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Electron scattering from diatomic polar molecules. II. Treatment by frame transformations

Charles W. Clark
Department of Physics, University of Chicago, Chicago, Illinois 60637

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The theory of Chang and Fano is applied to electron scattering by polar molecules. For collision energy $E > E_{\min}$ the problem can be treated accurately without numerical radial integration; the solution is presented in a form suited to an R-matrix treatment of the molecular core. The value of $E_{\min}$ (in a.u.) is determined through $D\,Bj/E_{\min} < \delta \ll 1$; when $E < E_{\min} \approx$ a few eV, more extensive calculation is required beyond the body-frame Born-Oppenheimer region. For this purpose a generalization of the Chang-Fano theory is developed. It consists of an *adiabatic* continuous transformation of frame, the frame used at each electron-molecule distance r being determined directly by the dynamics of the problem. This procedure generates a coordination diagram for the known solutions to limiting cases, a diagram analogous to that used in quantum chemistry for connecting the united-atom and separated-atom limits of molecular-orbital theory. A new type of symmetry in the problem is made apparent. Preliminary discussion is made of the applicability of this method to more general problems of close coupling in the asymptotic region.

I. INTRODUCTION

In this paper the problem of electron scattering by diatomic polar molecules is treated by a frame transformation theory.[1] A frame transformation treatment of the weakly polar CO molecule has been provided by Chandra[2]; the present application is to the case in which the dipole interaction is clearly dominant at intermediate and large electron-molecule distances r, as obtains in the alkali- and hydrogen-halides. Considerable literature exists dealing with the application of other methods to this problem[3]; the use of frame transformations in electron scattering by atoms and by nonpolar molecules is also well known.[4]

The basic idea of frame transformation theory is that different angular momentum coupling schemes are appropriate in different regions of the distance r. The equations of motion can be solved separately within each region, and the solutions are joined at the boundary between regions by application of appropriate transformations. In electron collisions with diatomic molecules the wave function at small r is best described in the molecular body frame; at large r, where the electron's motion becomes decoupled from the molecular axis, a laboratory frame description is more appropriate. The corresponding transformation theory has been given by Chang and Fano,[1] whose formalism and notation are adopted here. The electron-molecule configuration space is separated into three regions[5]: an inner region ($r < r_0$) where exchange is important; Region A ($r_0 < r < r_1$) in which the electron-molecule interaction is a static potential and the Born-Oppenheimer approximation holds; and Region B($r > r_1$) in which the angular momenta l and j of electron and molecule are nearly conserved separately (see Fig. 1). The value of r_0 is roughly equal to the electronic size of the molecule, i.e., 5–10 a.u. The magnitude of r_1 is determined by the requirement that the Born-Oppenheimer approximation have a specific degree of accuracy within Region A; it is dependent on the dynamical variables of the problem and may be as large as a few hundred a.u.

This paper will not deal in detail with the solution in the inner region. There the problem is essentially many particle and requires a different type of treatment than that appropriate in the outer regions. We shall develop here the solutions of the equations of motion in Regions A and B, with the solution in the inner region taken as input from some other calculation. This approach conforms to the general R-matrix philosophy of Burke and others[6]; the outer region solutions are cast here in a form suitable for use in an R-matrix calculation, but can be easily adapted to alternative treatments of the inner region.[7]

In Sec. II we start from the solution to the Schrödinger equation at $r = r_0$ and propagate it outward to $r = r_1$. In this region the electron-molecule interaction is a sum of electric multipole potentials. Experience indicates, however, that the effect of higher multipole moments is most important in the inner region and so only the electric dipole term is retained in the outer regions. Then the solution at r_1 can be obtained without numerical integration, for the wave function in Region A is a combination of known Bessel functions.[8] The identification of the frame in Region A requires numerical diagonalization of a matrix; the necessary formulas are summarized in the Appendix. These results have also been examined in other literature.[9]

In Sec. III we consider the propagation of the wave function from r_1 to infinity. Here, too, a

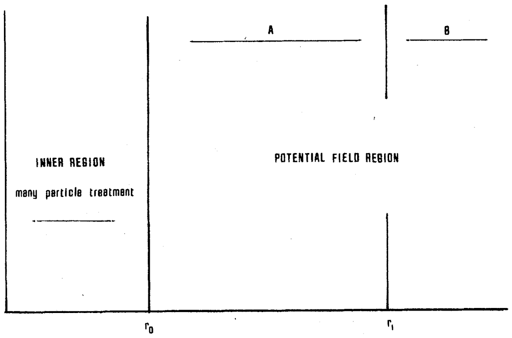


FIG. 1. Regions of electron-molecule configuration space (after Chang and Fano).

formal solution to the equations of motion is available. It does not, however, admit easy evaluation in general. We consider first the case in which the solution can be obtained from perturbation theory (essentially by a modified Born approximation). This completes the solution to the equations of motion in Regions A and B for collision energies E greater than a few eV; the low-energy limit to this approach $E_{\min}$ depends on molecular parameters through Eq. (29). The existence of this limit can be inferred from other literature,[10] but its origin and consequences have not received much serious consideration. When $E<E_{\min}$ a very considerable amount of numerical work will be required to solve the equations in Region B.

In the remainder of the paper we develop a new framework for analyzing the solution in Region B. It introduces an adiabatic transformation of the body frame into the laboratory frame; the frame transformation is thus performed continuously in r instead of at the point r_1 as in the Chang-Fano theory. The applicability of this method has not yet been evaluated in full, but the results obtained thus far are of considerable physico-mathematical interest in their own right. This type of transformation may be useful in more general problems of electron collision physics, for it reduces the strength of long-range interactions by an additional power of the distance.

This last remark underscores the motivation as well as broader implications of the present paper. Most of the extensive computational work on electron collisions with polar molecules has proceeded by close-coupling techniques, whether in the lab or in the body frame.[11] More generally, numerical solution of problems involving long-range noncentral interactions has become of considerable importance throughout atomic and molecular physics (e.g., in atomic photoionization). The very slow convergence of close-coupling calculations at large r—of which the subject of our Sec. III is an example—has been the cause of serious practical and conceptual difficulty. While accurate calculations of the inner region solutions over wide ranges of energy have become standard with present technology, the solutions in Region B need separate calculation at each energy and require far more computer time. It is, moreover, quite difficult to unearth the basic physics of a wave function which is only obtained by numerical integration of coupled radial equations over hundreds or thousands of Bohr radii. The strong noncentral interaction and closely spaced final states of the electron-polar molecule problem present an extreme case of this phenomenon. Thus the developments of the final section of this paper are intended as a first step towards understanding more general problems of close coupling at large distances.

II. BODY-FRAME TREATMENT IN REGION A

The Hamiltonian for the electron-molecule system in the outer regions A,B is (in a.u.)

$$H=-\tfrac{1}{2}\vec{\nabla}^2+V(\vec{r},\vec{R})+B\vec{j}^2+h_{\mathrm{vib}}\,, \tag{1}$$

where $\vec{\nabla}$ operates on the electron coordinate r; $\vec{R}$ is the molecular internuclear coordinate, B the molecular rotational constant, and $\vec{j}$ the molecular angular momentum. We shall not consider processes involving vibrational excitation[12] and so take the molecular vibrational energy h_{vib} to be constant. Only the dipole term in the interaction $V(\vec{r},\vec{R})$ will be retained; the contribution from higher multipole terms dies off faster with increasing r, and its short-range effect is primarily accounted for in the inner region. Thus we set $V(\vec{r},\vec{R})=-D\cos\vartheta'/r^2$ with ϑ' the angle between electron position and molecular axis.

In these units one has typically $B\sim10^{-7}$–10^{-5} and $D\sim1$–4. Thus for moderate values of $r\,(r<r_1)$ the rotational energy of the molecule may be disregarded in comparison with V. This defines Region A; the Schrödinger equation in that region is thus

$$\left(\frac{d^2}{dr^2}+k^2-(\vec{l}^2-2D\cos\vartheta')r^{-2}\right)\psi=0\,, \tag{2}$$

where $\frac{1}{2}k^2=E$ is the total energy. In this approximation the projection $\Lambda=\hat{R}\cdot\vec{l}$ of the electronic angular momentum upon the molecular axis is a constant of the motion.

Equation (2) may then be solved rather simply in two steps.

