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Physics, atomic

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Rotational Excitation in Slow Collisions of Helium with the Diatomic Hydrides: HF, DF, HCl, and DCl

by

Lee A. Collins

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Thesis Director's Signature:

Neal T. Lane

Houston, Texas
May, 1975
Holmes laughed. "Watson insists that I am the dramatist in real life," said he. "Some touch of the artist wells up within me, and calls insistently for a well staged performance. Surely our profession, Mr. Mac, would be a drab and sordid one if we did not sometimes set the scene so as to glorify our results. The blunt accusation, the brutal tap upon the shoulder—what can one make of such a denouement? But the quick inference, the subtle trap, the clever forecast of coming events, the triumphant vindication of bold theories—are these not the pride and the justification of our life's work? At the present moment you thrill with the glamour of the situation and the anticipation of the hunt. Where would be that thrill if I had been as definite as a timetable? I only ask a little patience, Mr. Mac, and all will be clear to you."

Sherlock Holmes

The Valley of Fear

A. Conan Doyle
Acknowledgements

The success of this project has its origins in the kindness and assistance of a large number of people. I hope that this brief acknowledgement will serve in some limited way to express my true gratitude.

Foremost, I wish to acknowledge the guidance, patience, and friendship of Dr. N. F. Lane. His constant encouragement, enthusiasm, and humor have considerably lightened the burden of the difficulties encountered in this project and heightened the sense of accomplishment in the successes.

I especially wish to thank Dr. J. C. Weisheit, Dr. C. B. Tarter, and the staff of T-division of the Lawrence Livermore Laboratory for their kind hospitality over last summer. Dr. Weisheit's suggestions, assistance, and encouragement are gratefully acknowledged. I also wish to thank the staff of the computation center of the Lawrence Laboratory, where the bulk of these calculations were performed, for their cooperation and helpfulness.

I am indebted to Dr. E. F. Hayes for supplying us with his coupled-channel integral equations code, to Dr. D. J. Kouri for the use of his $j_z$-conserving code, to Dr. C. F. Bender for calculating the RHF surface for He-HF, and to Dr. W. Lester for sending us the partial cross sections for the Li$^+$-$H_2$ system. I wish to acknowledge
useful discussions with Dr. A. Dalgarno, Dr. R. T. Pack, Dr. E. F. Hayes, Dr. D. J. Kouri, Dr. C. F. Bender, and Dr. H. F. Schaeffer.

The assistance offered by and the many stimulating discussions with members of the Rice Atomic Physics Group have been invaluable. I especially wish to acknowledge the friendship and help of Michael Morrison, Peet Hickman, and Walter Steets.

The preparation of this manuscript was made a much lighter task by the assistance of Horace Mitchell, who prepared the drawings, and Mary Comerford, who performed the typing.

The support of this research project by the U. S. Atomic Energy Commission and the Robert A. Welch Foundation is gratefully acknowledged.

Finally, "three cheers, and one cheer more" to Messrs. Gilbert and Sullivan whose "infernal nonsense" has lightened the darker moments of this project.
This thesis is dedicated to my parents, without whose constant encouragement, support, and love this work would have been impossible.
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In trying to achieve success
  No envy racks our hearts,
For all we know and all we guess,
  We mutually impart.    Princess Ida

Chapter 1. Introduction

Interest in heavy particle collisions involving various diatomic hydrides has recently arisen in several rather diverse fields. In laser physics, diatomic hydride lasers appear to offer the prospect of very high yield devices which may have applications to fusion research. The most widely studied of these hydride lasers is the chemical hydrogen fluoride (HF) laser. Chemical reactions between hydrogen and fluorine atoms and molecules produce HF in excited rotational-vibrational states. Radiative transitions from these excited levels to the ground vibrational state give rise to the lasing effects. Collisional mechanisms which de-excite or rearrange the populations of these excited rotational-vibrational levels are important to model studies aimed at increasing the efficiency of the laser. Therefore, rotational de-excitation of the excited rotational levels of HF by collisions with such buffer gas species as helium plays an important role in such model studies. Recently, lasing has been observed in HF produced by elimination reactions from chemically activated CH$_3$CF$_3$ and photo-excited CH$_2$CF$_2$. The lasing transitions occur between
high-lying rotational states, in which case de-excitation of these levels through collisions with atomic species (He) becomes an important quenching mechanism, which limits the efficiency of the laser. Since other diatomic hydrides such as hydrogen chloride (HCl) are known to lase, rotational de-excitation cross sections for transitions between various rotational levels of diatomic hydrides are important to studies of hydride laser systems.

In addition to laser physics, collisional excitations of the rotational states of diatomic hydrides are of interest in astrophysics. Within certain regions of the interstellar medium, known as dark clouds, the particle density is high enough (> 1000 cm\(^{-3}\)) to support molecular reactions and to shield the interior of the cloud from stellar ultraviolet photons which could dissociate the molecules. The average kinetic temperature of these regions is quite low (< 50°K). The energy balance for the dark clouds, which determines such important properties as the local temperature, is determined, in a steady state model, by the processes which heat and cool the particles. Although the relative abundance of hydrogen chloride is small compared to other cloud constituents such as H\(_2\) and He, rotational excitations of HCl by collisions with He and H\(_2\) provide an efficient cooling mechanism because of the large energy transfers that can occur between the widely spaced rotational levels of HCl.
Therefore, rotational excitation cross sections for collisions between HCl and He are important to model studies of the dark interstellar clouds.

In this thesis, we present and discuss the results of quantum mechanical calculations of the rotational excitation cross sections for collisions between helium and the diatomic hydrides: hydrogen fluoride (HF), deuterium fluoride (DF), hydrogen chloride (HCl), and deuterium chloride (DCl). Although we confine our attention to these systems, the techniques that we develop have applications to a wide variety of atom-molecule and other heavy particle systems. The remainder of the thesis consists of five chapters. In Chapters 2-4, we treat the quantum mechanical formulation of inelastic atom-molecule collisions in various references frames and in several approximations. We formulate the atom-molecule collision process in a reference frame fixed in space at the center-of-mass of the system in Chapter 2. By expanding the total scattering wave function in a set of complete states, we transform the Schrödinger equation into a set of coupled differential equations. From the asymptotic form of their solutions, we extract the scattering information which determines the excitation cross sections. We treat the molecule as either a symmetric top or linear rigid rotor. In addition, the distorted wave method, which approximates the complicated coupled equations, is derived in this
chapter. In Chapter 3 we rederive the scattering formalism of Chapter 2 in a reference frame whose origin is at the center-of-mass of the system and which rotates with the incident atom. We formulate the scattering theory in this frame in terms of a set of coupled differential equations from whose asymptotic solutions we extract the scattering information. We also derive the $j_z$-conserving coupled state approximation to these equations, which allows for a more rapid calculation of the cross sections. We transform the set of coupled differential equations into a set of coupled integral equations in Chapter 4. The numerical solutions of the set of integral equations are treated in detail since all excitation cross sections presented in this thesis are calculated by this technique. In order to solve this set of equations, we must know the interaction surface for the atom and molecule. Thus, Chapter 5 is devoted to a treatment of models of the potential energy surface for the interaction between an atom and molecule. Finally, the results of calculations of the rotational excitation cross sections for collisions between ground state helium atoms and the diatomic hydrides are presented and discussed in Chapter 6.
And I never use a big, big D - HMS Pinafore

Chapter 2. Atom-Molecule Scattering: Laboratory Frame

A. Introduction

In this chapter, we present the formalism which describes the rotational-excitation of a target molecule in a \( \Sigma \) electronic state by a collision with an incident ground state atom. We follow rather closely the formalism of Arthurs and Dalgarno.\(^1\) All motion is referred to the laboratory frame of reference which is a coordinate system fixed in space at the center of mass of the atom-molecule system. The atom is assumed to be a structureless, point particle incident along the laboratory z-axis with orbital angular momentum \( \mathbf{\ell}_h \). Since the lengths and orientations of the molecular bonds are considered fixed, the molecule can be treated as a rigid rotor with total rotational angular momentum \( j_h \). The Schrödinger equation which describes the collision of an atom and a rotating molecule has the form

\[
(H(\mathbf{R},\hat{f}) - E) \Psi(\mathbf{R},\hat{f}) = 0 ,
\]

in which both the hamiltonian and the total scattering wave function \( \Psi \) depend on the particle separation \( \mathbf{R} \) and the orientation \( \hat{f} \) of the molecule. The scattering equation is solved by expanding \( \Psi \) in a complete set of states of the angular variables \( \hat{R} \) and \( \hat{f} \) with the radial dependence appearing in the expansion coefficients. Under this expansion, the Schrödinger equation reduces to a set of coupled
differential equations whose solutions are the radial coefficients. By examining the asymptotic behavior of these coefficients, we draw the connection between the radial expansion coefficients and the rotational excitation cross sections. We investigate two types of rigid rotor molecules: 1) the asymmetric top and 2) the linear. Since the derivation of the scattering formalism is similar in both cases, we develop the quantum mechanical theory of rotational excitation of a symmetric top molecule by atomic collisions rather thoroughly in Section B and merely sketch the development for the linear molecule in Section C. Finally, in Section D we derive the distort wave approximation.
B. Rotational Excitation: Atom-Symmetric Top Molecule

The Hamiltonian $H$ in atomic units* which describes the collision between a structureless atom and a target symmetric top molecule has the form

$$H = -\frac{1}{2\mu} \tilde{\nabla}_R^2 + H_{\text{mol}}(\hat{\mathbf{r}}) + V(R, \hat{\mathbf{r}}). \quad (2.1)$$

The first term represents the kinetic energy operator in the laboratory frame for the relative motion of the center-of-mass of an atom and molecule with vector separation $\mathbf{R}$ (see Fig. 1). The reduced mass of the atom-molecule system is given by $\mu$. In the case that the molecular mass is much greater than the atomic mass, this operator describes the kinetic energy of the incident atom. The operator can be decomposed into radial and angular terms as

$$\tilde{\nabla}_R^2 = \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) - \frac{\mathbf{L}^2}{R^2}, \quad (2.2)$$

where $R$ is the length of $\mathbf{R}$ and $\mathbf{L}$ is the orbital angular momentum operator of the incident atom such that

$$\mathbf{L}^2 Y_{\ell m}^\ell(\hat{\mathbf{R}}) = \ell(\ell+1) Y_{\ell m}^\ell(\hat{\mathbf{R}}),$$

where $Y_{\ell m}^\ell(\hat{\mathbf{R}})$ is the spherical harmonic whose argument describes the angular position of the incident atom.

*Unless noted, all equations and parameters are given in atomic units.
Fig. 1 Geometry of atom-symmetric top system: space-fixed frame. (top) Definition of Euler angles giving the orientations of the body frame (x'y'z'), fixed along the principal axes of the symmetric top, with respect to the space-fixed frame (xyz). (bottom) Position of the atom with respect to the body and space-fixed frames. Line OA is coplanar with \( \hat{x} \) and \( \hat{y} \), and line OB is coplanar with \( \hat{x}' \) and \( \hat{y}' \).
The second term in Eq. (2.1) describes the rotational motion of the target molecule. The quantum mechanical hamiltonian for a rigid rotor can be obtained by replacing the angular momentum components of the classical hamiltonian with their corresponding operator forms.\(^2,^3\) In terms of the body frame of reference, which is a coordinate system fixed on the rotating molecule and oriented along the principal axes, the hamiltonian for a rigid rotor becomes

\[
H_{\text{mol}} = \frac{1}{2I_x'} \hat{j}_x'^2 + \frac{1}{2I_y'} \hat{j}_y'^2 + \frac{1}{2I_z'} \hat{j}_z'^2, \tag{2.2}
\]

where \(\hat{j}_i\) and \(I_i\) are respectively the rotational angular momentum operator and moment of inertia about principal axis \(i\). We always choose the body frame \(z\)-axis to lie along the symmetry (figure) axis of the molecule. For a symmetric top molecule, two of the moments are equal. The top is said to be oblate if \(I_x' = I_y', \langle I_z' \rangle\) and prolate if \(I_x' I_y' = I_z'\). For the case of an oblate symmetric top rotor, the hamiltonian has the form

\[
H_{\text{mol}} = A \hat{j}'^2 + (C-A) \hat{j}_z'^2, \tag{2.3}
\]

with the total rotational angular momentum operator given by \(\hat{j}'\) and the rotation constants \(A\) and \(C\) defined by \(1/(2I_x')\) and \(1/(2I_z')\).

The eigenfunctions and eigenvalues of the rotational hamiltonian are then given by

\[
H_{\text{mol}} \psi_{j m k}^{j} (\hat{\mathbf{r}}) = E_{j m k} \psi_{j m k}^{j} (\hat{\mathbf{r}}). \tag{2.4}
\]
The orientation of the body frame with respect to the laboratory frame is given by \( \hat{\mathbf{r}} \). The most general expression for this orientation is in terms of the Euler angles \((\alpha, \beta, \gamma)\). Since there is no net torque on the freely rotating molecule, whose motion is described by \( H_{\text{mol}} \), the total angular momentum and its projections on the laboratory and body z-axes are constants of the motion. In addition, the symmetric top hamiltonian \( H_{\text{mol}} \) is invariant under a reflection through a plane passing through the symmetry axis of the molecule. Thus, the eigenfunctions of \( H_{\text{mol}} \) are also eigenfunctions of the total rotational angular momentum operator \( \hat{j} \), the operators that represent the projections of \( \hat{j} \) along the body and space-fixed z-axes, \( \hat{j}_z \), and \( \hat{j}'_z \) respectively, and the reflection operator \( \hat{P}_v \). The following relations then hold:

\[
\begin{align*}
\hat{\mathbf{r}} \cdot \hat{j}_{m \pm m}^j \psi_{m j m_k}^j (\hat{\mathbf{r}}) &= j(j+1) \psi_{m j m_k}^j (\hat{\mathbf{r}}) \\
\hat{j}_z \psi_{m j m_k}^j (\hat{\mathbf{r}}) &= m_j \psi_{m j m_k}^j (\hat{\mathbf{r}}) \\
\hat{j}'_z \psi_{m j m_k}^j (\hat{\mathbf{r}}) &= m_k \psi_{m j m_k}^j (\hat{\mathbf{r}}) \\
\hat{P}_v \psi_{m j m_k}^j (\hat{\mathbf{r}}) &= (-1)^j \psi_{m j m_k}^j (\hat{\mathbf{r}}).
\end{align*}
\] (2.5)

The index \( \nu \) assumes values of either 0 or 1. A wave function with \( \nu = 0 \) does not change sign under a reflection in a plane passing through the symmetry axis, while a wave function with \( \nu = 1 \) changes sign under such a reflection. For an oblate symmetric top molecule, the energy becomes
\[ E_{jm_k} = A(j+1) + (C-A) m_k^2. \]

The rotational wave functions can be expressed in terms of the D-matrices as
\[ \psi_{mj_{m_k}}^j (\hat{\varphi}) = (2j+1)^{1/2} G_{jm_{m_k}}^j (\hat{\varphi}), \quad (2.6) \]

where
\[ G_{jm_{m_k}}^j = \begin{cases} \frac{1}{\sqrt{2}} \left[ D_{mj_{m_k}}^{j*} (\hat{\varphi}) + (-1)^\nu D_{mj_{m_k}}^{j*} (\hat{\varphi}) \right] & m_k > 0 \\ D_{mj_{j_0}}^{j*} (\hat{\varphi}) & m_k = 0 \end{cases}, \quad (2.7) \]

with \( \nu \) either 0 or 1. A more detailed description of the D-matrices is presented in Appendix B. We have used the symmetrized wave functions in order to display the invariance of the symmetric top Hamiltonian under reflections in a plane through the symmetry axis of the molecule. All additional expansions will be made with symmetrized functions to take full advantage of this symmetry property.

The third term in Eq. (2.1) is the interaction potential between the atom and molecule. We assume that the potential depends only on the radial separation \( R \) and angular orientation \( \Theta, \varphi \) of the atom and molecule. The appropriate geometry is displayed in Fig. 1. In Chapter 5 we discuss the methods used to generate the potential surface.
The Schrödinger equation for the atom-molecule collision may then be written in terms of the hamiltonian $H$ as

$$(H-E) \psi(R, \hat{r}) = 0 \quad (2.8)$$

The traditional procedure for solving this equation is to expand the total wave function $\psi$ in a complete set of target states of the molecule. However, because of the non-spherical nature of the potential, the rotational angular momentum of the molecule does not commute with $H$ and is, therefore, not a constant of the motion. However, since there are no external torques acting on the atom-molecule system, the total angular momentum $\mathbf{j}$, formed by coupling the rotational angular momentum $\mathbf{j}$ of the molecule to the orbital angular momentum $\mathbf{\ell}$ of the atom, is a constant of the motion. We can therefore find simultaneous eigenfunctions of $\mathbf{j}$ and $H$ since the total angular momentum commutes with $H$. In terms of these eigenfunctions, the hamiltonian $H$ is diagonal in $J$. We shall use the set of basis functions which are eigenfunctions of $\hat{J}^2$ and which are constructed by coupling the molecular wave function to the eigenfunctions of $\hat{\ell}^2$ in the form

$$\mathcal{Y}^{M}_{J, j m_j \mathcal{K}}(\hat{R}, \hat{r}) = \sum_{m_j = -j}^{j} \sum_{m_{\mathcal{K}} = -\mathcal{K}}^{\mathcal{K}} C(j, j; m_1 m_2 M) \mathcal{Y}^{J}_{j m_j \mathcal{K}}(\hat{r}) \mathcal{Y}^{M}_{j m_j \mathcal{K}}(\hat{R}),$$

(2.9)

where $M$ is the projection of $\mathbf{j}$ along the laboratory $z$-axis and $C$ is the Clebsch-Gordan coefficient in the notation of
These functions include all the angular dependence of the incident atom and target molecule. The Schrödinger equation for the system in an initial channel \((j m_k \nu \lambda)\) for each value of \(J\) becomes

\[
(H-E) \psi_{jm_k \nu \lambda}^{JM}(R, \hat{r}) = 0 \tag{2.10}
\]

The wave functions \(\psi^J\) may be expanded in terms of the complete set \(\psi^J_M\) as

\[
\psi_{jm_k \nu \lambda}^{JM}(R, \hat{r}) = \sum_{j' = 0}^{\infty} \sum_{\lambda' = |J-j'|} 1 \sum_{m_k' = 0}^{\nu} \sum_{\nu' = 0}^{\nu} u_{j'm_k' \nu' \lambda'}^{JM}(R) R^{-\frac{1}{2}} \psi_{j'm_k' \nu' \lambda'}^{M}(\hat{r}) \tag{2.11}
\]

with the radial expansion coefficient given by \(u^J(R)\).

Substituting Eq. (2.11) into Eq. (2.10), using Eqs. (2.1), (2.2), and (2.4), multiplying by \(\psi_{j'm_k' \nu' \lambda'}^{M^*}(\hat{r}, \hat{r})\), and integrating over \(d\hat{r}\) and \(d\hat{r}\), we find that the Schrödinger equation reduces to a set of coupled differential equations of the form

\[
\left[ \frac{d^2}{dR^2} - \frac{\lambda' (\lambda'' + 1)}{R^2} + k_{JJ'}^{m_k''} \right] u_{\gamma'}^{\gamma}(R) = \sum_{\gamma'} U_{\gamma'}^{\gamma''}(R) u_{\gamma'}^{\gamma''}(R), \tag{2.12}
\]

where

\[
U_{\gamma'}^{\gamma''}(R) = 2\mu \int d\hat{r} \int d\hat{r} \ \psi_{J \gamma''}^{M^*}(\hat{r}, \hat{r}) V(R, \hat{r}) \psi_{J \gamma'}^{M}(\hat{r}, \hat{r}) \tag{2.13}
\]

\[
k_{jjm_k}^2 = 2\mu [E - E_{jm_k}],
\]
and $\gamma$ represents the set of quantum numbers $(j m_k \forall \lambda)$, which label a scattering channel.

So far, we have assumed an expansion in terms of an infinite number of basis functions. The formulation with respect to this expansion is exact; however, treating an infinity of states is clearly not practical computationally even with the power of modern computers. We thus truncate the basis set $\{J_{\gamma}^M\}$ at a finite number of functions, $N$, such that the contribution to the cross section from the excluded channels is small. Such a treatment is termed the close coupling formulation. In general, the basis includes contributions from channels that are energetically accessible (open channels, $k^2 > 0$) and inaccessible (closed channels, $k^2 < 0$). For $N$ basis functions, there will be a set of $N$ coupled equations of the form of Eq. (2.12) with $2N$ solutions. However, we eliminate $N$ of these solutions by requiring each radial function $u_{\gamma}^{J_{\gamma}}$ be regular at the origin [$u_{\gamma}^{J_{\gamma}}(0) = 0$]. Each solution consists of a set of $N$ radial wavefunctions $\{u_{\gamma_1}^{J_{\gamma}}, u_{\gamma_2}^{J_{\gamma}}, \ldots, u_{\gamma_N}^{J_{\gamma}}\}$, having the same initial channel quantum number but different final channel quantum numbers. We therefore distinguish each of the $N$ solutions by the value of the initial channel index $\gamma$. Representing each of these $N$ solutions as a column vector whose elements consist of the radial functions $\{u_{\gamma i}^{J_{\gamma}} | i = 1, N\}$, we may then write the complete solution of Eq. (2.12) as an $N \times N$ matrix of the form $^7$
\[ u(R) = \begin{bmatrix} \gamma_1^J u_{\gamma_1} & \cdots & \gamma_N^J u_{\gamma_1} \\ \gamma_1^u u_{\gamma_1} & \cdots & \gamma_1^u u_{\gamma_1} \\ \vdots & & \vdots \\ \gamma_1^u u_{\gamma_N} & \cdots & \gamma_N^u u_{\gamma_N} \end{bmatrix} \]

With this simplification, we can then write Eq. (2.12)

in matrix form

\[ \frac{d^2}{dR^2} u(R) = A(R) u(R), \quad (2.12') \]

with

\[ A(R) = U(R) + L(R) - k^2, \]

and the matrix elements given by

\[ (U(R))_{\gamma', \gamma''} = U_{\gamma', \gamma''}(R) \]
\[ (L(R))_{\gamma'' \gamma'} = \kappa''(\kappa'' + 1)R^{-2} \delta_{\gamma'' \gamma'} \]
\[ (k^2)_{\gamma'' \gamma'} = k^2 j_{m^L} \delta_{\gamma'' \gamma'} . \]

In Appendix A, we describe the technique for obtaining the solution \( u(R) \) in terms of the numerical solutions of Eq. (2.12').

The only term of Eq. (2.12) that remains to be evaluated is the matrix element \( U_{\gamma', \gamma''}(R) \). We begin by expanding the interaction potential \( V \) which depends on the radial separation \( R \) and angular orientation \( (\Theta, \Phi) \) of the atom with respect to the molecular symmetry axis in terms of symmetrized spherical harmonics as
\[ V(R, \Theta, \phi) = \sum_{\lambda m_\lambda} v_{\lambda m_\lambda} \delta(R) Z_{\lambda m_\lambda} \delta(\Theta, \phi), \quad (2.14) \]

with
\[ v_{\lambda m_\lambda} \delta(R) = \int \int V(R, \Theta, \phi) Z_{\lambda m_\lambda} \delta(\Theta, \phi) \sin \Theta \, d\Theta \, d\phi, \quad (2.14') \]

and
\[
Z_{\lambda m_\lambda} \delta(\Theta, \phi) = \begin{cases} 
\frac{1}{\sqrt{2}} \left[ Y_{\lambda m_\lambda}(\Theta, \phi) + (-1)^{\delta} Y_{\lambda - m_\lambda}(\Theta, \phi) \right] & m_\lambda > 0 \\
Y_{\lambda 0}(\Theta, \phi) & m_\lambda = 0 
\end{cases}.
\quad (2.15) \]

We now employ the general form of the addition theorem for a spherical harmonic and a D-matrix \(^8\)
\[ Z_{\lambda m_\lambda} \delta(\Theta, \phi) = \sum_{\tilde{\mu}} \sum_{\tilde{m}_\lambda} G_{\lambda \tilde{\mu}}^{\lambda *}(\hat{\Theta}, \hat{\phi}) \cdot Y_{\lambda \tilde{m}_\lambda}^{\tilde{\mu}}(\hat{R}), \quad (2.16) \]

in order to express the symmetrized spherical harmonics in terms of the laboratory frame coordinates \(\hat{R}\) and \(\hat{\Theta}\).

