case of rotating molecules with $J \neq 0$. If $J$ is not too large, the rotational energy of a diatomic molecule in vibrational level $\tilde{v}$ is fairly accurately given by $J(J+1)\tilde{B}_n$ (although this assumption becomes less valid as the levels approach dissociation). In this approximation, equations (9), (32), and (33) allow the total energy of a level near $D$ to be written as:

$$G(v,J) = G(v,0) + J(J+1)\tilde{B}_n - G(v,0)^{1/2}$$

$$= D - ([v_n - \tilde{v}]\tilde{B}_n)^{1/2} + J(J+1)Q_n(v_n - \tilde{v})^{1/2}$$

and the inverse of the density of levels at any chosen $J$ is simply:

$$\frac{dG(v,J)}{dv} = \left\{ 1 - \frac{2J(J+1)\tilde{B}_n}{n[v_n - \tilde{v}]^{1/2}} \right\} \left( \frac{2n}{n-2} \right) \left( \frac{H_n}{\sqrt[2]{n^2}} \right) \left( \frac{v_n - \tilde{v}}{\sqrt[2]{n^2}} \right)$$

$$= \frac{dG(v,0)}{dv} \left\{ 1 - \frac{2J(J+1)\tilde{B}_n}{n[v_n - \tilde{v}]^{1/2}} \right\} \left( \frac{H_n}{\sqrt[2]{n^2}} \right)$$

(34)
Table 7 Coefficients of $[J(J+1)]^n$ in expressions for the $J$-dependence of the number of levels supported by $R^{-n}$-tailed potentials

<table>
<thead>
<tr>
<th>$n$</th>
<th>Number of bound levels: $[N(J) - N(0)]$</th>
<th>Number of quasi-bound levels: $[N^*(J) - N(0)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From equation (36)</td>
<td>From equation (37)</td>
</tr>
<tr>
<td>3</td>
<td>1.0000</td>
<td>Exact</td>
</tr>
<tr>
<td></td>
<td>1.2861</td>
<td>0.2360</td>
</tr>
<tr>
<td>4</td>
<td>0.5000</td>
<td>0.5642</td>
</tr>
<tr>
<td>5</td>
<td>0.3333</td>
<td>0.3584</td>
</tr>
<tr>
<td>6</td>
<td>0.2500</td>
<td>0.2625</td>
</tr>
<tr>
<td>8</td>
<td>0.1666</td>
<td>0.1712</td>
</tr>
</tbody>
</table>

* See footnote on p. 128; † equal to $(n-2)^{-1}; ‡$ see ref. 21.

the total number of levels lying below this maximum, as a function of $J$, is

$$N^*(J) = N(0) - (2J)(J+1)(P_2)/B_2$$

Combined with equation (36), this result yields an expression for the number of quasi-bound levels:

$$N^*(J) - N(J) = [J(J+1)]^n[(1-(2n)/(J+1)](P_2)/B_2$$

Values of the coefficient of $[J(J+1)]^n$ in equation (37) are given in Table 7, where they are seen to be in relatively poor agreement with the corresponding coefficients from the analogous exact semi-classical expressions for Sutherland potentials.21 This increased error of equation (37) relative to that of equation (36) is clearly attributable to the fact that the former is concerned with following the vibrational levels to relatively higher $J$ values.

It should be remembered that the exact semi-classical and quantal expressions used to test equations (36) and (37) can only estimate the total number of bound or quasi-bound levels. In contrast, the results presented here also describe the distribution of these levels. Furthermore, these tests only examined the effect of cutting-off the $G(v,J)$ expansion [equation (34)] at the linear term in $J(J+1)$, and this is not the dominant source of error in equations (34)–(37) for real molecular systems (see footnote on p. 130).

Discussion and Prognosis.—The main weakness of the results presented in Section 4 is that they are much more sensitive to the effect of additional terms in the long-range potential [equation (3)] than was the case for the vibrational problem discussed in Section 3. For real systems, this sensitivity has much more serious consequences for equations (34)–(37) than does the approximation of including only a linear $J(J+1)$ term in equation (34). This weakness must be shared equally by the Tani–Inokuti equation (13) since it rests on precisely the same foundation as the present results. On the other hand, since $B$ values are relatively more sensitive to higher-power terms in equation (3) with $m > n$, they may prove to be a useful probe of these interactions.

An additional deficiency of equations (34) and (35) and the results based on them (see Table 7) is their neglect of quadratic and higher-power terms in $J(J+1)$. However, expressions analogous to equations (32) and (33) should be able to be derived for the rotational constant $D$ in the near future. In addition to its spectroscopic implications, the inclusion of the ensuing $[J(J+1)]^n$ terms in equations (34) and (35) should lead to significantly improved predictions for $[N(J) - N(0)]$ and $[N^*(J) - N(0)]$.

5 Rotational Predissociation and Long-range Potentials

Background: The Limited Curve of Dissociation (LCD).—The total effective internuclear potential of a rotating $(J \neq 0)$ diatomic molecule is the sum of the electronic interaction potential plus a repulsive centrifugal term:

$$V_2(R) = V(R) + J(J+1)\mu^2/2\mu R^2$$

If the attractive long-range part of $V(R)$ dies off more rapidly than $R^{-3}$, then $V_2(R)$ will have a potential maximum at large $R$ (for $J > 0$). Classically, all levels lying behind the maximum of such a barrier are truly bound, even if they are above the molecular dissociation limit. However, as $J$ increases this centrifugal barrier grows and moves to smaller $R$; concurrently, the vibrational levels are shifted to higher energies and eventually they move above the potential maximum and become part of the continuum. As this occurs, rotational progressions will suddenly break off at a critical $J$ characteristic of the particular vibrational level, with the last observed line(s) perhaps being measurably broadened. This is the phenomenon known as rotational predissociation.46, 47

The more highly excited vibrational levels will clearly be predissociated at relatively smaller $J$ values. Thus, the energy associated with the onset of predissociation will yield an ever decreasing upper bound to $D$ as $v$ increases. Büttenbender and Herzberg 44 noted this trend and proposed the use of plots of the energy of the first predissociating level for each $v$, $G^*(v,J)$ versus $J(J+1)$. The $[J(J+1)] = 0$ intercept of a curve of this sort, now known as a 'limiting curve of dissociation' or LCD, is a least upper bound to the dissociation limit $D$. If $V(R)$ has no rotationless potential maximum this intercept should be $D$ itself; otherwise it is the height of the electronic potential energy barrier.

Schmid and Gerö6 expanded upon the LCD approach by noting that the tangent to the curve at any point is given by:

$$dG^*(v,J)/d[J(J+1)] = \mu^2/2\mu[R^2(J)(J+1)]^{1/2}$$

where $R^*(J)$ is the position of the centrifugal barrier maximum. The main application of their result has been as a test of whether the electronic potential $V(R)$ has a potential maximum at some distance $R_0$. In this case, $R^*(J)$ will be constant and equal to $R_0$, and the LCD will have a constant finite slope near the $[J(J+1)] - 0$ intercept. On the other hand, if $V(R)$ is monotonically attractive at long-range (with $n > 2$), then $R^*(J)$ smoothly approaches infinity as $J(J+1) \to 0$ and the LCD will have zero slope at the intercept and positive curvature everywhere. It is important to be able to distinguish between these two cases since the methods described in this section apply only to the latter.