(i) Find the eigenvalues $N(N+1)$ and the eigenfunctions $\Omega_N^{(\Lambda)}$ of the operator $\vec{l}^2-2D\cos\vartheta'$,

$$(\vec{l}^2-2D\cos\vartheta')\Omega_N^{(\Lambda)}=N(N+1)\Omega_N^{(\Lambda)}\,. \tag{3}$$

(ii) With $\psi(\vec{r})=\sum_{N,\Lambda}\Omega_N^{(\Lambda)}g_N^{(\Lambda)}(r)$, solve the radial equations

$$\left(\frac{d^2}{dr^2}+k^2-\frac{N(N+1)}{r^2}\right)g_N^{(\Lambda)}(r)=0\,. \tag{4}$$

By expanding the eigenfunctions $\Omega_N^{(\Lambda)}$ in spherical harmonics

$$\Omega_N^{(\Lambda)} = \sum_l A_{Nl}^{(\Lambda)} Y_{l\Lambda}(\vartheta', \varphi'), \tag{5}$$

the eigenvalues $N(N+1)$ and coefficients $A_{Nl}^{(\Lambda)}$ are readily obtained by diagonalizing a tridiagonal matrix; explicit formulas are given in the Appendix. The eigenvalues $N(N+1)$ depend on both $|\Lambda|$ and D; for $D=0$ they are given by $N=l=|\Lambda|, |\Lambda|+1, \ldots$. For sufficiently large l the dipole term of (3) may be treated perturbatively,

$$N \to l + 0(D^2/l^2).$$

The first few eigenvalues for $\Lambda=0,1,2$ are shown as functions of D in Fig. 2. Note that the lowest eigenvalue for each Λ decreases monotonically with increasing D, whereas the higher eigenvalues increase at first near $D=0$; in other words, the dipole interaction is effectively repulsive for higher partial waves.

When N is known, the solution of Eq. (4) is immediate:

$$g_N^{(\Lambda)}(r) = \alpha_N^{(\Lambda)} \tilde{j}_N(kr) - \beta_N^{(\Lambda)} \tilde{y}_N(kr), \tag{6}$$

where $\tilde{j}_N(kr) = k^{1/2} r j_N(kr)$ and $j_N(kr), y_N(kr)$ are the regular and irregular spherical Bessel functions; the Wronskian $W\{\tilde{j}_N, \tilde{y}_N\} = 1$. For sufficiently strong dipole moments, the eigenvalues $N(N+1)$ will become negative. When $N(N+1) < -\frac{1}{4}$, the "centrifugal" potential of Eq. (4) becomes attractive; this occurs when the dipole moment is greater than a critical value, $D > D_c(\Lambda)$. Then $N = -\frac{1}{2} + i\mu$, and the definition of $\tilde{j}_N, \tilde{y}_N$ must be revised to keep g real and $W=1$:

$$\tilde{j}_N(kr) = (\tfrac{1}{2}\pi r)^{1/2}[1/\sinh(\tfrac{1}{2}\pi\mu)]\ \mathrm{Im}(J_{i\mu}(kr))$$

$$\tilde{y}_N(kr) = (\tfrac{1}{2}\pi r)^{1/2}[-1/\cosh(\tfrac{1}{2}\pi\mu)]\ \mathrm{Re}(J_{i\mu}(kr)). \tag{7}$$

The analytic properties of these functions are discussed by Greene *et al.*[13] and we have a computer code to evaluate them numerically. In this context the D_c of interest are $D_c(\Lambda=0) = 0.639$ a.u. and $D_c(\Lambda=1) = 3.79$ a.u. For polar molecular ions the same treatment is applicable: the angular functions $\Omega_N^{(\Lambda)}$ are the same, and the radial functions (6) are given by replacing j_N, y_N by the Coulomb wave functions[14] F_N, G_N.

The ratio between the constants α, β of Eq. (6) is determined from the *inner* region solution; on the other hand, their actual magnitude depends upon boundary conditions imposed at *large r* (i.e., normalization of incoming or outgoing waves). Since at this stage we are dealing only with the solution in Region A, it is not yet appropriate to specify α and β. Instead, we use them to construct a transformation, diagonal in N and Λ, which expresses the values of each radial function (6) and its derivative at $r=r_1$ in terms of their values at $r=r_0$.

Equation (6) and its derivative can be expressed as

$$\begin{pmatrix} g_N^{(\Lambda)}(r) \\ g_N'^{(\Lambda)}(r) \end{pmatrix} = \begin{bmatrix} \tilde{j}_N(kr) & -\tilde{y}_N(kr) \\ \tilde{j}_N'(kr) & -\tilde{y}_N'(kr) \end{bmatrix} \begin{pmatrix} \alpha_N^{(\Lambda)} \\ \beta_N^{(\Lambda)} \end{pmatrix}, \tag{8}$$

where primes denote the radial derivative. More generally,

$$\begin{pmatrix} g(r) \\ g'(r) \end{pmatrix} = \begin{bmatrix} \tilde{j}(kr) & -\tilde{y}(kr) \\ \tilde{j}'(kr) & -\tilde{y}'(kr) \end{bmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \tag{8'}$$

where g, α are to be understood as column vectors whose elements are the $g_N^{(\Lambda)}(r)$ and $\alpha_N^{(\Lambda)}$, respectively; $\tilde{j}, \tilde{y}$ are diagonal matrices whose elements are $\tilde{j}_N(kr), \tilde{y}_N(kr)$. By applying the transformation (8′) at $r=r_1$ and its reciprocal at $r=r_0$, we obtain

$$\begin{pmatrix} g(r_1) \\ g'(r_1) \end{pmatrix} = \begin{bmatrix} \tilde{j}(kr_1) & -\tilde{y}(kr_1) \\ \tilde{j}'(kr_1) & -\tilde{y}'(kr_1) \end{bmatrix} \times \begin{bmatrix} \tilde{y}'(kr_0) & -\tilde{y}(kr_0) \\ \tilde{j}'(kr_0) & -\tilde{j}(kr_0) \end{bmatrix} \begin{pmatrix} g(r_0) \\ g'(r_0) \end{pmatrix}. \tag{9}$$

The determination of g and g' at r_0 is obtained from the inner region solution. If the wave function is expanded in spherical harmonics

$$\psi(r) = \sum_{l\Lambda} f_l^\Lambda(r) Y_{l\Lambda}(\vartheta, \varphi), \tag{10}$$

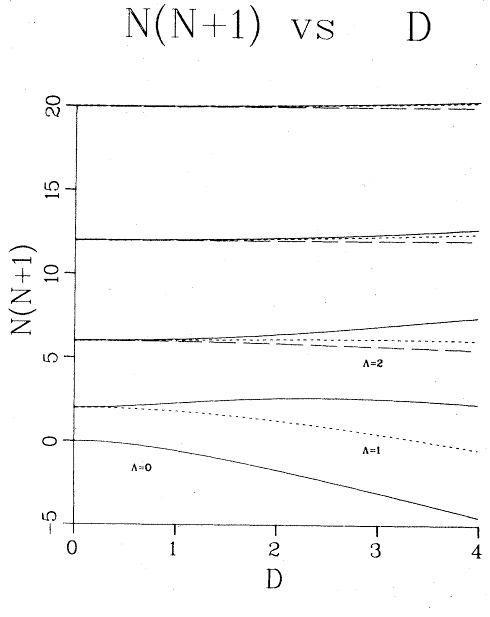


FIG. 2. Eigenvalues $N(N+1)$ of Eq. (3) as a function of dipole moment. The solid lines are successive eigenvalues for $\Lambda=0$; the dashed and chain dotted lines correspond to $\Lambda=1$, 2, respectively.

at $r \sim r_0$ then the inner region solution specifies a homogeneous relation between the f_l^Λ and their radial derivatives at $r = r_0$.[15] In terms of the R matrix of Burke[6] (with $b = 0$ and $a = r_0$),

$$f_l^\Lambda(r_0) = r_0 \sum_{l'} R_{ll'}^{(\Lambda)}(r_0) \frac{d}{dr} f_{l'}^\Lambda \Big|_{r_0} . \tag{11}$$

The equivalent expression for (11) in terms of the dipole radial functions is thus

$$g_N^{(\Lambda)}(r_0) = \sum_{N'} \overline{R}_{NN'}^{(\Lambda)}(r_0) \frac{d}{dr} g_{N'}^{(\Lambda)} \Big|_{r_0} , \tag{12}$$

where

$$\overline{R}_{NN'}^{(\Lambda)}(r_0) = r_0 \sum_{l,l'} A_{Nl}^{(\Lambda)} A_{N'l'}^{(\Lambda)} R_{ll'}^{(\Lambda)}(r_0) . \tag{13}$$

In the matrix notation of Eqs. (8′) and (9), Eq. (12) is equivalent to:

$$\begin{pmatrix} g(r_0) \\ g'(r_0) \end{pmatrix} = \begin{bmatrix} \overline{R} & 0 \\ 0 & 1 \end{bmatrix} \begin{pmatrix} g'(r_0) \\ g'(r_0) \end{pmatrix} , \tag{14}$$

where $\overline{R}$ is a matrix block-diagonal in Λ whose elements are the $\overline{R}_{NN'}^{(\Lambda)}(r_0)$ of Eq. (13).

Since partial waves with sufficiently large N do not penetrate the inner region, the elements of $\overline{R}$ will tend to

$$\overline{R}_{NN'}^{(\Lambda)}(r_0) \xrightarrow[N \to \infty]{} \delta_{NN'}/N+1 \tag{15}$$

as N increases. The dimensionality of the systems of Eqs. (9), (14) is thus determined by the range of N, Λ over which $\overline{R}$ is significantly different from the trivial form (15). The partial waves which do not penetrate the inner region can be treated independently, by setting $\beta_N^{(\Lambda)} = 0$ in Eq. (6).