Using Eqs. (2.9) and (2.16), we may write the matrix element in the form
\[
U_{\lambda^\prime \mu^\prime}^{\lambda \mu}(R) = 2 \mu \sum_{\lambda m_\lambda} \delta \sum_{\tilde{\mu}} \sum_{\tilde{m}_\lambda} \sum_{m_\lambda} \sum_{m_\lambda'} \frac{(2j'+1)}{8\pi^2} \frac{1}{8\pi^2} v_{\lambda m_\lambda} \delta(R) \\
\times C(j^\prime \mu^\prime j; m_\lambda, m_\lambda') C(j \mu j'; m_\lambda', m_\lambda; M) \quad I_1 I_2,
\]

where
\[
I_1 = \int G_{m_\lambda m_\lambda'}^{j^\prime *}(\hat{\Theta}, \hat{\phi}) \cdot G_{\lambda \tilde{m}_\lambda}^{\lambda *}(\hat{\Theta}, \hat{\phi}) \cdot G_{m_\lambda}^{j^\prime}(\hat{\Theta}, \hat{\phi}) \, d\hat{\Theta}.
\]
\[
I_2 = \int \hat{Y}_{j^\prime}^{\lambda *}(\hat{R}) \cdot \hat{Y}_{\mu^\prime}^{\lambda *}(\hat{R}) \cdot \hat{Y}_{\mu}^{\lambda}(\hat{R}) \, d\hat{R}.
\]


The integrals $I_1$ and $I_2$ can be evaluated using the properties of the D-matrices and spherical harmonics. Performing these integrations and rearranging the resulting equation, we find that

$$U_{j^1j^2}^\nu\gamma^\nu'\gamma' (R) = \frac{\Sigma}{4\pi(2\lambda+1)} \left[ \frac{(2j^1+1)(2j^2+1)(2\lambda'+1)(2\lambda''+1)}{4\pi(2\lambda+1)} \right]^{1/2} (-1)^{j''-j'-j} C(\lambda', \lambda'', \lambda; 000)$$

$$\times W(j', \lambda', j'', \lambda) \left\{ \frac{\Sigma}{4\pi(2\lambda+1)} \delta^{\nu'\gamma'\nu''\gamma''} (m_k', m_k'' 0) \right\}$$

$$+ \sum_{\lambda=1}^\lambda \sum_{\delta=0}^1 (\frac{1}{2})^{2/3} \nu_{\lambda\lambda} \delta (R) \Delta^{\nu'\gamma'\nu''\gamma''} (m_k', m_k'' m_k') \right\}, \quad (2.17)$$

with

$$\Delta^{\nu'\gamma'\nu''\gamma''} (m_k', m_k'' m_k') = [1 + (-1)^{\nu' + \nu'' + \delta + j' - j'' - \lambda}] (-1)^{m_k''} \quad (2.17')$$

$$\times \left\{ C(j', j'' \lambda; m_k', -m_k'' m_k') + (-1)^{\nu'} C(j', j'' \lambda; -m_k', m_k'' m_k') \right\}$$

$$+ (-1)^{\delta} C(j', j'' \lambda; m_k', -m_k'' - m_k')$$

$$+ (-1)^{\nu' + \delta} C(j', j'' \lambda; -m_k', -m_k'' - m_k') \right\},$$

where $W$ is a Racah coefficient. We notice that the potential matrix element and therefore the scattering equations (2.12) are diagonal in $J$ and independent of $M$. The equations are independent of the projection of the total angular momentum on the laboratory z-axis, $M$, since the scattering hamiltonian does not depend explicitly on the operator $\hat{J}_z$ which represents the projection of $\hat{J}$ along the z-axis.
The reflection symmetry of the symmetric top molecule and therefore the atom-molecule system about a plane through the molecular symmetry axis imposes the condition on the potential that

$$V(R, \Theta, \phi) = V(R, \Theta, 2\pi - \phi).$$

Using this condition in the angular integral over $\phi$ in Eq. (2.14'), we discover that only values of delta equal to zero ($\delta = 0$) are allowed by the symmetry. This result and the restrictions imposed by the first Clebsch-Gordan coefficient in Eq. (2.17) and the leading term of Eq. (2.17') imply that the matrix element $U^{\gamma_1}_{\gamma}(R)$ is zero unless the following relation holds among the channel quantum numbers:

$$(j' + \nu' + \lambda') + (j'' + \nu'' + \lambda'') = \text{even number}.$$  

We refer to the term $(-1)^{j_1 + \nu' + \lambda'}$ as the parity of channel $(jm_k \nu \lambda)$. Since the matrix elements connecting channels with different parities vanish, the coupled equations divide into two distinct sets, each with a definite parity. Each set can in turn be solved independently for the wave functions $\{u^{\gamma}_{\gamma_1}(R)\}$.

Having established the form of the coupling matrix elements, we now return to a discussion of the solutions $u^{\gamma}_{\gamma_1}(R)$ of the coupled set of equations (2.12). We are interested in the asymptotic form of the wave functions,
since it is in this limit that we may extract scattering information. As \( R \) approaches infinity, the molecular interaction potential elements, for systems considered in this study, all approach zero faster than \( R^{-2} \). Thus, at large values of \( R \), the potential terms in Eq. (2.12) vanish and the radial wave function for an open channel \( (k_{ji}^2 \gg 0) \) has the asymptotic form

\[
\lim_{R \to \infty} u_{\gamma''}^\gamma(R) = \delta_{\gamma \gamma''} \exp[-i(k_{\alpha}R-\lambda\pi/2)] \quad \text{(open)}
\]

\[
-\left(\frac{\hbar}{k_{\alpha''}}\right)^{1/2} S_{\gamma''}^J(\gamma'', \gamma) \exp[i(k_{\alpha''}R-\lambda''\pi/2)], \quad (2.19a)
\]

where \( \alpha \) represents the set of quantum numbers \( (jm_k) \). Since closed channels represent states that are energetically inaccessible to the system, the closed channel radial functions are not scattering solutions and must vanish at large distances as

\[
\lim_{R \to \infty} u_{\gamma''}^\gamma(R) \to \exp[-|k_{\alpha''}|R], \quad \text{(closed)} \quad (2.19b)
\]

with \( |k_{\alpha''}| \), the magnitude of the purely imaginary closed channel wave number \( k_{\alpha''} (k_{\alpha''}^2 < 0) \). The scattering matrix element is given by \( S_{\gamma'}^J(\gamma', \gamma) \). The scattering equations (2.12) are diagonal in \( J \) and independent of \( M \) as is the \( S \)-matrix. The square modulus of this element \( |S_{\gamma'}^J(\gamma', \gamma)|^2 \) gives the probability for a transition between channels \( \gamma \) and \( \gamma' \) and obeys the unitarity relation

\[
\sum_{\gamma'} |S_{\gamma'}(\gamma', \gamma)|^2 = 1 \quad (2.19c)
\]
and the symmetry condition

\[ S^J(\gamma'', \gamma) = S^J(\gamma, \gamma''). \]

Therefore, by solving the coupled equations (2.12) for the wave functions \( u^J_{\gamma'}(R) \) and comparing the resulting values to the asymptotic form of Eq. (2.19a), we can determine the values of \( S^J(\gamma', \gamma) \). We now seek the connection between the S-matrix and the rotational excitation cross section.

Asymptotically the total scattering wave function \( \psi_{jm_k \nu}(R, \hat{r}) \) must have the form of a plane wave incident upon the initial target state \((jm_k \nu)\) plus a superposition of outgoing spherical waves in each of the allowed channels. If we choose the laboratory z-axis as the incident direction, the form of the total wave function is given by

\[
\psi_{jm_j \nu}(R, \hat{r}) \rightarrow \lim_{R \to \infty} \exp(-ik_{\alpha} \cdot R) \psi^j_{jm_j \nu}(\hat{r}) + \sum_{j'm_k \nu'} \left( \frac{k_{\alpha}}{k_{\alpha'}} \right)^{1/2} R^{-1} \exp(ik_{\alpha} \cdot R) f(j'm_k \nu', jm_k \nu | \hat{R}),
\]

where \( f \) is the scattering amplitude. The total wave function may also be formed as a superposition of the wave functions \( \psi^{JM}_{\nu} \) given by Eq. (2.11) as

\[
\psi_{jm_j \nu}(R, \hat{r}) = \sum_{JM} \sum_{\ell'm_k \nu'} a^{JM}_{\ell'm_k \nu'} \psi^{JM}_{\nu}(R, \hat{r}).
\]
The asymptotic form of Eq. (2.21) is determined by substituting for the \( u_{\gamma}^{J,\nu} \) term of Eq. (2.11) its asymptotic expansion given by Eq. (2.19). This substitution splits Eq. (2.21) into two distinct types of terms, the first set depending on \( \exp(-ik_{\alpha} R) \) and the second set on \( \exp(ik_{\alpha} R) \). The expansion coefficient \( a_{J}^{M} \) can be determined by forcing the first set of terms to give the incident plane wave of Eq. (2.20). The resulting value for \( a_{J}^{M} \) is given by

\[
a_{J}^{M} = \frac{i}{2k_{\alpha}} \frac{\bar{k}'+1}{(2\bar{k}'+1)\frac{1}{2} (4\pi)^{\frac{1}{2}}} C(j', \bar{k}', \bar{J}; m'_{J}, M) \delta_{\bar{k}', \bar{k}'} \delta_{j, j'} \times \delta_{m_{J}, m_{J}'} \delta_{\nu, \nu'} \delta_{m_{k}, m_{k}'}.
\]

Using this value for \( a_{J}^{M} \) in the set of terms depending on \( \exp(ik_{\alpha} R) \), and comparing this to the second term in Eq. (2.20), we discover that

\[
f(\gamma', \gamma|\hat{R}) = \frac{i}{k_{\alpha}} \sum_{m_{J}} q(j', m_{J}, m_{k}', \nu'; jm_{J}, m_{k}, \nu) \phi_{m_{J}, m_{k}', \nu}^{j'}, (\hat{f}), \quad (2.22)
\]

with

\[
q(j', m_{J}, m_{k}', \nu'; jm_{J}, m_{k}, \nu) = \sum_{J}^{J} \sum_{\bar{J}}^{J} \sum_{m_{\bar{J}}}^{J} \frac{i^{\bar{k}'+1}}{\pi^{\frac{1}{2}} (2\bar{k}'+1)^{\frac{1}{2}}} \times C(j, \bar{J}; m_{J}, M) C(j', \bar{J}; m_{J}', M) T^{J}(\gamma', \gamma) Y_{\bar{J}, m_{\bar{J}}}, (\hat{R}) \quad (2.23)
\]

and

\[
T^{J}(\gamma', \gamma) = \delta_{\gamma', \gamma} - S^{J}(\gamma', \gamma). \quad (2.24)
\]

The differential cross section for a transition from \((jm_{J}, m_{k}, \nu)\) to \((j', m_{J}', m_{k}', \nu')\) is given by
\[ \frac{d\sigma}{d\Omega}(jm_{j'}m_{k'} \gamma \rightarrow jm_{j}m_{k} \gamma') = |f|^2 = \frac{1}{k\alpha} |\alpha(j'm_{j}m_{k} \gamma', jm_{j}m_{k} \gamma')|^2. \]  

(2.25)

The rotational excitation cross section for the transition \( jm_{k} \rightarrow jm'_{k} \) can be determined from Eq. (2.25) by averaging over the initial \( (m_{j} \gamma) \) values and summing over the final \( (m'_{j} \gamma') \) values and integrating over \( d\hat{R} \) as

\[ \sigma(jm_{k} \rightarrow jm'_{k}) = \frac{\pi}{2k\alpha} \sum_{J=0}^{\infty} \frac{1}{(2J+1)} |J+j| |J+j'| \sum_{J'=|J-j'|}^{J-j'} \sum_{\gamma'\gamma} (2J+1) |T^{J}(\gamma', \gamma)|^2. \]  

(2.26)

We define the partial cross section for a given \( J \) as

\[ \sigma^{J}(jm_{k} \rightarrow jm'_{k}) = \frac{\pi}{2k\alpha} \frac{(2J+1)}{(2j+1)} \sum_{J'} \sum_{\gamma'\gamma} |T^{J}(\gamma', \gamma)|^2. \]  

(2.27)

with \( J' \) restricted by the triangular relation on \( J, j, \) and \( j' \).

In conclusion, we briefly review the procedure for calculating rotational excitation cross sections in the coupled channel close coupling formulation (CCCCF). We assume that the total energy \( E \) is fixed. For each value of the total angular momentum quantum number \( J \), we choose a finite set of rotor states, for example, the symmetric top states, each of which is designated by the quantum numbers \( (jm_{k} \gamma) \) and energy \( E_{jm_{k}} \), with \( j \) between zero and \( j_{\text{max}} \). We shall assume that there are \( N_{s} \) such states.

\( \gamma \) We use the notation \( (0-j_{\text{max}}) \) to denote a rotor basis consisting of all basis functions with \( j \) between 0 and \( j_{\text{max}} \).
Using the triangular relation between $J$, $j$, and $\lambda$,
\[ |J-j| \leq \lambda \leq |J+j|, \]
we determine the 2$j+1$ values of the channel quantum numbers $\gamma = (jm_K^l \lambda \lambda)$ associated with each rotor state. For the $N_g$ rotor states, we shall assume that there are $N_c$ such channels and therefore $N_c$ basis functions of the form $u^M_{J\gamma}$. Having identified the channels, we then numerically solve the set of $N_c$ coupled equations (2.12') for the channel wave functions $u^M_{J\gamma}(R)$. Comparing the asymptotic behavior of these wave functions with Eq. (2.19), we determine the scattering matrix elements $S^J(\gamma', \gamma)$. We now repeat the calculation using a larger basis set (0-$j_{\text{max}}+1$) and compare the resulting S-matrix with our previous calculation. If the corresponding S-matrix elements agree to within an allowed tolerance, we use the S-matrix elements to calculate the partial cross section $\sigma^J(jm_k^l - j'm_k^l)$ of Eq. (2.27). However, if the S-matrices have not converged, the calculation is continued with larger and larger basis sets until two successive S-matrices agree to within the allowed tolerance. In this manner, we determine the partial cross section for each $J$ value. The total cross section $\sigma(jm_k^l - j'm_k^l)$ is given as the sum of the partial cross sections. In theory the sum over partial cross sections is infinite; however, in practice, we must truncate this sum. We choose to do so once the contribution from one of the addition of another $\sigma^J'$ is less than one tenth of the percent (0.1%) of the value of the total cross section.
calculated from all \( J < J' \). Since many cross sections oscillate over a fairly wide range of \( J \) values before eventually vanishing, we calculate the partial cross section over an extensive range of \( J \) values and apply the above procedure only in the region in which all oscillation has died and the cross section is monotonically approaching zero.
C. Rotational Excitation: Atom-Linear Molecule

In this section we briefly outline the formalism which describes the rotational excitation of a linear rigid rotor molecule by collisions with a ground state structureless atom. Since the derivation closely parallels that of the symmetric top molecule, we merely describe the differences and then present the final form of the scattering formalism. The hamiltonian which describes the collision has the same form as Eq. (2.1). The kinetic energy operator is identical to that of the atom-symmetric top system. The rotational hamiltonian, however, changes since the linear molecule has one less degree of rotational freedom than the symmetric top. In addition, the interaction potential is less complicated since it no longer depends on the azimuthal orientation of the atom-molecule system. We now discuss the consequences of each of these changes on the scattering formalism of the last section.

A new form for the molecular hamiltonian will mean changes in the basis functions and matrix elements. For a linear rigid rotor, the molecular hamiltonian has the form (see Eq. (2.2))

\[ H_{\text{mol}} = \frac{1}{2I} \hat{j}^2, \]  

(2.29)

where \( \hat{j} \) is the total rotational angular momentum operator. The eigenfunctions of \( H_{\text{mol}} \) are the spherical harmonics.
Fig. 2  Geometry of atom-linear rotor system: space-fixed frame. The position of the rigid rotor is \((\theta_R, \phi_R)\) and of the atom \((R, \theta_R, \phi_R)\).
\( Y_{jm_j}(\hat{r}) \) with \( m_j \) the projection of \( j \) on the laboratory z-axis. The eigenvalue equation of \( H_{\text{mol}} \) then becomes

\[
H_{\text{mol}} Y_{jm_j}(\hat{r}) = E_j Y_{jm_j}(\hat{r}),
\]

(2.29')

with \( E_j = \frac{1}{2I} j(j+1) \). As before, we choose our expansion basis \( \{ Y_{jm_j}(\hat{R},\hat{r}) \} \) to be the states formed by coupling the rotational angular momentum \( \hat{j} \) of the molecule to the orbital angular momentum \( \hat{k} \) of the incident atom as

\[
Y_{jm_j}(\hat{R},\hat{r}) = \sum_{m_k} C(j\hat{A}, m_j m_k M) Y_{jm_j}(\hat{r}) Y_{km_k}(\hat{R}).
\]

(2.29'')

We expand the wave function in terms of this complete basis and substitute the result into Eq. (2.1). After eliminating the angular dependence by multiplying by \( Y_{jm_k}^{JM^*} \) and integrating over \( d\hat{R} \) and \( d\hat{r} \), we are left with a set of coupled differential equations of the form of Eq. (2.12) with \( \gamma = (j\hat{k}) \) and \( E_{jm_k} \) replaced by \( E_j \). Following the same line of argument as in Section B, we find the rotational excitation cross section is given by

\[
\sigma(j\rightarrow j') = \sum_J \sigma^J(j\rightarrow j'),
\]

(2.30a)

with

\[
\sigma^J(j\rightarrow j') = \frac{\pi}{k_j^2} \frac{(2J+1)}{(2j'+1)} \sum_{\hat{k}\hat{l}} |T^J(j', \hat{k}'; j\hat{l})|^2.
\]

(2.30b)

The matrix elements which appear in Eq. (2.12) are affected by changes in the basis and the interaction poten-
tial. We assume that we know the interaction surface $V_1$ as a function of the atom-molecule radial separation $R$ and angular orientation $\Theta$. We then expand $V(R, \Theta)$ in a Legendre series as

$$V(R, \Theta) = \sum_{\lambda=0}^{\infty} v_\lambda(R) P_\lambda(\cos \Theta),$$

(2.31)

and use the addition theorem of spherical harmonics to express $P_\lambda(\cos \Theta)$ in terms of the laboratory coordinates $\hat{\hat{R}}$ and $\hat{\hat{f}}$. Using the new basis of Eq. (2.29"), we find that the matrix element becomes 1

$$U^\gamma_{\gamma'}(R) = \sum_{\lambda} f_\lambda(j' \lambda'; j'' \lambda''; J) v_\lambda(R)$$

where

$$f_\lambda(j' \lambda'; j'' \lambda''; J) = \frac{(-1)^{j'+j''-J}}{(2\lambda+1)} \left[ \frac{(2j'+1)(2j''+1)(2\lambda'+1)(2\lambda''+1)}{(2j'+1)(2j''+1)(2\lambda'+1)(2\lambda''+1)} \right]^{1/2}$$

$$\times \, \tilde{W}(j' \lambda'; j'' \lambda''; J\lambda) C(\lambda' \lambda'' \lambda; 000) C(j' j'' \lambda; 000);$$

(2.32)

the $f_\lambda$ are the Percival-Seaton coefficients. 1

From the restrictions imposed by the final two Clebsch-Gordan coefficients of Eq. (2.32), we note that the matrix element $U^\gamma_{\gamma'}$ is non-zero only if the two channels have the same value of the parity defined by $(-1)^{j'+\lambda'}$. Therefore as in the symmetric top case, the coupled differential equations may be separated into two distinct sets, one with even parity and one with odd parity. Each set may be handled independently and the resulting cross sections added to give the total rotational excitation cross section.
D. Distorted Wave Method

The distorted wave method\textsuperscript{12} is an approximation to the coupled channel differential equations (2.12) for the case of weak coupling. In the weak coupling limit, we assume that the potential matrix elements $U_{\gamma'\gamma}$ which connect different channels ($\gamma' \neq \gamma$) are small compared to the diagonal matrix elements $U_{\gamma\gamma}$. As a first approximation to the coupled channel equations, we assume that all coupling between different channels vanishes. The system thus remains in the initial (incident) channel $\gamma$ throughout the collision with the incident atom scattering elastically. The wave function for this case becomes

$$u_{\gamma'\gamma}(R) = u_{\gamma\gamma}(R) \delta_{\gamma \gamma'} \quad (2.33)$$

and the coupled equations (2.12) reduce to a single channel, one-dimensional equation

$$\left[ \frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k_\alpha^2 - U_{\gamma\gamma}(R) \right] U_{\gamma\gamma}(R) = 0 \quad (2.34)$$

whose solution satisfies the boundary conditions

$$u_{\gamma\gamma}(0) = 0$$

$$u_{\gamma\gamma}(R) \rightarrow \exp[-i(k_\alpha R - \lambda \pi/2)] S_{\gamma\gamma}(\gamma, \gamma) \exp[i(k_\alpha - \lambda \pi/2)], \quad R \rightarrow \infty$$

or

$$u_{\gamma\gamma}(R) \rightarrow -2i e^{-i\eta_{\gamma}} \sin(k_\alpha R - \lambda \pi/2 - \eta_{\gamma}), \quad R \rightarrow \infty$$

(2.34')
with the channel index $\gamma (\gamma = (\alpha, \ell))$ representing the quantum numbers associated with the rotor, $\alpha$, and the orbital angular momentum quantum number of the incident atom, $\ell$. We have used the fact that for a single channel equation the $S$-matrix can be expressed in terms of the channel phase shift $\eta_\gamma$ as

$$S^J(\gamma, \gamma) = e^{2i \eta_\gamma}.$$ 

In addition, we shall label the particular solution to Eq. (2.34) that asymptotically behaves as the sine function as $g^J_\gamma(R)$ so that

$$u^J_\gamma(R) = -2ie^{i \eta_\gamma} g^J_\gamma(R). \quad (2.35)$$

While the reduction of the coupled equations to a single equation is certainly a major simplification, it is, alas, a rather uninteresting one since inelastic scattering has been ignored. We now assume that the coupling between different channels is non-zero and weak, obeying the relation

$$|U^\gamma'(R)| \ll |U^\gamma(R)| \text{ and } |U'^\gamma(R)| \quad (\gamma \neq \gamma'). \quad (2.36)$$

Substituting Eq. (2.33) into Eq. (2.12) and using relation (2.36), we obtain a set of differential equations of the form

$$\left[ \frac{d^2}{dR^2} - \frac{\ell(\ell+1)}{R^2} + k_\alpha^2 - U^\gamma(R) \right] u^J_\gamma(R) = 0 \quad (2.37a)$$
\[
\left[ \frac{d^2}{dr^2} - \frac{\ell' (\ell' + 1)}{r^2} + k_\alpha^2 - U_\gamma'(R) \right] u_{\gamma'}^J(R) = U_\gamma'(R) u_{\gamma}^J(R),
\]

for all \( \gamma' \neq \gamma \) with \( U_\gamma'(R) \neq 0 \). The excited channel wave function \( u_{\gamma'}^J(R) \) satisfies the asymptotic boundary condition

\[
u_{\gamma'}^J(R) \rightarrow -\left( \frac{k_\alpha}{k_\alpha'} \right)^{1/2} S^J(\gamma', \gamma) \exp[i(k_\alpha, R-\ell' \pi/2)].
\]

An equation of the form of Eq. (2.37) is associated with each excited channel \( (\gamma' = (\alpha', \ell')) \) that is coupled to the initial channel \( \gamma \). Since the excited channel is coupled only to the initial channel, we may solve Eqs. (2.37b) separately for each excited channel once the solution of Eq. (2.37a) has been determined. We recall that more than one channel can be associated with each rotor state. We therefore find a set of equations (2.37) for each incident channel \( \gamma \) arising from the initial rotor state \( \alpha \). For each of these sets of equations labeled by the initial channel, we solve for the S-matrix and channel cross section \( \sigma^J(\alpha \ell - \alpha' \ell') \). The total cross section for the transition between initial and final rotor states \( \sigma^J(j-j') \) is calculated by summing over all allowed values of \( \ell \) and \( \ell' \).

We now concentrate our attention on the solution of Eq. (2.37b). Mott and Massey have shown that the differential equation

\[
\left[ \frac{d^2}{dr^2} + k^2 - U(R) \right] \psi(R) = F(R)
\]

has a solution
\[ \psi(R) = \psi_1(R) \int_\infty^R \psi_2(R') F(R') dR' - \psi_2(R) \int_0^R \psi_1(R') F(R') dR' \]

(2.39)

subject to the conditions that

\[ \psi(0) = 0 \]
\[ F(R) \to 0 \quad R \to \infty \]
\[ \psi(R) \to e^{i k R} \quad R \to \infty \]
\[ RU(R) \to 0 \quad R \to \infty . \]

(2.40)

The wave functions \( \psi_1 \) and \( \psi_2 \) are solutions to the homogeneous equation

\[ \left[ \frac{d^2}{dR^2} + k^2 - U(R) \right] \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = 0 \]

(2.41)

with

\[ \psi_1(0) = 0 \]
\[ \psi_1(R) \to \sin(kR + \eta) \quad R \to \infty \]
\[ \psi_2(R) \to \frac{1}{k} e^{i(kR + \eta)} , \]

where \( \eta \) is the phase shift. Since the conditions imposed by Eq. (2.40) are satisfied by the solutions and matrix elements of Eq. (2.37b), the solution to Eq. (2.37b) is given by Eq. (2.39) if the following identifications are made: \( F(R) \) with \( U'_Y(R) u^Y(\gamma, R) \), \( \psi(R) \) with \( u^Y(\gamma, R) \), \( U(R) \) with \( U'_Y(R) \), \( \eta \) with \( \eta_{\gamma'} \), and \( \phi_{\gamma'} \) with \( \psi_1 \). We are most interested in the asymptotic form of this solution since in this
limit we can compare the solution with Eq. (2.38) to find the form of the S-matrix. In the asymptotic limit, Eq. (2.39) becomes

$$\psi(R) \to -\frac{1}{k} e^{i(kR+\eta)} \sum_{R'=0}^{\infty} \psi_1(R') F(R') dR'. $$

Making the identifications with Eq. (2.37b) and using the asymptotic form (Eq. (2.34')) for $u^\gamma_Y(R)$, we have

$$u^-\gamma_Y(R) \to \frac{2i}{k\alpha'} \exp[i(\eta_\gamma+\eta_{\gamma'})] \exp[i(k_\alpha', R-\ell' \pi/2)]$$

$$\times \sum_{R'} g^{\gamma}_{\gamma'}(R') U^-\gamma_Y(R') g^\gamma_Y(R') dR'. \quad (2.42a)$$

where $g^{\gamma}_{\gamma'}$ and $g^\gamma_{\gamma'}$ satisfy

$$\left[ \frac{d^2}{dR^2} - \frac{\ell''(\ell''+1)}{R^2} + k_{\alpha''} - U''_{\gamma''}(R) \right] g^{\gamma}_{\gamma''}(R) = 0$$

$$g^{\gamma}_{\gamma''}(0) = 0 \quad (2.42b)$$

$$g^{\gamma}_{\gamma''}(R) \to \sin(k_{\alpha''} R - \ell'' \pi/2 + \eta_{\gamma''}),$$

for $\gamma'' = \gamma$ or $\gamma'$. Comparing Eqs. (2.42a) and (2.38), we find that the inelastic S-matrix is given by

$$S^\gamma(\gamma', \gamma) = -2i \exp[i(\eta_\gamma+\eta_{\gamma'})] \left(\frac{k_{\alpha'}}{k_\alpha}\right)^{1/2} \beta^\gamma_{\gamma'}, \quad (2.43a)$$

with

$$\beta^\gamma_{\gamma'} = \frac{2i}{k_{\alpha'}} \sum_{R'} g^{\gamma}_{\gamma'}(R') U^\gamma_{\gamma'}(R') g^\gamma_Y(R') dR'. \quad (2.43b)$$

Thus, the S-matrix can be calculated from the solutions of the homogeneous equations (2.42b) and the coupling matrix
element $U_{\gamma'}(j)$. The inelastic cross section for the case of the linear rigid rotor ($\alpha = j$) is then found from Eq. (2.30) as

$$
\sigma(\alpha-\alpha') = \sum_{J=0}^{\infty} \sigma^J(j-j'),
$$

(2.44)

with

$$
\sigma^J(j-j') = \frac{\pi}{k_j^2} \frac{2J+1}{(2J+1)} \sum_{k=|J-j|} \sum_{k'=|J-j'|} |S^J(j,j',j,j')|^2.
$$

We review briefly the procedure for calculating inelastic cross sections for transitions between two rotor levels ($j$ and $j'$). We first determine all channels associated with the initial and final rotor states. For a given initial channel $\gamma$, we solve Eq. (2.37a) for the elastic initial channel wave function $g^J_{\gamma}(R)$. Using this solution, we calculate the S-matrices $S_{\gamma'}(j,j')$ by solving Eq. (2.37b) for each final channel $\gamma'$ that is coupled to this particular initial channel. We repeat this procedure for all initial channels until we have generated the S-matrices which connect all allowed pairs of initial and final channels. The resulting S-matrices are then used in Eq. (2.44) to find the cross section. The S-matrix calculated by the distorted wave method is not unitary since it satisfies the relation

$$
\sum_{j',k',k} |S^J(j,k,j',k')|^2 = 1 + \sum_{j',k',k} \frac{k_i}{k_j} \frac{J_{j,k}}{\kappa_j} (2\theta_{j,k}).
$$

(2.45)
Therefore, one condition for the validity of the distorted wave method is that the second term on the right side of Eq. (2.45) is small compared to one (1). In this case we approximately regain the unitarity of the S-matrix. Finally, if the elastic matrix element is neglected in Eqs. (2.42b), the distorted wave approximation reduces to the Born approximation. In the Born approximation, the wave functions are plane waves. Thus, the effect of including the potential matrix element in Eq. (2.42b) is to "distort" the solution from the plane wave form; it is from this effect that the method derives its name.