The data requirements for an LCD analysis are somewhat more sophisticated than those for the methods discussed in Sections 3 and 4. First of all, the rotational structure of each vibrational band must be resolved and the correct absolute rotational assignments made. In addition, the observed rotational series for each band must be followed to the critical value of $J$ at which the vibrational level in question predissociates. Unfortunately it is sometimes very difficult to determine whether or not this latter criterion is in fact satisfied, since the sudden breaking-off of a rotational progression can occur for reasons other than rotational predissociation. For instance, the radial wavefunctions of highly excited levels shift to larger $R$ at an accelerating rate as $J$ increases. This could lead to a sharp decrease in Franck–Condon overlap and a concomitant drop in the intensity of the rotational progression so that the latter appeared to break off when the vibrational level was still some distance below the potential maximum. Furthermore, difficulties of this sort are most serious for the highly excited vibrational levels which have the most influence on the determination of $D$. For example, for the highest bound level ($v = 14$) of ground-state $\text{H}_2$, $[d<\psi(t,J)\psi(t,J)/dJ]_{t=\infty}$ is more than 30 times larger than it is for the $v = 0$ level.

In general, errors of the type described above would cause the LCD estimate of $D$ to be too low. An example of a situation in which this appears to have occurred is the $B^1\Pi_{u}^o$ state of $\text{Br}_2$. Here the vibrational analysis which superseded the original LCD treatment of this molecule showed that some of the unobserved levels which had been assumed to be rotationally predissociated actually lay below the dissociation limit, and hence were not even upper bounds to $D$.

Doubt about proximity to the barrier maximum is dispelled if a broadening of levels is observed immediately preceding the break-off of a rotational progression. This type of behaviour is due to quantum-mechanical tunneling, and hence can occur only if the level in question lies above the dissociation limit and fairly near the barrier maximum. It is most often observed for species with small reduced mass, since they can tunnel most efficiently.

---

Bernstein's 'Locus of Barrier Maxima' (LBM): Derivation and Analysis.— Bernstein was the first to make use of the dependence of the heights of centrifugal potential barriers on the attractive long-range electronic potential. He noted that at a maximum $R^*(J)$ of the total effective potential expression (38):

$$dV[R^*(J)]/dR = \{dV[R^*(J)]/dR\} - [J(J+1)\hbar^2/\mu(R^*(J))]$$

(40)

Substituting into equation (40) the long-range potential form [equation (4)], $V(R) = D - C_n/R^n$, then yields an expression for the position of the barrier maximum:

$$R^*(J) = [\mu C_n/J(J+1)]^{1/(n-1)}$$

(41)

Since this maximum corresponds to $V'(R^*(J))$, one obtains:

$$E_n(J) = D + S_n[J(J+1)]^{n/(n-1)}$$

(42)

for the 'locus of barrier maxima' or LBM, where the constant $S_n = S_0[\mu(C_n)]^{1/2}$. Values of the numerical factor $S_n$ for various $n$ are listed in Table 1.

There is an important distinction between equation (42) and the expressions (8)–(10) and (32)–(33), which describe the vibrational energies and $R$ constants. The latter quantities depend on the potential over the whole of the region between the classical turning points, although for levels near $D$ they are largely dominated by the effect of the attractive long-range part of $V(R)$. In contrast, equation (42) is a purely classical result and it depends only on the nature of $V(R)$ right at the barrier maximum $R^*(J)$. As a result, it will be less seriously affected by errors associated with replacing the actual
potential by the long-range form [equation (4)]. In addition, the fact that the barrier corresponding to the predissociation of a given vibrational level \( \nu \) lies at a distance \( R^c(\nu) = R_d(\nu, \nu') \) somewhat larger than the \( R_d(\nu, 0) \) turning point makes the use of equation (4) even more appropriate here.

In an analysis based on equation (42) the experimental observables are the energies of the rotational levels preceding the onset of predissociation. Since the levels are sometimes widely spaced, the determination of the energy and \( J \) value for which a given vibrational level lies at the centrifugal maximum can be a serious problem. Possible choices are the \( J \) and energy of the last sharp observed level, those of any broadened levels which may have been observed, the extrapolated energy and \( J \) of the first missing level in the series, or any intermediate values. Thus an experimental LCD may have many definitions and need not coincide with the actual LBM described by equation (42).

This problem has been studied for ground-state \( \text{H}_2 \), \( \text{HD} \), and \( \text{D}_2 \), for which the exact energies and the widths of all quasi-bound vibrational–rotational levels have been calculated from the accurate ab initio potential. For this case, many of the quasi-bound levels lying behind centrifugal barriers had sufficiently large widths (of from 5 to 80 cm\(^{-1}\)) that they would be extremely difficult to observe experimentally. Figure 15 compares the LBM with 'predicted experimental LCDs' defined as the loci of measurably broadened levels with widths

\[
0.05 < \Gamma < 0.25 \text{ cm}^{-1}
\]  

(43)

A mass-reduced abscissa scale is used so that the LBM curves for the three isotopes are identical. Note that the differences \( \Delta E \) between the LBM and the LCD curves are from 10% to 40% of the LBM energy, with the greatest relative error occurring at small \( J \). This implies that any simple algorithm such as equation (43) will tend to be proportionately most seriously in error at the small \( J \) values where Bernstein's expression [equation (42)] should be appropriate. The trend of the results for the different isotopes is in accord with the decreased efficiency of tunneling with increasing reduced mass \( \mu \). However, effects of this sort will clearly only become negligible for large \( \mu \gg 1 \) amu. In conclusion, therefore, the results described above suggest that the best empirical definition of an LCD corresponds to the extrapolated energy and \( J \) value of the first unobserved level in the given rotational series. However, for hydrides and deuterides this apparently missing level might still lie well below the centrifugal barrier maximum.

Applications of the LBM Expression: Results and Non-results.—If rotational predissociation is observed for three or more highly excited vibrational levels of a given state, the corresponding energies \( E_a(J) \) may in principle be fitted to equation (42) by least squares to yield values of the parameters

\[
D, n, \text{ and } C_n \text{ (from } S_n). \text{ In practice, however, the small number of data and the uncertainties discussed above seriously hamper any such direct determination of } n. \text{ These difficulties are compounded by the fact that the power } n(n-2) \text{ in equation (42) is only half as sensitive to changes in } n \text{ as are the powers } 2n(n-2) \text{ and } 4(n-2) \text{ appearing in equations (9) and (33)}. \text{ As a result, it is almost always necessary to assume a value for } n, \text{ and in practice it is always set equal to its theoretically-known asymptotic value } \bar{n}. \text{ Plots of } E_a(J) \text{ versus } [J(J+1)]^{n/2} \text{ may then be made, and } D \text{ obtained from the } J=0 \text{ intercept and } C_n \text{ from the limiting slope. Unfortunately this puts a fairly severe constraint on the present approach, since it may only be used in the asymptotic region where the interaction potential is mostly due to the leading } n \neq \bar{n} \text{ term in equation (3)}.