Substitution of Eq. (14) on the right-hand side of Eq. (9) yields on expression for the radial functions $g_N^{(\Lambda)}$ and their derivatives on the surface $r = r_1$ in terms of the derivative vector $g'(r_0)$. From the resulting expression

$$\begin{pmatrix} g(r_1) \\ g'(r_1) \end{pmatrix} = \begin{bmatrix} A_1 & A_2 \\ A_3 & A_4 \end{bmatrix} \begin{pmatrix} g'(r_0) \\ g'(r_0) \end{pmatrix} , \tag{16}$$

one can obtain the R matrix at r_1, defined analogously to that of Eq. (12) by

$$g_N^{(\Lambda)}(r_1) = \sum_{N'} \overline{R}_{NN'}^{(\Lambda)}(r_1) \frac{d}{dr} g_{N'}^{(\Lambda)} \Big|_{r_1} .$$

The matrix $\overline{R}(r_1)$ is then

$$\overline{R}(r_1) = (A_1 + A_2)(A_3 + A_4)^{-1} ,$$

where the matrices A are constructed from products of $\overline{R}(r_0)$ and of the matrices in Eq. (9).

At this point the calculation in Region A is completed. Much previous work has taken the electron's motion in Region B to be that of a free particle; when this is appropriate, Eq. (16) can be used to generate the body-frame S and K matrices. We shall not carry out this development just yet, as the Region B solutions require specific examination. This is provided in Sec. III.

III. LABORATORY-FRAME TREATMENT OF REGION B

The boundary $r = r_1$ of Region B is defined by the condition that the rotational energy of the molecule be no longer negligible in comparison to the dipole potential energy. This definition will be made explicit at the end of this section. For the moment we will consider the laboratory-frame solution of the equations of motion in Region B, without restriction on the actual value of r_1.

Since molecular rotation is to be taken into account and, presumably, l and j are nearly constants of the motion, the appropriate basis of angular functions consists of the $\Phi_{JM}^{(lj)}$ of Chang and Fano[1]

$$\Phi_{JM}^{lj} = \sum_m Y_{lm}(\vartheta, \varphi) Y_{jM-m}(\theta, \phi)(lmjM-m \,|\, ljJM) .$$

The arguments of the spherical harmonics are the angles of the electron position and the molecular orientation in a laboratory-fixed frame. It will be convenient to employ a single index L to denote the set of indices $ljJM$; the results of this section do not depend on M.

We shall obtain a formal solution to the equations of motion in $r > r_1$ using the phase-amplitude method of Chang and Fano (CF). The electron-molecule wave function is written as

$$\psi = \sum_L F_L(r) \Phi^{(L)} , \tag{17}$$

and we introduce new dependent variables $f_L(r)$, $\overline{f}_L(r)$ through

$$\begin{aligned} F_L(r) &= f_L(r) \tilde{j}_L(r) - \overline{f}_L(r) \tilde{y}_L(r) , \\ \tilde{j}_L f'_L &= \tilde{y}_L \overline{f}'_L , \end{aligned} \tag{18}$$

where $\tilde{j}_L(r) = r(k_L)^{1/2} j_l(k_L r)$ and $\frac{1}{2}k_L^2 = \frac{1}{2}k_j^2 = \frac{1}{2}k^2 - Bj(j+1)$. This representation is analogous to that of Eq. (6) for the body-frame solutions, except that the coefficients of $\tilde{j}, \tilde{y}$ vary with r. The Hamiltonian of Eq. (1) is then equivalent to a system of integral equations for $f, \overline{f}$, in accordance with Eq. (32) of CF:

$$
\begin{aligned}
f_L(r) &= f_L(r_1) - 2D\sum_{L'} (k_L k_{L'})^{1/2} \langle L\,|\cos\vartheta'|\,L'\rangle \int_{r_1}^{r} dp\, y_l(k_j p)\left[f_{L'} j_{l'}(k_{j'} p) - \bar{f}_{L'} y_{l'}(k_{j'} p)\right] , \\
\bar{f}_L(r) &= \bar{f}_L(r_1) - 2D\sum_{L'} (k_L k_{L'})^{1/2} \langle L\,|\cos\vartheta'|\,L'\rangle \int_{r_1}^{r} dp\, j_l(k_j p)\left[f_{L'} j_{l'}(k_{j'} p) - \bar{f}_{L'} y_{l'}(k_{j'} p)\right] .
\end{aligned} \tag{19}
$$

Here $\langle L\,|\cos\vartheta'|\,L'\rangle = \langle ljJM\,|\cos\vartheta\,|\,l'j'J'M'\rangle$ is diagonal in J, M and independent of M. From the linearity of Eq. (19) we may write

$$
\begin{pmatrix} f(r) \\ \bar{f}(r) \end{pmatrix} = \left[1 + \begin{pmatrix} W(r;r_1) & \bar{W}(r;r_1) \\ \bar{V}(r;r_1) & V(r;r_1) \end{pmatrix} \right] \begin{pmatrix} f(r_1) \\ \bar{f}(r_1) \end{pmatrix} , \tag{20}
$$

where, as in the body-frame treatment, f and $\bar{f}$ are to be understood as column vectors whose components are the $f_L(r), \bar{f}_L(r)$; and W, V are square matrices to be evaluated below. As $r \to \infty$, $f_L(r)$ and $\bar{f}_L(r)$ become constant; with $f_L, \bar{f}_L = \lim_{r\to\infty} f_L(r), \bar{f}_L(r)$ we have $\bar{f}_L = \tan\delta_L f_L$, where δ_L is the phase shift in the radial function of channel L. Thus this representation leads us directly to the laboratory-frame reactance matrix K as follows.

Equation (18) yields

$$
\begin{pmatrix} f(r_1) \\ \bar{f}(r_1) \end{pmatrix} = \begin{bmatrix} \bar{y}'(r_1) & -\bar{y}(r_1) \\ \bar{j}'(r_1) & -\bar{j}(r_1) \end{bmatrix} \begin{pmatrix} F(r_1) \\ F'(r_1) \end{pmatrix} \tag{21}
$$

in the vector notation utilized previously; $\bar{j}, \bar{y}$ are again diagonal matrices with elements $\bar{j}_L(r_1), \bar{y}_L(r_1)$. The functions $F_L(r_1), F'_L(r_1)$ are expressed in terms of $g_N(r_1), g'_N(r_1)$ by transforming the dipole body-frame angular functions $\Omega_N^{(\Lambda)}$ into the lab-frame angular functions Φ_{JM}^{lj}. Thus

$$
\begin{pmatrix} F(r_1) \\ F'(r_1) \end{pmatrix} = \begin{bmatrix} B & 0 \\ 0 & B \end{bmatrix} \begin{pmatrix} g(r_1) \\ g'(r_1) \end{pmatrix} , \tag{22}
$$

where B is the square matrix $B_{LN} = A_{Nl}^{(\Lambda)} U_{j\Lambda}^{(lJ\eta)}$, the $U_{j\Lambda}^{(lJ\eta)}$ being the standard frame transformation coefficients of CF:

$$
U_{j\Lambda}^{(lJ\eta)} = (-1)^{J+\Lambda} \frac{\left[1+\eta(-1)^{J-l-j}\right]}{\left[2(1+\delta_{\Lambda 0})\right]^{1/2}} \times (2j+1)^{1/2} \begin{pmatrix} l & J & j \\ \Lambda & -\Lambda & 0 \end{pmatrix} . \tag{23}
$$

By combining Eqs. (22), (21), and (16), and denoting $W(r_1) = \lim_{r\to\infty} W(r, r_1)$, etc., we have

$$
\begin{pmatrix} f \\ \bar{f} \end{pmatrix} = \begin{pmatrix} K_1 & K_2 \\ K_3 & K_4 \end{pmatrix} \begin{pmatrix} g'(r_0) \\ g'(r_0) \end{pmatrix} , \tag{24}
$$

where

$$
\begin{pmatrix} K_1 & K_2 \\ K_3 & K_4 \end{pmatrix} = \left(1 + \begin{pmatrix} W(r_1) & \bar{W}(r_1) \\ \bar{V}(r_1) & V(r_1) \end{pmatrix} \right) \times \begin{pmatrix} \bar{y}'(r_1) & -\bar{y}(r_1) \\ \bar{j}'(r_1) & -\bar{j}(r_1) \end{pmatrix} \begin{pmatrix} B & 0 \\ 0 & B \end{pmatrix} \begin{pmatrix} A_1 & A_2 \\ A_3 & A_4 \end{pmatrix} . \tag{25}
$$

By eliminating the $g'(r_0)$ in Eq. (24) we then find the reactance matrix K, defined by $\bar{f} = Kf$:

$$
K = (K_3 + K_4)(K_1 + K_2)^{-1} . \tag{26}
$$

Of the quantities occurring in Eq. (25) all are either standard functions or are computed in Region A, except for the matrices $W, \bar{W}, \bar{V}, V$. These are determined entirely by the equation of motion in Region B; a pure body-frame treatment is equivalent to setting them equal to zero.