In this chapter we have presented the scattering formalism for atom-molecule collisions in the laboratory frame of reference. In the next chapter, we will rederive this formalism in terms of a coordinate system which follows the incident atom.
And we are right, I think you'll say,  
To argue in this kind of way.  
The Mikado

Chapter 3. Atom-Molecule Scattering: Rotating Atom Frame

A. Introduction

We now wish to derive the scattering formalism for 
the rotational excitation of a $\Sigma$ state molecule by colli-
sions with a ground state atom in a reference frame 
which rotates about the center-of-mass of the system so 
as to follow the motion of the incident atom. For this 
reason, we refer to the coordinate system, whose z-axis 
points along the incident particle direction and whose 
y-axis lies in the laboratory x-y plane, as the rotating 
atom (RA) frame.\(^1\) The RA frame is related to the laboratory 
or space-fixed (SF) frame of Chapter 2 by the unitary rota-
tion operator $\hat{\Lambda}$. The two frames are formally equivalent; 
however, practically certain problems are better handled 
in one frame or the other. In Section B, we derive the 
RA scattering equations from the SF hamiltonian and wave 
function by the direct application of the rotation operator 
$\hat{\Lambda}$. We follow rather closely the development of Pack\(^2\) and 
limit our discussion to the case of a linear rigid rotor. 
In Section C, we consider the $j_z$-conserving coupled state 
approximation\(^3\) to the RA scattering equations. This 
approximation greatly simplifies the computation of rota-
tional excitation cross sections. We conclude this chapter with a comparison of the coupled channel close coupling (CCCC) method and the $j_z$-conserving coupled state approximation, (JZCS).
B. Rotating Atom Frame: Coupled Channels

Since all scattering information is given by the solutions to the Schrödinger equation, our first task is to find the form of this equation in the RA frame. We accomplish this by transforming the SF hamiltonian and wave function by the unitary rotation operator $\hat{\Lambda}$ which represents rotation of the SF coordinate axes into a RA coordinate system whose z-axis $\hat{z}'$ lies along the direction of the incident particle $\hat{R}$ and whose y-axis $\hat{y}'$ lies in the SF x-y plane. The appropriate geometry is displayed in Fig. 3. We shall use primed (unprimed) symbols to denote quantities referred to the RA(SF) coordinate systems. Thus, the radial atom-molecule separation, the orientation of the incident atom, and the orientation of the rigid rotor are given in the SF frame by $R$, $\hat{R} = (\theta_R, \phi_R)$, and $\hat{r} = (\theta_r, \phi_r)$ and in the RA frame by $R'$, $\hat{R}' = (0, 0)$, and $\hat{r}' = (\theta_{r'}, \phi_{r'})$. In this notation, the Euler angles $^4(\alpha \beta \gamma)$ which describe the rotation are given by $(\phi_R, \theta_R, 0)$. The hamiltonian $H'$ and the wavefunction $\psi'$ in the RA frame are then given by

$$H' = \hat{\Lambda}^{-1}H\hat{\Lambda} \quad (3.1a)$$
$$\psi' = \hat{\Lambda}^{-1}\psi \quad (3.1b)$$

where $H$ is the SF hamiltonian of Eqs. (2.1) and (2.2) of the form
Fig. 3 Geometry of atom-linear rotor system: rotating atom frame. The rotating atom frame (x'y'z') has its z axis along R and its y axis in the space-fixed xy plane.
\[ H = -\frac{1}{2\mu} \nabla_R^2 + \frac{e^2}{2\mu R^2} + H_{\text{mol}}(\hat{r}) + V(R, \hat{r}) , \]

with \( \nabla_R^2 = \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) \), and \( \psi \) is the SF wave function.

The Schrödinger equation in the RA frame becomes

\[ (\hat{\Lambda}^{-1} H \hat{\Lambda}) \hat{\Lambda}^{-1} \psi = E \hat{\Lambda}^{-1} \psi . \tag{3.1c} \]

We now seek to determine the form of the RA hamiltonian \( H' \). The fact that the magnitude of \( \mathbf{R} \) is unchanged by the rotation (i.e., \( R = R' \)) implies that the radial kinetic energy operator has the same form in both frames with

\[ \hat{\Lambda}^{-1} \frac{1}{2\mu} \nabla_R^2 \hat{\Lambda} = \frac{1}{2\mu} \nabla_{R'}^2 . \tag{3.3} \]

The potential depends only the radial and angular separation of the atom and molecule. In the SF frame, the potential has the form \( V(R, \hat{r}) \). Since the potential is a scalar quantity, its magnitude is invariant under the rotation. Therefore, to find \( V \) in the rotating frame, we simply replace \( R \) by \( R' \) and \( \hat{r} \) by \( \cos \theta_{r'} \), (see Fig. 3) and thus write

\[ \hat{\Lambda}^{-1} V(R, \hat{r}) \hat{\Lambda} = V(R', \cos \theta_{r'}) . \tag{3.4} \]

The molecular hamiltonian \( H_{\text{mol}} \) depends only on the relative orientation of the molecular figure axis with respect to a set of coordinate axes and is invariant under the rotation described by \( \hat{\Lambda} \). Thus, \( H_{\text{mol}} \) is found in the rotated frame.
by replacing \( \hat{r} \) by \( \hat{r}' \) with the result

\[
\lambda^{-1} H_{\text{mol}}(\hat{r}) \hat{\lambda} = H_{\text{mol}}(\hat{r}') \quad .
\] (3.5)

The operator \( \hat{\lambda}^2 = \lambda^{-1} \hat{\lambda}^2 \hat{\lambda} \) describes the orbital angular momentum of the incident particle in the RA frame. The RA orbital angular momentum, together with the angular momentum due to the rotation of the coordinate axes must equal the orbital angular momentum in the SF frame. Further, since the radial motion of the atom is along the \( z \)-axis in the RA frame, there is no net orbital angular momentum about this axis \( [\hat{\lambda}_z = R' \hat{\lambda}' \times \hat{\mu}_z = 0] \), and the \( z \)-components of the total angular momentum \( J'_z \), and the rotational angular momentum \( j_z \), are equal. We could represent \( \hat{\lambda}^2 \) in terms of differential expressions as is usually done with \( \hat{\lambda}^2 \); however, it is more convenient to express \( \hat{\lambda}^2 \) in terms of formal vector operators whose effects on the RA wave functions are known. In the SF frame, we recall that the total angular momentum \( \hat{\lambda} \) is formed by coupling the orbital angular momentum \( \hat{\lambda} \) with the rotational angular momentum \( j \) \( (\hat{\lambda} = \hat{\lambda} + j) \). In operator notation, this relation has the form

\[
\hat{\lambda}^2 = (\hat{\lambda} - j)^2 .
\]

Since \( \hat{\lambda} \) and \( j \) are vector operators, the application of the rotation simply changes the axes to which the operators refer from the SF to the RA as

\[
\hat{\lambda}'^2 = \lambda^{-1} (\hat{\lambda} - j)^2 \hat{\lambda} = (\hat{\lambda}' - j')^2 \quad , \text{or}
\]

\[
\hat{\lambda}'^2 = (\hat{\lambda}' - j') \cdot (\hat{\lambda}' - j') \quad .
\] (3.6)
If we expand this dot product in terms of the operator components referred to the RA axes and use the relations that

\[ 2 \hat{j}_x' \hat{J}_x' + 2 \hat{j}_y' \hat{J}_y' = \hat{j}_- ' \hat{J}_+ ' + \hat{j}_+ ' \hat{J}_- ' , \quad \text{and} \]

\[ [\hat{J}_i ', \hat{j}_i '] = 0 \quad \text{with} \quad i = x, y, z, \]

then Eq. (3.6) can be written

\[ \hat{\rho}'^2 = \hat{j}_- ' \hat{J}_- ' + \hat{j}_+ ' \hat{J}_+ ' + \hat{j}_x' \hat{J}_y' + \hat{j}_y' \hat{J}_x' \]

where \( \hat{J}_\pm ' \) and \( \hat{j}_\pm ' \) are the raising and lowering operators defined by

\[ \hat{J}_\pm ' = \hat{J}_x' \pm i\hat{J}_y' \]

\[ \hat{j}_\pm ' = \hat{j}_x' \pm i\hat{j}_y' \]

Thus, combining Eqs. (3.3), (3.4), (3.5), and (3.8), we form the hamiltonian \( H' \) in the RA coordinate system as

\[ H' = - \frac{1}{2\mu} \overline{v} R' R' + H_{mol}(\hat{r}') + V(R', \cos \theta_z') \]

\[ + \frac{1}{2\mu R'_2} [\hat{\rho}'^2 - 2\hat{J}_z'^2 + \hat{j}_- ' \hat{J}_+ ' - \hat{j}_+ ' \hat{J}_- '] . \]

We now consider the form of the wave function in the RA frame. Formally, this wave function is related to the SF wave function by the rotational operator \( \hat{R} \) as in Eq. (3.1b). We can place this operator equation in a more convenient form by choosing a particular representation. If we choose as our representation the eigenfunctions of the
total angular momentum $J'$ and its projection along the $z'$-axis, the wave functions in the RA frame $\psi_{\Omega', j\Omega}^{J'}(R', \hat{z}')$, which are eigenfunctions of $J'$ and $J'_{z'}$, are obtained from the known SF wave functions $\psi_{j\lambda}^{JM}(R, \hat{r})$, which are eigenfunctions of $\hat{J}$ and $J'$, by the relation
\begin{equation}
\psi_{\Omega', j\Omega}^{J'}(R', \hat{z}') = \sum_{M'=-J}^{J} D_{M', \Omega}^{J}(\psi_{R', \theta', 0}) \psi_{j\lambda}^{JM}(R, \hat{r}) , \tag{3.11}
\end{equation}
with
\begin{equation}
\hat{J}^2 \psi_{\Omega', j\Omega}^{J'}(R', \hat{z}') = J(J+1) \psi_{\Omega', j\Omega}^{J'}(R', \hat{z}') \tag{3.12}
\end{equation}
\begin{equation}
\hat{J}_{z'} \psi_{\Omega', j\Omega}^{J'}(R', \hat{z}') = \Omega' \psi_{\Omega', j\Omega}^{J'}(R', \hat{z}') .
\end{equation}
The subscripts $(j\lambda)$ and $(j\Omega)$ represent the initial channel quantum numbers in SF and RA frames respectively. We have dropped the prime from $\hat{J}'$ since the magnitude of the total angular momentum is the same in both frames ($J' = J$). The $D$-matrix is the representation of the rotational operator $\hat{\Lambda}$ in terms of the SF and RA eigenfunctions. In Dirac notation, it has the form $\langle J M | \hat{\Lambda} | J \Omega \rangle = D_{M \Omega}^{J}$ with $\psi_{J\Omega}^{JM}$ and $\psi_{\Omega'}^{J}$ defined as $\langle R' \hat{r} | JM \rangle$ and $\langle R' \hat{r}' | J \Omega \rangle$ respectively. Substituting $\psi_{\Omega', j\Omega}^{J}$ and Eq. (3.10) into Eq. (3.1c) and using the relations of Eq. (3.12), we find that the RA Schrödinger equation becomes
\begin{equation}
-H_{\Omega', \Omega'-1} \psi_{\Omega', j\Omega}^{J'}(R', \hat{z}') + (E-H_{\Omega', \Omega'} \psi_{\Omega', j\Omega}^{J'}(R', \hat{z}') - H_{\Omega', \Omega'+1} \psi_{\Omega', j\Omega}^{J'}(R', \hat{z}') = 0 , \tag{3.13}
\end{equation}
where

\[ H_{\Omega',\Omega'} = -\lambda_{\pm}(J,\Omega') \frac{\hat{J}_{z}^{2}}{2\mu R'^{2}} \]

\[ H_{\Omega',\Omega'} = -\frac{1}{2\mu} \nabla_{R'}^{2} + [J(J+1) - 2\Omega'^{2} + \hat{j}'^{2}] / 2\mu R'^{2} \]

\[ + H_{\text{mol}}(\hat{\xi}') + V(R',\cos\theta_{r}') . \]

In deriving Eq. (3.13), we have used the following properties of the raising and lowering operators:

\[ J_{\pm} \psi_{\Omega}^{J} j \Omega = \lambda_{\pm}(J,\Omega') \psi_{\Omega}^{J} j \Omega , \]

with \( \lambda_{\pm}(J,\Omega') = [(J\pm\Omega'+1)(J\mp\Omega')]^{\frac{1}{2}} \). In the SF frame, the coupling between channels is provided by the potential matrix elements. However, in the RA frame, the coupling between channels is provided not only by the potential but also by the raising and lowering operators. We recall that the SF Hamiltonian was diagonal in both \( J \) and \( M \); however, the RA Hamiltonian, while still diagonal in the total angular momentum \( J \), is no longer so with respect to the projection of the total angular momentum on the RA z-axis, \( \Omega \). We now eliminate the angular dependence in Eq. (3.13) by expanding the wave function in a complete set of linear rigid rotor states \( \{ Y_{j',\Omega'}(\hat{\xi}') \} \) with the properties

\[ H_{\text{mol}}(\hat{\xi}') Y_{j',\Omega'}(\hat{\xi}') = \frac{1}{2I} j'(j'+1) Y_{j',\Omega'}(\hat{\xi}') \]

\[ j'^{2} Y_{j',\Omega'}(\hat{\xi}') = j'(j'+1) Y_{j',\Omega'}(\hat{\xi}') \]

\[ \hat{j}_{z} Y_{j',\Omega'}(\hat{\xi}') = \Omega' Y_{j',\Omega'}(\hat{\xi}') = m_{j'} Y_{j',m_{j}'}(\hat{\xi}') \text{ with} \]

\[-j' \leq \Omega' \leq j' \].
In the final relation we have used the fact that in the RA frame \( \hat{j}_z \), is equal to \( \hat{J}_z \). The expansion of the wave functions \( \psi^{J}_{\Omega', J} \) can then be written as

\[
\psi^{J}_{\Omega', J} (R', \hat{\theta}') = \sum_{j''} R'_{j''}^{-1} u^{J}_{j''} \Omega' (R') \psi^{J}_{j''} \Omega' (\hat{\theta}') .
\]  \( (3.15) \)

Substituting Eq. (3.15) into Eq. (3.13), multiplying by \( \psi^{*}_{j', \Omega'} (\hat{\theta}') \), and integrating over \( d \hat{\theta}' \), we find the set of coupled equations\(^2\)

\[
\begin{align*}
&h^{j'}_{\Omega', J} u^{J}_{j'} \Omega' \cdot 1 (R') + h^{j'}_{\Omega', J} u^{J}_{j'} \Omega' \cdot 1 (R') + h^{j'}_{\Omega', J} u^{J}_{j'} \Omega' \cdot 1 (R') \\
&= \sum_{j''} \sum_{J''} R''_{j''} (R') u^{J}_{j''} \Omega' (R') ,
\end{align*}
\]  \( (3.16) \)

where

\[
\begin{align*}
h^{j'}_{\Omega', J} &= \frac{d^2}{dR^2} + k^{j'}_{\Omega', J} - \frac{[J(J+1) - 2\Omega' \cdot 2 + j'(j'+1)]}{R'} \\
h^{j'}_{\Omega', J} \pm 1 &= \lambda_{+}(J, \Omega') \lambda_{-}(j', \Omega' \pm 1) R' - 2 \\
u^{j'}_{j''} (R') &= 2 \mu \int d \hat{\theta}' \psi^{*}_{j', \Omega'} (\hat{\theta}') V(R', \cos \theta_x) \psi_{j''} \Omega' (\hat{\theta}') \\
k^{j'}_{\Omega', J} &= 2 \mu (E - j'(j'+1) \frac{1}{2I}) .
\end{align*}
\]

Because of the long-range coupling provided by the terms \( h^{j'}_{\Omega', J} \pm 1 \), the asymptotic behavior of the radial wavefunctions \( u^{J}_{j'} \Omega' (R') \) is not as obvious as in the SF case. Pack\(^2\) has shown that the correct asymptotic form is given by
\[ u_{j'j'\Omega'}(R') \rightarrow k_j, \frac{-i}{2} \delta_{j',j'} \delta_{\Omega',\Omega} \exp[-i(k_j R' - (J+j) \pi/2)] \]

\[-SJ(j'\Omega';j'-\Omega) \exp[i(k_j R' - (J+j') \pi/2)]. \tag{3.17} \]

For an infinite basis set, the formulation of the scattering problem in terms of the coupled set of equations (3.16) is exact. In order to handle these equations computationally, we must truncate the basis at a finite number of functions. Each basis function is associated with a particular scattering channel \((j'\Omega')\). For each value of the rotational angular momentum quantum number \(j'\) which designates a particular rigid rotor state with energy \(E_{j'}\), there are \(2j'+1\) associated scattering channels of the form \((j'\Omega')\) since

\[-j' \leq \Omega' \leq j'. \]

For a fixed value of the total angular momentum \(J\) and a given number of rotor states \(\left[ j'|0 \leq j' \leq j_{\text{max}} \right]\), we can construct \(N\) (\(N = \sum_{j'=0}^{j_{\text{max}}} (2j'+1)\)) scattering channels \((j'\Omega')\) which correspond to a set of \(N\) coupled equations of the form of Eq. (3.16). These equations can then be solved numerically for the \(N\) channel radial wave functions \(\{u_{j'j'\Omega'}(R)|0 \leq j' \leq j_{\text{max}}; -j' \leq \Omega' \leq j'\}\). The scattering \(S\)-matrix element is obtained by comparing the numerical values of the \(u_{j'j'\Omega'}(R')\) functions at large values of \(R'\) with their asymptotic form given by Eq. (3.17). The procedure for testing the convergence of the \(S\)-matrix with
respect to basis size is the same as outlined in Chapter 2 for the SF case.

We now seek to determine the rotational excitation cross section in terms of the S-matrix elements found from the numerical solution of Eq. (3.16). Since the procedure follows rather closely that of Chapter 2, we briefly outline the important points and refer the reader to the article by Pack\(^2\) for a more thorough treatment. We begin by forming the total scattering wave function \( \psi_j \) as a superposition of RA wave functions. Since we wish to use the asymptotic form of the total wave function given by Eq. (2.20) in the SF frame,\(^7\) we expand \( \psi_j \) in terms of a set of RA wave functions which have been transformed into the laboratory (SF) frame. This transformation is accomplished through the use of the inverse of relation (3.11). We thus have in the laboratory frame

\[
\psi_j(R,\hat{\ell}) = \sum_{JM\Omega} a(Jm_j\Omega) \sum_{\Omega'} D_{JM\Omega'}^J(\hat{R}) \psi_{\Omega'}^J j\Omega (R',\hat{\ell}') . \tag{3.18}
\]

Using the expansion of the \( \psi_{\Omega'}^J j\Omega \) wave functions of Eq. (3.15) and the asymptotic form of the \( u_{j\Omega}^J \) wave functions of Eq. (3.17) in Eq. (3.18), we determine the asymptotic behavior of the total wave function \( \psi_j \). The expansion coefficients \( a(Jm_j\Omega) \) are trapped by equating the incident parts of the asymptotic forms of Eqs. (3.18) and (2.20). Substituting these coefficients into the scattering part of Eq. (3.18), we find the relation between the S-matrix
calculated in the RA frame and the rotational excitation
cross sections referred to the SF frame. The resulting
cross sections found by averaging over the initial states
and summing over the final are given by

\[ \sigma(j \rightarrow j') = \sum_{J=0}^{\infty} \sigma^J(j \rightarrow j') , \]  

(3.19)

where

\[ \sigma^J(j \rightarrow j') = \frac{\pi}{k_j} \frac{(2J+1)}{(2j'+1)} \sum_{M=-j}^{j} \sum_{\Omega'=-j'}^{j'} |T^J(j', \Omega'; jM)|^2 , \]

\[ T^J(j', \Omega'; jM) = \delta_{j,j'} \delta_{\Omega, \Omega'} - S^J(j', \Omega'; jM) , \]

with \( j < \) the lesser of \( j \) and \( J \) and \( j' < \) the lesser of \( j' \)
and \( J' \). Since the atom is assumed incident along the \(-\hat{z}\)
axis,\(^2\) the RA and SF axes are initially parallel and the
initial channel quantum number \( \Omega \) may be replaced by \(-M\).
A method of solution similar to that outlined at the end
of Section B of Chapter 2 can be used to solve for the
rotational excitation cross section.

We conclude this section with a comparison of the
scattering formalism in the SF and RA frames. We accom-
plish this by comparing Eqs. (3.16) and (2.12). In the
close coupling formalization, the formalism in the two
frames is equivalent. For a given value of \( J \) and choice
of rotor bases, the same number of coupled equations
appear in Eq. (3.16) as in Eq. (2.12). The SF equations
decouple at large values of \( R \) since all the coupling is
provided by the potential matrix elements which die faster than $R^{-2}$. On the other hand, due to the $h_{\Omega',\Omega\pm 1}$ terms, the RA equations remain coupled to very large distances. However, in the short-range region, where the $v_{\lambda}$ terms are large, the RA equations are less strongly coupled than the SF equations. In addition, the $\Omega$ and $j$ couplings are distinct since the $h_{\Omega\Omega\pm 1}$ terms are diagonal in $j$ and the potential matrix elements are diagonal in $\Omega$. In the SF frame the $\lambda$ and $j$ couplings are always connected by the Percival-Seaton coefficients and cannot be separated. These observations suggest that the SF representation be used in cases of weak, long-range coupling problems and that the RA representation be used in problems involving short-range, strong coupling.\(^2\) In our coupled channel studies we have used only the SF representation. The derivation of the $jz$-conversing approximation to the RA equation is our main reason for introducing the RA representation. An alternate approach, which takes into account the advantages of both representations, is to use the RA formalism in the short-range region and transform to the SF formalism in the long-range limit by means of a frame transformation.\(^8\) This procedure would minimize the coupling in all regions and is a topic we hope to pursue at some later time.
C. \( j_z \)-Conserving Coupled State Approximation

Several recent methods, which employ approximations to the coupled channel scattering equations, show promise as rapid, accurate procedures for calculating rotational excitation cross sections. The \( j_z \)-conserving coupled state (JZCS) method,\(^3\) the effective hamiltonian technique,\(^9\) the sudden approximation,\(^10\) and the exponential distorted wave method\(^11\) have been applied with some success to a wide variety of atom-molecule systems. We have selected the JZCS method for its versatility in treating different coupling strengths, its ability to handle closed channels, and its adaptability to our coupled channel numerical codes.

Under the JZCS approximation, we neglect the non-diagonal terms of the \( \hat{J}_z^2 \) operator and replace its diagonal terms with a constant expression. Since the coupling between channels with different values of \( m_j \) (\( \Omega \)) vanishes, the only remaining coupling is between the various rotor states labeled by the rotational angular momentum \( j \). Thus, the RA coupled channel equations reduce to a set of coupled state equations diagonal in both \( J \) and \( m_j \). This reduction in the dimensionality of the coupled equations leads to a more rapid numerical solution. In order to determine the cross section, we make the additional approximation that the RA and SF wave functions are the same.\(^{12a}\) This approxi-
mation allows us to associate the S-matrix, which is obtained from the numerical solution of the coupled state equations, directly with the laboratory frame cross sections.

We derive the JZCS method by approximating various expressions in the RA hamiltonian and wave function. First, we replace the operator $\hat{\ell}^2$ of Eq. (3.8) by the constant operator expression $J(J+1)$ $\hat{1}$ such that

$$\hat{\ell}^2 = J(J+1) \hat{1}, \quad (3.19')$$

where $\hat{1}$ represents the identity operator. It should be noted that this particular choice of the constant expression is not unique. In fact, various choices are made in order to better approximate different coupling strengths.\textsuperscript{12b} If we substitute this expression into Eq. (3.10), the Schrödinger equation becomes

$$(E-H)\psi_{m_jj_m_j}^J(R',\hat{r}') = 0, \quad (3.19'')$$

with

$$H = -\frac{1}{2\mu} \nabla_{R'}^2 + J(J+1)/2\mu R'^2 + H_{\text{mol}}(\hat{r}') + V(R',\cos\theta_{R'}).$$

We note that the Hamiltonian is diagonal in both $J$ and $m_j$.