A major source of error in past applications of equation (42) appears to
have arisen from a literal belief in Bernstein's suggestion that the electronic potential achieved its asymptotic form \((D - C_\infty R^s)\) for \(R \geq 1.5 R_e\), where \(R_e\) is the equilibrium internuclear distance of the given state. This criterion is valid for model potentials of the Lj(a) or exp(a) type, and probably also for some van der Waals molecules such as ground-state \(\Delta R_6\). However, it is far too liberal of a requirement for the chemically bound species to which this approach has most often been applied, and consequently most of the results which have been obtained using equation (42) are invalid.

The latter conclusion was based on an examination of the \(R^s(J)\) values obtained on substituting the reported \(C_\infty\) values into equation (41) together with \(\eta\) and the values of the points \(E_\eta(J)\) used in the analyses. Many of these barrier maxima did not satisfy equation (5), and an even larger fraction of them failed to satisfy Swallow's alternative requirement \(R^s(J) \geq 5 \AA\) for the validity of the inverse-power potential equation (3). Furthermore, since these criteria refer only to the region of validity of the expansion (3), the leading \(m = \eta\) term in the latter may not come to dominate the potential until \(R\) is considerably larger than this minimum value. For the hydrides and deuterides (which comprise half the species studied) there are serious additional uncertainties associated with the effect of tunneling and with the problem of determining \(E_\eta(J)\) values from the relatively widely-spaced rotational levels. In view of the above, the present conclusion is that the Bernstein-type predissociation analyses reported for \(N_2\) (\(C^2\Pi_g\)), \(CO\) (\(B^1\Sigma^+\)), \(HgH\) (\(X^1\Sigma^+\)), and \(HgD\) (\(X^1\Sigma^+\)), and \(DF\) (\(X^1\Sigma^+\)) are invalid.

Table 8 Results of predissociation analyses using Bernstein's LMB expression [equation (42)]

<table>
<thead>
<tr>
<th>Species</th>
<th>(D/cm^{-1})</th>
<th>(\eta)</th>
<th>(C_\infty/cm^{-1} \AA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH ((B^1\Pi))</td>
<td>34492.5(±0.5)</td>
<td>6</td>
<td>0.402 \times 10^4</td>
</tr>
<tr>
<td>(Se_2) ((1,2,3,4,5,6,7))</td>
<td>35999.0(±2.5)</td>
<td>5</td>
<td>1.5 \times 10^4</td>
</tr>
<tr>
<td>(Se_2) ((2,3,4,5,6,7))</td>
<td>29690 (±20)</td>
<td>5</td>
<td>1.6 \times 10^4</td>
</tr>
</tbody>
</table>

* See footnote on p. 140. 1 \(C_\infty\) held fixed at the theoretical value; 2 These potential parameters characterize the predissociating \(1\) state and not the predissociated \(B^1\Sigma^+\) state; 3 expressed relative to the ground-state potential minimum.

The results for the other cases to which equation (42) has been applied are summarized in Table 8. The first, LiH (\(B^1\Pi\)), is an example of Herzberg's case III predissociation involving only a single potential-energy curve. In this case, only one vibrational level \((n = 2)\) predissociates at small enough \(J\) that the corresponding centrifugal barrier maximum lies in the long-range region. Therefore Swallow and Way \(^{44}\) calculated the asymptotic potential coefficient for this case \((\eta = 6)\) and used it to yield a theoretical value of the constant \(C_\infty\) in equation (42). Combining the latter with their one datum then yielded the improved dissociation limit of \(34492.5(±0.5)\) \(cm^{-1}\), a value significantly different from the experimental's estimate of \(34495(±2)\) \(cm^{-1}\). An additional noteworthy feature of this analysis was the fact that they used trial calculations of quasi-bound level positions and widths for different assumed potentials to estimate the effects of higher-power potential terms \((R^{-4}, R^{-6}, \ldots\) etc.\) and of quantum-mechanical tunnelling. \(^{44}\)

The discussion accompanying Figure 15 suggests that for hydrides or deuterides, such model calculations should probably accompany any predissociation analysis.

The other problems to which equation (42) has been applied are examples of Mulliken's case IIB\(^+\) predissociation (a subcase of Herzberg's case Iib). Here the observed predissociation arises from the intersection of the attractive outer branches of two potential curves of different but related symmetry which have different dissociation limits. The pure vibrational \((J = 0)\) level spectrum of both states will be oblivious to this intersection. However, rotational motion causes a mixing of states such that \(J > 0\) levels of the potential with the higher asymptote may be predissociated if they lie above the centrifugal barriers associated with the long-range part of the potential curve with the lower dissociation limit. In this case, the \(J\)-dependence of the onset of predissociation for vibrational levels of the first state lying below the asymptote of the second may be used to determine the long-range potential of the latter.

In the absorption and emission spectra of \(S_2\) \((B^3\Sigma_g^+\)) Ricks and Barrow \(^{56}\) observed predissociations of this sort, caused by the intersection of the \(B^1\Sigma^+\) curve with a \(1\) state which dissociates to yield \(3\Sigma^+\) \(\pi\) atoms. They analysed the data for the three \(S_2\) isotopomers \(^{35}\)S\(^{35}\)S, \(^{35}\)S\(^{37}\)S, and \(^{37}\)S\(^{37}\)S in terms of equation (42) while assuming \(n = \eta = 5\) and obtained the \(D\) and \(C_\infty\) (experimental) given in Table 8. There are three different \(1\) states correlating with these dissociation products, all of which correspond to \(\eta = 5\). However, theory shows \(^{31}\) that the \(R^{-3}\) term is only attractive for the one \(1\) state whose calculated \(C_\infty\) is given in Table 8, while the \(C_\infty\) values for the other two possible \(1\) curves are negative (repulsive).\(^*\) Note that the theoretical \(C_\infty\) quoted by Ricks and Barrow \(^{56}\) erroneously corresponds to one of these latter states.

The disagreement between the theoretical and experimental \(C_\infty\) for \(S_2\) (see Table 8) is rather large, and the agreement shown in Table 2 implies

\(^*\) Of course, this does not necessarily mean that the states in question are repulsive, since the dispersion potential terms \((R^{-4}, R^{-6}, \ldots\) etc.\) are probably attractive, while the exchange forces could have either sign.


that it should not be attributed to error in the former. This appears to leave three possible explanations. If the predissociation is correctly assigned to the \( 1_s \) state with an attractive \( C_s \), either some of the data are in error, or the additional attractive \( R^{-4}, R^{-6}, \ldots \) etc. terms contributing to the long-range potential are significant over the range of the experimental \( R^* (J) \) values. In the latter case, an analysis which assumes pure \( n = \bar{n} = 5 \) behaviour would be inaccurate. On the other hand, if the predissociating \( 1_s \) state is one of those with a repulsive asymptotic \( R^{-4} \) tail, then any analysis based on equation (42) will be spurious. In any case, there is clearly some uncertainty as to the actual significance of the \( S_2 \) results quoted here.