A formal expression for these matrices may be obtained by solving the integral Eq. (19) by iteration. With $M_{LL'} = 2D\langle L\,|\cos\vartheta'|\,L'\rangle$, one finds for $W_{LL'}$ the series

$$
\begin{aligned}
W_{LL'}(r;r_1) = {} & -M_{LL'} \int_{r_1}^{r} dp\, y_l(k_j p) j_{l'}(k_{j'} p) \cdot (k_j k_{j'})^{1/2} + \sum_{L''} M_{LL''} M_{L''L'} \\
& \times \int_{r_1}^{r} dp \int_{r_1}^{p} dp'\, y_l(k_j p) y_{l''}(k_{j''} p) j_{l''}(k_{j''} p') j_{l'}(k_{j'} p') \cdot (k_j k_{j''}^2 k_{j'})^{1/2} + \dots ,
\end{aligned} \tag{27}
$$

where each successive term involves an additional integration. The expansions for $\bar{W}, \bar{V}, V$ are the same up to changes of sign and exchanges of j and y.

Though the convergence of this series is formally guaranteed, actual evaluation in the general case is a substantial numerical task. At each additional iteration the number of terms in the sum over intermediate L'' increases by a factor of 4, and an additional multiplicative factor of D is introduced. Each product of Bessel functions in (27) can be separated into a sum of oscillatory terms with radial frequencies $k_{\pm}=k_j \pm k_{j'}$. We consider the case in which the total collision energy is much greater than the difference in energy between typical molecular rotational states, so that $k_+ \approx 2k$ and k_- is small (it will be seen below that this restriction is consistent with the results). The term with k_+ then converges rapidly in successive integrations. The dominant contribution to $W(r, r_1)$ comes from the integration of oscillatory functions of long wavelength $1/k_-$, modulated by inverse powers of r. These converge rather slowly; by evaluating $W_{LL'}$ to first order only we find[16] that

$$W^{(r_1)}_{LL'} \approx D/\varkappa_{LL'} r_1 , \quad \varkappa_{LL'} = (k_L k'_L)^{1/2} . \tag{28}$$

Thus the contribution to the scattering matrix from Region B vanishes only as the inverse of the frame transformation distance r_1.

This slow convergence is not due to a poor choice of representation, but is an essential consequence of the slow "beat" frequencies between wave functions of adjacent l_j. This same phenomena arises in a variety of electron collision calculations, in which adequate convergence of phase shifts is obtained only after numerical integration out to very large r, as mentioned in Sec. I.

Since the frame transformation theory in its present form is not adapted to deal with the coupled Eqs. (19) in the general case, we consider the circumstances in which the Region B solution may be obtained from perturbation theory, i.e., by evaluation of $W(r_1)$ to first order only. This is equivalent to applying a modified Born approximation[17] in Region B; the fractional error introduced is then of the order of the typical value of the matrix elements $W(r_1)$, $\overline{W}(r_1)$, etc. Thus to obtain a given accuracy δ' in the Region B solution we must have $r_1 > \overline{r}_1 = D/\delta'(2E)^{1/2}$, from Eq. (28). This criterion must be reconciled with having r_1 small enough so that the methods employed in Region A are accurate.

As is well known,[1,3] the body-frame propagation matrices are accurate to order δ if $(\Delta k) r_1 < \delta$. Here Δk is the variation of k_j over the range of j in the problem. If the total energy E is greater than the spacings between molecular rotational states so that $\Delta k = (2Bj/E)^{1/2}$, we must have $r_1 < \delta/(\Delta k) = \delta(\frac{1}{2}E)^{1/2}/(Bj)$. Then in order that $r_1 > \overline{r}_1$ we must have

$$DBj/E < \delta\delta' . \tag{29}$$

When this criterion holds, the methods of Secs. II and III provide the solution to the scattering problem with minimal numerical calculation (i.e., without radial integration) beyond that for the inner region. For a given required accuracy, Eq. (29) implies a lower limit $E_{\min}$ to the range of energies over which this treatment is valid. If, for example, a total error of 10% is regarded as tolerable, then $\delta \sim 0.1$ and $\delta' \sim 0.01$. For some typical polar molecules at room temperature we find the values of $E_{\min}$ and r_1 listed in Table I.

TABLE I. Values of $E_{\min}$ and r_1 for some typical polar molecules at 300 °K.

Molecule	$E_{\min}$ (eV)	r_1 (a.u.)
LiF	5	40
KCl	2.7	92
CsF	2.2	71
KBr	1.6	114
HBr	1.6	10

On the other hand, for many applications (e.g., magnetohydrodynamics (MHD) kinetics[18] and perturbation of Rydberg series[19]) one needs to deal with energies considerably lower than these. Since r_1 decreases with decreasing energy, the calculation in Region B becomes more important. The structure of the equations of motion in the laboratory frame does not offer much of a hint toward the essential physics in this region. In the remainder of this paper we shall develop an approach towards a more general qualitative understanding of the problem, by introducing a continuous transformation of frame.

IV. ADIABATIC FRAME TRANSFORMATION

In recent years there have been successful applications of adiabatic methods to a number of problems,[20-23] in which adiabaticity was not indicated at the outset, as it usually is,[24] by the existence of intrinsically different time scales in the problem. The principal value of the adiabatic classification of states in these problems seems to have been in providing a scheme for interpolating the character of solutions between limiting cases of solutions between limiting cases of known symmetry.

In the remainder of this paper an adiabatic-diabatic approach to the problem of electron scattering from polar molecules will be developed. The full range of applicability of this method, in the sense of providing an accurate description of the electron radial motion, has not yet been tested adequately. However, it generates a coordination diagram for the angular wave functions between the limit $r=0$ and $r=\infty$. In those two limits the problem admits known solutions with specific symmetries. Another definite symmetry in the adiabatic solutions appears at one intermediate value of $r=(2B)^{-1/2}$ a.u. It will be shown that although symmetries exist strictly only in these three cases, a quasisymmetry of the adiabatic solutions can be traced in an unambiguous manner throughout the entire range of electron distances. This suggests an approximate separability of the equations of motion.[25] An analogous quasisymmetry of the type to be described has emerged for the collision of polar molecules, which also involves a noncentral interaction.[26]

The meaning of "adiabatic" used here in accordance with general collision theory[20-23] *contrasts* with the meaning of the same term in much of the specific literature of electron-molecule collisions. In this field the term "adiabatic approximation" generally[3] denotes various calculational schemes in which the molecular axis is regarded as fixed in space during the time of the collision. These schemes may be regarded as variants of the body-frame approximation of Sec. II. In the following development, however, the adiabatic frame is generated by the instantaneous dynamics of the problem. It nearly coincides with the body frame at small r and with the lab frame at large r. At intermediate distances it does not have such simple geometrical interpretations, but is nevertheless defined unambiguously. "Adiabatic approximation" amounts here specifically to disregarding certain velocity-dependent terms in the equation of motion; this term has also been so used in a recent calculation of electron scattering by N_2.[27]

Near avoided crossings of adiabatic potentials, the nature of the adiabatic channels changes suddenly, thus violating conservation of some approximate symmetry. For sufficiently high radial speeds the conservation rule tends to prevail, and the system changes from one adiabatic channel to another. This behavior is called diabatic. For example, in the first case of Sec. V A, diabaticity results from separate conservation of l and j.

As in the problem of atomic collisions, the adiabatic approximation gives elastic scattering only, because the system exists in the same channel that it enters. This is also the case if the collision process is perfectly diabatic at particular crossings. On the other hand, there is substantial inelasticity in electron scattering from polar molecules. In the context of this paper, inelasticity may be considered as being produced by two distinct mechanisms. Near the avoided crossings of adiabatic potential curves, the motion of the electron will be neither entirely adiabatic nor entirely diabatic. There are a finite number of these points at which inelastic transitions may occur. Away from avoided crossings the adiabatic and diabatic approximations are identical. In this case there may be a cumulative failure of the approximation due to interchannel coupling by velocity-dependent terms.

Section V details the construction of the adiabatic potentials and the characteristics of the adiabatic states. In Sec. VI the applicability of the method is discussed.