We now expand the wave function $\psi_{m_j}^J$ in terms of a complete set of rotor states $\{\chi_{j'}^{m_j}(\hat{r}')\}$ as

$$\psi_{m_jj_m_j}^J(R',\hat{r}') = \sum_{j'} u_{j'}^{j_m_j} (R') R'^{-1} \chi_{j'}^{m_j}(\hat{r}').$$
Substituting this expansion into Eq. (3.19), multiplying by \( Y_{j m_j}^* (\hat{r}') \), and integrating over \( d\hat{r}' \), we find that the Schrödinger equation becomes

\[
\left[ \frac{d^2}{dr'^2} + k_j^2 - \frac{j(j+1)}{r'^2} \right] u_{j m_j}^{j'}(r') = \sum_j U_{j''}'(r') u_{j'' m_j}^{j'}(r'),
\]

where

\[
k_j^2 = 2\mu \left[ E - \frac{j(j+1)}{2l} \right]
\]

\[
U_{j''}^j(r') = 2\mu \int d\hat{r}' Y_{j m_j}^* (\hat{r}') V(R', \cos \theta', j') Y_{j m_j} (\hat{r}').
\]

(3.20')

Expanding the potential in a Legendre series, we find that

\[
U_{j''}^j(r') = \sum_\lambda V_\lambda (R') d_{\lambda}^{j'' j}
\]

(3.20'')

with

\[
d_{\lambda}^{j'' j} = \left[ \frac{(2j''+1)}{2j'} \right]^\lambda C(j'' j'; m_j 0 m_j) C(j'' j'; 000).
\]

From the first Clebsch-Gordan coefficient, we discover that only transitions which leave the initial and final projection of \( j \) unchanged are allowed. Thus, since the projection of \( \hat{j}' \) along the \( z' \)-axis, \( j_z' \), is conserved during collision, the method is referred to as the \( j_z \) conserving technique. This fact is a consequence of the diagonality of the scattering equations in \( m_j \).

Since the potential matrix elements die faster than \( R^{-2} \), the asymptotic form of Eq. (3.20) is the Bessel equation. The radial wave function \( u_{j m_j}^{j'} \) has the asymptotic form
As before, we may find the values of the $S$-matrix elements by solving the set of coupled equations (3.20) numerically in the close coupling formulation and compare the behavior of the solutions at large $R'$ with the form of Eq. (3.21). Equations (3.20) and (3.21) bear a remarkable similarity to Eqs. (2.12) and (2.19) if the $J$-coupling is ignored in the latter equations. However, we recall that the radial wave functions which are solutions to Eq. (3.20) are referred to the RA frame. The $S$-matrix derived from Eq. (3.21) cannot be directly used in the SF cross section equations.

The second step of our approximation is to ignore the difference between the RA and SF wave functions. We, therefore, solve Eq. (3.20) in the RA frame under the asymptotic boundary conditions of Eq. (3.21) and the condition that the wave function is regular at the origin. We then proceed directly to associate the RA $S$-matrix elements with the SF cross sections, without transforming between the RA and SF frames. Using the now familiar technique of constructing the total scattering wave function at large distances by use of the asymptotic behavior of the radial wave function and of comparing this asympt-
totic form against Eq. (2.20) in order to determine the cross sections from the scattering part, we can write the rotational excitation cross section in the JZCS approximation as

$$
\sigma(j\rightarrow j') = \sum_{J=0}^{\min(j,j')} \sum_{m_{j}\leq-\min(j,j')} \sigma^J(jm_j\rightarrow jm_j'),
$$

(3.22)

where

$$
\sigma^J(jm_j\rightarrow jm_j') = \frac{\pi}{k_{j}} \frac{(2J+1)}{(2J+1)} |T^J(j'm_j; jm_j)|^2,
$$

(3.23)

and

$$
T^J(j'm_j; jm_j) = \delta_{j',j} - S^J(j'm_j; jm_j).
$$

Since the potential matrix elements are symmetric with respect to a sign change on $m_j$, the cross section may be rewritten as

$$
\sigma(j\rightarrow j') = \sum_{J=0}^{\infty} \left[ \sigma^J(j0\rightarrow 0') + 2 \sum_{m_j=1}^{\min(j,j')} \sigma^J(jm_j\rightarrow jm_j') \right].
$$

(3.24)

We now review the procedure for calculating the rotational excitation cross sections by the JZCS method. We fix the value of $J$ and choose a finite basis

$$\{Y_{j m_j} | 0 \leq j \leq j_{\text{max}} \}$$

of $N$ functions. For a given value of $m_j$ between zero and $j_{\text{max}}$, we solve numerically a set of coupled state equations of the form (3.20), which are enumerated by the basis states whose $j$ values have projection $m_j$, and obtain the $S$-matrix elements.
\{S^J(j'm_j;j_{m_j}) \mid 0 \leq j \leq m_{\text{max}} \}$. Using these elements in Eq. (3.23), we find the partial cross sections $a^J(j_{m_j}-j'_{m_j})$. The total cross section is found by summing the partial cross sections over all allowed values of $m_j$. In a more systematic manner, the procedure may be described as follows: (1) for $m_j = 0$, we solve the $N$ coupled equations, which result from all states with $m_j = 0$, for the partial cross sections; (2) we increment $m_j$ by one and solve the resulting $N$-1 coupled equations, formed by all states with $m_j = 1$, for the partial cross sections (the state with $j = 0$ has no $m_j > 0$ projection and does not contribute to the coupled equations); (3) we continue to increment $m_j$ and reduce the number of coupled states until $m_j = m_{\text{max}}$, solving for the partial cross sections at each $m_j$ value; (4) the resulting partial $m_j$ cross sections are then summed to give the total cross section.

We conclude this chapter with a comparison of the CCCC and JZCS methods. Both methods employ the close coupling approximation and involve the solution of a finite set of coupled equations. The dimensionality of these coupled equations is determined by the number of channels, labeled by $(j\ell)$, in the CCCC method and the number of rotor states in the JZCS technique labeled by $j$. Since the number of rotor states is always less than or equal to the number of channels, the JZCS method provides a more rapid numerical procedure. To demonstrate this point
in more detail, we compare the two methods for the case of a fixed value of the total angular momentum \((J = 4)\) and a particular choice of basis \((0-2)\). Using Eq. (2.28), we find the following nine scattering channels, which enumerate the nine coupled channel equations:

\[
\begin{align*}
  j = 0 & \quad j = 1 & \quad j = 2 \\
  (0, 4) & \quad (13) & \quad (22) \\
  (14) & \quad (23) & \\
  (15) & \quad (24) & \\
  & \quad (25) & \\
  & \quad (26).
\end{align*}
\]

Noting that only states of like parity have non-zero coupling matrix elements, we separate these nine coupled equations into two distinct sets, one of five equations, representing channels of even parity, and one of four equations, representing channels of odd parity. We numerically solve each set separately for the S-matrix elements and rotational excitation cross sections \(\{\sigma_{\text{even}}^J(j\rightarrow j') | 0 \leq j, j' \leq 2\}\). The cross sections of even and odd parity are then added to determine the partial cross section \(\sigma_J^J(j\rightarrow j')\),

\[
\sigma_J^J(j\rightarrow j') = \sigma_{\text{even}}^J(j\rightarrow j') + \sigma_{\text{odd}}^J(j\rightarrow j').
\]

Applying the JZCS procedure to this example, we construct three sets of coupled equations, one for each allowed value of \(m_j (0,1,2)\). For \(m_j = 0\), there are three coupled
equations; for \( m_j = 1 \), two coupled equations; and for \( m_j = 2 \), one equation. We solve each set of equations separately for the \( S \)-matrices and rotational excitation cross sections \( \{ \sigma^J(jm_j-j'm_j,)|0 \leq j,j' \leq 2 \} \) and determine the partial rotational excitation cross section \( \sigma^J(j-j') \) from Eq. (3.24), with \( m_j \) ranging from zero to two. Since the coupled equations can be placed in matrix form (see Eq. (2.12')) the numerical operations involved in solving a set of coupled equations are those of matrix algebra. The relative time to perform a matrix operation (e.g., inversion) is proportional to at least the square of the dimension of the matrix. Thus if we assume that a representative operation for a 2 x 2 matrix takes one unit of computation time, then the time to evaluate the rotational excitation cross section by the CCCC methods is at least three times longer than that required in the JZCS method. The larger the size of the initial basis, the more efficient the JZCS method becomes in comparison to the CCCC procedure.

In the CCCC method, channels with different \( j \) values are coupled by several values of \( \lambda \). In our example, the (14) channel is coupled to the (22), (24), and (26) channels. In the JZCS method, the value of \( J \) plays the same role as \( \lambda \) with respect to the form of the radial functions \( u^J \) (compare Eq. (2.19) with Eq. (3.21)). We may therefore view the JZCS method as a coupled "channel" procedure in which the "channels" are denoted by \((jJ)\) with \( J \) fixed.
Unlike the CCCC method in which many different $\lambda$ values may couple, only "channels" with the same value of $J$ can couple in the JZCS procedure. Thus, for the case in which the coupling between channels with the same initial and final $\lambda$ values dominates, the JZCS method may provide an adequate approximation to the CCCC formulation. The analogy is rather crude since the corresponding coupling matrix elements have different values for each method. Another case in which the JZCS method may prove a good approximation to the CCCC procedure is that in which the coupling between two states in the JZCS method represents somehow the coupling between all channels of the CCCC method associated with these states. We shall investigate this point in more detail in Chapter 6. We are, however, led by these general arguments to believe that the JZCS method may give accurate cross sections in certain cases.
I'm very good at integral and differential calculus.

Pirates of Penzance

Chapter 4. Integral Equations Formulation

A. Introduction

In the last two chapters, we have formulated the atom-molecule collision problem in the close coupling approximation in terms of a set of coupled differential equations. Under certain conditions, a set of coupled differential equations can be transformed into a set of coupled integral equations whose solutions are identical with those of the differential equations. For a wide variety of problems of physical interest, including the JZCS and CCC collision problems, the conditions which guarantee the existence of this transformation are easily met. Although formally the two formulations are equivalent, some systems are better treated practically by one method or the other. In Section B, we transform the set of coupled differential equations (2.12') into a set of integral equations. From the solutions to this set of equations, we then extracted the scattering information. We confine our discussion to the laboratory frame although the formulation can be readily extended to other coordinate systems. Throughout this chapter, we follow rather closely the development of Sams and Kouri. Since we use the integral equations technique to determine the cross
sections for systems discussed in this paper, we describe the numerical procedure for solving the coupled integral equations in detail in Section C. We have selected the integral equations technique over the standard differential equations procedures (e.g., the Numerov algorithm\textsuperscript{2}, since the integral equations technique is computationally faster,\textsuperscript{3} since its solutions are numerically more stable, and since no special treatment is required for the closed channels. While we discuss the integral equations method for atom-molecule scattering, the method can be applied to a wide variety of coupled channel problems such as atom-atom, electron-atom, and electron-molecule collisions.\textsuperscript{4}
B. Coupled Integral Equations

In this section, we transform a set of coupled differential equations of the form of Eq. (2.12') into a set of coupled integral equations by a Green's function technique. We then determine the solutions of this set of equations and, from their asymptotic behavior, find the S matrix and cross sections. We seek to transform a set of coupled differential equations of the form

$$\frac{d^2}{dR^2} \mathbf{u}(R) = \mathbf{U}(R) + \mathbf{L}(R) - k^2,$$  \hspace{1cm} (4.1)

with the elements of the matrices are given by

$$\begin{align*}
(U(R))_{\gamma'' \gamma'} &= U_{\gamma'}^{\gamma''}(R) \\
(L(R))_{\gamma'' \gamma'} &= \lambda''(\lambda''+1)R^{-2} \delta_{\gamma'' \gamma'} \\
(k^2)_{\gamma'' \gamma'} &= k_{\alpha''}^2 \delta_{\gamma'' \gamma'} .
\end{align*}$$

The channel index $\gamma$ labels a set of quantum numbers ($\alpha'' \lambda''$) with $\alpha''$ representing the quantum number(s) of internal molecular motion (e.g., rotation) and with $\lambda''$ representing the orbital angular momentum quantum number of the incident particle; the potential matrix elements are given by $U_{\gamma'}^{\gamma''}(R),$ the centrifugal term by $\lambda''(\lambda''+1)R^{-2},$ and the wave number by $k_{\alpha''}$. The $N \times N$ solution matrix $\mathbf{u}(R)$ of the radial expansion functions of the total scattering wave function has the form
Each column vector represents one of the $N$ regular solutions of Eq. (4.1). The elements of each column vector satisfy the set of coupled equations

\[
\left[ \frac{d^2}{dr^2} - \frac{\ell''(\ell'' + 1)}{r^2} + k_{\alpha''}^2 \right] u_{\gamma''}^{\gamma'}(r) = \sum_{\gamma'} u_{\gamma'}^{\gamma'}(r) u_{\gamma'}^{\gamma'}(r).
\]  

(4.3)

The radial expansion functions satisfy the boundary conditions

\[
u_{\gamma''}^{\gamma'}(0) = 0
\]

\[
u_{\gamma''}^{\gamma'}(R) \to \begin{cases} 
\delta_{\gamma'' \gamma'} \sin[k_{\alpha''} R - \ell'' \pi/2] & \text{(open)} \\
\frac{k_{\alpha''}}{k_{\alpha''}} R^{\gamma''} \gamma) \cos[k_{\alpha''} R - \ell'' \pi/2] & \text{(closed)}.
\end{cases}
\]

(4.4)

In Eq. (4.4) we have used elements of the $R$ matrix instead of the $S$ matrix to describe the asymptotic behavior of the open channel functions. The two scattering matrices are related by

\[
S = (1 + iR)(1 - iR)^{-1}.
\]

Although the scattering formulations in terms of the $S$ and
and R matrices are equivalent, numerical solutions are more easily handled with the real-valued R matrix rather than the complex-valued S matrix. We leave the form of the wave number \( k_\alpha^2 \) and the potential matrix elements \( U_{\gamma'}^\gamma(R) \) completely general, except to demand that the potential matrix elements die faster than \( R^{-2} \) asymptotically. Thus, our formulation of the integral equations technique applies to any scattering system whose Schrödinger equation can be written in the form of Eq. (4.1) and whose solutions satisfy the boundary conditions of Eq. (4.4). This procedure therefore applies to both the CCCC and JZCS methods and to a wide variety of collision problems. We begin our derivation by considering the transformation of the coupled differential equations associated with a particular column vector solution of the form of Eq. (4.3). We then generalize our results to obtain the complete solution matrix of Eq. (4.2).

We recall that a general solution \( u_{\gamma'}^\gamma(R) \) to an inhomogeneous differential equation (4.3) can be constructed as the sum of the solution \( h_{\gamma'}^\gamma(R) \) of the homogeneous equation and a particular solution \( p_{\gamma'}^\gamma(R) \) of the inhomogeneous equation as

\[
    u_{\gamma'}^\gamma(R) = h_{\gamma'}^\gamma(R) + p_{\gamma'}^\gamma(R). 
\]

The homogeneous solution satisfies the equation
\[
\left[ \frac{d^2}{dR^2} - \frac{\ell''(\ell''+1)}{R^2} + k_{\alpha''}^2 \right] h_{\ell'\ell''}(R) = 0, \quad (4.6)
\]

which can be easily rearranged into a form of the Bessel equation with solution
\[
h_{\ell'\ell''}(R) = (k_{\alpha''}R) \ j_{\ell''}(k_{\alpha''}R). \quad (4.7)
\]

This solution is regular at the origin and is given in terms of the spherical Bessel function \( j_{\ell''}(k_{\alpha''}R) \) of order \( \ell''. \) We now determine a particular solution of Eq. (4.3) by employing a Green's function technique. According to this procedure,\(^7\) a particular solution \( y(R) \) to an inhomogeneous differential equation of the form
\[
\left( \frac{d^2}{dR^2} + q \right) y(R) = \hat{h}(R), \quad (4.6a)
\]

which satisfies the homogeneous boundary conditions
\[
\alpha y(R) + \beta \ \frac{dy}{dR} = 0
\]
on the domain \((a,b)\), is given by
\[
y(R) = \int_a^b G(R,R') \ \hat{h}(R') \ dR', \quad (4.6b)
\]

provided that a function \( G(R,R') \) can be found which satisfies the equation
\[
\left[ \frac{d^2}{dR^2} + q \right] G(R,R') = \delta(R-R') \quad (4.6c)
\]

Replacing \( q \) by \(-\ell''(\ell''+1)R^{-2} + k_{\alpha''}^2\), \( y(R) \) by \( u_{\ell'\ell''}(R) \), and
\( \mathcal{S}(R) \) by \( \sum \mathcal{U}_{\gamma'}^{\gamma''}(R) \mathcal{U}_{\gamma'}^{\gamma''}(R) \), in Eq. (4.6a), we can then write a particular solution of Eq. (4.3) as

\[
P_{\gamma'}^{\gamma''}(R) = \int_0^\infty G_{\gamma''}(R,R') \left[ \sum \mathcal{U}_{\gamma'}^{\gamma''}(R') \mathcal{U}_{\gamma'}^{\gamma''}(R') \right] \, dR' ,
\]

provided we can find a function \( G_{\gamma''}(R,R') \) such that

\[
\left[ \frac{d^2}{dR^2} - \frac{\ell''(\ell''+1)}{R^2} + \kappa_{\alpha''}^2 \right] G_{\gamma''}(R,R') = \delta(R-R') .
\]

We use the procedure outlined in Mathews and Walker\(^8\) to determine the form of the Green's function which satisfies Eq. (4.8). The resulting Green's function, for open channels, has the form

\[
G_{\gamma}(R,R') = \begin{cases} 
- (k_{\alpha RR'}) j_\ell(k_{\alpha R}) \eta_{\ell}(k_{\alpha R'}) & R < R' \\
- (k_{\alpha RR'}) j_\ell(k_{\alpha R'}) \eta_{\ell}(k_{\alpha R}) & R > R' 
\end{cases}
\]

and, for closed channels, has the form

\[
G_{\gamma}(R,R') = \begin{cases} 
- (k_{\alpha RR'}) h^{(1)}_{\ell}(i|k_{\alpha}|R) j_\ell(i|k_{\alpha}|R') & R < R' \\
- (k_{\alpha RR'}) h^{(1)}_{\ell}(i|k_{\alpha}|R') j_\ell(i|k_{\alpha}|R) & R > R' 
\end{cases}
\]

with \( \eta_{\ell}(kR) \) and \( h^{(1)}_{\ell}(kR) \) respectively the spherical Neumann function of order \( \ell \) and the spherical Hankel function of the first kind of order \( \ell \).\(^9\) Having thus established the form of the particular and homogeneous solutions, we can write the general solution of Eq. (4.3) as
\[ u_{\gamma}^{J}(R) = k_{\alpha}^{\gamma}R \delta_{\gamma}^{\gamma} \sum_{\gamma'} \int_{0}^{\infty} G_{\gamma'}^{\gamma}(R, R') u_{\gamma'}^{J}(R') u_{\gamma'}^{J}(R') dR' \quad (4.10) \]

A linear integral equation of this form is known as a Fredholm equation of the second kind. We can write Eq. (4.10) in a more convenient notation by defining three new quantities \( G_{\gamma}^{1}, G_{\gamma}^{2}, \) and \( G_{\gamma}^{12} \) as

\[
G_{\gamma}^{1}(R) = k_{\alpha}^{R} \begin{cases} j_{\ell}(k_{\alpha}R) & \text{(open)} \\ j_{\ell}(i|k_{\alpha}|R) & \text{(closed)} \end{cases} \quad (4.11)
\]

\[
G_{\gamma}^{2}(R) = R \begin{cases} \eta_{\ell}(k_{\alpha}R) & \text{(open)} \\ h_{\ell}^{(1)}(i|k_{\alpha}|R) & \text{(closed)} \end{cases}
\]

\[
G_{\gamma}^{21}(R, R') = G_{\gamma}^{2}(R_{\triangleleft}) G_{\gamma}^{1}(R_{\triangleright})
\]

\[
G_{\gamma}^{12}(R, R') = G_{\gamma}^{1}(R_{\triangleleft}) G_{\gamma}^{2}(R_{\triangleright}),
\]

with \( R_{\triangleleft} = \min(R, R') \) and \( R_{\triangleright} = \max(R, R') \), and by separating the integrals of Eq. (4.10) into two distinct intervals of \( R > R' \) and \( R < R' \) as

\[ u_{\gamma}^{J}(R) = G_{\gamma}^{1}(R) \delta_{\gamma}^{\gamma} \sum_{\gamma'} \int_{0}^{R} G_{\gamma}^{21}(R, R') u_{\gamma'}^{J}(R') u_{\gamma'}^{J}(R') dR' \]

\[ + \int_{R}^{\infty} G_{\gamma}^{12}(R, R') u_{\gamma'}^{J}(R') u_{\gamma'}^{J}(R') dR' \] \quad (4.12)
Since the derivation of Eq. (4.12) as valid for any one of the N solutions of Eq. (4.1), we can, by analogy with Eqs. (2.12) and (2.12'), write the complete matrix solution \( \mathbf{u}(R) \) as

\[
\mathbf{u}(R) = G^1(R) - \int_{0}^{R} G^{21}(R,R') \cdot \mathbf{u}(R') \cdot \mathbf{u}(R') dR' \\
- \int_{R}^{\infty} G^{12}(R,R') \cdot \mathbf{u}(R') \cdot \mathbf{u}(R') dR' ,
\]

(4.13)

with the matrix elements given by

\[
\begin{align*}
(G^1(R))_{\gamma' \gamma} &= G_{\gamma' \gamma}^1(R) \\
(G^{2}(R))_{\gamma' \gamma} &= G_{\gamma' \gamma}^2(R) \\
(G^{12}(R,R'))_{\gamma' \gamma} &= G_{\gamma' \gamma}^{12}(R,R') \delta_{\gamma' \gamma} ,
\end{align*}
\]

with a similar form for \( G^{21} \). The "dot" product is used to specifically denote matrix multiplication. We now write Eq. (4.13) in a slightly different form by expanding the second integral as the sum of an integral from zero to infinity and the negative of an integral from zero to \( R \) as

\[
\mathbf{u}(R) = G^1(R) - \int_{0}^{R} G^{21}(R,R') \cdot \mathbf{u}(R') \cdot \mathbf{u}(R') dR' \\
+ \int_{R}^{\infty} G^{12}(R,R') \cdot \mathbf{u}(R') \cdot \mathbf{u}(R') dR' \\
- \int_{0}^{\infty} G^{12}(R,R') \cdot \mathbf{u}(R') \cdot \mathbf{u}(R') dR' .
\]

(4.14)
Thus, we have accomplished the transformation of the set of coupled differential equations (4.1) into a set of coupled integral equations (4.14).

We now seek to find the solutions of this set of coupled integral equations. Proceeding as with the differential equations, we try a solution of the form

\[ u(R) = u^0(R) + u^1(R) , \quad (4.15) \]

such that \( u^0 \) satisfies a "homogeneous" equation

\[
u^0(R) = g^1(R) + \int_{\Omega} \left[ g^{12}(R, R') \cdot \mathbf{u}(R') \cdot u^0(R') \right. \\
- g^{21}(R, R') \cdot \mathbf{u}(R') \cdot u^0(R') \left. \right] dR' \quad (4.16)
\]

and \( u^1(R) \) satisfies the inhomogeneous equation

\[
u^1(R) = \int_{\Omega} \left[ g^{12}(R, R') - g^{21}(R, R') \right] \cdot \mathbf{u}(R') \cdot u^1(R') dR' \\
- \int_{\Omega} g^{12}(R, R') \cdot \mathbf{u}(R') \cdot [u^0(R') + u^1(R')] dR' . \quad (4.17)
\]

An integral equation like Eq. (4.16), whose upper limit of integration is the current value of variable, is known as a Volterra equation of the second kind.\(^6\) We define \( \zeta \) as

\[
\zeta = - \int_{\Omega} g^{2}(R', R') \cdot \mathbf{u}(R') \cdot [u^0(R') + u^1(R')] dR' \quad (4.18)
\]

and try a solution to the inhomogeneous equation (4.17) of the form

\[
u^1(R) = \zeta(R) \cdot \zeta(R) , \quad (4.19)
\]
where \( \zeta(R) \) is the solution matrix that we seek. Substituting Eq. (4.19) into Eq. (4.17), we find

\[
\begin{align*}
\{ \zeta(R) & - \left[ g^{1}(R) + \int_{0}^{R} g^{12} (R,R') \cdot u(R') \cdot \zeta(R')dR' \right. \\
& \quad \left. - \int_{0}^{R} g^{21} (R,R') \cdot u(R') \cdot \zeta(R')dR' \right]\} \cdot \mathcal{C} = 0
\end{align*}
\]

Since \( \mathcal{C} \) is not the zero matrix, the expression in brackets must equal zero. However, this expression has the same form as the homogeneous equation (4.16), whose solution we know to be \( u^{o}(R) \). Thus, we have

\[
\zeta(R) = u^{o}(R), \quad \text{and}
\]

the inhomogeneous equation has a solution

\[
u^{1}(R) = u^{o}(R) \cdot \mathcal{C}.
\]

The solution to Eq. (4.13) then becomes

\[
u(R) = u^{o}(R) \cdot (1 + \mathcal{C}) .
\]  \hspace{1cm} (4.20)

Substituting this expression into Eq. (4.18), we find that \( \mathcal{C} \) can be represented as

\[
\mathcal{C} = \left[ 1 + \int_{0}^{R} g^{2}(R') \cdot u(R') \cdot u^{o}(R')dR' \right]^{-1}
\]

\[
\cdot \left[ - \int_{0}^{R} g^{2}(R') \cdot u(R') \cdot u^{o}(R')dR' \right] .
\]  \hspace{1cm} (4.21)

Thus, the general solution to the set of coupled integral
equations (4.13) is obtained uniquely from the solution $u^0$ of the homogeneous Volterra equation (4.16), subject to the boundary conditions of Eq. (4.4).