An analysis using equation (42) has also been reported for similar case \( 1b^3 \) predissociations of \( \text{Se}_2 \) (\( B^3\Sigma^– \)).\(^{91}\) In this case there are two sets of observations corresponding to intersections of the \( B \Omega \) curve by \( 1_s \) states whose dissociation limits are separated by the atomic \( 3P_1 - 3P_2 \) excitation energy.\(^{92}\) Barrow et al.\(^{93}\) pointed out that there are three possible electronic assignments for this pair of dissociation limits, yielding three different estimates of the ground-state dissociation energy, \( D_s (X) \). Using qualitative spectroscopic arguments they chose the middle value of \( D_s (X) \), and recent spectroscopic evidence (R. F. Barrow, personal communication, 1972) appears to confirm this assignment. On the other hand, photoionization measurements strongly favour the largest of these three \( D_s (X) \) values,\(^{94}\) which would imply that the observed predissociating \( 1_s \) states correlate with \( 3P_1 + 2P_2 \) (upper \( D \) value) and \( 3P_2 + 2P_0 \) atoms (lower \( D \) value).

Byrne et al.\(^{95}\) analysed the \( 3s \) predissociation corresponding to the upper dissociation limit (\( 3P_1 + 3P_2 \)) using \( \bar{n} = 5 \). As in the analogous \( S_2 \) situation, there are three different \( 1_s \) states correlating with these dissociation products, all corresponding to \( \bar{n} = 5 \). If the predissociations are correctly assigned as case \( 1b^3 \),\(^{96}\) they must be due to the one curve with an asymptotic \( R^{-6} \) tail. However, the theoretical \( C_s \) for this case (given in Table 8) is significantly smaller than the experimental value of Byrne et al.\(^{95}\) This fact casts further suspicion upon the electron assignment of the predissociation products favoured by the photoionization measurements. On the other hand, Stwalley pointed out that if either of the two lower values of \( D_s (X) \) were correct, the \( 1_s \) state yielding the higher set of predissociations would correlate with \( 1P_1 + 3P_2 \) or \( 3P_1 + 3P_0 \) atoms, cases for which the \( C_s \) \( = \) 0.\(^{31} \) This would have meant that \( \bar{n} = 6 \) for the data in question and hence that the reported \( \bar{n} = 5 \) analysis was wrong. Note also that Chang’s\(^{97}\) discussion of the theoretical \( C_s \) for this case is erroneous, since he mistakenly assumed that the predissociating potentials had the same \( 0^+_1 \) symmetry as the predissociated state.

**Discussion and Prognosis.**—The dearth of valid applications of equation (42) seems surprising in view of the fact that in principle this expression is more accurate than those discussed in Sections 3 and 4. This shortage of results appears to be largely due to the experimental difficulty of observing the predissociation of (highly excited) vibrational levels for which \( R^* (J) \) are sufficiently large that equation (42) can be expected to be valid. Compounding these problems are uncertainties as to whether a breaking-off of a rotational series actually corresponds to a barrier maximum, and uncertainties in determining experimental \( E_s (J) \) values from the observed energy levels.

Stwalley suggested that problems of the latter sort will diminish if broadened levels are observed and their widths measured, since in this case trial calculations should be able to locate barrier maxima \( E_s (J) \) fairly accurately. However, such techniques have as yet only been qualitatively applied,\(^{98}\) and in any case they would only really be useful for hydrogenic or other light molecules for which tunneling is fairly efficient.

As an alternative to equation (42), Stwalley\(^{100}\) suggested using Schmid and Gerô’s\(^{86}\) expression [equation (39)] to determine a potential numerically without assuming any analytic form. This would be done by using the derivatives in equation (39) to yield values of \( R^* (J) \) which can then be substituted into equation (40) to yield ‘experimental’ values of \( dV (R^* (J)) / dR \). Interpolation and integration over the latter would then yield \( V (R) \) itself. This type of approach has the advantage of being free from any constraints associated with the validity of the inverse-power form [equation (4)]. However, the determination of accurate derivatives \( dG^* (\nu, J) / dJ (J + 1) \) requires both very accurate values for the energies \( G^* (\nu, J) = E_s (J) \) and a fairly high density of such points, both of which are rather difficult criteria to fulfill. These difficulties will be compounded by additional uncertainties arising from the integration of \( dV (R^* (J)) / dR \). As a result, it seems unlikely that this approach will find very wide usage in the near future.

Very recently Goscinksi and Tapia\(^{100}\) derived a generalized version of Bernstein’s LBM equation (42) which takes account of higher-power terms \( (m > \bar{n}) \) in the long-range potential expansion (3). They represented the first few terms in (3) with the [1,0] \( \text{Padé} \) approximation:

\[
V_1 (R) = D - C_{1s} [R^2 (1 - C_{1s} / C_{1s} R^{-6})]
\]

\[
= D - C_{1s} R^2 - C_{1s} / R^6 - \ldots
\]

where \( \bar{n} \) is the power of the first \( m > \bar{n} \) term in (3). Their approach then yielded

\[
E_s (J) = D - S_3 (J + 1)^{(\bar{n} - \nu) / 2} \left( 1 + \frac{C_{1s} (S_3)^{(\bar{n} - \nu) / 2} [J (J + 1)^{(\bar{n} - \nu) / 2}]}{\nu (\bar{n} - 2) C_{1s}^{(\bar{n} - \nu) / 2}} \right)
\]

as the generalization of equation (42) for cases in which

\[
\nu (J) = C_{1s} / C_{1s} [R^2 (J)]^{-6}
\]


Molecular Spectroscopy

is small. The latter requirement does not limit the usefulness of equation (43b), since unless \( n(J) \) is significantly less than one, the inverse-power expansion (3) becomes inappropriate for describing the interaction potential (see Section 2: Validity of the Inverse-power Expansion). However, the utility of the improved LBM expression (43b) is still restricted by the difficulty of obtaining experimental data suitable for analysis. In this vein it should be noted that the barrier maxima \( R^b(J) \) in the two sample problems considered by Goscinski and Tapia,\(^{109}\) \( \text{H}_2(\text{B}^1\Sigma_u^+) \) and \( \text{H}_2\text{H}(\text{X}^1\Sigma_u^+) \) do not satisfy criterion (5), and hence their conclusions about these species should be regarded with some suspicion.

In conclusion, therefore, it appears that the methods described in this section are of relatively limited applicability. On the other hand, since the difficulties discussed above are partly experimental, the ever-improving techniques of measurement should eventually uncover more examples in which the LBM equations (42) and (43b) may be profitably applied.