V. ADIABATIC AND DIABATIC POTENTIALS AND EIGENSTATES

The Hamiltonian to be considered is that of Eq. (1) of Sec. II,

$$H=\tfrac{1}{2}p^2+B\vec{\mathrm{j}}^2-D(\cos\vartheta'/r^2)\quad(\text{in a.u.}),$$

where p is the electronic momentum; B, $\vec{\mathrm{j}}$, and D are defined as previously. We shall proceed without neglecting any terms; the appropriate Schrödinger equation is then

$$\left(\frac{d^2}{dr^2}+k^2-\frac{V}{r^2}\right)\psi=0\,, \tag{30}$$

where

$$V=\vec{\mathrm{l}}^2+\rho\,\vec{\mathrm{j}}^2-2D\cos\vartheta'\,, \tag{31}$$

where $\rho=2Br^2$. The diagonalization of V at fixed r provides a complete set of angular functions $\phi_i(\Omega;r)$:

$$V\phi_i(\Omega;r)=\epsilon_i(r)\phi_i(\Omega;r)\,.$$

Whereas in Secs. II and III the angular functions for electron and molecule were chosen according to the prescription of Chang and Fano, we shall now refer all angular functions to the basis of eigenvectors of V. These eigenfunctions reduce to the body- and laboratory-frame basis functions of Chang and Fano in the limits $r=0$ and $r=\infty$. Setting $\psi=\Sigma b_i(r)\phi_i(\Omega;r)$ the Schrödinger equation becomes

$$\left(\frac{d^2}{dr^2}+k^2-\frac{\epsilon_i(r)}{r^2}\right)b_i(r)$$

$$=-\sum_j 2(\phi_i|\phi_j')\frac{d}{dr}b_j(r)+(\phi_i|\phi_j'')b_j(r)\,, \tag{32}$$

where $\phi_j'=(d/dr)\phi_j$ and the brackets denote as usual integration over all angular coordinates. The adiabatic approximation disregards the right-hand side of (32). Since the resultant equation then admits standing-wave solutions confined to single adiabatic channels, the scattering process in this approximation is entirely elastic.

The total angular momentum J and the parity $\eta(-1)^J$ commute with V. For each $J>0$ there are then two families of states which do not couple, corresponding to $\eta=\pm1$ (favored or unfavored, respectively).[1] The component M of J along a fixed direction is also a constant of the motion, but since $\cos\vartheta'$ is a scalar with respect to J the value of M does not enter the problem. V is most easily studied in the basis of functions $|lj\eta JM\rangle$:

$$
\begin{aligned}
|lj\eta JM\rangle = i^{l+j}\sum_m\, & (lmjM-m\,|ljJM) \\
& \times Y_{lm}(\vartheta,\varphi)Y_{jM-m}(\theta,\phi)\,, \\
= i^{l+j}\Phi_{JM}^{(lj)}\,. &
\end{aligned}
\tag{33}
$$

The choice of phase i^{l+j} standardizes the signs of matrix elements of tensor operators.[28] It is convenient to write the set of vector components representing a superposition $\phi=\sum_{l,j}a_{lj}\,|lj\eta JM\rangle$ in a tabular form. Setting $\mu=\frac{1}{2}(1-\eta)$, we arrange the components a_{lj} in a rectangular array

$$
\begin{array}{ccccc}
a_{\mu J} & a_{\mu+1,J+1} & \cdots & a_{\mu+n,J+n} & \cdots \\
a_{\mu+1,J-1} & a_{\mu+2,J} & \cdots & \cdot & \\
a_{\mu+2,J-2} & & & \cdot & \\
\cdot & \cdot & & \cdot & \\
\cdot & \cdot & & & \\
\cdot & \cdot & & & \\
a_{J\mu} & a_{J+1,\mu+1} & \cdots & a_{J+n,\mu+n} & \cdots
\end{array}
\quad . \tag{34a}
$$

The elements of each column of (34a) have an equal value of $l+j$; those of each row have equal $l-j$.

It will prove convenient to relabel the subscript by a single index,

$$
\begin{array}{ccccc}
a_1 & a_{J+2-\mu} & \cdots & a_{n(J+1-\mu)+1} & \cdots \\
a_2 & a_{J+3-\mu} & & & \\
\cdot & \cdot & & & \\
\cdot & \cdot & & & \\
\cdot & \cdot & & & \\
a_{J+1-\mu} & a_{2(J+1-\mu)} & \cdots & a_{(n+1)(J+1-\mu)} & \cdots
\end{array}
\quad . \tag{34b}
$$

In the basis thus defined the matrix of V can be arranged as a tridiagonal array of submatrices $D^{(i)}$ and $T^{(i)}$,

$$
V=\begin{bmatrix}
T^{(1)} & D^{(1)} & 0 & 0 & \cdots \\
D^{(1)} & T^{(2)} & D^{(2)} & 0 & \cdots \\
0 & D^{(2)} & T^{(3)} & D^{(3)} & 0
\end{bmatrix}. \tag{35}
$$

The $T^{(i)}$ are themselves symmetric tridiagonal matrices, the $D^{(i)}$ are diagonal. The diagonal elements of $T^{(i)}, D^{(i)}$ are

$$T_{kk}^{(i)}=l_k(l_k+1)+\rho j_k(j_k+1)\,, \tag{36a}$$

$$D_{kk}^{(i)}=-D\{[(l_k+j_k+2)^2-J^2]\,[(l_k+j_k+2)^2-(J+1)^2]/[(2l_k+2)^2-1]\,[(2j_k+2)^2-1]\}^{1/2}\,, \tag{36b}$$

where in the notation of (34b) $(i-1)(J+1-\mu)+1\leq k\leq i(J+1-\mu)$ and the values of l_k and j_k are determined from the correspondence between the single index k of (34b) and the double index lj of (34a). The off-diagonal elements of $T^{(i)}$ are

$$T_{k,k+1}^{(i)}=-D\{[(l_k-j_k+1)^2-J^2]\,[(l_k-j_k+1)^2-(J+1)^2]/[(2l_k+2)^2-1]\,[(2j_k)^2-1]\}^{1/2}\,. \tag{37}$$

A rough indication of the variation of the off-diagonal matrix elements (36b), (37) over the (infinite) range of allowed lj values may be seen from

$$D_{kk}^{(i)}\approx -D\cos^2(\tfrac{1}{2}\psi)\,,\quad T_{k,k+1}^{(i)}\approx -D\sin^2(\tfrac{1}{2}\psi)$$

for $(l,j)\gg 1$. ψ is the angle shown in Fig. 3—note that $\psi\to 0$ as $i\to\infty$. This relation indicates that the *total* strength of dipole interaction on a given state (lj) is relatively independent of its position in (34). With reference to the lattice of amplitudes (34), the terms (36b), (37) couple each lattice point to its *first nearest* neighbors.[29] It should also be noted that the interaction terms (36b), (37) are invariant under interchange of l and j. This operation to be denoted by R amounts to a reflection of the lattice (34) through a line bisecting its columns.

A. Limiting cases

In order to categorize the symmetries which arise in this scheme, it is useful to examine two limiting cases.

$D=0$. When there is no interaction between electron and molecule, l and j are separately conserved. The eigenvalues of V are linear in ρ—if they are denoted $N_i(N_i+1)$, then $N_i(N_i+1)=l(l+1)+\rho j(j+1)$. The eigenvectors of V are of the form $a_i=\delta_{ij}$ [in (34b)]. The first ten eigenvalues of V in this case, for $J=4$, even parity, are shown as functions of ρ in Fig. 4(a). For arbitrary J the figure remains basically the same, except for a change in the slopes of the lines. If the symmetry operation R is exploited, it is only necessary to plot $N_i(N_i+1)$ in the interval $0\leq\rho\leq 1$ because if $\phi_i(\rho)$ is the eigenvector of V corresponding to the ith smallest value of $N_i(N_i+1)$ at ρ, then

$$\phi_i(\rho^{-1})=R\phi_i(\rho) \tag{38}$$

and

$$N_i(N_i+1)\Big|_{\rho^{-1}}=\rho^{-1}N_i(N_i+1)\Big|_{\rho}\,. \tag{39}$$

The radial motion of the electron in this case will be completely diabatic. Since l and j are con-

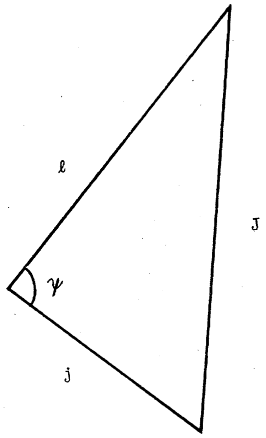
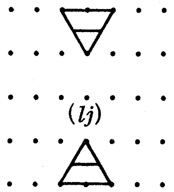


FIG. 3. Angle Ψ indicating the strength of the dipole matrix elements (36b), (37).

served quantities, the many curve crossings in Fig. 4(a) do not influence the radial motion at all.

Each line (lj) in Fig. 4(a) will cross a finite number of other lines $(l'j')$ between $\rho = 0$ and $\rho = \infty$. The number of such crossings will be less than or equal to $(J+1-\mu)^2$. In particular the curve of Fig. 4(a) corresponding to a state (lj) will eventually cross all those corresponding to the states $(l'j')$ lying within the shaded regions indicated in the diagram:



(40)

which are right triangles with hypotenuses on the top and bottom rows of (34). Of principal interest are the crossings which occur at $\rho = \rho_c = 1$. Since $[R, V(\rho_c)] = 0$ and (usually) $R\phi_i \neq \phi_i$ it is seen from (38) and (39) that at ρ_c each eigenvalue $N_i(N_i+1)$ is doubly degenerate (except for those corresponding to states with $l = j$).