Our next task is to determine the $R$ matrix from the asymptotic form of the radial solution functions $u^{JY}_n$. Before proceeding, we place Eq. (4.16) in yet another convenient form. We accomplish this by separating the Green's functions to give

$$u^0(R) = G^1(R) \cdot \left[ 1 + \int_0^R G^2(R') \cdot \overline{u}(R') \cdot u^0(R') \, dR' \right]$$

$$- G^2(R) \cdot \int_0^R G^1(R') \cdot \overline{u}(R') \cdot u^0(R') \, dR' .$$

(4.22)

Defining two new quantities $i_1$ and $i_2$ as

$$i_i(R) = \delta_{i2} + \int_0^R G^i(R') \cdot \overline{u}(R') \cdot u^0(R') \, dR' , \quad i = 1, 2,$$

(4.23)

we may write

$$u^0(R) = G^1(R) \cdot i^2(R) - G^2(R) \cdot i^1(R)$$

(4.24a)

$$z = [i^2(R)]^{-1} \cdot [1 - i^2(R)].$$

(4.24b)

We now take the asymptotic limit of Eq. (4.24) and compare the resulting expression with Eq. (4.4) in order to determine the form of the $R$ matrix. Since $G^1$ and $G^2$ are expressed in terms of Bessel functions, their asymptotic forms are known with

$$G^1(R) \to g(R) \quad \text{as} \quad R \to \infty,$$

$$G^2(R) \to -c(R) \cdot k^{-1},$$

(4.25)
with the elements of the matrices $\mathbf{S}$ and $\mathbf{C}(\mathbf{R})$ given by

$$
[s(\mathbf{R})]_{\gamma'' \gamma'} = \sin[k_{\alpha} R - \lambda'' \pi/2] \delta_{\gamma'' \gamma'}
$$

$$
[c(\mathbf{R})]_{\gamma'' \gamma'} = \cos[k_{\alpha} R - \lambda'' \pi/2] \delta_{\gamma'' \gamma'} .
$$

Using Eqs. (4.25) in Eq. (4.24) and defining

$$
\mathbf{I}^{1,2}(\mathbf{R}) \rightarrow \mathbf{I}^{1,2}(\infty),
$$

we can write the asymptotic limit of the radial function $u$ as

$$
u(\mathbf{R}) \rightarrow \frac{[s(\mathbf{R}) \cdot \mathbf{I}^{2}(\infty) + c(\mathbf{R}) \cdot k^{-1} \cdot \mathbf{I}^{1}(\infty)]}{[1 + [\mathbf{I}^{2}(\infty)]^{-1} \cdot (1-\mathbf{I}^{2}(\infty))]} \quad (4.27)
$$

Using the identity that $1 = [\mathbf{I}^{2}(\infty)]^{-1} \cdot \mathbf{I}^{2}(\infty)$, we find that

$$
[1 + [\mathbf{I}^{2}(\infty)]^{-1} \cdot (1-\mathbf{I}^{2}(\infty))] = [\mathbf{I}^{2}(\infty)]^{-1}.
$$

Thus, the asymptotic form of the solution matrix radial functions has the form

$$
u(\mathbf{R}) \rightarrow \frac{[s(\mathbf{R}) + c(\mathbf{R}) \cdot k^{-1} \cdot \mathbf{I}^{1}(\infty) \cdot [\mathbf{I}^{2}(\infty)]^{-1})}{[1 + [\mathbf{I}^{2}(\infty)]^{-1} \cdot (1-\mathbf{I}^{2}(\infty))]} \quad (4.28)
$$

The matrix form of Eq. (4.4) which describes the asymptotic limit of the open channel radial functions, is given by

$$
u(\mathbf{R}) \rightarrow \frac{[s(\mathbf{R}) + c(\mathbf{R}) \cdot (k^{-1} \cdot \mathbf{I}^{\frac{1}{2}} \cdot \mathbf{R} \cdot \mathbf{I}^{\frac{1}{2}})]}{[1 + [\mathbf{I}^{2}(\infty)]^{-1} \cdot (1-\mathbf{I}^{2}(\infty))]} \quad (4.29)
$$

Finally, comparing Eqs. (4.29) and (4.28), we find

$$
R = k^{-\frac{1}{2}} \cdot (\mathbf{I}^{1}(\infty) \cdot [\mathbf{I}^{2}(\infty)]^{-1} \cdot k^{\frac{1}{2}}) .
$$

(4.30)
The T matrix, in which form the cross sections are given, is related to the R matrix by

\[ T = 1 - (1 + iR) \cdot (1 - iR) \quad \] (4.31)

Representing the complex T matrix in terms of its real T_{real} and imaginary T_{imag} parts, we find, after some manipulation, that

\[ T_{\text{real}} = 2 \cdot R \cdot R \cdot [1 + R \cdot R]^{-1} \quad \text{and} \quad \] (4.32)

\[ T_{\text{imag}} = -2 \cdot R \cdot [1 + R \cdot R]^{-1} \cdot \]

The T matrix elements calculated in this manner are then used in expressions like Eqs. (2.27) and (3.23) to determine the cross sections. Again, we emphasize that the radial function y(R) and the R matrix, which contains the scattering information, are completely determined by the solution y^0 to the homogeneous Volterra equation (4.16) or (4.24). We now discuss numerical techniques for obtaining the solutions to this equation.
C. Numerical Solution of Coupled Integral Equations

In this section, we discuss the numerical solution of a set of coupled integral equations of the form

\[ u^O(R) = g^1(R) \cdot \left[ 1 + \int_0^R g^2(R') \cdot u(R') \cdot u^O(R') \, dR' \right] \]

\[ - g^2(R) \cdot \int_0^R g^1(R') \cdot u(R') \cdot u^O(R') \, dR' . \]  \hspace{1cm} (4.33)

One of the simplest and most accurate procedures for evaluating an integral is quadrature.\textsuperscript{11} In this technique, the integral is replaced by a sum over weighted values of the integrand which is evaluated at selected points within the domain. Thus, an integral of the form

\[ I = \int_a^b f(x) \, dx \]

can be approximated by the following N-point quadrature relation

\[ I = \sum_{i=1}^{N} f(x_i) w_i , \]

where the mesh of points of the variable x is given by \([x_i | i=1, N; a \leq x_i \leq b]\) and where \(w_i\) assigns a weight or relative importance to each mesh point. The mesh points and weighting factors are determined by the particular quadrature method. For example, in an N-point trapezoidal quadrature, the mesh consists of N equally spaced
points within the domain \( (x_1, x_N) \) such that

\[
x_{i+1} - x_i = (x_N - x_1)/N ,
\]

and the weighting factors are given by

\[
w_i = \begin{cases} 
\frac{1}{2} & i = 1 \text{ or } N \\
1 & i = 2, \ldots, N-1 
\end{cases}.
\]

Replacing the integrals in Eq. (4.33) by quadrature sums over a mesh \([R_i | i = 1, m]\), we determine the value of \( u^0 \) at \( R = R_m \) as

\[
u^0(R_m) = G^1(R_m) \cdot \left[ 1 + \sum_{i=1}^{m-1} G^2(R_i) \cdot u(R_i) \cdot u^0(R_i) w_i \right] 
- G^2(R_m) \cdot \left[ \sum_{i=1}^{m-1} G^1(R_i) \cdot u(R_i) \cdot u^0(R_i) w_i \right]. \tag{4.34}
\]

Initially the sums in Eq. (4.34) range from 1 to \( m \); however, for the case that \( i = m \), the two summations cancel each other. This result is quite significant. Since the sums in Eq. (4.34) extend only over points interior to the point at which the radial function is evaluated \( R_m \), Eq. (4.34) can be solved non-iteratively. In other words, the value of \( u \) at \( R_m \) can be found in terms of the values of \( u \) at points interior to \( R_m \) and values of the known functions \( G^1 \) and \( G^2 \) at \( R_m \). Using our previous definitions of the integrals, we may write the numerical solution to the coupled differential equations in the following compact form
\[ u^0(R_m) = G^1(R_m) \cdot I^2(R_{m-1}) - G^2(R_m) \cdot I^1(R_{m-1}) , \quad (4.35a) \]

where

\[ I^2(R_{m-1}) = \sum_{i=1}^{m-1} [G^2(R_i) \cdot U(R_i) \cdot U^0(R_i)] w_i \]

\[ I^2(R_{m-1}) = 1 + \sum_{i=1}^{m-1} [G^2(R_i) \cdot U(R_i) \cdot U^0(R_i)] w_i . \quad (4.35b) \]

We now develop a general procedure for systematically solving the set of coupled integral equations (4.35). Since \( G^1, G^2, \) and \( U \) are expressed in terms of known functions (e.g., \( G^1 \) in terms of the spherical bessel function, \( G^2 \) in terms of the spherical neumann or hankel functions, and \( U \) in terms of the radial potential expansion coefficients and vector-coupling coefficients), we can evaluate them explicitly at any point within the integration domain independent of the value of \( u^0 \). Using the boundary conditions on the radial wave function at the origin \( (R_o = 0) \) that

\[ u^0(R_o) = 0 , \]

and therefore

\[ I^1(R_o) = 0 \]

\[ I^2(R_o) = 1 \]

to start the solution, we calculate the radial function at a new point \( R_1 = R_o + \Delta \) by Eq. (4.35a) as

\[ u^0(R_1) = G^1(R_1) \cdot I^2(R_o) - G^2(R_1) \cdot I^1(R_o) \]

\[ = G^1(R_1) , \]
where $\Delta$ is the step size between successive mesh points. 

From the value of $u^0$ at $R_1$, we generate the integrals $I^1$ and $I^2$ at $R_1$ using Eq. (4.35b) as

\[
I^1(R_1) = G^1(R_1) \cdot U(R_1) \cdot u^0(R_1) w_1
\]

\[
I^2(R_1) = 1 + G^2(R_1) \cdot U(R_1) \cdot u^0(R_1) w_1.
\]

Then, using these integrals in Eq. (4.35a), we calculate the radial function at $R_2 = R_1 + \Delta$. The procedure is continued until a point $R_{\text{max}}$ in the asymptotic region is reached. At this point, we calculate the $R$ matrix by Eq. (4.30) and, from the $R$-matrix, the cross sections.

The numerical procedure can be summarized by the following simple algorithm:

\[
\begin{align*}
\text{m} & = 0 \\
u^0(R_0) & = 0 \\
I^1(R_0) & = 0 \\
I^2(R_0) & = 1 \\
R_{m+1} & = R_m + \Delta \\
u^0(R_{m+1}) & = G^1(R_{m+1}) \cdot I^2(R_m) - G^2(R_{m+1}) \cdot I^1(R_m) \\
I^i(R_{m+1}) & = G^i(R_{m+1}) \cdot U(R_{m+1}) \cdot u^0(R_{m+1}) w_{m+1} \\
& + I^i(R_m) \quad i = 1 \text{ or } 2 \\
R_{m+1} & : R_{\text{max}} \\
\text{Calculate } R \text{ and } o^J
\end{align*}
\]
Thus, from the initial boundary conditions, we start the integration and generate the radial scattering solution $\mathbf{u}^0$ and cross sections at any exterior point by the algorithm of Eq. (4.36).

The solutions of the coupled integral equations and consequently the cross sections are sensitive to the various parameters of the numerical algorithm, in particular step size $\Delta$ and matching radius $R_{\text{max}}$. These parameters are systematically varied until a region of convergence is found for which the solution to the integral equations and the scattering matrix $R$ are insensitive to changes in $\Delta$ and $R_{\text{max}}$. The standard procedure is to choose a step size $\Delta_0$ and matching radius $R^0_{\text{max}}$ and solve the integral equations for the $R$-matrix, $R^0$. The step size is then halved, $\Delta_1$, and the matching radius increased, $R^1_{\text{max}}$, and the calculation repeated to obtain a new $R$-matrix $R_1$. If corresponding elements of the $R$-matrices ($R^0$ and $R^1$) have converged to within a given tolerance (usually better than three significant figures), the $R$-matrix, $R^1$, is used to evaluate the cross sections. On the other hand, if the tolerance condition is not met, the procedure continues until successive $R$-matrices agree to within the given tolerance ($R^i \approx R^{i+1}$). We should note that the longer the range of the potential matrix elements, the larger the value of $R_{\text{max}}$. For example, an $R_{\text{max}}$ between 20-30 $a_0$ is generally sufficient for poten-
tials decaying as $R^{-6}$, while an $R_{\text{max}} \geq 100 \ a_0$ is needed to guarantee the convergence of the R-matrix for potentials decaying as $R^{-3}$. The procedures outlined are meant to serve as general guidelines since they have been tested only on the systems presented in Chapter 6. For any other system, the sensitivity of the solution and R-matrix to changes in the step size and matching radius should be thoroughly investigated in order to find a range of values that guarantee convergence.

The symmetry and unitarity of the S-matrix provide indirect tests of the performance of the numerical algorithm. The agreement between symmetric elements of the S-matrix gives some indication of the stability of the numerical solution. Poor S matrix symmetry usually implies either a step size too large to properly follow the oscillatory wave function or a loss of the linear independence of the solutions. The former problem can be easily rectified by decreasing the step size. For the integral equations associated with systems described in this paper, we have found that at least twenty (20) integration points are needed within a de Broglie wavelength ($\lambda_\alpha = 1/k_\alpha$) in order to guarantee an accurate numerical wave function. This rule is empirical and should be thoroughly tested for any new system. Formally, the solutions to the integral equations are linearly independent, and starting values of the wave function can be chosen to guarantee the initial independence of the numerical solutions. However, at larger distances the solutions may become linearly dependent
due to errors arising from the limitations of the numerical techniques or devices. In Appendix C, we outline a procedure which can guarantee a linearly independent solution at any point within the integration domain. The use of such a method is strongly advised in cases of barrier penetration.

We recall that the solutions to Eqs. (4.35) are obtained for a particular value of $J$ and choice of basis. From this solution we can calculate the partial rotational excitation cross sections $\sigma^J(j\rightarrow j')$ for all energetically allowed transitions $(j\rightarrow j')$. We should then test the convergence of these cross sections with respect to the size of the basis by the method outlined in Chapter 2. For each new choice of basis, we must solve a new set of coupled equations of the form of Eqs. (4.35). Finally, after obtaining a converged set of cross sections at a particular $J$, we repeat the procedure at other $J$ values in order to find the partial cross sections that contribute to the total rotational excitation cross sections $\sigma(j\rightarrow j')$. Usually, the basis which guarantees convergence of the cross sections at one $J$ value will also guarantee convergence at all other $J$ values that have non-negligible contributions to the total cross section. By the above procedure, we have generated total cross sections at one energy. We should repeat the calculations at various energies to obtain behavior of the cross sections as a
function of energy, always being careful to check convergence of the solution and cross sections.

In this chapter, we have transformed the collision formalism from a set of coupled differential equations to a set of coupled integral equations of the Volterra form. We have found the solutions to this set of integral equations, and derived an algorithm which obtains these solutions numerically. By comparing the asymptotic behavior of the solutions with the form of Eq. (4.3), we have found a relationship between the $R$ matrix and the integrals evaluated in the numerical solution. Finally, we have discussed various practical procedures for simplifying and stabilizing the numerical solutions.
On fire that glows with heat intense
We turn the hose of common sense
And out it goes at a small expense! Iolanthe

Chapter 5. Atom-Molecule Interaction Potentials

A. Introduction

The only quantity that remains to be specified in the scattering equations is the potential energy $V$ for the interaction between the atom and molecule. In all derivations to this point we have implicitly made the Born-Oppenheimer approximation,¹ which allows the nuclear and electronic motion of the atom-molecule system to be separated. In this approximation, the electronic energy $E_e$ and the repulsive Coulomb interaction between the atomic and molecular nuclei $V_{am}$ act as an effective potential energy for the motion of the atomic and molecular nuclei. Since we are only interested in rotational excitations of the molecule, the molecular nuclei are assumed to be fixed throughout the collision at their equilibrium internuclear distance. Under this assumption, the potential energy that arises from the Coulomb interaction between the nuclei of the molecule is constant, and we define the zero of energy so as to remove this term from the total system hamiltonian. The electronic energy $E_e$ is the expectation value of the electronic hamiltonian,

$$E_e = \langle \psi_e | H_e | \psi_e \rangle,$$
where $\psi_e$ is the electronic wave function. The electronic hamiltonian has the form

$$H_e = T_e + U_{ee} + U_{en},$$

(5.1)

where $T_e$ is the kinetic energy operator for the electrons, $U_{ee}$ represents the total electron-electron Coulomb interaction, and $U_{en}$ represents the total electron-nucleus Coulomb interaction. The Schrödinger equation for the nuclear motion becomes

$$H_{\text{nuc}} \psi_n = (T_n + V_{am} + E_e) \psi_n = E \psi_n,$$

(5.1')

where $T_{\text{nuc}}$ is the nuclear kinetic energy, $\psi_n$ is the nuclear wave function, and $E$ is the total energy of the system. We can thus identify the term $(V_{am} + E_e)$ of Eq. (5.1') with the total interaction potential energy $V$ and $H_{\text{nuc}}$ with the hamiltonian of Eq. (2.1). There are a plethora of methods for calculating the electronic energy and wave function of an atom-molecule system, the most common being Hartree-Fock and configuration interaction.² Since these methods are computationally very time consuming and since complete ab initio surfaces for the hydride systems were unavailable, we have developed a technique for rapidly computing an approximate potential energy surface for the interaction between an atom and a molecule. We separate the potential energy into long- and short-range regions and treat each region under a separate set of approximations. There is no absolute demarcation between
the short- and long-range regions. The long-range region is usually characterized by the lack of overlap between the electron clouds of the atom and molecule and by the vanishing of exchange effects. These two criteria are met at large internuclear separations. On the other hand, the short-range region is characterized by the opposite conditions: cloud overlap and non-negligible exchange effects. For a repulsive potential with a small attractive well, the short-range region is generally considered to be the region interior to the position $R_m$ of the well minimum and the long-range region as that exterior to $R_m$. In Section B, we derive a method for generating the interaction potential energy in the short-range region by averaging the effective potential energy between an electron and an atom over the charge distribution of the molecular electrons. The resulting potential energy surface includes to some degree of approximation Coulomb, kinetic, and exchange effects. We derive the method in general in the first part of Section B. In the second part of Section B, we illustrate the technique by applying it to interactions between helium atoms and molecules. In Section C, we discuss the long-range form of the interaction potential energy. We use a generalization of the London formula to describe the long-range interaction. The total interaction potential energy surface is constructed by smoothly merging the long- and short-range
potential energy surfaces. Finally, in Section D, we present the results of calculations of model potential energy surfaces for interactions between helium and the diatomic hydrides, hydrogen fluoride and hydrogen chloride.

We restrict our discussion and derivations to a number of conditions. First, we consider only interactions between an atom and a diatomic molecule, although the formalism can be extended to nonlinear polyatomic molecules. Second, since we treat only rotational excitation, we consider the diatomic molecule to be a rigid rotor with the molecular nuclei fixed at their equilibrium separation. Third, we perform the calculation of the potential energy in the body frame (see Chap. 2). In this frame, the origin of the coordinate system is at the center-of-mass of the molecule and the z-axis lies along the molecular symmetry axis. Since the interaction potential energy depends only on the relative separation and orientation of the atom with respect to the molecular symmetry axis, the position of the atom, given by the coordinates \((R, \Theta, \phi)\), and vector \(R\), uniquely determines the interaction potential energy in the body frame (see Fig. 4). The interaction potential energy in another reference frame is found by applying a similarity transformation to the body-frame potential energy. We have already implicitly made this transformation in the SF frame of Chap. 2 and the RA frame of Chap. 3. Thus, the radial expansion coefficients of the
body-frame interaction potential energy surface can be used directly in Eqs. (2.32) and (3.20). Fourth, at large intermolecular separations the interaction between the atom and molecule vanishes and the electronic energy equals the sum of the internal energies of the free atom and molecule. We shall use the convention that the interaction potential energy goes to zero as the distance \( R \) between the atom and molecule becomes infinite. We, thus, redefine the interaction potential energy as

\[
V(R) = \left[ E_e(R) - E_e(\infty) \right] + V_{am}(R)
\]

such that

\[
V(R) \to 0 \quad \text{as} \quad R \to \infty.
\]

For future discussions, we consider the terms in brackets to be the "adjusted electronic energy." Fifth, we consider only closed-shell, ground-state systems. The short-range interaction potential energy is generally repulsive for such systems since, according to the Pauli principle, the spin-paired electrons of the closed-shell molecule have the smallest probability of being found in the vicinity of the spin-paired electrons of the closed-shell atom.\(^3\)

The repulsion prevents the electron clouds from greatly overlapping and consequently being distorted. With these conditions in mind, we now proceed to derive an approximate form for the potential energy surface \( V(R) \) for interactions between an atom and molecule.
B. Short-Range Interaction Potential

1) General Form

The electronic energy $E_e$ is a complicated expression which includes electrostatic, kinetic energy, exchange, and correlation effects.\(^2\) The electrostatic interactions, the kinetic energy, and the correlation effects, which arise from the instantaneous interactions between the electrons, have classical counterparts. On the other hand, exchange, which arises from the indistinguishability of the electrons, is purely a quantum mechanical effect. In deriving the form of the short-range interaction potential energy $V(E_e - E_e(\infty) + V_{am})$ we make the following assumptions: 1) that the interaction potential energy can be separated explicitly into terms representing Coulomb $V_C$, kinetic energy $V_{KE}$, exchange $V_{ex}$, and correlation $V_{corr}$ effects as

$$V = V_C + V_{KE} + V_{ex} + V_{corr} \quad (5.2)$$

2) that the coulomb interaction potential energy $V_C$ can be further divided into interactions of i) atomic electrons with molecular nuclei $V_{em}$, ii) molecular electrons with the atomic nucleus $V_{ea}$, iii) atomic electrons with molecular electrons $V_{ee}$, and iv) molecular nuclei with the atomic nucleus $V_{am}$ as
\[ V_c = V_{em} + V_{ea} + V_{ee} + V_{am}, \]  

(5.3)

3) that the electron clouds of the atom and molecule are not distorted by the interaction. In regard to the first assumption it should be pointed out that it has not been possible to find a one-to-one correspondence between each term in Eq. (5.2) and a particular part of the Hartree-Fock or configuration interaction electronic energy. However, a procedure by which the total interaction potential energy is built up from local potentials that approximate the major contributions to the electronic energy has been successfully used in recent statistical methods for calculating potential energy surfaces. For example, in the Gordon-Kim method, the Coulomb terms are treated by perturbation theory and the kinetic energy, exchange, and correlation terms are approximated by those of a free electron gas. The second assumption is based on the additive nature of the Coulomb potential energy. Since the electrostatic interactions themselves can be grouped according to the interacting species, it is reasonable to believe that their expectation values can be treated likewise. The third assumption is justified since we calculate the potential energy in the region of small overlap between the electron clouds of the atom and molecule. This assumption also allows us to use the unperturbed atomic and molecular charge densities.
In Eq. (5.3) the simplest term to evaluate is the interaction potential energy between the atomic and molecular nuclei. The term is purely electrostatic and has the form

$$V_{am}(R) = \frac{Z_a Z_m^i}{|R - R_m^i|}, \quad (5.4)$$

where $Z_a$ and $Z_m^i$ are the charge on the atomic nucleus and $i^{th}$ molecular nucleus respectively, and $R_m^i$ and $R$ are the vector positions with respect to the molecular center-of-mass (CM) of the $i^{th}$ molecular nucleus and the atomic nucleus respectively.

We group the electronic terms associated with the electrostatic electron-electron interaction, $V_{ee}$ and (molecular electrons) - (atomic nucleus) interaction $V_{ea}$, the kinetic energy $V_{KE'}$, and exchange $V_{ex}$ into one term $V'$ that can be expressed in terms of a one-electron effective potential energy. By the method of pseudopotentials, we can construct an effective potential energy, $V_{eff'}$, which approximately describes the interaction between a single electron and an atom. This effective potential energy includes not only the electrostatic interactions but also exchange and kinetic energy effects. In Appendix D, we present a short discussion of the methods by which pseudopotentials can be used to construct effective electron-atom potential energy curves. We now use this one-electron potential energy to generate the total potential energy $V'$.
for interactions between all molecular electrons and an atom. We first assume that the molecular electrons are fixed in space. The interaction potential energy $V'(\mathbf{R}, \mathbf{r}_1)$ is just the sum of the effective potential energies for each of the $N$ molecular electrons

$$V'(\mathbf{R}, \mathbf{r}_1) = \sum_{i=1}^{N} V_{\text{eff}}(\mathbf{r}_i),$$  \hspace{1cm} (5.5)$$

where $\mathbf{s}_i = \mathbf{R} - \mathbf{r}_i$ and $\mathbf{r}_i$ is the position vector of the $i^{\text{th}}$ molecular electron from the molecular CM. The molecular electrons, however, are not fixed but have a finite probability, determined by the ground state wave function, of being at any point in space. We thus replace the sum in Eq. (5.5) with an integral over all space and weight the effective potential energy by the total probability density $\rho(\mathbf{r})$ of the molecular electrons in order to determine the interaction potential energy between a distribution of molecular electrons and the atom. We can thus write

$$V'(\mathbf{R}) = \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{eff}}(\mathbf{r}),$$  \hspace{1cm} (5.6)$$

where the geometry is given in Fig. 4 and $s^2 = r^2 + R^2 - 2Rr \cos \vartheta$. Thus, the interaction potential energy given by Eq. (5.6) is just the expectation value of Eq. (5.5) with respect to the ground state electronic wave function $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ as

$$V'(\mathbf{R}) = \langle \psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) | V'(\mathbf{R}, \mathbf{r}_1) | \psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \rangle.$$
Fig. 4 Geometry for the interaction of a molecular electron with an atom. All parameters refer to the body frame with the molecular figure axis lying along $\hat{z}$.
In Appendix E, we discuss the form of the probability density in more detail. The potential energy surface $V'(\mathbf{R})$ describes the interaction between all molecular electrons and the atom and includes electrostatic (Coulomb), kinetic energy, and exchange effects. We therefore make the identification with Eq. (5.2) that

$$V'(\mathbf{R}) = V_{ee} + V_{ea} + V_{ex} + V_{KE}. $$

The technique of calculating an interaction potential energy surface for a distribution of electrons about a charged core and an atom by averaging the effective interaction potential energy for a single electron and the atom over the probability density of all the electrons is similar to that used by Hickman and Lane\textsuperscript{7} to generate atom-atom potentials.