6 Analysis of Long-range RKR Turning Points

Background: Calculating RKR Potentials near Dissociation.—The three methods considered heretofore were all based on expressions relating the long-range interatomic potential directly to the energies or \( B \) values of levels near dissociation. In contrast, the techniques described below involve the analysis of actual points on the 'true' potential in terms of the theoretically-known long-range form [equation (3)]. Although the latter approach is more straightforward, it is also more restrictive since the calculation of RKR turning points for a given level necessarily involves knowledge of the energies and \( B \) values for all lower vibrational levels. In practice, however, these extensive data requirements may be partially relaxed for highly excited levels.

The Rydberg–Klein–Rees (RKR) procedure\(^{10,12,101–109}\) is based on an exact inversion of the first-order WKB eigenvalue criterion [equation (6)] which involves integrals of the form


\( (k, v) = \int_{k=0}^{k=1} (B_0) [G(v') - G(v)]^{-1} dv' \) (44)

where \( k = 0 \) and 1. The \( k = 0 \) integral, which utilizes no rotational data, determines the distance between a pair of turning points:

\( R_0(v) - R_0(v) = (\hbar / 2\mu)^{1/2} I(0,v) \) (45)

while the \( B_r \)-dependent \( k = 1 \) integral yields

\( 1/R_0(v) - 1/R_0(v) = (2\mu / \hbar^2)^{1/2} I(1,v) \) (46)

and effectively determines their means.

The most important contributions to \( I(k,v) \) are associated with the integrand at \( v' \) near the singularity at \( v \), and this weighting is particularly significant for levels near dissociation for which \( G(v') \) approaches \( G(v) \) slowly. Thus, it is essential that the interpolation over the discrete experimental \( G(v') \) values be highly accurate as \( v' \) approaches \( v \). Unfortunately, for the highest observed levels the absence of data for yet higher levels makes accurate interpolations most difficult for precisely those cases which are most sensitive to this type of error. However, such effects may be minimized through use of the natural 'near-dissociation' expressions [9] and [33] (rather than the customary polynomials in \( v \)) when interpolating in this region. In contrast to the difficulties described above, the dominance of \( I(k,v) \) values by the integrand at \( v' \) near \( v \) also means that errors in the vibrational numbering or in the experimental \( G(v') \) or \( B_r \) at \( v' < v \) will have little effect on the turning points of a highly excited level.

It is often much easier to measure the energies of highly excited vibrational levels than it is to obtain reliable \( B \) values for them. Fortunately, the distinction between the roles of \( G(v) \) and \( B \) in equations (45) and (46) means that this difficulty need not prevent the determination of reliable \( R_0(v) \) values for such levels. The inner turning points for all but the lowest vibrational levels rise so steeply that virtually any reasonable extrapolation beyond the range of the \( R_0(v) \) values calculated for the lower levels should yield a fairly accurate repulsive potential wall. The vibrational energies in the region where the \( B \) values are not known may then be used in equation (45) to yield accurate turning-point differences, which when added to the extrapolated inner branch of the potential should yield reliable outer turning points. This type of RKR-extrapolation, first used by Verma,\(^{75}\) has proved to be fairly useful \(^{88,101–106,107}\) since the limited availability of rotational data for highly excited levels would otherwise seriously restrict the availability of RKR turning points in the long-range region.

One great strength of the RKR procedure is that it is model-independent, i.e., its validity does not depend on the appropriateness of any particular functional form for the potential. However, a concomitant disadvantage is the fact that the method has no built-in way of extrapolating to yield information about the dissociation limit or the long-range potential. To
this end, Ginter and Battino\textsuperscript{102} suggested that one simply use analytic extrapolations to estimate $G(o)$ and $B_e$ values beyond the range of the experimental data, and then calculate the turning points in this region from these projected data. Although this may yield plausible results over a narrow internal, it merely shifts the uncertainties onto the shoulders of the assumed $G(o)$ and $B_e$ expressions, and hence solves nothing.

Another way in which RKR potentials have been used to estimate dissociation energies involved using the calculated turning points to test the appropriateness of different model potential functions. The analytic potential in closest agreement with the RKR turning points was then assumed to give the best estimate of $D$.\textsuperscript{110-112} This scheme is clearly just a modification of the model-potential approach discussed in Section 1, with the appropriateness of a particular functional form being examined through the intermediary of the calculated turning points rather than by a direct comparison with experimental data. Since no new physical or theoretical information is introduced by such an extrapolation, this approach should not be taken too seriously.

Graphical Methods.—This section describes diverse ways of analysing outer RKR turning points in terms of the long-range potential forms [equations (3) and (4)]. The fundamental assumption of any such treatment is that the use of these expressions is appropriate over the range of the given turning points, and hence a criterion such as equation (5) must always be kept in mind. Of course, turning points satisfying equation (5) should not be expected to depend only on the asymptotic inverse-power potential term $R^{-n}$, since competing higher-power terms in equation (3) with $m > n$ will usually be present also.

Perhaps the simplest way of analysing turning points in the long-range region is by utilizing the expression

$$ D - G(o) = C_n(R_e(o))^m $$

obtained on substituting $G(o) = V[R_e(o)]$ into equation (4). If $D$ is accurately known, equation (47) suggests using a log-log plot of binding energy versus $R_e(o)$ to determine the power $n$ and coefficient $C_n$ of the effective outer potential over the range of the given turning points. This approach can indicate whether this effective local inverse power approaches its (assumed known) asymptotic value $n$, and when this occurs it will also yield the theoretically interesting coefficient $C_n$. Unfortunately, $D$ is usually not known with particularly high accuracy, and relatively small errors in it can significantly affect log-log plots of this sort (e.g. see ref. 51). An additional difficulty, shared with the methods of Sections 3–5, is that equation (47) does not offer any natural way of taking account of higher-power contributions to the long-range potential.

Swalley pointed out that a much more flexible type of RKR analysis is possible if one utilizes the first few terms in the long-range potential expansion [equation (3)] for the particular state under consideration.\textsuperscript{43} Substituting $G(o) = V[R_e(o)]$ into equation (3) yields:

$$ G(o) = D - \sum_{n > 4} C_n[R_e(o)]^m $$

where the allowed values of $m$ for the first few terms are assumed to be known (see Section 2). This expression may be used in a number of different ways, depending on whether or not reliable values of $D$ and some $C_n$ are already known. If none are, equation (48) suggests making a plot of $G(o)$ versus $[R_e(o)]^{-m}$, which in the limit of large $R_e(o)$ should be linear with intercept $D$ and slope $C_n$. However, as with the log-log plots discussed above, this neglect of all $m > n$ terms in equation (48) will tend to make the thus-obtained $C_n$ an upper bound to the true value.