This enumeration of properties of V for $D = 0$ does not shed any new light on the solution of the free-particle problem. It has been made in order to set the stage for consideration of the general case $D > 0$. In this limiting case, as in the next example, simple knowledge of the eigenvectors and eigenvalues of V suffices to solve the equations of motion.

$B = 0$. When the rotational constant B vanishes, ρ vanishes irrespective of r. In this limit, which corresponds to an infinitely large moment of inertia of the molecule, a system of electronic coordinates fixed in the molecule (body frame) is appropriate. As is well known (and shown in Sec. II) V is then diagonal in Λ, the projection of $\vec{l}$ upon the direction $\vartheta' = 0$. The eigenvalues $N_i(N_i+1)$ of V coincide then with the $N_i(N_i+1)$ of Sec. II; from Eq. (32) it is apparent they generate potential curves for which the *adiabatic* approximation gives an exact solution to the equations of motion $[\epsilon_i \equiv N_i(N_i+1)$, and $(d/dr)\,\phi_i = 0$ everywhere$]$. In analogy with molecular-orbital theory the eigenstates of V for arbitrary D may be identified by their $l\Lambda$ designation at $D = 0$ (see Fig. 4). The value of $l - \Lambda$ represents the number of nodal surfaces, $\vartheta' = \text{const}$, of the $l\Lambda$ eigenfunction. In order of increasing $\eta_i(\eta_i+1)$, the eigenstates are $s\sigma, p\pi, p\sigma, d\Delta, d\pi, d\sigma, \ldots$ etc. These results are independent of the value of the total angular momentum J, except for the implied restriction $\mu \leq \Lambda \leq J$.

B. General case

Thus in two extreme cases $D = 0$ and $B = 0$ it is seen that the diagonalization of V at each r provides exact diabatic and adiabatic solutions, respectively. The angular functions generated in these two cases are just those of the laboratory and body frames of CF. This separability of the equations of motion should persist to a certain extent in the general case. In the remainder of this section the plausibility of this hypothesis is verified by tracing the evolution of the symmetries of the eigenstates of V away from the two limiting cases. Consider first the simplest, "one-dimensional" solutions for $J = 0$ and for $J = 1$ even parity.

Lowest J. Both sets of conditions, $J = 0$ and $J = 1, \eta = -1$ require the values of l and j in the indices of (34a) to coincide. Then

$$V = (1+\rho)\,\vec{l}^{\,2} - 2D\cos\vartheta' = (1+\rho)\,V' \tag{41}$$

with

$$\begin{aligned} V' &= \vec{l}^{\,2} - 2D(r)\cos\vartheta' , \\ D(r) &= D/(1+2Br^2) . \end{aligned} \tag{42}$$

Thus the eigenvalues and eigenvectors of V' are the same as described for $B = 0$, provided one substitutes for D an effective dipole moment $D(r)$. These eigenvalues are those for $\Lambda = J$ in Fig. 2. It is also seen from that figure that the adiabatic potential curves generated from these eigenvalues are always well separated.

From (42) it is apparent that the effective dipole moment is nearly constant at small r and so the adiabatic solution to the equations of motion is essentially the same as that in the body-frame approximation of Sec. II. At large r the effective dipole moment falls off as r^{-2}. Since the eigenvalues of (42) are even functions of D, the asymptotic expansion of the adiabatic potential ϵ_i/r^2 of

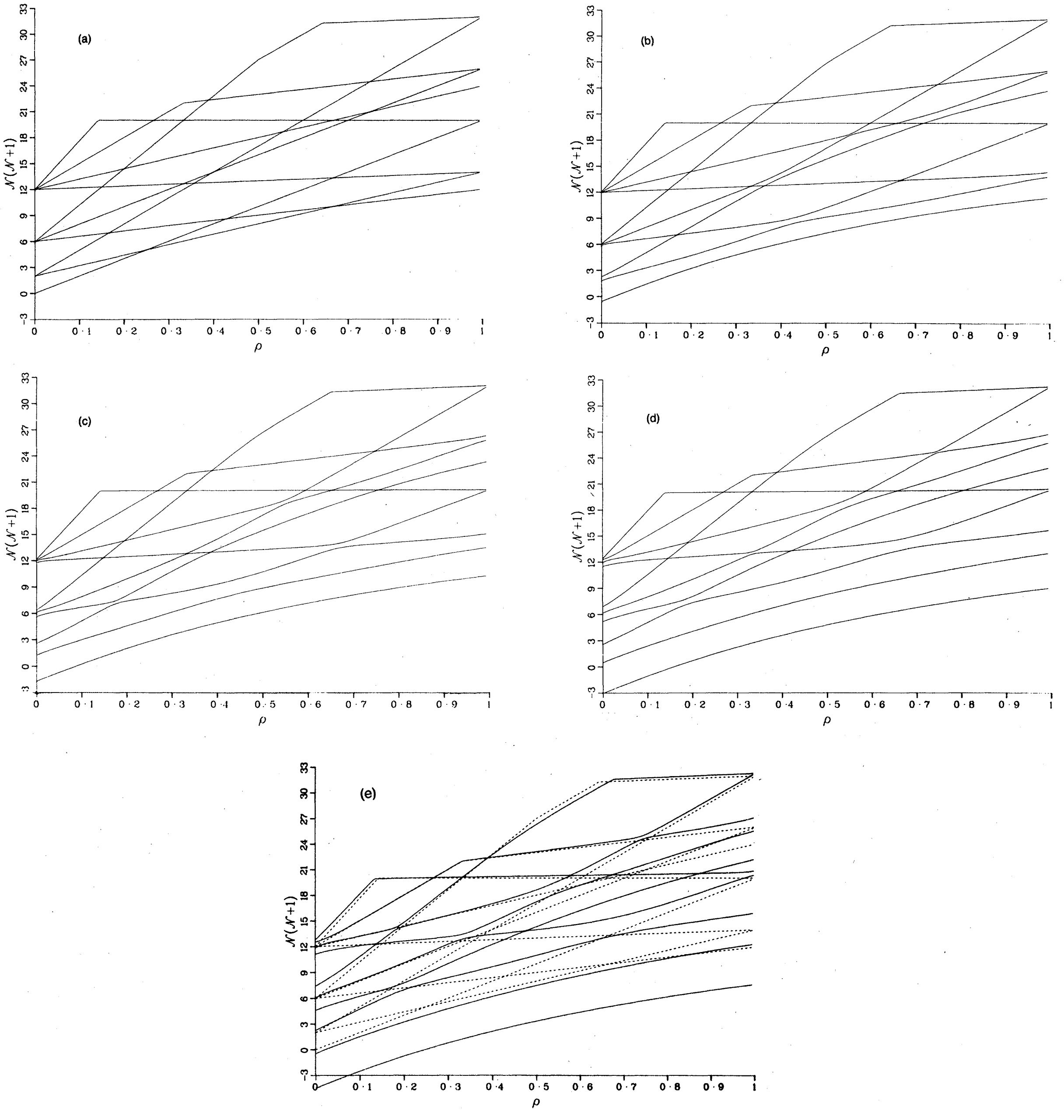


FIG. 4. First ten lowest eigenvalues of V for $J=4$, even parity. (a)–(e) correspond to $D=0,1,2,3,4$, respectively. The dashed lines inset on (e) show the $D=0$ eigenvalues for comparison.

(32) gives a strong r^{-4} polarization interaction. Specifically, for $i=1,2,\ldots$ at large r,

$$(\epsilon_i/r^2) \to 2B(i+J-1)(i+J) + [(i+J-1)(i+J)/r^2] + \beta_i(D^2/B)(1/r^4) + O(r^{-6}), \qquad (43)$$

where successive terms represent the final-state molecular rotational energy, the centrifugal barrier, and the polarization potential. The coefficient β_i is a dimensionless constant depending only on i, which may be calculated from second-order perturbation theory: it is equal to $\frac{1}{4}d^2N(N+1)/dD^2\,|_{D=0}$. It is of interest to note that while $\beta_1<0$ corresponds to an attractive interaction, we have $\beta_j>0$ for $j>1$. Thus, for all channels but the lowest, the effect of the dipole interaction is actually repulsive at large distances, and for typical values of dipole moment the adiabatic potentials for these higher channels are repulsive at all r. The first few values of β are shown below.

$$\begin{array}{cccccc} & i= & 1 & 2 & 3 & 4 \\ & J=0 & -\frac{1}{3} & +\frac{1}{5} & +\frac{1}{21} & +\frac{1}{45} \\ \beta_i & J=1 & -\frac{1}{10} & +\frac{1}{42} & +\frac{1}{60} & +\frac{17}{1540} \end{array}$$

For most of the hydrogen and alkali halides D lies between 0.5 and 4.5 a.u., and B ranges from 10^{-7} to 10^{-5} a.u., whereby the adiabatic polarizabilities $\beta_i D^2/B$ are several orders of magnitude larger than those arising from the distortion of the molecular charge distribution.