Since the interaction potential energy for an atom and molecule in a $\Sigma$ state is axially symmetric, we can now expand the interaction potential energy $V'$ in a Legendre series

$$V'(R, \Theta) = \sum_{\lambda} v_{\lambda}'(R) P_{\lambda}(\cos \Theta) \quad (5.7)$$

with

$$v_{\lambda}'(R) = \frac{2\lambda+1}{2} \int_0^\pi V'(R, \Theta) P_{\lambda}(\cos \Theta) \sin \Theta \, d\Theta \quad (5.7')$$

and attempt to find a closed form for the radial expansion coefficients $v_{\lambda}'$, which appear in the scattering equations.
The one-electron probability density $\rho(\mathbf{r})$ for the molecular electrons is obtained from an electronic structure calculation. The results can either be found in the literature\textsuperscript{2h} or calculated using a packaged computer code. Since the form of $\rho(\mathbf{r})$ is known, we can also expand the probability density in a Legendre series as\textsuperscript{8}

$$\rho(r,\theta) = \sum_{\lambda} a_\lambda(r) P_\lambda(\cos\theta), \quad (5.8)$$

with

$$a_\lambda(r) = \frac{2\lambda+1}{2} \int_0^\pi \rho(r,\theta) P_\lambda(\cos\theta) \sin\theta \, d\theta, \quad (5.8')$$

where $r$ is the distance of the molecular electron from the molecular CM and $\theta$ is the orientation of the electron with respect to the molecular symmetry axis [$\mathbf{r} = (r, \theta)$]. We also know the form of the one-electron effective potential energy $V_{\text{eff}}$ and thus can expand $V_{\text{eff}}$ in a Legendre series as

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{eff}}(R, r, \Psi) = \sum_{\lambda} \tilde{V}_\lambda(R, r) P_\lambda(\cos\Psi), \quad (5.9)$$

with

$$\tilde{V}_\lambda(R, r) = \frac{2\lambda+1}{2} \int_0^\pi V_{\text{eff}}(R, r, \Psi) P_\lambda(\cos\Psi) \sin\Psi \, d\Psi. \quad (5.9')$$

Substituting Eqs. (5.8) and (5.9) into Eq. (5.6) and the resulting expression into Eq. (5.7'), using the addition theorem of spherical harmonics,
\[ P_{\lambda}(\cos \psi) = \frac{4\pi}{2\lambda + 1} \sum_{m} Y_{m}(\theta, \phi) Y_{\lambda, m}(\theta, \phi), \quad (5.10) \]

and the orthogonality of the spherical harmonics, we find that

\[ v_{\lambda}^{\prime}(R) = \frac{4\pi}{2\lambda + 1} \int_{0}^{\infty} a_{\lambda}(r) \bar{v}_{\lambda}(r, R) \, r^2 dr. \quad (5.11) \]

Thus, we have expressed the radial expansion coefficient \( v_{\lambda}^{\prime} \) in terms of the radial expansion coefficients of the molecular electron probability density and the effective one electron potential energy.

The interaction \( V_{em} \) between the atomic electrons and molecular nuclei and the correlation terms remain to be evaluated. We evaluate the term \( V_{em} \) by a perturbation technique similar to that used by Gordon and Kim.\(^5\) The interaction of the atomic electrons with the molecular nuclei is given by

\[ V_{em}(R) = \sum_{i} \int d \mathbf{r}_{a} \, \rho_{i}(\mathbf{r}_{a}) \, Z_{i}^{\prime} \left[ |R - R_{m} + \mathbf{r}_{a}| \right]^{-1}, \quad (5.12) \]

where \( \rho_{i}(\mathbf{r}_{a}) \) is the probability density of the atomic electrons at position \( \mathbf{r}_{a} \) from the atomic center, and the sum runs over all nuclei of the molecule. This expression is similar in form to Eq. (5.6) in that the interaction of all atomic electrons with a molecular nucleus is given by the electrostatic interaction of a single atomic electron with the molecular nucleus averaged over the probability density of the atomic electrons. In other words,
both forms generate a many-electron interaction potential energy from an effective one-electron potential energy and the probability density of all the electrons. Since we are in the region of small electronic overlap, the correlation term $V_{\text{corr}}$, which arises from the instantaneous electron-electron interactions, should be small compared to $V'$. In fact, it can be shown that in this region the correlation term is given approximately by the long-range dispersion potential energy (see Section C). Thus, we shall consider the correlation term to be the long-range potential energy for large internuclear separations and to be approximated, in part, at intermediate intermolecular distances by the potential energy which results from smoothly merging the long- and short-range potential energies. The total atom-molecule potential energy in the short-range region is thus given by

$$V(R) = V'(R) + V_{\text{am}}(R) + V_{\text{em}}(R). \quad (5.13)$$

The radial Legendre expansion coefficients $v_\lambda(R)$ for the total interaction potential energy $V(R)$ can be found by adding the radial expansion coefficients of each term in Eq. (5.13) The radial expansion coefficients $v_\lambda(R)$ are then used in the scattering equations (2.12) to determine cross sections.
2) He-Diatomc Molecule

The potential energy surface for interactions between a tightly bound, small atom and a molecule is dominated by the term $V'(R)$ of Eq. (5.13). In the limit that the atomic charge distribution can be considered concentrated at the atomic center, the attractive interaction $V_{em}$ of the atomic electrons with the molecular nuclei is exactly balanced by the repulsive interaction $V_{am}$ between the atomic nucleus and molecular nuclei. For the case in which the atomic charge density has a finite, but small extent, the terms $V_{em}$ and $V_{am}'$, although large in magnitude, approximately cancel and leave the term $V'(R)$ as the dominant contribution to the potential energy. We thus assume that the short-range potential energy surface for interactions between a small atom and molecule is given by

$$V(R) = V'(R),$$

with the short-range radial expansion coefficients given by Eq. (5.11) and labeled as $\nu_{\lambda}^{SR}(R)$. We thus seek expressions for the radial expansion coefficients of the molecular probability density $\rho$ and the effective one-electron potential $V_{\text{eff}}$.

From an electronic structure calculation, such as Hartree-Fock or configuration interaction, for the diatomic molecule, we obtain a molecular wave function. Since the
wave function for a closed shell system is not particularly sensitive to correlation effects; we can use the Hartree-Fock wave function and the rather simple expression for the one-electron probability density \( \rho(\mathbf{r}) \) given by Eq. (E8) in terms of the spatial orbitals. Knowing the functional form of \( \rho \), we calculate the radial expansion coefficients \( a_\lambda \) of the probability density from Eq. (5.8') by a numerical integration technique. We have found that a 32-point Gauss-Legendre quadrature is sufficient to evaluate the integrals for the diatomic hydrides. Since the \( a_\lambda \) coefficients are rather expensive to calculate, we evaluate them over a mesh of widely spaced radial points (e.g., \( r_{i+1} - r_i = 0.25 \, a_0 \)). We then fit these points with a cubic spline technique and evaluate all other points from the resulting spline fit. The cubic spline fit should be applied with care. Regions in which the \( a_\lambda \) coefficients vary rapidly should be fit with more points than those regions in which the coefficients are slowly varying. The resulting spline fit should be tested for accuracy and smoothness over a mesh much smaller than the one used to determine the fit.

The radial expansion coefficients for the effective potential energy are determined from Eq. (5.7'). Hickman has shown that the effective potential energy \( V_{\text{eff}}(S) \) which represents the interaction of a single electron with a tightly bound atom, in particular helium, can be accurately fit to the form
\[ V_{\text{eff}}(s) = -\frac{2}{s} \exp(-as) + b \exp(-s^2/2\sigma^2) \] (5.14)

where \( a \) and \( \sigma \) are parameters determined by the fit. In terms of this functional form, the radial expansion coefficients \( \tilde{v}_\lambda(r) \) have exact analytical expressions. In Appendix F, we discuss the method for calculating the analytical expressions for the \( \tilde{v}_\lambda \) coefficients. Having determined this analytic form for \( \tilde{v}_\lambda \) and having determined a numerical fit to the \( a_\lambda \), we obtain the radial expansion coefficients of the atom-diatom potential energy surface by numerically integrating Eq. (5.11). We have found that using a Gauss-Legendre quadrature\(^9\) in the inner region \( r < R+2 \) and a Gauss-Laquerre quadrature in the outer regions \( r > R+2 \) lead to a rapid, accurate integration of Eq. (5.11). In this manner we generate the interaction potential energy surface for a small, tightly bound atom and a diatomic molecule from the unperturbed molecular electron probability density and an analytical fit to the one-electron effective potential.
C. Long-Range Interaction Potential

We now seek a form for the interaction potential energy in the region in which the overlap of the electron clouds of the atom and molecule and the exchange effects are small. In the limit of infinite atom-molecule separation, the electronic hamiltonian reduces to the sum of the free atom and free molecule hamiltonians as

\[ H_e \rightarrow H_a + H_m. \]  \hspace{1cm} (5.15)

The hamiltonians \( H_a \) and \( H_m \) each have a discrete spectrum of bound states associated with the sets of wave functions \( \{ \psi_a^i \} \) and \( \{ \psi_m^j \} \) such that

\[ H_a \psi_a^i = E_a^i \psi_a^i, \quad i = 0,1,2,\ldots \] \hspace{1cm} (5.16)

\[ H_m \psi_m^j = E_m^j \psi_m^j, \quad j = 0,1,2,\ldots \]

where \( E_a^i \) and \( E_m^j \) are the eigenvalues of the atomic and molecular hamiltonians respectively. The hamiltonians \( H_a \) and \( H_m \) depend only on the internal coordinates of their respective systems and describe an atom (\( H_a \)) and a molecule (\( H_m \)) in a space free of all external forces. In this limit the electronic energy of a ground-state atom (\( \psi_a^o \)) and a ground-state molecule (\( \psi_m^o \)) becomes simply

\[ E_e \rightarrow E_a^o + E_m^o. \]  \hspace{1cm} (5.17)
At large, but finite atom-molecule separations, we must add to the electronic hamiltonian of Eq. (5.15) the electrostatic potential energy $U$ between all charged particles of the atom-molecule system

$$U = \sum_{i_a^j} q_i^{a^j} q_j^{a^j} \frac{R_i^{-1}}{r_{i_a^j}},$$

where $q_i^{a^j}$ and $q_j^{a^j}$ are the charge on the $i^{th}$ particle of the atom and the $j^{th}$ particle of the molecule respectively, $R_i^{-1}$ is the distance between the $i^{th}$ atomic and $j^{th}$ molecular particle, and the sum runs over all electrons and nuclei of the atom and molecule. We have thus included the term $V_{am}$ in the definition of $U$. In the limit of large atom-molecule separation the electronic hamiltonian is still dominated by the separated atom and molecule energies. We can thus treat the potential energy $U$ as a perturbation and apply perturbation theory to calculate the electronic energy and therefore the interaction potential energy. Using the adjusted electronic energy and recalling that the nuclear repulsion term $V_{am}$ has been included in $U$, we can write the interaction potential energy $V$ for an atom and molecule to second order in the perturbation as:

$$V = \langle \psi_a^o \psi_m^o | U | \psi_a^o \psi_m^o \rangle - \sum_{i,j} \frac{|\langle \psi_a^o \psi_m^o | U | \psi_a^i \psi_m^j \rangle|^2}{(E_a^i - E_a^o) + (E_m^j - E_m^o)},$$

where $\psi_a^i$ ($\psi_m^j$) is an excited state of the unperturbed atomic (molecular) hamiltonian. The leading term of Eq. (5.18)
gives the first order correction to the unperturbed energy and is designated the electrostatic term $V_{\text{elect}}$. The second term in Eq. (5.18), which gives the second-order correction to the unperturbed energy, contains both induction $V_{\text{ind}}$ and dispersion $V_{\text{disp}}$ contributions. These terms will be explained in more detail in the subsequent discussion.

We now place the potential energy $U$ in a form which depends explicitly on the separation and orientation of the atom and molecule. We accomplish this by expanding $U$ in a multipole series as

$$U = T_2 q_a q_m + T_{2\alpha}(q_a \mu_m - q_m \mu_a)$$

$$+ T_{2\alpha\beta}(\frac{1}{3} q_a \theta_m \alpha\beta + \frac{1}{3} q_m \theta_a \alpha\beta - \mu_a \mu_m \alpha\beta)$$

$$+ T_{2\alpha\beta\gamma}(\frac{1}{3} \mu_m \alpha\beta \gamma - \frac{1}{3} \mu_a \theta_m \alpha\beta \gamma) + ...$$

$$(5.19a)$$

where, if $\mathbf{R}$ is the vector connecting the center of the atom to the center-of-mass of the molecule then

$$T_2 = R^{-1}$$

$$T_{2\alpha} = \nabla_\alpha R^{-1} = -R_\alpha R^{-3}$$

$$T_{2\alpha\beta} = \nabla_\alpha \nabla_\beta R^{-1} = (3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}) R^{-5}$$

$$T_{2\alpha\beta...\gamma} = \nabla_\alpha \nabla_\beta... \nabla_\gamma R^{-1}$$

$$(5.19b)$$
with \( R_\alpha \) the components of \( R \). We have used the convention that repeated indices are summed as

\[
T_{2\alpha}^{\mu\mu\alpha} = -\frac{1}{R^3} \left( \mu_{mX} R_x + \mu_{mY} R_y + \mu_{mZ} R_z \right).
\]

The permanent charge, dipole, and quadrupole moments of the atomic (molecular) change distributions are given by \( q_a(q_m) \), \( \mu_a(\mu_m) \), and \( \theta_a(\theta_m) \). The first term in Eq. (5.19a) represents the interaction of the charge on the atom with the charge on the molecule or the monopole-monopole interaction. The second term represents the monopole-dipole interaction, and the third term gives the monopole-quadrupole and dipole-dipole interactions. Since we consider collisions only between neutral atoms and molecules, all terms in Eq. (5.19a) which depend on the permanent charge on the atom or molecule vanish. For neutral systems, we can then write

\[
U = -T_{2\alpha\beta}^{\mu\alpha\mu\beta}
+ T_{2\alpha\beta\gamma} \left( \frac{1}{3} \mu_{m\alpha} \theta_{a\beta\gamma} - \frac{1}{3} \mu_{a\alpha} \theta_{m\beta\gamma} \right) + \ldots \tag{5.20}
\]

Substituting Eq. (5.20) into the first-order perturbation term of Eq. (5.18), we find the leading term of the electrostatic interaction potential energy becomes

\[
V_{\text{elect}} = T_{2\alpha\beta}^{\mu^O\alpha\mu^O\beta} + \ldots, \tag{5.21}
\]

where \( \mu^O_{m\alpha} \) is the permanent dipole moment of the molecule in its ground state, \( \psi^O_m \); that is,
\[ \mu_{m\alpha}^o = \langle \psi_m^o | \mu_{m\alpha} | \psi_m^o \rangle, \]  

with a similar definition holding for the atom. The electrostatic term represents the interaction between the permanent multipole moments of the atom and molecule. Since we consider only collisions involving closed shell, ground state, spherical atoms which have no permanent moments, the electrostatic contribution vanishes.

The electrostatic potential energy \( V_{\text{elect}} \) has a direct classical correspondence; however, the second-order perturbation term of Eq. (5.18) is purely quantum mechanical in origin. This term represents "virtual" transitions to the excited states of the atom and molecule which give rise to instanteneous multipole moments. The instantaneous moments of one particle (atom or molecule) can 1) induce moments in the other particle which then interact with the original moments or 2) interact with the permanent moments of the other particle. The former case of interaction of mutually induced moments is termed dispersion, while the latter case of the interaction of a permanent moment with an induced moment is called induction. We can thus separate the second-order perturbation term into induction and dispersion terms.

Since the ground state atom has no permanent moments, the induction term \( V_{\text{ind}} \) due to the interactions between the permanent molecular moments and the induced moments of
the atom becomes\textsuperscript{13}

\[
V_{\text{ind}} = \Sigma \frac{\langle \psi_a^\circ \psi_m^\circ | U | \psi_a^i \psi_m^o \rangle^2}{(E_a^i - E_a^o)}
\]

\[
= -\frac{1}{2} \alpha_{\alpha \beta} F_{\alpha \gamma} F_{\alpha \beta} - \frac{1}{3} A_{\alpha \beta \gamma} F_{\alpha \gamma} F_{\alpha \beta} + \ldots ,
\]

(5.23)

where $F_{\alpha \alpha}$ and $F_{\alpha \beta \gamma}$ are the electric field and field gradient at the center of the atom arising from the permanent moments of the neutral molecule and are given by

\[
F_{\alpha \alpha} = T_{2\alpha \beta \alpha} \mu_{\beta \gamma} - \frac{1}{3} T_{2\alpha \beta \alpha} \theta_{\beta \gamma} + \ldots
\]

(5.24)

\[
F_{\alpha \beta \gamma} = T_{2\alpha \beta \gamma} \mu_{\beta \gamma} - \frac{1}{3} T_{2\alpha \beta \gamma} \theta_{\beta \gamma} + \ldots ;
\]

$\alpha_{\alpha \beta}$ and $A_{\alpha \beta \gamma}$ are the dipole and quadrupole polarizabilities of the atom and have the form\textsuperscript{13,14}

\[
\alpha_{\alpha \beta} = S(\alpha, \beta) \Sigma \frac{\langle \psi_a^n | \mu_{\alpha \beta} | \psi_a^i \rangle \langle \psi_a^i | \mu_{\alpha \beta} | \psi_a^n \rangle}{E_a^i - E_a^n}
\]

\[
A_{\alpha \beta \gamma} = 2 \Sigma \frac{\langle \psi_a^n | \mu_{\alpha \beta} | \psi_a^i \rangle \langle \psi_a^i | \theta_{\alpha \beta \gamma} | \psi_a^n \rangle}{E_a^i - E_a^n}
\]

(5.25)

where $S(\alpha, \beta)$ implies a summation of all the tensor components in which $\alpha$ and $\beta$ are permuted. Buckingham\textsuperscript{13} has shown that the leading terms of a Legendre expansion of the induction contribution $V_{\text{ind}}$ to the long-range interaction potential energy $V$ between a polar molecule and a spherical atom can be written as
\[ V_{\text{ind}} = - \sum_{\lambda=0}^{4} v_{\lambda}^{\text{ind}}(R) P_{\lambda}(\Theta), \]

(5.26)

with

\[ v_{0}^{\text{ind}}(R) = \alpha_{a} \mu_{m}^{2} R^{-6} \]

\[ v_{1}^{\text{ind}}(R) = \frac{18}{5} \alpha_{a} \mu_{m} \theta_{m} R^{-7} \]

\[ v_{2}^{\text{ind}}(R) = \alpha_{a} \mu_{m}^{2} R^{-6} \]

\[ v_{3}^{\text{ind}}(R) = \frac{12}{5} \alpha_{a} \mu_{m} \theta_{m} R^{-7} \]

\[ v_{4}^{\text{ind}}(R) = \frac{18}{5} \alpha_{a} \theta_{m} R^{-8}, \]

(5.27)

where \( \alpha_{a} \) is the isotropic polarizability of the atom

\( \mu_{m} (= \mu_{mz}) \) is the dipole moment and \( \theta_{m} (= \theta_{mzz}) \) is the quadrupole moment of the molecule. All moments and polarizabilities are referred to the center-of-mass of their respective systems.

The dispersion contribution to the second-order perturbation correction \( V_{\text{disp}} \) is given by

\[ V_{\text{disp}} = - \sum_{i \neq o} \frac{|\langle \psi_{a}^{o} \psi_{m}^{o} | U | i \psi_{a}^{i} \psi_{j}^{j} \rangle|^{2}}{(E_{a}^{i} - E_{a}^{o}) + (E_{m}^{i} - E_{m}^{o})}. \]

London\textsuperscript{15} has shown that by making the approximation that

\[ [(E_{a}^{i} - E_{a}^{o}) + (E_{m}^{i} - E_{m}^{o})]^{-1} \]

\[ = I_{a}^{o} I_{m}^{o} (I_{a}^{o} + I_{m}^{o})^{-1} (E_{a}^{i} - E_{a}^{o})^{-1} (E_{m}^{j} - E_{m}^{o})^{-1} \]
and setting the terms $I_a^O$ and $I_m^O$ equal to fixed energies associated with the ground states of the atom $\psi_a^O$ and molecule $\psi_m^O$ (e.g., the ionization energies), the dispersion term can be considerably simplified to\(^{13}\)

$$V_{\text{disp}} = -\frac{I_a^O I_m^O}{4(I_a^O + I_m^O)} \left[ T_{2a\beta} T_{2\gamma\delta} \alpha_{a\alpha\gamma} \alpha_{m\beta\gamma} \right.$$  

$$+ \frac{2}{3} T_{2a\beta} T_{2\gamma\delta\varepsilon} (\alpha_{a\alpha\gamma} A_{m\beta\delta\varepsilon} - \alpha_{m\alpha\gamma} A_{a\beta\delta\varepsilon})$$  

$$+ \ldots \right], \quad (5.28)$$

where $\alpha_{m\alpha\beta}$ and $A_{m\alpha\beta\delta}$ are the dipole and quadrupole polarizabilities of the molecule and have definitions similar to those of the atomic polarizabilities given in Eqs. (5.25). Finally, Buckingham\(^{13}\) has shown that the leading terms of a Legendre expansion of the approximate dispersion contribution $V_{\text{disp}}$ of Eq. (5.28) to the long-range interaction potential energy of a polar molecule and spherical atom can be written as

$$V_{\text{disp}} = -\sum_{\lambda} v_{\lambda}^{\text{disp}}(R) P_{\lambda}(\Theta),$$

with

$$v_{\lambda}^{\text{disp}}(R) = \alpha_a \bar{a}_m \Delta R^{-6}$$  

$$v_{1}^{\text{disp}}(R) = \frac{6}{15} \alpha_a (3A_m|| + 6A_m\perp) \Delta R^{-7}$$  

$$v_{2}^{\text{disp}}(R) = \frac{\alpha_a}{2} (\alpha_m|| - \alpha_m\perp) \Delta R^{-6}$$  

$$v_{3}^{\text{disp}}(R) = \frac{4}{15} \alpha_a (3A_m|| - 4A_m\perp) \Delta R^{-7}, \quad (5.29)$$
where $\Delta = 3/2 \frac{I_a^0 I_m^0}{(I_a^0 + I_m^0)}$, $\alpha_{m,\parallel}$ and $\alpha_{m,\perp}$ are the parallel and perpendicular components of the dipole molecular polarizability, $\bar{\alpha}_m = 1/3 (\alpha_{m,\parallel} + 2\alpha_{m,\perp})$, and $A_{m,\parallel}$ and $A_{m,\perp}$ are the parallel and perpendicular components of the quadrupole molecular polarizability. Thus, the London approximation allows the dispersion contribution to interaction potential energy to be written in terms of molecular parameters which can be calculated by ab initio methods or derived from experimental results. The total long-range interaction potential energy is given as the sum of the dispersion and induction terms as

$$v^{LR}_\lambda(R) = -(v^{\text{disp}}_\lambda(R) + v^{\text{ind}}_\lambda(R)).$$

(5.30)
D. Atom-Molecule Potential Surfaces

In this section we apply the formalism developed in Sections B and C to calculate the potential energies for interactions between ground state helium atoms (He) and other closed-shell, ground state atoms and molecules. In the first subsection, we treat the interactions between helium and other rare gas atoms. The parameters of the one-electron effective potential energy $V_{\text{eff}}$ are set for all subsequent calculations by forcing the short-range He-He interaction potential energy curves, generated by the effective potential method (EPM) of Section B, to agree with ab initio results. Using these parameters, the EPM interaction potential energy curves for helium and neon (He-Ne) and helium and argon (He-Ar) agree well with more detailed ab initio calculations. We also use these parameters to calculate the short-range potential energy surfaces for interactions between helium and hydrogen fluoride (He-HF) and helium and hydrogen chloride (He-HCl). The results of these calculations are presented in the second subsection. The He-HF surface calculated with the EPM compares favorably with a restricted Hartree-Fock surface. Finally, from molecular and atomic parameters, we calculate the long-range potential energy surfaces for these systems by the method outlined in Section C and smoothly merge them with the appropriate short-range component to give the total atom-molecule interaction surface.
1) Helium-Rare Gas Atom Potentials

We can calculate the short-range potential energy curve for interactions between helium and other rare gas atoms by the effective potential method (EPM), described in Section B, by setting $\lambda$ equal to zero and replacing $a_0(r)$ in Eq. (5.11) with the rare-gas electron probability density. The atomic probability density of the rare gas atoms is calculated from the Hartree-Fock wave functions of Clementi.\textsuperscript{16} Using the one-electron effective potential parameters, $a$ and $\sigma$, which give the best fit to the electron-helium pseudopotential of Kestner and co-workers,\textsuperscript{6c} in an EPM calculation of He-He interaction potential energy, we find that the resulting EPM potential energy curve is much stronger than are potential energy curves calculated by \textit{ab initio} electronic structure techniques. We thus vary the parameters $a$ and $\sigma$ of the one-electron effective potential energy (Eq. 5.14) until the EPM He-He potential energy curve agrees with the more accurate \textit{ab initio} results. We obtain good agreement if we choose $\sigma$ to be 0.90 and $a$ to be 3.00. To test the validity of this choice of parameters, we calculated the short-range potential energy curves for helium-neon and helium-argon by the EPM and compared the results with \textit{ab initio} calculations.\textsuperscript{17} The EPM and \textit{ab initio} curves for He-He, and He-Ne are shown in Fig. 5. The rather good agreement between the two sets of potential energy curves indicates that the effective poten-
Fig. 5 Potential energy curves for the interaction of He with He and Ne. Dashed line represents EPM calculation and solid line represents ab initio calculations.
tial method, with the above choice of parameters, may be applicable to the calculation of potential energy surfaces for interactions between helium and other closed shell systems, in particular, molecules.