If one of the $C_n$ values is already known, say $C_n$, then a simple rearrangement of equation (48) suggests the use of a plot of $\{G(o) + C_n[R_e(o)]^m\}$ versus $[R_e(o)]^{-n}$, where $n$ is the power of the second term in the long-range potential expansion [equation (3)]. In this case, the intercept at $R_e(o) \rightarrow \infty$ is again equal to $D$ while the limiting slope should yield the coefficient $C_n$. Figure 16 illustrates how Swalley first used this type of plot in his analysis of the turning points of $\text{Mg}_2$ ($X^1\Sigma_g^+$).\textsuperscript{42} In this example, the leading terms in equation (48) have powers $m = 6, 8, 10$, and a theoretical $C_6 = 3.29 (\pm 0.17) \times 10^6 \text{ cm}^{-1} \text{ Å}^6$ had been reported.\textsuperscript{113}

A somewhat more sophisticated version of such plots was proposed by Cummings\textsuperscript{29} for use in cases where reasonably accurate values of $D$ are known. In its simplest form, appropriate when none of the $C_n$ constants

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure16.png}
\caption{RKR turning points for $\text{Mg}_2$ ($X^1\Sigma_g^+$),\textsuperscript{42} for which $m = 6, 8, 10, \ldots$ etc., plotted according to equation (48) utilizing the theoretically known\textsuperscript{113} values of $C_n$. Energies are in cm$^{-1}$ and lengths in Å. (Reproduced by permission from Chem. Phys. Letters, 1970, 7, 600.)}
\end{figure}

\textsuperscript{112} V. M. Trivedi and V. B. Gohel, J. Phys., (B), 1972, 5, L38.
are known, Cummings' approach suggests plotting $[R_0(0)]^n[D - G(0)]$ versus $[R_0(0)]^{\bar{n} - m}$, where $\bar{n}$ and $\bar{m}$ are again the powers of the first and second terms contributing to equation (48). Here, a linear extrapolation as $R_0(0) \to \infty$ will clearly yield $C_6$ as the intercept and $C_8$ as the slope. On the other hand, for the problem to which this approach was first applied, Cl$_2$ ($B^3\Pi_u$, $\Sigma^+$), for which the leading terms in equation (48) correspond to $m = 5, 6, 8, 10, \ldots$ etc., reliable values of both $D$ and $C_6$ are known (see Table 2). Thus, Cummings used plots of $[R_0(0)]^n \times [(D - G(0)) - C_0[R_0(0)]^{\bar{n}}]$ versus $[R_0(0)]^{-\bar{n}}$ such as that shown in Figure 17 to obtain values of $C_6$ from the intercept and $C_8$ from the slope.

![Figure 17](image_url)  
**Figure 17** RKR turning points for Cl$_2$ ($B^3\Pi_u$, $\Sigma^+$) for which $m = 5, 6, 8, 10, \ldots$ etc., plotted according to equation (48) utilizing the known (Table 2) $D$ and $C_6$ in the manner suggested by Cummings. Units as in Figure 16.

It should be quite clear that an approach such as that of Figure 17 will be very sensitive to errors in the assumed-known values of $D$ and $C_6$. Hence, it should not be used unless these constants are believed to be quite accurate. In addition, such plots should also be fairly sensitive to errors in the RKR turning points. The increasing scatter of the last few points on Figure 17 is the type of behavior one might expect to reflect the interpolation errors which can arise when calculating turning points for the highest observed levels.

Results of RKR Analyses.—The results which have been obtained using the techniques described above are summarized in Table 9. Also given there are the range of the turning points used in the analysis, and the minimum internuclear distance $R(5)$ corresponding to the right-hand side of equation (5).

Although the criterion of equation (5) for the appropriateness of the long-range potential form equation (48) is satisfied by the turning points for the halogens, this is not so for ground-state M$_8$ ($X^4\Sigma^+_u$). The turning-point analysis for this case was performed using a calculated $^{113}$ value of $C_6$ and a plot similar to that shown in Figure 16. It is clear that the $D$ and $C_6$ values obtained in this way really depend only on the two points corresponding to

---

**Table 9** Results of graphical analysis of long-range RKR potentials; energies are in cm$^{-1}$ and lengths in Å

<table>
<thead>
<tr>
<th>Species</th>
<th>$n$</th>
<th>Turning Point</th>
<th>$R(5)$</th>
<th>$D$</th>
<th>$C_6$</th>
<th>$C_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgHgHg</td>
<td>6</td>
<td>7.2</td>
<td></td>
<td>4.5</td>
<td>R &lt; 7.2</td>
<td></td>
</tr>
<tr>
<td>nCHCl</td>
<td>7.2</td>
<td>4.5</td>
<td>R &lt; 7.2</td>
<td>8.7</td>
<td>$C_6 = 1.22 \times 10^4$</td>
<td>$C_8 = 0.10 \times 10^4$</td>
</tr>
<tr>
<td>nBrBr</td>
<td>4.7</td>
<td>R &lt; 7.9</td>
<td></td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nHBr</td>
<td>4.7</td>
<td>R &lt; 7.9</td>
<td></td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Intermolecular distance corresponding to the criterion of equation (5): $R(5) = 2[C_0(R_0(0))]^{1/3} \times \langle \gamma \rangle^{1/2}$.*
v = 11 and 12. For these levels, the calculated turning points Rκ(v) = 6.8 and 7.2 Å come fairly close to satisfying equation (5), and are significantly larger than the minimum distance of 5 Å suggested by Stwalley. Thus, in spite of the violation of the criterion of equation (5), the reported D and Cₖ values may be significant. Evidence favouring this possibility is provided by Stwalley's report (W. C. Stwalley, personal communication, 1972) that an additional point corresponding to the recently identified v = 13 level lies right on the solid line in Figure 16. In any case, the trend of this plot suggests that the inclusion of additional turning points farther into the long-range region would mainly tend to increase the reported (Table 9) D and Cₖ values. Such a change would merely improve the accord between Stwalley's 'experimental' Cₖ = \(48 \times 10^6\) cm⁻¹ Å⁻¹ and his approximate theoretical bounds for it:\(^{45}\)

\[48 \times 10^6 \leq C_k \leq 77 \times 10^6 \text{ cm}^{-1} \text{ Å}^{-1}\]

while slightly increasing the difference between his D value and the experimental estimate \(^{11}\) of \(D_k = 399 \pm 5\) cm⁻¹.

For the \(\text{B}(^3\Pi_g^+)^\text{a state halogens, the first few terms in equations (3 and (48) correspond to } m = 5, 6, 8, \text{ and 10, and the corresponding } C_m \text{ values are all positive (attractive). Since reliable } D \text{ and } C_k \text{ values are known for } B\text{-state } C_\text{l}, B_\text{r}, \text{ and } I_\text{s} \text{ (see Table 2), utilization of their turning points in the manner suggested by Cummings }^{38} \text{ can yield values of } C_k \text{ and } C_\text{s}. \text{ The } C_\text{l} \text{ results in Table 9 were thus obtained from a linear least-squares fit to the points for } v = 22 - 30 \text{ in Figure 17. The point for } v = 31 \text{ was ignored because of its inconsistency with the others, a difficulty probably due to error in the RKR turning point for this highest observed level.}