Preliminary exploration of the validity of the adiabatic approximation in these cases will be done in Sec. VI.

Arbitrary J. When $D \neq 0$ and $\phi_i \equiv \phi_i(D, \rho)$, Eqs. (38) and (39) become

$$\phi_i(D/\rho, \rho^{-1}) = \pm R\phi_i(D, \rho) , \qquad (38')$$

and

$$N_i(N_i+1)\big|_{D/\rho, \rho^{-1}} = \rho^{-1} N_i(N_i+1)\big|_{D, \rho} , \qquad (39')$$

since the dipole interaction term is symmetric in l and j. Thus for a given dipole moment D_0, diagonalization of V for $D \leqslant D_0$, $0 \leqslant \rho \leqslant 1$ suffices to determine its eigenvalues and eigenvectors for all ρ. Figures 4(b)–4(e) show the lowest ten eigenvalues of $V(J=4, \eta=1)$ in the interval $0 \leqslant \rho \leqslant 1$ for $D = 1, 2, 3, 4$. Figures 5(a)–5(d) show the four lowest eigenvalues of this system as continuous functions of D and ρ, respectively. All the crossings noted for $D=0$ are avoided when the dipole moment is finite (though the width of the line obscures this effect for the higher channels).

The symmetry operation R now enforces a particular symmetry of the solutions ϕ_i at $\rho = \rho_c = 1$. Since $R^2 = 1$, and since V and R commute $[V, R] = 0$ at ρ_c, all solutions $\phi_i(D, \rho_c)$ must be either even or odd under R; in the representation (34a) they must be symmetric or antisymmetric under reflection through the central row. In the basis (33) the ϕ_i are characterized by a remarkable regularity at ρ_c. The lowest eigenstate of V has all components a_{lj} of the same sign; the next lowest has one node (i.e., a change of sign) along the central row of (34); the next, two nodes along rows. The number of nodes along *rows* increases by one for each successive eigenstate up to the

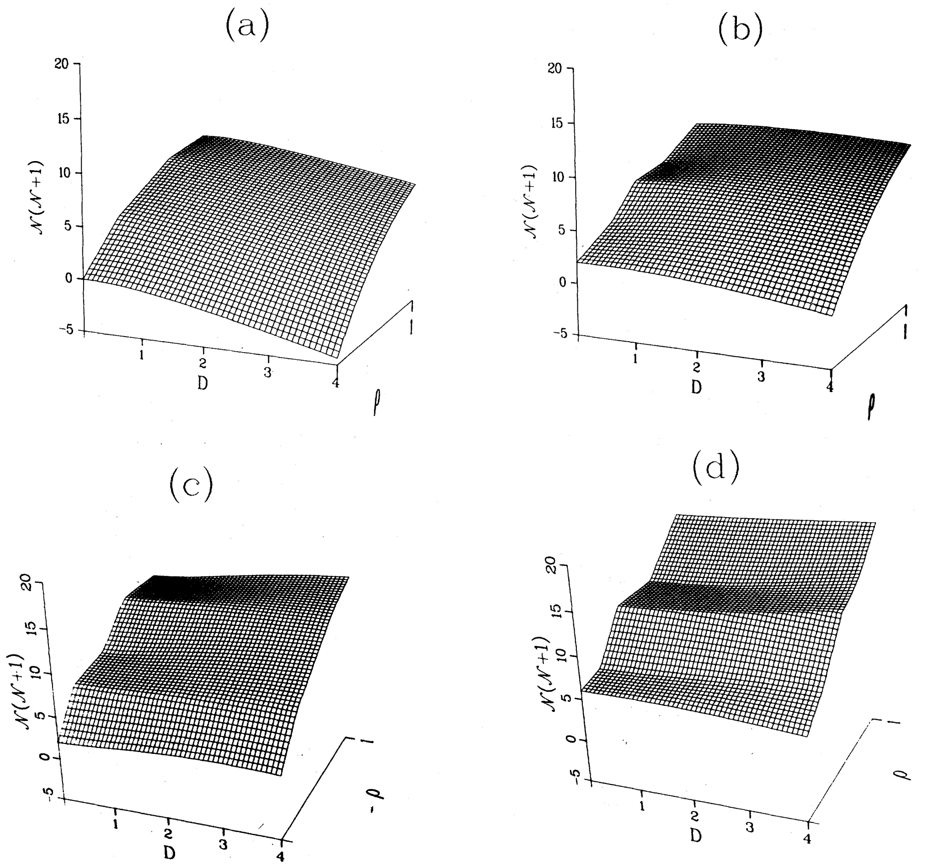


FIG. 5. Four lowest eigenvalues of V for $J=4$, even parity, as continuous functions of the dipole moment D.

$(J+1-\mu)$th lowest, for which adjacent rows are of opposite sign. The next eigenstate is symmetric within each *column*, but has a node between the first and second columns. The pattern then repeats itself until the number of nodes along rows is again exhausted, at which point a second node breaks across columns, and so on. As an example the signs of the a_{lj} for successive states are indicated below for $J=4, \eta=-1$:

$$\begin{array}{ccc} \text{First} & \text{Second} & \text{Third} \\ ++\cdots & ++\cdots & ++\cdots \\ ++ & ++ & -- \\ ++ & -- & -- \\ ++\cdots & --\cdots & ++\cdots \\ \text{Fourth} & \text{Fifth} & \text{Sixth} \\ ++\cdots & +-\cdots & +-\cdots \\ -- & +- & +- \\ ++ & +- & -+ \\ --\cdots & +-\cdots & -+\cdots \end{array} \tag{44}$$

When $J+1-\mu$ is odd the central row vanishes for all states odd under R.

This nodal pattern persists to arbitrary values of ρ, though it is not so easily described. The symmetry between $\vec{l}$ and $\vec{j}$ in V at ρ_c makes the pattern "rectangular." Values of $\rho\neq 1$ alter the relative weight of $\vec{j}^2$ and $\vec{l}^2$ thus distorting the nodal lines—much like the pattern of water waves would change in a rectangular canal of uniform depth, if the depth varied. However, the components a_{lj} of the lowest channel are always of the same sign for arbitrary ρ, and the number of nodal lines in (34) always increases by unity between successive states or the direction of the nodal line changes.

Small values of ρ correspond approximately to $B=0$. It is then appropriate to expand the eigenstates of V in the basis $|l\Lambda JM\rangle$ employed in Sec. II:

$$\phi_i=\sum_{l,\Lambda} \alpha_{l\Lambda} X_{JM}^{(l\Lambda\eta)}, \tag{45}$$

where $X_{JM}^{(l\Lambda\eta)}$ are the body-frame wave functions of Chang and Fano. The components $\alpha_{l\Lambda}$ may be placed in an array similar to (34),

$$\begin{array}{ccc} \alpha_{\mu\mu} & \alpha_{\mu+1,\mu} & \cdots \\ \alpha_{\mu+1,\mu+1} & \alpha_{\mu+2,\mu+1} & \cdots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \alpha_{JJ} & \alpha_{J+1,J} & \cdots \end{array} \tag{46}$$

whose rows correspond to constant Λ. A nodal pattern emerges from this representation as well. The components of the lowest eigenvectors lie primarily along a single row, reflecting the near constancy of Λ. Their structure is the same as that shown for $B=0$ – in increasing order, they are basically $s\sigma, p\pi, p\sigma, d\Delta, d\pi, d\sigma, \ldots$, where now $l-\Lambda$ gives the number of sign changes between successive components in the row corresponding to Λ. This order is eventually broken in the higher states, when the term $\rho j(j+1)$ is comparable to D.

It has not been possible to identify uniquely an "effective" dipole moment $D(r)$, as was done for $J=0$. However, the asymptotic form of the adiabatic potentials is the same as in (43),

$$\begin{aligned} \epsilon_i/r^2 \to 2Bj_i(j_i+1) + [l_i(l_i+1)/r^2] \\ + \beta_i(D^2/Br^4) + 0(r^{-6}) \,, \end{aligned} \tag{47}$$

where the pair l_i, j_i identify the ith adiabatic channel in the large-r limit. The values of β_i will only be of practical interest for small l values. The first one, β_i, for which $l_1=\mu$, is always positive for $\mu=0$ and negative for $\mu=1$. Thus the effect of the dipole on the electronic s wave is always *repulsive* at large distances, except for $J=0$. The magnitude of a given β falls off with increasing J roughly as $1/J$.

In conclusion, the adiabatic (or diabatic) channels provide a well-defined basis which reduces to known solutions for limiting values of the parameters. The strong identity of the channels, maintained for arbitrary variation of the parameters, suggests a quasi-separability of the row and column indices in Eqs. (34) or (41).