2) Helium-Diatomic Hydride Potential Surfaces

We have used the parameters of the effective potential energy $V_{\text{eff}}$ determined in the previous subsection to calculate the short-range interaction surfaces of helium-hydrogen fluoride and helium-hydrogen chloride. The surface is determined in terms of the short-range Legendre coefficients $v_{\lambda}^{\text{SR}}$, which are calculated by Eq. (5.11). We determine the expansion coefficients $a_{\lambda}$ of the unperturbed molecular probability densities for HF and HC\textsubscript{2} from the near Hartree-Fock wave functions of Cade and Huo.\textsuperscript{18} The first three radial expansion coefficients for HF are shown in Fig. 6. The non-spherical radial coefficients $v_{\lambda}$ ($\lambda \neq 0$), which will result from the EPM calculation, are repulsive at intermediate atom-molecule distances ($4.0 \leq R \leq 7.0 \, \text{a}_0$) but turn over and eventually become negative at small atom-molecule distances ($R < 4.0 \, \text{a}_0$) due to the attractive term of $V_{\text{eff}}$. As noted earlier, the EPM short-range potential energy surface is only valid in the region of small electron cloud overlap and distortion and is not necessarily accurate at very small atom-molecule separations. However, since these closed-shell systems do not form bonds and since the electrostatic repulsion of the
Fig. 6 Radial expansion coefficients $a_\lambda(r)$ for the probability density of HF.
Table 1
Radial Expansion Coefficient Parameters: $v_\lambda(R)$

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>$A_\lambda$</th>
<th>$\zeta_\lambda$</th>
<th>$C_\lambda$</th>
<th>$m_\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>128.275</td>
<td>2.494</td>
<td>3.42</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>10.356</td>
<td>2.151</td>
<td>6.78</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>29.253</td>
<td>2.379</td>
<td>1.55</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>10.739</td>
<td>2.173</td>
<td>1.41</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>3.875</td>
<td>2.115</td>
<td>1.23</td>
<td>8</td>
</tr>
<tr>
<td>HCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>81.132</td>
<td>2.062</td>
<td>12.10</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>63.992</td>
<td>2.146</td>
<td>19.12</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>228.385</td>
<td>2.416</td>
<td>1.96</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>86.054</td>
<td>2.168</td>
<td>8.78</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>53.050</td>
<td>2.166</td>
<td>29.20</td>
<td>8</td>
</tr>
</tbody>
</table>

*All parameters are given in atomic units.*
atomic and molecular electron clouds grows with decreasing separation, we expect the potential energy surface to be repulsive even at small separations. Smith\textsuperscript{19} and Toennies\textsuperscript{20} have shown that the short-range repulsive interaction potential between rare gas atoms can be accurately fit by an exponential over a rather wide range of interatomic distances. Extending these results to interactions between closed shell atoms and molecules, we fit the EPM radial expansion coefficients to an exponential form as

\[ V^\text{SR}_\lambda(R) = A_\lambda \exp(- \zeta_\lambda R). \quad (5.31) \]

The fit is performed in the region in which the short-range radial expansion coefficients are repulsive and are smoothly varying, monotonically decreasing functions with increasing \( R \). The fit was made in the region between 4.0 and 5.0 \( a_0 \) for He-HF and between 5.0 and 6.0 \( a_0 \) for He-HCl. This exponential form is used then to represent the short-range expansion coefficients at all atom-molecule separations. The values of \( A_\lambda \) and \( \zeta_\lambda \) are given in the first two columns in Table 1 for the He-HF and He-HCl surfaces.

We compare EPM short-range He-HF surface with a restricted Hartree-Fock (RHF) surface calculated by Bender.\textsuperscript{21} The RHF surface was calculated at eight angular positions for each of three radial distances. The results of the calculation are given in Table 2a. This surface was expanded in a Legendre series so that it could
Table 2a. RHF Surface: He-HF

<table>
<thead>
<tr>
<th>θ</th>
<th>R</th>
<th>V(R,θ) - V(∞)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>0°</td>
<td>4.490(-1)</td>
<td>1.219(-1)</td>
</tr>
<tr>
<td>30°</td>
<td>2.136(-1)</td>
<td>7.833(-2)</td>
</tr>
<tr>
<td>45°</td>
<td>1.653(-1)</td>
<td>6.039(-2)</td>
</tr>
<tr>
<td>60°</td>
<td>1.404(-1)</td>
<td>4.994(-2)</td>
</tr>
<tr>
<td>90°</td>
<td>1.327(-1)</td>
<td>4.578(-2)</td>
</tr>
<tr>
<td>120°</td>
<td>1.376(-1)</td>
<td>4.717(-2)</td>
</tr>
<tr>
<td>135°</td>
<td>1.384(-1)</td>
<td>4.689(-2)</td>
</tr>
<tr>
<td>150°</td>
<td>1.347(-1)</td>
<td>4.536(-2)</td>
</tr>
<tr>
<td>180°</td>
<td>1.318(-1)</td>
<td>4.362(-2)</td>
</tr>
</tbody>
</table>

* All parameters are given in atomic units.
be more easily compared with the EPM results. For a particular value of $R$, we know the value of the RHF potential energy $V(R, \Theta_i)$ at, say, $n$ values of the angle $\Theta_i$ ($\Theta = \Theta_i | i = 1, n$). Since we can explicitly evaluate the Legendre coefficient $P_\lambda(\Theta)$ at each of these angles, we can construct a set of $n$ simultaneous equations of the form

$$\begin{align*}
V(R, \Theta_1) &= \sum_{\lambda=0}^{n-1} v_\lambda(R) P_\lambda(\Theta_1) \\
& \vdots \\
V(R, \Theta_n) &= \sum_{\lambda=0}^{n-1} v_\lambda(R) P_\lambda(\Theta_n),
\end{align*}$$

(5.32)

whose solutions are the radial expansion coefficients $v_\lambda(R)$ with $0 \leq \lambda \leq n-1$. For a particular choice of $n$ values of the potential energy $V(R, \Theta)$, all at the same radial distance but for different angular orientations, we obtain all radial expansion coefficients up to order $n-1$. We continue to add potential energy points for a given $R$ until the radial coefficients of interest (in our case those with $\lambda \leq 4$) converge to within a given tolerance for successive evaluations of Eqs. (5.32). The procedure is repeated at each value of $R$ at which the ab initio surface was evaluated to obtain the radial dependence of the expansion coefficients. We found that at a given $R$ at least eight angular positions are needed in order to guarantee convergence of the first three expansion terms ($v_0$, $v_1$, and $v_2$). The results of our calculation of the
expansion coefficients of the RHF surface are given in Table 2b and compared with the EPM coefficients given by Eq. (5.30) and Table 2 in Fig. 7. The rather good agreement leads us to believe that for interactions between small, tightly bound atoms and closed-shell molecules the effective potential method may give a rather accurate short-range interaction potential energy surface.

We have used the recent RHF surface of Bender for comparison, although other He-HF surfaces have been calculated by Gelb and co-workers\textsuperscript{22} and by Lischka.\textsuperscript{23} Unfortunately, the \textit{ab initio} surfaces of Bender and Lischka are over different intermolecular regions,\textsuperscript{24} and the Lischka surface is evaluated at only two orientations (\(\Theta = 0^\circ\) and \(180^\circ\)). However, the potential surface at \(\Theta = 0^\circ\) formed by summing the first five EPM radial expansion coefficients is of the same order as that of Lischka in the region beyond 4.5 \(a_o\). Since this EPM surface closely parallels that of Bender, the model and the two \textit{ab initio} surfaces seem to be consistent with each other. The Gelb surface is considerably stronger than the Bender or Lischka surface. Since only three angular positions for each \(R\) were used to determine the radial expansion coefficients of the Gelb surface, the lack of convergence of the radial coefficients due to insufficient angular resolution could account from the discrepancies between this and the Bender surface.
Fig. 7 Comparison of EPM and restricted Hartree-Fock radial expansion coefficients $v_\lambda(R)$ of the short-range potential energy surface for He-HF.
Table 2b. RHF Surface: Radial Expansion Coefficients

<table>
<thead>
<tr>
<th>R \ (a_0)</th>
<th>v_0 \ (-1)</th>
<th>v_1 \ (-2)</th>
<th>v_2 \ (-2)</th>
<th>v_3 \ (-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>1.506</td>
<td>4.229</td>
<td>5.501</td>
<td>7.072</td>
</tr>
<tr>
<td>3.0</td>
<td>5.219</td>
<td>1.536</td>
<td>1.740</td>
<td>1.741</td>
</tr>
<tr>
<td>4.0</td>
<td>5.286</td>
<td>2.263</td>
<td>2.213</td>
<td>1.911</td>
</tr>
</tbody>
</table>

*All quantities are in atomic units. Eight angular positions were used at each R to determine the v_λ coefficients. The v_3 coefficients have not stabilized with respect to an increase in the number of angular points.*
The long-range radial expansion coefficients for both induction and dispersion effects were calculated from Eqs. (5.27) and (5.29) using the molecular parameters listed in Table 3, which presents the parallel $\alpha_{||}$, perpendicular $\alpha_{\perp}$, and average $\alpha$ dipole polarizabilities, the permanent dipole moment $\mu$, the permanent quadrupole moment $\Theta$, the ground state ionization energies $I$, the parallel $A_{||}$ and perpendicular $A_{\perp}$ quadrupole polarizabilities, and the displacement of the centers of mass and charge for HF, HCl, and He. In addition, we give the rotational constant $B (= \frac{1}{2}I)$ for each molecule and its isotopic relative. The total long-range expansion coefficients given by Eq. (5.30) were then placed in the form

$$v_{LR}^{\lambda}(R) = - C_\lambda R^{-m_\lambda}. \quad (5.33)$$

The values of $C_\lambda$ and $m_\lambda$ are given in the last two columns of Table 1 for the He-HF and He-HCl surfaces. We have considered only induction contributions to $v_4$ for He-HCl and to $v_3$ and $v_4$ for He-HF, since the higher order polarizabilities are unavailable for these systems. For He-HF, the dispersion contribution to $v_1$ was calculated by an expression given by Margenau and Kestner in terms of the separation of the molecular center-of-mass and center-of-charge, $d$. Using the HF parameters of Bender and Davidson, we were able to estimate the value of $d$ by the procedure outlined by Herman. Finally, the long- and
Table 3: Molecular Parameters*: HF (DF) and HCl (DCL)

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>HCl</th>
<th>He</th>
</tr>
</thead>
<tbody>
<tr>
<td>a_∥</td>
<td>5.34</td>
<td>21.14</td>
<td>31</td>
</tr>
<tr>
<td>a_⊥</td>
<td>2.48</td>
<td>16.14</td>
<td>31</td>
</tr>
<tr>
<td>a</td>
<td></td>
<td></td>
<td>1.42</td>
</tr>
<tr>
<td>μ</td>
<td>0.765</td>
<td>0.472</td>
<td>32</td>
</tr>
<tr>
<td>θ</td>
<td>0.541</td>
<td>2.83</td>
<td>29</td>
</tr>
<tr>
<td>r</td>
<td>0.581</td>
<td>0.468</td>
<td>18b</td>
</tr>
<tr>
<td>d</td>
<td>0.220</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A_∥</td>
<td>-</td>
<td>11.04</td>
<td>33</td>
</tr>
<tr>
<td>A_⊥</td>
<td>-</td>
<td>2.27</td>
<td>33</td>
</tr>
<tr>
<td>B</td>
<td>9.54(-5)</td>
<td>4.82(-5)</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>[DF 5.01(-5)]</td>
<td>[DCL 2.48(-5)]</td>
<td>24</td>
</tr>
</tbody>
</table>

* All parameters are in atomic units and are referred to the center of mass of the molecular or atom.
short-range radial expansion coefficients were smoothly merged at intermediate atom-molecule separations by the form

$$v_{\lambda}(R) = v_{\lambda}^{SR}(R) + v_{\lambda}^{LR}(R)[1 - \exp[-(R/R_0)^m]]$$  \hspace{2cm} (5.34)

to give the total radial expansion coefficient $v_{\lambda}(R)$. In general, the value of $m$ determines the rapidity with which the long-range term is truncated within the short-range region, while the value of $R_0$ estimates the distance at which the short-range term begins to dominate. There is not a unique choice for these parameters. In fact, in scattering calculations which use coefficients of this form, the sensitivity of the cross sections to changes in $R_0$ and $m$ should always be carefully checked.

In Fig. 8, we present the radial expansion coefficients $v_0$, $v_1$, and $v_2$ as a function of the atom-molecule distance $R$ for He-HF. The $v_3$ coefficient closely parallels $v_2$, and the $v_4$ coefficient is a factor of two smaller than $v_2$. Higher order terms ($\lambda > 4$) make successively smaller contributions and can be neglected in calculations involving the lowest few rotational levels ($j \leq 3$). We have omitted $v_3$ and $v_4$ from the figure for clarity. The long-range terms have not been truncated, so $R_0 << 1$. The surface is rather asymmetric with the non-spherical terms $v_1$, $v_2$, and $v_3$ making comparable contributions. Since the spherical term $v_0$ is somewhat stronger overall than the non-spherical ones,
Fig. 8 EPM radial expansion coefficients $v_\lambda(R)$ of the total potential energy surface for He-HF. The term $v_3$ closely parallels $v_1$, and $v_4$ is about half the size of $v_2$. 
we consider this a case of intermediate anisotropy, hence intermediate coupling. In contrast, a weak anisotropy corresponds to the case where the spherical term is much larger than the non-spherical components, while a strong anisotropy implies one or more of the non-spherical terms becomes larger than $v_o$. In Fig. 9, we present the radial expansion coefficients $v_o$, $v_2$, and $v_3$ as a function of intermolecular distance $R$ for He-HC with $R_o = 5.0$ and $m = 12$. The $v_1$ and $v_4$ terms are parallel to the $v_2$ coefficient and are omitted from the figure for clarity. Higher order terms make successively smaller contributions. The He-HC surface is more asymmetric and has a larger extent than the He-HF surface. These differences arise from the fact that HC is a larger and more loosely bound molecule than HF. Since the $v_3$ term is larger than the spherical term over a certain range of $R$, this case corresponds to a strong anisotropy and will thus lead to strong coupling between the scattering channels.

Finally, to first order, we may use the He-HF and He-HC surfaces to approximate the He-DF and He-DCl surfaces. The introduction of an isotopic species does not greatly change the features of a potential curve as can be seen from the slight difference in the equilibrium separations of HF and DF. The most important consequence of an isotopic substitution is manifest in the change of the moment of inertia and therefore the rotational spectrum.
Fig. 9 EPM radial expansion coefficients $v_\lambda(R)$ of the total potential energy surface for He-HCl. The terms $v_1$ and $v_4$ closely parallel $v_2$. 
We shall pursue this point in more detail in the discussion of the scattering results. In conclusion, we have developed a procedure for generating model interaction potential energy surfaces between a small, tightly bound atom and other closed shell atoms and molecules. We have used this procedure to calculate the potential energy surfaces of He-HF and He-HCl with the hydrogen fluoride surface in good agreement with more accurate \textit{ab initio} calculations. In the next chapter, we shall discuss the results of scattering calculations for these systems.
My natural instinct teaches me  
And instinct is important, O!
You're everything you ought to be,  
And nothing that you oughtn't, O! Princess Ida

Chapter 6. Rotational Excitation Cross Sections:
Helium-Diatom Collisions

A. Introduction

In this chapter, we present and discuss the results of calculations of cross sections for excitation of the lowest few rotational levels of the diatomic hydrides by collisions with ground state helium atoms at energies (c.m.) \(^1\) between 0.015 eV and 0.15 eV above the ground rotor state. Specifically we consider collisions involving hydrogen fluoride (HF), deuterium fluoride (DF), hydrogen chloride (HCl), and deuterium chloride (DCl) and treat these molecular hydrides as linear rigid rotors. Computer codes INEQCC and INEQJZ were developed to numerically calculate rotational excitation cross sections in the coupled-channel close coupling (CCCC) and \(j_z\)-conserving coupled state (JZCS) formulation respectively by the integral equations technique discussed in Chapter 4. Before applying these integral equations codes to the hydride systems, we ran various tests to compare our results with those of previous calculations. Several of these tests are discussed in Section B. In Section C, we present the results of calculations of the rotational excitation cross
sections for the diatomic hydrides in collisions with helium. We treat each of the four hydride systems in a separate subsection and, where applicable, use simple models to explain the behavior of the partial and total rotational excitation cross sections of each system. In addition, we compare corresponding cross sections of different systems and discuss the trends in the behavior of these cross sections in terms of the relative strength of the potential energy expansion coefficients and the spacings of the energy levels of the rotors.

B. Test Cases: Atom-Molecule Collisions

We have developed two numerical codes, INEQCC and INEQJZ, which calculate rotational excitation cross sections for atom-molecule (linear rotor) collisions in the CCCC and JZCS formulations respectively using the method of integral equations presented in Chapter 4. Both codes use an integration package, developed by Dr. E. F. Hayes and other members of the Rice Quantum Chemistry Group, which performs the integration algorithm of Eq. (4.36), calculates the proper Green's functions, and stabilizes the solution by the method outlined in Appendix C. In addition, the codes include routines which evaluate the radial expansion coefficients of the potential energy surface and the Clebsch-Gordon and Racah coefficients of the matrix elements. The codes thus require only a small
amount of input data—the incident atom energy $E$, the reduced mass $\mu$, the molecular rotation constant $B$, the number of states in the rotor basis ($0-j_{\text{max}}$), the step size $\Delta$, the matching radius $R_{\text{max}}$, the total angular momentum $J$, the parameters of the potential fit, and the frequency at which the solution is to be stabilized. From this information, the codes determine the channels associated with each basis state, construct the appropriate wave functions and potential energy matrices, integrate the solution out to the matching radius $R_{\text{max}}$, and calculate the R-matrix and cross sections from the solutions at $R_{\text{max}}$. In order to test these codes, we have compared results of calculations with INEQCC and INEQJZ with those of previous calculations for the system He-H$_2$. We have also tested INEQCC for the systems Ar-TAF and Li$^+$-H$_2$. Each of these systems provides a test of a particular aspect of the codes.

The hydrogen molecule H$_2$ has rather widely spaced rotor levels (e.g., $\Delta E_{02} \simeq 0.044$ eV) and the He-H$_2$ interaction surface has a rather weak anisotropy. Because of these two properties, the scattering channels for collisions between ground-state helium atoms and H$_2$ are weakly coupled and only a small basis, usually representing only open channels, is required to guarantee the convergence of the partial rotational excitation cross sections $\sigma^J(j\rightarrow j')$. In addition, at low energies ($E < 0.20$ eV), a small number
of partial cross sections \((J \leq 20)\) is sufficient to determine the total rotational excitation cross section \(\sigma(j\rightarrow j')\). Rotational excitation cross sections for the elastic \((0\rightarrow 0)\) and inelastic \((0\rightarrow 2)\) and \((0\rightarrow 4)\) excitations of \(H_2\) by collisions with helium were calculated at several energies with an open channel basis by INEQCC and the coupled-channel numerov code, OPCHAN, developed by A. P. Hickman. In all cases, the rotational excitation cross sections calculated by these two codes are in excellent agreement. While these calculations tested only the even parity case, the transition \((1\rightarrow 3)\) provides a test of the ability of the code INEQCC to handle different parities. Selected partial rotational excitation cross sections \(\sigma^J(1\rightarrow 3)\) for an energy of 0.15 eV, calculated with INEQCC and the coupled-channel numerov code of N. F. Lane are compared in Table 4a. The excellent agreement between these two sets of cross sections suggests that the open-channel and parity routines of INEQCC are functioning properly. In addition, test runs with the coupled state code INEQJZ gave total cross sections for the elastic \((0\rightarrow 0)\) and inelastic \((0\rightarrow 2)\) excitations of \(H_2\) by He in agreement with those of McGuire and Kouri. These comparisons indicate that both codes are properly handling the open channels for a weakly coupled system and correctly evaluating the partial rotational excitation cross sections at small values of \(J\). In addition, they indicate that the code INEQCC is correctly evaluating cross sections for different parities.
Table 4a. Partial Rotational Excitation Cross Sections: He-H\(_2\)

<table>
<thead>
<tr>
<th>J</th>
<th>(\sigma^J_{(1-3)}) (even parity)</th>
<th>(\sigma^J_{(1-3)}) (odd parity)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>INEQCC</td>
<td>NUMEROV(^6)</td>
</tr>
<tr>
<td>4</td>
<td>0.0254</td>
<td>0.025</td>
</tr>
<tr>
<td>6</td>
<td>0.0330</td>
<td>0.033</td>
</tr>
</tbody>
</table>

Table 4b. Partial Rotational Excitation Cross Sections: Ar-T\&F

<table>
<thead>
<tr>
<th>J</th>
<th>basis</th>
<th>(\sigma^J_{(0-2)})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>INEQCC</td>
</tr>
<tr>
<td>20</td>
<td>(0-4)</td>
<td>9.64(-2)</td>
</tr>
<tr>
<td>20</td>
<td>(0-6)</td>
<td>5.41(-2)</td>
</tr>
<tr>
<td>40</td>
<td>(0-4)</td>
<td>1.38(-1)</td>
</tr>
</tbody>
</table>

\(^\dagger\) All cross sections are in units of \(\sigma^2\). The scattering parameters for the He-H\(_2\) system are as follows: \(E = 0.15\) eV, \(\mu = 2440.89\), the basis is (0-2), \(R_{\text{max}} = 20.0\) a\(_o\), \(\Delta = 0.01\) a\(_o\), and the potential is that of Roberts.\(^4\)

\(^*\) All cross sections are in units of \(\sigma^2\). The scattering parameters for the Ar-T\&F system are as follows: \(E = 0.1158\) eV, \(\mu = 61,776.2\), \(R_{\text{max}} = 20.0\) a\(_o\), \(\Delta = 0.01\) a\(_o\), and the potential is given in Ref. 8. The T\&F molecule is treated as a homonuclear rigid rotor so that the basis (0-6) implies about the rotor states with \(j\) equal to 0, 2, 4, and 6 are included in the basis.
In treating collisions between ground state argon Ar and the molecule T&F, we are dealing with a system whose properties contrast vividly with those of the He-H₂ system. The rotational levels of T&F are very closely spaced (e.g., ΔE₀₁ ≈ 5.5×10⁻⁵ eV) due to its large moment of inertia, and the Ar-T&F potential energy surface is strongly anisotropic. We thus expect that the scattering channels are strongly coupled and that a large basis and many partial cross sections are needed to guarantee a converged total rotational excitation cross section. Tsien, Parker, and Pack⁸ have calculated partial rotational excitation cross sections for the (0-2) excitation of T&F by Ar using a coupled-channel Gordon's method⁹ routine. In Table 4b we compare the results of their calculations with those of INEQCC. The rather good agreement indicates that the coupled channel integral equations code, INEQCC, can accurately calculate partial cross sections for large values of the total angular momentum J and for a large basis whose corresponding channels are strongly coupled.

We also tested the closed channel routine of INEQCC by calculating partial inelastic cross sections for the rotational excitation of H₂ by collisions with ground state Li⁺ ions. In Table 5, we compare our results for the (0-2) transition with those of Lester and Schaeffer¹⁰ which were calculated with a coupled-channel Gordon's method. The agreement between the two sets of partial cross sections
Table 5. Partial Rotational Excitation Cross Sections: \( \text{Li}^+-\text{H}_2 \)

<table>
<thead>
<tr>
<th>( J )</th>
<th>INEQCC ( \sigma^J(0\rightarrow2) )</th>
<th>Gordan's Method ( \sigma^J(0\rightarrow2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.909(-2)</td>
<td>2.859(-2)</td>
</tr>
<tr>
<td>20</td>
<td>0.1908</td>
<td>0.1989</td>
</tr>
<tr>
<td>26</td>
<td>0.5482</td>
<td>0.5600</td>
</tr>
<tr>
<td>30</td>
<td>0.5324</td>
<td>0.4847</td>
</tr>
</tbody>
</table>

\( \neq \) All cross sections are in units of \( a_0^2 \). The scattering parameters are as follows: \( E = 0.10 \text{eV}, \mu = 2856.10 \), the basis is (0-4), \( R_{\text{max}} = 120.0 \text{a}_0^2 \), \( \Delta = 0.01 \text{a}_0 \), and the potential is given by Ref. 10.
is not as good as with the other two systems, although the difference is never more than ten percent (10%). In Gordon's method,\textsuperscript{9} the potential energy surface is approximated in various regions by a linear fit. Thus, the two codes do not employ exactly the same potential energy surface since no such linearization is made by INEQCC. The differences in the partial cross sections probably arise largely from this fact. The agreement does seem to indicate that the closed channel routine of INEQCC is functioning properly.

Having tested the integral equations codes for a number of atom-molecule systems, we conclude that INEQCC and INEQJZ can be used to accurately calculate partial cross sections for open channel, weakly coupled systems. In addition, INEQCC is found to give accurate partial rotational excitation cross sections for systems with bases of open and closed channels which are strongly coupled. The success of these tests leads us to believe that the integral equations codes can be applied with confidence to the calculation of rotational excitation cross sections for other systems such as the collisions between He and the diatomic hydrides.
C. Helium-Diatomic Hydride Collisions

In this section we present and discuss the results of calculations, by the coupled channel and coupled state integral equations codes INEQCC and INEQJZ, of the rotational excitation cross sections for collisions between ground state helium atoms and the following diatomic hydrides: HF, DF, HC\textsubscript{\ell}, and DC\textsubscript{\ell}. We treat each atom-molecule system in a separate subsection. Within each subsection, we present the total rotational excitation cross sections for transitions between the lowest four rotor levels of the molecule (j \leq 3) at several energies and, for one or more of these energies, discuss the variation with J of the various partial cross sections \sigma^J(j\rightarrow j'). In order to understand the important features of the partial cross sections, we discuss simple models which approximate the complicated scattering processes. Although cross sections estimated by these models are usually not quantitatively very accurate, nevertheless, the models serve to explain the relative orderings and general functional behavior of the partial cross sections. Thus, we use the models to give only a very qualitative description of the behavior of the cross sections. We should remember that this behavior actually depends on complicated quantum mechanical interference effects between the various coupled channels which are only approximately
described by these models. We also use these models to explain the changes in the behavior of a particular cross section that arise from changes in the spacing of the rotor levels and the strength of the potential energy surfaces. In this manner, we can understand the differences in cross sections for the same transitions of different atom-molecule systems.