In his related analysis of the outer turning points of \(C_\text{r}(B,^3\Pi_g^+)^\text{a}, \text{ Cummings also allowed for variations in the 'assumed-known' } D \text{ and } C_k \text{ values.}^{38} \text{ For a number of trial } C_k \text{ values he determined the } D \text{ for which the } v = 24 - 30 \text{ points on a plot such as Figure 17 give the best straight line, the line's intercept and slope yielding estimates of } C_k \text{ and } C_\text{s}. \text{ The results corresponding to the } C_k = 1.22 \times 10^6 \text{ cm}^{-1} \text{ Å}^{-1} \text{ used here are: } D = 20879.40 \pm 0.05\text{ cm}^{-1}, C_k = 0.37 \times 10^6 \text{ cm}^{-1} \text{ Å}^{-1}, \text{ and } C_\text{s} = 6.6 \times 10^5 \text{ cm}^{-1} \text{ Å}^{-1}. \text{ The differences between Cummings' results and those given in Table 9 are partly due to the different assumed } D \text{ values, and partly associated with the fact that he used slightly different turning points. Although the theoretical } C_k \text{ in Table 10 is in better agreement with the present value (in Table 9) than with Cummings' estimate (above), the difference is not really sufficiently large to determine which of the latter is 'better'. Other } C_\text{l} \text{ analyses by } \text{ Le Roy}^{77} \text{ and Gosciniski}^{118} \text{ are less reliable than that reported here since they ignore or misrepresent the influence of the first (R⁻³) and third (R⁻⁴) terms contributing to equation (48). In addition, in their prior analysis of } B\text{-state } C_\text{l} \text{ and } B_\text{r}, \text{ Byrne et al.}^{11} \text{ concluded that the potential tails asymptotically died off as } R^{-4} \text{ rather than } R^{-3}. \text{ However, a re-examination of their data showed that this conclusion was erroneously based on an incorrect assumed value of } D_\text{r} \text{ and a neglect of the turning points for the highest observed levels.}^{41}

Figure 18 shows the Br₂ (B,^3\Pi_g^+) state plot analogous to that of Figure 17, the intercept and slope of the solid line yielding the Cₖ and C₈ given in Table 9. The RKR turning points used for this case are those reported by Todd, Richards, and Byrne,\(^{41}\) since the more recent RKR calculation by Coxon\(^{107}\) was later shown\(^{71}\) to be based on an incorrect vibrational assignment of levels v = 49 - 52. The RKR analyses for this state reported by Le Roy\(^{77}\) and Gosciniski\(^{118}\) should therefore be disregarded, since they were based on Coxon's\(^{107}\) potential.

\[
\begin{array}{|c|c|c|c|}
\hline
& \text{Experimental} & \text{Theoretical} & \text{Experimental} & \text{Theoretical} \\
\hline
\text{Cl₂} & 0.42(±0.02) & 0.45(±0.05) & 5.9(±0.5) & 2.8(±0.6) \\
\text{Br₂} & 0.84(±0.03) & 0.83(±0.08) & 11.8(±1.0) & 6.3(±1.3) \\
\text{I₂} & 1.63(±0.01) & 1.85(±0.2) & 33.1(±0.4) & 19(±4) \\
\hline
\end{array}
\]

\(^{4}\) From Table 9; \(^{5}\) from ref. 38; the error bounds are only estimates.

A similar analysis of long-range RKR turning points for I₂(B,^3\Pi_g^+) yielded the Cₖ and C₈ for this state shown in Table 9.\(^{117}\) Prior work by Steinfield, Campbell, and Weiss\(^{114}\) had concluded that the v = 45 - 51 turning points


\(^{115}\) J. D. Brown, G. Burns, and R. J. Le Roy, to be published.

in the region 4.6—5.0 Å displayed pure $R^{-6}$ behaviour. However, both the RKR potential and the $D$ value used in their analysis have since been shown to be invalid, and in any case the turning points considered lie at too small $R$ for the long-range potential form (3) [or (47)] to be valid. In a more recent study of this state, Tellinghuisen independently noted the lack of pure $R^{-6}$ asymptotic behaviour and re-emphasized the "anomalous accuracy" of the Le Roy—Bernstein results for this case (see discussion on p. 145).

Long-range analyses of outer RKR turning points have been reported for a number of other systems for which the results are believed to be invalid because of violations of the criterion of equation (5). For example, ground-state HF and DF turning points in the region $1.8 < R < 2.2$ Å were reported to display the asymptotic $R^{-4}$ behaviour, a conclusion upon which the $R(5) = 3.1$ Å value for this species casts considerable doubt. In another type of situation, studies of the outer turning points of ground-state $I_{0}$ which assumed the asymptotic $C_{g}/R^{6}$ functionality are deemed invalid because the levels whose turning points lie in the long-range region actually belong to a different electronic state.

Discussion and Prognosis.—An important product of the above analyses is the conclusion for the $B^{(+)}$state halogens that the outer branch of the potential in the neighbourhood of the highest observed levels is not purely $R^{-6}$. The results in Table 9 indicate that the $R^{-4}$ and $R^{-6}$ terms in equation (48) are responsible for between 30% and 60% of the binding at the outer turning points of the levels used to obtain the halogen data in Table 2. Fortunately, most of this non-$R^{-6}$ contribution is due to the $R^{-4}$ term. As was discussed earlier (p. 145), a fortuitous cancellation of errors in this $\tilde{n} = \tilde{n} + 1$ case means that the Table 2 results obtained by using equation (9) with $n = n = 5$ are not compromised by the significant $R^{-4}$ contribution.

As the halogen results indicate, a long-range RKR analysis and the method of Le Roy and Bernstein (see Section 3) complement each other very effectively. In almost any problem for which turning points are available in the long-range region, the energy levels will be close enough to dissociation to be treated using equation (9).* If the power describing the distribution of levels is effectively equal to $\tilde{n}$, then fitting the energies to equation (9) will yield a $D$ and $C_{6}$ which may be used in equation (48) to yield the coefficients of the first two terms with $m > \tilde{n}$ (e.g. see Figures 17 and 18). On the other hand, if the highest observed levels do not correspond to $n = \tilde{n}$, a fit to equation (9) will still yield a reliable value of $D$ which when used in equation (48) can yield estimates of $C_{6}$ and $C_{8}$.

One rather important use of results such as those in Table 9 is as a test of theoretically calculated $C_{n}$ coefficients. To this end, Table 10 compares the present best $C_{6}$ and $C_{8}$ values for the $B^{(+)}$-state halogens with values calculated by Cummings. The good agreement between the experimental and theoretical $C_{n}$ values attests to the usefulness of Cummings methods. The fact that the theoretical $C_{n}$ values are roughly twice as large as the experimental values may be due to the approximations involved in the calculation of the former. On the other hand, it might also be a reflection of our neglect of yet higher-power ($m > 8$) contributions to the long-range potential (3).

The discussion in this section has considered only the inverse-power sum representation for the long-range potential. However, for cases in which $D$ is known, it might be preferable to utilize Goscinski's [1,0] Padé approximate representation, equation (43a). In this setting $G(\omega) = V[R_{2}(\omega)]$ would yield:

$$[R_{2}(\omega)]^{-4}[D - G(\omega)]^{-1} = (C_{6})^{-1} - [C_{6}/(C_{6})^{2}]R_{2}(\omega)$$

(49)

A plot of the left-hand side of equation (49) vs. $[R_{2}(\omega)]^{-5}$ will clearly yield $C_{6}$ and $C_{8}$ from its intercept and slope. Although the results Goscinski obtained on applying this technique to $B$-state CI and BrCl are less reliable than those presented in Table 9, his approach should prove to be of considerable use in the future.