VI. VALIDITY OF THE ADIABATIC APPROXIMATION

The principal theoretical difficulty in the understanding of the electron-polar molecule interaction has been the coupling between electron partial waves of small l at large distances. Thus the motivation for this work has been to determine whether the interaction at large distance can be comprehended from an adiabatic point of view. We now examine this question, which was first raised in Sec. I.

The equations of motion for electron scattering from any atom or molecule reduce at large r to a form in which the interaction between electron and target may be expanded in inverse powers of r. The expansion coefficients depend upon the choice of the basis of target and electron angular wave functions; in the laboratory frame (33) these coefficients are just the electric multipole moments of the target. The leading power of r in the noncentral part of the long-range interaction will always be r^{-2} in this frame.

However, if the equations of motion are written instead in the adiabatic frame, as in (32), the off-diagonal terms are just the P matrix elements defined in (48) below. As we shall see for our particular example, the leading power of r in the noncentral part of the interaction in the adiabatic frame is then r^{-3}. This substantially improves the speed of convergence of numerical solutions at large r.

Thus there is some qualitative utility in thinking in terms of an adiabatic basis rather than of a fixed one, even if the adiabatic approximation to the solution of the Eqs. (32) is inaccurate. The remainder of this paper is given to showing how the reduction in the strength of the long-range noncentral interaction takes place in the electron-dipole problem. The discussion of the influence of the avoided crossings of adiabatic potential curves on the electron motion is deferred to further study, without implying it is unimportant.[30,31]

The inhomogenous part of Eq. (32) may be written as $-2P_{ij}b'_j - Q_{ij}b_j$ with

$$\begin{aligned} P_{ij} &= (\phi_i|\phi'_j)\,, \\ Q_{ij} &= (\phi_i|\phi''_j) = \Sigma_k P_{ik}P_{kj} + \frac{d}{dr}P_{ij}\,. \end{aligned} \tag{48}$$

Since also $P_{ij} = (\epsilon_j - \epsilon_i)^{-1}(\phi_i|dV/dr|\phi_j)$,

$$P_{ij} = 4Br(\epsilon_j - \epsilon_i)^{-1}(\phi_i|\vec{\mathrm{j}}^2|\phi_j)\,. \tag{49}$$

The P and Q matrices are most easily evaluated for $J=0$ or $\beta = 1, \eta = -1$. In this case the P matrix becomes

$$P_{ij} = (\bar{\epsilon}_j - \bar{\epsilon}_i)^{-1}\frac{8DBr}{(1+2Br^2)^2}(\phi_i|\cos\vartheta'|\phi_j)\,, \tag{50}$$

where $\bar{\epsilon}_i = \epsilon_i/(1-\rho) \to l_i(l_i+1)$ as $r \to \infty$. Nevertheless the off-diagonal P dies off less rapidly than the diagonal polarization term of (43). Similarly (48) shows that Q provides a diagonal term of order r^{-6} and off-diagonals with a leading power r^{-4}. In this case the inelastic contribution to scattering, i.e., molecular rotational excitation, will be due to the smooth off-diagonal coupling induced by the P and Q matrices. Since there are no avoided crossings, localized nonadiabatic transitions are not likely to occur.

The special case of $J=0$ differs from that of larger J in two ways. For $J=0$ there are no avoided crossings of the adiabatic potentials, and each potential curve corresponds to a different final-state value of j at $r=\infty$. When $J>0$ there are many avoided crossings, and each value of j at $r=\infty$ corresponds to a number ($\leq J+1-\mu$) of different adiabatic potentials. Thus the P matrix elements for $J>0$ are not monotonic like those (50) for $J=0$; near each avoided crossing they generally have a local maximum and their sign may reverse between two crossings. Nevertheless, in the limit of large r their form will be seen to reduce to that of (50). Thus for any value of J the off-diagonal coupling in the adiabatic basis goes as r^{-3} at large r.

Consider first the interaction between two channels i and k which correspond to different molecular rotational states j_i, j_k at $r=\infty$. Equation (49) may be rewritten

$$\begin{aligned} P_{ik} &= 4Br(\epsilon_k - \epsilon_i)^{-1} \\ &\quad \times [\phi_i|(2D\cos\vartheta' - \vec{\mathrm{l}}^2)\rho^{-1}|\phi_k]\,. \end{aligned} \tag{49$'$}$$

At large r, $\epsilon_i \to l_i(l_i+1) + \rho j_i(j_i+1)$ and $(\phi_i|\vec{\mathrm{l}}^2|\phi_k)$ vanishes because $j_i \neq j_k$; therefore

$$P_{ik} \to \left[\Delta j(j+1)\right]^{-1}\frac{8DBr}{(2Br^2)^2}(\phi_i|\cos\vartheta'|\phi_k) \tag{51}$$

at large r—compare with (50). For channels converging to the same j, but with different l, the situation is similar even though their separate adiabatic potential curves draw together at ∞. Then in (49) $\epsilon_k - \epsilon_i$ goes to $l_k(l_k+1) - l_i(l_i+1)$ and so

$$P_{ik} \to 4Br[\Delta l(l+1)]^{-1}(\phi_i|\vec{\mathrm{j}}^2|\phi_k)\,. \tag{52}$$

At large r, ϕ_i and ϕ_k can be expanded in inverse powers of D/ρ:

$$\phi_i = |l_i j_i\rangle + \sum_{m,n}(D/\rho)^n\Gamma^n_{im}|l_m j_m\rangle\,.$$

Since $j_i = j_k$ and $\Gamma^n_{im} = 0$ unless $j_i + j_m + n = \text{even}$, only even powers of D/ρ will be retained in the expression for P_{ik},

$$P_{ik} \to [\Delta l(l+1)]^{-1}[4D^2Br/(2Br^2)^2]\Gamma_{ik}$$

where Γ_{ik} is just a geometrical coefficient.

Sample numerical integration of the equations of motion in the adiabatic approximation has been performed, and the results compared with those obtained from direct integration of the coupled equations in the body frame. In these "experiments," which involve rather low angular momenta, moderate to large dipole moments[32] ($J<10$, $D\sim 1-3$) and collision energies $E<1000B$, the adiabatic approximation gives quite reasonable agreement with the exact solutions. A quantitative comparison of the results and investigation of the behavior of the radial wave functions near the avoided crossings are currently in progress.

Thus it is apparent that the validity of the adiabatic approximation at large r should not depend strongly on the value of J, except perhaps indirectly through differences in allowed rotational thresholds and the strengths of the effective dipole moments. If the adiabatic approximation can be shown to yield solutions of reasonable accuracy—

which is the goal of future work—it will provide a substantial qualitative understanding of the effect of long-range forces in this problem.

VII. CONCLUSION

The use of an adiabatic frame transformation enables one to trace the character of solutions between body and laboratory frames and reduces the magnitude of off-diagonal coupling by a factor r at large distances. These considerations do not depend on classical criteria for the use of adiabatic approximations: i.e., there are no distinct "fast" and "slow" motions. The origins of the approximate separability of the problem are not yet fully understood, but are similar to those arising in other cases.

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APPENDIX: CALCULATION OF THE BODY-FRAME EIGENFUNCTIONS

The eigenvalue Eqs. (3) and (5) are equivalent to

$$l(l+1)A_{Nl}^{(\Lambda)} - 2D \sum_{l'} \langle l\Lambda | \cos\vartheta | l'\Lambda \rangle A_{Nl'}^{(\Lambda)}$$
$$= N(N+1)A_{Nl}^{(\Lambda)} .$$

The matrix elements $T_{ll'}^{(\Lambda)} = \langle l\Lambda | \cos\vartheta | l'\Lambda \rangle = T_{l'l}^{(\Lambda)}$ are then

$$T_{l\,l+1}^{(\Lambda)} = \{[(l+1)^2 - \Lambda^2]/(2l+3)(2l+1)\}^{1/2} .$$

Mittleman and von Holdt[9] have shown how to calculate $N(N+1)$ and A_{Nl} by iterative methods. This procedure can be easily carried out on a programmable pocket calculator to an accuracy of eight or nine decimal places. The convergence of this system is so rapid, however, that one can use any standard matrix diagonalization code.

The diagonalization is performed separately for each value of Λ. If one wishes an accuracy of about 10^{-9} for the first m eigenvalues, truncation to a $2m$ dimensional system will usually be adequate (i.e., $l = \Lambda, \Lambda+1, \ldots, \Lambda+2m$).

The eigenvalues so obtained are independent of J, M and of the total parity $\eta(-1)^J$. We have used as a basis functions $Y_{l\Lambda}(\vartheta, \varphi)$ which do not correspond to definite J, η; but it can be shown that these coefficients $A_{Nl}^{(\Lambda)}$ determine an eigenfunction of J, M and η by

$$|N\Lambda JM\eta\rangle = \sum_{l} A_{Nl}^{(\Lambda)} X_{JM}^{(l\Lambda\eta)} ,$$

where $X_{JM}^{l\Lambda\eta}$ is as defined by Chang and Fano. This procedure is thus consistent with the frame transformation of Eq. (22).

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