In summary, therefore, it appears that long-range RKR analyses have a very bright future as a source of information about long-range potential coefficients $C_{n}$, particularly when coupled with a priori use of the vibrational eigenvalue expression (9).

7 Concluding Remarks

A feature common to all four of the methods described above is the fact that they readily allow the concurrent treatment of data for different isotopic forms of a molecule in a given electronic state. This is possible because within the Born—Oppenheimer approximation the internuclear potentials for the different isotopes are precisely the same. Furthermore, equations (6) and (38) imply that the vibrational—rotational eigenvalues of the different isotopes may be expressed as a single function of mass-reduced quantum numbers. In view of this, Stwalley has suggested replacing the normal $\nu$ and $J$ by

$$\eta = (\nu + \frac{1}{2})/\mu$$

and

$$\zeta = (J + 1)/\mu$$

He demonstrated that all the observed eigenvalues of HgH, HgD, and HgT could be expressed as a single function of these new variables. It is readily seen that the vibrational eigenvalue expressions (equations (8)–(13)) and the LBM equation (42) may be rewritten in terms of this \( \eta \) and \( \xi \). This is also possible for the \( B_r \) and RKR-potential expressions, equations (32) and (33) and (44)–(46), respectively, if \( B_r \) is replaced by the mass-reduced quantity \( \bar{B}_r = \mu B_r \). Concomitant mass-independent forms of all other expressions described above are also readily obtainable.

The great advantage of the type of ‘combined-isotope analysis’ which this mass scaling makes possible is that it provides a larger number of independent data in any given region than are available for any single isotopic form. As a result, uncertainties in the results of an analysis of such data would be much smaller than if the data for individual isotopes were analysed separately. This feature is particularly important for a species with a small reduced mass, for which case the density of levels is relatively small. For example, in the case of ground-state HgH the small number of vibrational levels seriously limits the accuracy with which an RKR curve may be obtained. However, using Stwalley’s variables \( \eta \) and \( \xi \) and treating the three isotopes HgH, HgD, and HgT as a single species allows the calculation of a much more reliable RKR potential. This feature was also exploited in the analysis of the functionality of the energies and \( B_r \) values of the highest observed levels of \( \text{Br}_2 \) (\( B^1 \)).

Another type of situation in which this ‘combined-isotope’ approach proves useful is one in which data for different isotopes happen to be available in mutually exclusive regions of the potential well. This occurs for \( \text{Br}_2 \) (\( B^\text{III} \)), for which there exist pure isotopes (\( ^{80}\text{Br}^{80}\text{Br} \) and \( ^{80}\text{Br}^{81}\text{Br} \)) measurements in the neighbourhods of both the potential minimum and the dissociation limit, but only mixed-isotope \( ^{80}\text{Br}^{81}\text{Br} \) results in the intermediate region. In calculating the RKR potential for this case one should ideally utilize Stwalley’s \( \eta \) and \( \xi \) to join smoothly the different sets of data.

It is perhaps noteworthy that all of the molecular species studied in this chapter are formed from uncharged atoms. In contrast, for ionic or ionized molecules, for which \( n = 1 \) and \( 4 \), respectively, the asymptotic potential tail will tend to bind a relatively higher density of levels in the immediate neighbourhood of \( D \). Thus, the present techniques, particularly those of Sections 3 and 4, should be even more important here than for the neutral–neutral interactions considered heretofore.

One point which deserves re-emphasis is the importance of verifying the validity of the inverse-power potential expansion [equation (3)] for the data under consideration. The significance of this question is underlined by the discovery in Section 5 that most of the reported applications of Bernstein’s \( \text{LBM} \) expression [equation (42)] were invalid. This problem was first quantitatively considered by Stwalley, who suggested \( R > 5 \) Å as a minimum requirement for the validity of equation (3). However, it seems clear that any such criterion should take account of the differing sizes of different atoms, and equation (5) seems to fulfill this requirement admirably. On the other hand, one may obviously formulate any number of analogous criteria for \( R \) which utilize other properties of the interacting atoms. In this vein, the RKR analysis of Mm suggested that the present criterion [equation (5)] might be somewhat pessimistic for atoms of the alkali metals or alkaline earths.

Prior to the development of the methods discussed in this chapter, the best way of studying experimentally long-range interaction potentials was via atomic beam scattering. It is interesting to note how effectively these two approaches complement one another. In spectroscopic observations, the selection rules for optical transitions readily distinguished between the several molecular states formed by the interaction of a pair of atoms with unfilled valence shells. This type of situation would be quite unsuited to the application of scattering techniques once all the energetically accessible potential curves would concurrently contribute to the observed cross-sections, and it would be virtually impossible to separate them. On the other hand, this latter approach may be very profitably applied to the study of interactions in which at least one of the atoms has a closed-shell electronic configuration, for which case the collision partners effectively interact according to a single potential function. However, this type of species is usually weakly bound and supports few vibrational levels. In addition to being relatively difficult to observe spectroscopically, the small number of levels makes any results that might be obtained quite difficult to analyse using the methods described above.

A particularly interesting connection between beam scattering and spectroscopic measurements is their mutual observation of the broadened rotationally predissociating levels discussed in Section 5.99 In a scattering experiment these levels, called ‘orbiting resonances’, manifest themselves as small peaks or dips in the cross-section plotted as a function of collision energy, their position yielding the energy of the particular level above the dissociation limit. Since the spectroscopic observation of such a broadened level

generally gives its position relative to the potential minimum, combining these two types of results should yield an accurate estimate of the molecular dissociation energy. However, these broad quasi-bound levels are relatively hard to observe by either technique so that this type of result is unlikely to be obtainable for many systems.

In conclusion, we have seen that spectroscopic studies of highly-excited vibrational–rotational levels are capable of yielding much hitherto unobtainable information about long-range intermolecular potentials. The comparisons in Tables 2 and 10 promise that such results will provide a very useful foil in the development of improved theoretical techniques for calculating interatomic forces. Although the utility of the methods described herein clearly depends on the availability of spectroscopic data for levels near dissociation, the growth of selective excitation and fluorescence techniques using lasers has made this region much more open to investigation. At present it appears that the methods of vibrational energy analysis introduced by Le Roy and Bernstein 16, 41 (see Section 3) and the long-range RKR analysis techniques proposed by Stwalley 42 and Cummings 38 (see Section 6) are the most useful. However, future developments 88 may also make $B_0$ values for levels near dissociation (see Section 4) another potent source of information about long-range potential, and improved versions of all the techniques discussed will almost certainly be obtained.

I am very grateful to Professors R. B. Bernstein and W. C. Stwalley for numerous helpful discussions, and to them, Dr. D. M. Gass and Professor W. J. Meath for critical comments on the manuscript. I would also like to thank Drs. F. E. Cummings and O. Goscinksi for sending me results prior to publication.