1) He-HF Collisions

We first consider the behavior of the partial rotational excitation cross sections for various transitions at a particular energy. This behavior can be understood in terms of the spacing of the rotor levels and the relative strength of the coupling matrix elements. From Fig. 10, we note that hydrogen fluoride has the widest spacing between rotor levels of the hydrides that we consider. In fact, of the first and second row hydrides only $\text{H}_2$ has levels more widely separated. The He-HF system is an example of intermediate coupling since the non-spherical radial expansion coefficients of the potential-energy surface are somewhat smaller in magnitude than the spherical term, $v_0$ (see Fig. 8). In addition, the non-spherical terms $v_1$, $v_2$, and $v_3$ are approximately equal. In Fig. 11 we present the partial rotational excitation cross sections for collisions between He and HF for transitions between the ground rotational state ($j = 0$) and the lowest three excited states for an energy (c.m.) of 0.05 eV.
Fig. 10 Rotational spectra of HF, DF, HCl, and DCl.
The general shape of the partial cross section curves can be understood from a simple analogy with a classical rigid rotor. We replace the molecule with a rigid rotor consisting of two spherical masses, each with a radius \(a\), which are separated by a distance \(R\) and are connected by a thick rod and replace the atom with a very small spherical mass. We assume that the rotor and incident particle interact only by direct collisions and that initially the symmetry axis of the rotor points along the \(z\)-axis of the space-fixed (SF) coordinate system. For a particle incident parallel to the \(z\)-axis in the \(x\)-\(z\) plane, the amount of torque exerted on the rotor through the collision with the incident particle is proportional to the impact parameter, which is the \(x\)-coordinate of the particle. The greater the applied torque, the greater the excitation or angular speed of the rotor. For a diatomic hydride, which consists of a heavy atom located very near the molecular center-of-mass and a light hydrogen atom located at a distance \(r_H\) from the center-of-mass approximately equal to the internuclear separation (i.e., \(r_H \approx R\)), torque is exerted most efficiently through collisions between the hydrogen atom and incident particle. We consider in this discussion only the case of collisions with the hydrogen atom, since the torque exerted through collisions with the heavy atom is much smaller. A particle with zero impact parameter strikes the rotor at its center-of-mass and
can therefore exert no torque. As the impact parameter increases in magnitude, the torque, which can be exerted on the rotor through the collision, and consequently the excitation of the rotor increase. A maximum excitation is reached when the particle is incident on the center of the spherical mass. Once the particle misses the rotor, torque can no longer be exerted through the collision. In this picture, the degree of excitation of the rotor as a function of impact parameter starts at zero for a zero impact parameter, rises to a maximum for the impact parameter \( r_H \), and falls to zero once the impact parameter exceeds \( r_H + a \). If the rotor and incident particle interact through a long-range force (e.g., van der Waals), then torque can be exerted on the rotor even for an impact parameter equal to zero or greater than \( r_H + a \). The degree of excitation then starts at a finite value for zero impact parameter, rises to a maximum for an impact parameter corresponding approximately to the center of the spherical rotor mass, and gradually decreases as the impact parameter increases. The resulting excitation curve as a function of impact parameter would closely resemble in form the curves displayed in Fig. 11. In fact, the value of the total angular momentum \( J \) is related to an orbital angular momentum of the incident atom which in turn can be related semi-classically to an impact parameter. Similarly, the degree of excitation of the classical rotor roughly corres-
ponds to the quantum mechanical probability of exciting
the rotor and therefore to the excitation cross section.
Thus, we might expect the quantum mechanical excitation
cross section as a function of J to exhibit a behavior
similar to that of the degree of excitation of a classical
rotor as a function of impact parameter. For excitations
between the lowest few rotational levels of a molecule
and large values of J, we can make the identification
that J and \( \ell \) are approximately equal (J \( \sim \) \( \ell \)) since \( j \) is
small. Further, using the correspondence between the
classical and quantum mechanical angular momenta, we can
write

\[
J \sim \ell \sim \mu v b,
\]

where \( b \), \( \mu \), and \( v \) are the impact parameter, reduced mass,
and velocity of the incident particle respectively. Since
for the case of direct contact between the rotor and inci-
dent particle, the greatest torque is exerted for an impact
parameter equal to \( r_H \), the value of the angular momen-
tum \( J_{\text{max}} \) at which the excitation of the rotor is largest
is given by

\[
J_{\text{max}} \sim \mu v (r_H),
\]

or, in terms of the incident energy \( E \), by

\[
J_{\text{max}} \sim \sqrt{2 \mu E} (r_H). \tag{6.1}
\]
For collisions between He and HF at 0.05 eV, $J_{\text{max}}$ is approximated equal to ten ($r_H \approx 1.6 \ a_0$, $a \approx 0.5 \ a_0$).

Since He and HF interact through a potential, the impact parameter $b_{\text{max}}$ at which the maximum torque is exerted is somewhat larger than $r_H + a$. Therefore, we expect the partial rotational excitation cross section for He-HF to peak for a value of $J$ somewhat greater than ten. In fact, investigation of Table 6 shows that the partial cross sections for the transition (0-1) peaks for a $J$ value equal to sixteen (16). While this model explains the general form of the partial cross section, it is quite crude, for it fails to account for the subtle interference effects that can occur between the quantum mechanical scattering channels.

We next wish to understand the relative ordering of the various rotational excitation cross sections. Although, in general, the relative ordering of the cross sections for various transitions is determined by the complicated interplay between all coupled channels, for cases of weak or intermediate coupling, the ordering can be qualitatively understood in terms of the magnitudes of the matrix elements $U_{\gamma \gamma'}$, which couple the channels directly associated with initial and final states and the ratio of the wave numbers $k_\alpha$ of these states. The dependence of the ordering on these properties can most easily be understood by investigating the distorted wave method. We only use the
Fig. 11  Sensitivity of the partial rotational excitation cross sections at $E = 0.05$ eV for He-HF to changes in the manner in which the long- and short-range surfaces are joined. The cut-off parameters for the curves represented by the a) solid line, b) the crosses (+), and c) the circles (○) are as follows: a) $R_o \ll 1$, $m = 6$, b) $R_o = 5.0 \ a_o$, $m = 6$, and c) $R_o = 6.0 \ a_o$, $m = 6$. 
distorted wave picture to gain insight into the qualitative behavior of the cross sections, since the method does not give very accurate results for the hydride systems. We note from Eq. (2.43) that the stronger the matrix element which connects initial and final channels, the larger the rotational excitation cross section. The matrix element for transitions between the ground \((j = 0)\) and excited \(j'\) rotor states depends only on the radial expansion coefficient \(v_j(R)\) and the Percival-Seaton coefficient \(f_{\lambda}\). Since the non-spherical terms \(v_1, v_2,\) and \(v_3\) are approximately equal for the He-HF system, the relative ordering of the coupling matrix elements between the ground state and the three excited states \((j = 1, 2, \text{and} 3)\) is determined by the relative magnitude of the Percival-Seaton coefficients. Since the magnitude of the Percival-Seaton coefficients \(f_{\lambda}(j'; \lambda'; 0; J)\) decreases as the magnitude of the excited state rotational quantum number increases (see Table 6a), the matrix elements for the transition \((0-1)\) are larger than those for the transition \((0-2)\), which in turn exceed those for the transition \((0-3)\). Thus, from the relative magnitude of the coupling matrix elements, we obtain an ordering of the partial rotational excitation cross sections in agreement with that of Fig. 11. The rather large spacing of the rotor levels of HF is another effect which works in favor of the ordering displayed in Fig. 11. To see this, we must examine the dis-
Table 6a. Percival-Seaton Coefficients

<table>
<thead>
<tr>
<th>J</th>
<th>λ</th>
<th>j'</th>
<th>λ'</th>
<th>j</th>
<th>λ</th>
<th>f_λ^{j λ';0 λ; J}</th>
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<td>4</td>
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<td>0.2624</td>
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<td>2</td>
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<td>2</td>
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<td>-0.2232</td>
</tr>
</tbody>
</table>

≠ Coefficients are rounded off to the fourth decimal place.
torted wave approximation in more detail. For two states with approximately the same values of the wave number \((k_{\alpha} \approx k_{\alpha'})\) and matrix element, the wave functions \(g_{\gamma}^J\) and \(g_{\gamma'}^J\) are nearly in phase and therefore constructively interfere over most of the domain of the integral. On the other hand, for states with widely differing wave numbers \((k_{\alpha}/k_{\alpha'} \gg 1)\), the wave functions \(g_{\gamma}^J\) and \(g_{\gamma'}^J\) are considerably out of phase and constructively interfere over a much smaller domain. Thus, the integral in Eq. (2.43b) for the case of widely separated levels is smaller than that for closely spaced ones. Therefore, we expect the partial rotational excitation cross sections \(\sigma^J(0\rightarrow j')\), which are calculated from this integral, to decrease in magnitude as the value of \(j'\) increases, since \(k_0/k_1 < k_0/k_2 < k_0/k_3\). This is exactly the behavior of the cross sections shown in Fig. 11. Thus, the relative ordering of the cross sections for transitions from the ground rotational state can be understood in terms of the relative strength of the coupling matrix elements and spacing of the rotor levels.

In Fig. 11 and Table 6b, we display the dependence of the partial rotational excitation cross sections on the manner in which the short- and long-range potential energy surfaces are joined. We consider three models in which the long-range potential energy surface is truncated [see Eq. (5.34)] at: a) very small atom-molecule separations, \(R_o \ll 1\), \(m = 6\), b) \(R_o = 5.0\ a_o\), \(m = 6\), and
Table 6b. Comparison of Cross Sections for Various Model Interaction Surfaces: He-HF

<table>
<thead>
<tr>
<th>J</th>
<th>$\sigma^J(0-1)$ (a)</th>
<th>$\sigma^J(0-2)$ (a)</th>
<th>$\sigma^J(0-3)$ (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(b)</td>
<td>(c)</td>
<td>(b)</td>
</tr>
<tr>
<td>4</td>
<td>0.168</td>
<td>0.202</td>
<td>0.226</td>
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<tr>
<td>8</td>
<td>0.308</td>
<td>0.366</td>
<td>0.414</td>
</tr>
<tr>
<td>12</td>
<td>0.412</td>
<td>0.480</td>
<td>0.556</td>
</tr>
<tr>
<td>16</td>
<td>0.418</td>
<td>0.476</td>
<td>0.574</td>
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<tr>
<td>20</td>
<td>0.258</td>
<td>0.289</td>
<td>0.379</td>
</tr>
<tr>
<td>24</td>
<td>0.038</td>
<td>0.046</td>
<td>0.083</td>
</tr>
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</table>

$\neq$ All cross sections are in units of $a_o^2$. The scattering parameters are as follows: $E = 0.05 \text{ eV}$, $\mu = 6120.0$, the basis in (0-3), the starting radius is $3.0 a_o$, $R_{\text{max}} = 20.0 a_o$, $\Delta = 0.01 a_o$, and the rotational constant is given in Table 3. The short- and long-range interaction surface parameters for He-HF are given in Table 1. The long-range cut-off parameters are as follows:
(a) $R_o \ll 1$; (b) $R_o = 5.0 a_o$, $m = 6$; (c) $R_o = 6.0 a_o$, $m = 6$. 
c) $R_o = 6.0 \ a_o$, $m = 6$. Since the long-range potential energy surface is attractive, the greater the range over which the long-range potential is allowed to penetrate the repulsive short-range region, the smaller the magnitude of the resulting total potential energy surface. The radial expansion coefficients of the potential energy surface are therefore largest for model (c) and smallest for model (a). Since larger non-spherical coefficients can provide greater coupling, the partial cross sections are expected to increase in magnitude in going from model (a) to (c). The differences between partial cross sections for a particular transition for different models of the long-range cut-off are less than twenty-five percent (25%), indicating that the rotational excitation cross section for (He-HF) are relatively insensitive to the manner in which the long- and short-range interaction surfaces are joined.

We next investigate the behavior of the partial cross sections at a higher energy. In Fig. 12, we present the rotational excitation cross sections for transitions between the ground state and the lowest three excited states at an energy of 0.10 eV. Since the energy is higher, the helium atom can penetrate deeper into the region of strong coupling where the non-spherical interaction coefficients are larger. The total excitation cross section is therefore expected to be larger for the case of a higher incident energy (see Table 9). The greater strength of the
Fig. 12 Partial rotational excitation cross sections at $E = 0.10$ eV for He-HF: transitions from the ground state.
potential also means that more channels are coupled. For this reason, we must use a larger basis at 0.10 eV than was required at 0.05 eV in order to guarantee the convergence of the partial cross sections. Since the lowest vibrational level of the hydrides that we consider is well above 0.15 eV, we include only rotational states in our bases. The partial cross sections at 0.10 eV peak at larger values of J than those at 0.05 eV. The total angular momentum J is related to an orbital angular momentum ℓ of the incident particle. As the orbital angular momentum increases, the centrifugal barrier, given by the second term in Eq. (2.12) becomes more repulsive. The growth in the magnitude of the repulsive barrier acts to "exclude" the incident particle from the region of strong coupling. Since a higher energy particle can penetrate a more repulsive centrifugal barrier, we expect contributions from higher values of J to be more important for higher incident energies. This behavior can be seen by comparing Figs. 11 and 12. According to our simple model, the maximum value of J increases as the square root of the energy [see Eq. (6.1)]. For the He-HF system in the case of direct contact interactions, an incident energy of 0.10 eV corresponds to a $J_{\text{max}}$ of fourteen. Since He and HF interact by a potential, the value of $J_{\text{max}}$ is somewhat larger than fourteen. From Table 7 we observe that the actual maximum in the partial cross section $\sigma^J(0-1)$ occurs
near a J of twenty. However, the relative increase of \( J_{\text{max}} \) from 10 to 14 as the energy is increased from 0.05 eV to 0.10 eV is in good agreement with the actual shift from 16 to 20. The relative ordering of the various cross sections can be explained by the same simple model invoked at 0.05 eV.

In Fig. 13, we display the partial rotational excitation cross sections for transitions among the three lowest excited levels of HF at 0.10 eV. Explanation of the relative ordering of these cross sections is much more complicated, since several radial expansion coefficients are coupled for each transition and the relative incident energies are different for cross sections corresponding to different initial states (recall that \( E \) is always the energy relative to \( j = 0 \)). Nevertheless, we can qualitatively understand the relative ordering of the cross sections from the models we have introduced. In the distorted wave treatment, the partial cross section \( \sigma^J(1-2) \) is determined from matrix elements which depend on \( v_1, v_2, \) and \( v_3, \) while the cross section \( \sigma^J(1-3) \) is determined by matrix elements involving \( v_2, v_3, \) and \( v_4. \) Since the expansion coefficient \( v_1 \) is much larger than \( v_4, \) the matrix elements for the transition (1-2) are larger than those for the transition (1-3). Therefore, for the same value of \( J, \) we expect the partial cross section \( \sigma^J(1-2) \) to be larger than the partial cross section \( \sigma^J(1-3). \) We are
Fig. 13 Partial rotation excitation cross sections at $E = 0.10$ eV for He-HF: excited state transitions.
also led to expect this ordering to be favored by the fact that the ratio of the wave numbers associated with the transition (1-3) is larger than that for the transition (1-2). The partial cross section $\sigma^J(2-3)$ is determined by matrix elements depending on $v_1$, $v_2$, $v_3$, $v_4$ and $v_5$. Since the matrix elements for the transition (2-3) depend on the same dominant expansion terms $v_1$, $v_2$, and $v_3$ as the transition (1-2) and both transitions have wave numbers in approximately the same ratio, the partial cross section $\sigma^J(2-3)$ is of approximately the same magnitude as the cross section $\sigma^J(1-2)$. We repeat that this explanation is qualitative and that in general the actual ordering is a consequence of complicated interactions between all coupled channels.

We have also performed calculations of the partial rotational excitation cross sections for collisions between He and HF in the $j_z$-conserving coupled state formulation. In Tables 7 and 8, we compare the partial rotational excitation cross sections at 0.10 eV for transitions between the lowest four rotor levels calculated by the coupled channel (CCCC) and coupled state (JZCS) methods. The agreement between partial cross sections calculated by these two methods is quite good for all transitions, and the total excitation cross sections agree to within a few percent. We recall that in the CCCC approach each rotor state, designated by the rotational quantum number $j$, can
Table 7. Comparison JZCS and CCCC Partial Cross Sections: He-HF

<table>
<thead>
<tr>
<th>J</th>
<th>( \sigma^J_{(0-1)} ) (JZCS)</th>
<th>( \sigma^J_{(0-2)} ) (JZCS)</th>
<th>( \sigma^J_{(0-3)} ) (JZCS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.044</td>
<td>0.036</td>
<td>0.015</td>
</tr>
<tr>
<td>4</td>
<td>0.083</td>
<td>0.061</td>
<td>0.027</td>
</tr>
<tr>
<td>8</td>
<td>0.159</td>
<td>0.113</td>
<td>0.052</td>
</tr>
<tr>
<td>12</td>
<td>0.237</td>
<td>0.158</td>
<td>0.076</td>
</tr>
<tr>
<td>16</td>
<td>0.311</td>
<td>0.185</td>
<td>0.093</td>
</tr>
<tr>
<td>20</td>
<td>0.364</td>
<td>0.179</td>
<td>0.096</td>
</tr>
<tr>
<td>24</td>
<td>0.355</td>
<td>0.129</td>
<td>0.080</td>
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<tr>
<td>28</td>
<td>0.246</td>
<td>0.054</td>
<td>0.047</td>
</tr>
<tr>
<td>32</td>
<td>0.083</td>
<td>0.007</td>
<td>0.015</td>
</tr>
</tbody>
</table>

All cross sections are in units of \( a_0^2 \). The reduced mass is 6120.0, the basis is (0-4), the starting value is 3.0 \( a_0 \), the matching radius \( R_{\text{max}} \) is 20.0 \( a_0 \), the step size is 0.01 \( a_0 \), and the rotation constant \( B \) is given in Table 3. The potential parameters are given in Table 1 with \( R_0 \ll 1 \). The CCCC calculations include both odd and even parity cases, and the JZCS calculations are for all \( m_j \leq 2 \).
Table 8. Comparison JZCS and CCCC Partial Cross Sections: He-HF

<table>
<thead>
<tr>
<th>J</th>
<th>$\sigma^J(1\rightarrow2)$</th>
<th>$\sigma^J(1\rightarrow3)$</th>
<th>$\sigma^J(2\rightarrow3)$</th>
</tr>
</thead>
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<tr>
<td></td>
<td>CCCC</td>
<td>JZCS</td>
<td>CCCC</td>
</tr>
<tr>
<td>12</td>
<td>0.244</td>
<td>0.243</td>
<td>0.117</td>
</tr>
<tr>
<td>16</td>
<td>0.317</td>
<td>0.319</td>
<td>0.129</td>
</tr>
<tr>
<td>20</td>
<td>0.353</td>
<td>0.363</td>
<td>0.111</td>
</tr>
<tr>
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<tr>
<td>28</td>
<td>0.193</td>
<td>0.203</td>
<td>0.028</td>
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</table>

* All cross sections are in units of $a_0^2$. The scattering parameters used in these calculations are the same as those of Table 7.

* The incident energy with respect to the following states is: 0.10 eV ($j = 0$), 0.0948 eV ($j = 1$), and 0.0844 eV ($j = 2$).
give rise to a number of scattering channels \((j\ell)\) which are labeled not only by \(j\) but also by the orbital angular momentum quantum number \(\ell\) of the incident atom. The channels associated with a particular rotor state are coupled to the channels of another state by terms which depend on the values of \(j\) and \(\ell\) for the initial and final channels [see Eq. (2.32)]. In the \(J_z\)-conserving coupled state method, the terms which couple the various channels associated with one rotor state to those of another state are approximated by a single effective coupling term that directly couples the two states and that depends only on the rotational quantum number \(j\) of the initial and final states [see Eq. (3.20")]. Thus, the multiple couplings between channels are replaced by an effective coupling between states. The agreement between the cross sections calculated by these two methods indicates that the coupling between the various channels in the CCCC methods is being modeled by the effective coupling between the various states in the JZCS method. The differences between the JZCS and CCCC partial cross sections become more pronounced for transitions involving the higher excited states. Since the higher excited states are characterized by larger values of the rotational angular momentum \(j\), in the CCCC formulation, these levels have a larger number of associated channels. The single effective coupling term of the JZCS formulation connecting two rotor states one or both of which
is highly excited must therefore approximate a larger number of channel coupling terms than the effective coupling term between low-lying states with few associated channels. Therefore, it is not surprising that the JZCS method is less accurate for transitions involving highly excited states. Although the JZCS method gives cross sections in excellent agreement with those of the CCCC method for the He-HF system, there are no well established criteria under which the JZCS method can be guaranteed to yield accurate results for other systems. We, therefore, recommend that the \( j_z \)-conserving method be used as a means of very rapidly and economically calculating a large number of partial rotational excitation cross sections for a system once the JZCS results have been checked at selected values of \( J \) with those of a coupled channel method.

The total rotational excitation cross sections for collisions between He and HF are presented in Table 9 as a function of energy (c.m.) above the ground rotational state \( (j = 0) \). The partial excitation cross sections for both even and odd parities were calculated at even values of \( J \). The partial cross sections at odd values of \( J \) were found by graphically extrapolating the even \( J \) results. The total cross section at a particular energy was then determined by summing the exact even \( J \) and extrapolated odd \( J \) partial excitation cross sections. From Table 9 we observe that the total rotational excitation cross sections
Table 9. Rotational Excitation Cross Sections  

\textit{vs} Energy: He-HF*  

<table>
<thead>
<tr>
<th>E (eV)</th>
<th>(\sigma(0\rightarrow1))</th>
<th>(\sigma(0\rightarrow2))</th>
<th>(\sigma(0\rightarrow3))</th>
<th>(\sigma(1\rightarrow2))</th>
<th>(\sigma(1\rightarrow3))</th>
<th>(\sigma(2\rightarrow3))</th>
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<td>0.017</td>
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<tr>
<td>0.025</td>
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<tr>
<td>0.050</td>
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<td>0.100</td>
<td>7.5</td>
<td>3.5</td>
<td>2.0</td>
<td>7.0</td>
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<td>6.3</td>
</tr>
<tr>
<td>0.150</td>
<td>7.4</td>
<td>4.4</td>
<td>2.7</td>
<td>7.2</td>
<td>3.3</td>
<td>7.1</td>
</tr>
</tbody>
</table>

*The scattering and potential parameters are the same as those of Table 6 except that the following basis is associated with each energy: \((0\rightarrow3)\) for 0.017 eV, 0.025 eV, and 0.05 eV, \((0\rightarrow4)\) for 0.10 eV, and \((0\rightarrow5)\) for 0.15 eV. All cross sections were calculated in the CCCC formulation. The incident energy \(E\) is defined with respect to the ground state \((j = 0)\). The incident energy relative to the excited states can be found by subtracting from \(E\) the following level energies: 0.0052 eV for \(j = 1\), 0.0156 eV for \(j = 2\), and 0.0312 eV for \(j = 3\).
as a function of energy rise rapidly from their threshold values and then gradually level off. We may understand this behavior in terms of a semi-classical model. The trajectory of the incident atom is mainly determined by the expansion term $v_0(R)$. The atom "moves along $v_0(R)$" until it arrives at the classical turning point (CTP), where the repulsive potential and incident kinetic energies are equal, at which point it reverses and then moves back along $v_0(R)$. The higher the incident energy, the smaller the magnitude of the CTP and therefore the closer the approach of the atom and molecule. The magnitudes of both the spherical term $v_0$ and the anisotropic expansion terms which provide the coupling between channels increase as the atom-molecule separation decreases. Thus, the closer the approach of the atom, the stronger are the coupling coefficients. Since stronger coupling coefficients make for larger rotational cross sections, we expect the cross sections to rise as the incident energy increases. This trend is off-set by two other processes. First, since the expansion coefficients of the short-range potential energy surface increase exponentially with decreasing atom-molecule separation $R$, eventually a region is encountered in which large increases in the incident kinetic energy change the CTP and therefore the magnitude of the non-spherical radial expansion coefficients by only small amounts. Since the cross section is directly proportional
to the coupling matrix elements which depend on the radial expansion coefficients and inversely proportional to the energy, the cross section for this case would be expected to level off or even decrease for increasing energies. A second effect which tends to oppose the rapid increase of the cross section with energy is the strong competition between the coupled channels. At low energies, the distance of closest approach is large and only the lowest few channels are substantially coupled. However, as the energy rises, the magnitude of the coupling matrix elements increases and a greater number of channels are coupled. Since the sum of the probabilities for excitation to other channels from a given channel is a constant [see Eq. (2.19c)], the more channels that must be included in the sum, the smaller the individual probabilities. Thus, the cross section for transitions between low-lying states is expected to level off or even decrease with increasing energy due to the competition from the strongly coupled higher excited states. The interplay of these three processes leads to the behavior of the total cross section similar to that displayed in Table 9. Finally, we note that the rotational excitation cross sections involving the higher excited states are not negligible as in the case of He-H₂. In fact, the importance of these cross sections grows with increasing energy. Thus, the transitions to the higher excited states of HF must be included in any model study of kinetics of the HF laser, for example.
...What further inferences can we draw?'
'Do none suggest themselves? You know my methods.
Apply them!'

Sherlock Holmes to Dr. Watson, The Hound of the Baskervilles

2) He-DF Collisions

In this subsection, we present the results of calculations of the rotational excitation cross sections for collisions between ground state helium atoms and deuterium fluoride (DF). We use for the He-DF interaction surface that of He-HF with the cut-off parameters $R_o = 5.0 \, a_o$ and $m = 6$ (see Fig. 8 and Table 1). In the Born-Oppenheimer approximation, the electronic potential energy depends only on the charge of the nuclei, and the He-HF and He-DF surfaces are identical. The two surfaces differ only when correction terms are introduced which couple the nuclear and electronic motions. These corrections are usually small, and we have ignored them in this treatment. Since the interaction surfaces are the same, the coupling matrix elements $U^\gamma_\gamma$, connecting channels or states of the He-DF system are the same as those which connect corresponding channels or states of the He-HF system. However, DF has a moment of inertia almost twice as large as HF, and therefore, the rotational levels of DF have a much smaller separation than those of HF (see Fig. 10).

We first present a rather detailed discussion of the partial excitation cross sections at 0.05 eV and then briefly
discuss the energy dependence of the total cross sections. We formulate our discussion in terms of several of the models developed in the previous subsection, with special emphasis placed on explaining the differences between corresponding cross sections of the He-DF and He-HF systems.

In Fig. 14, we present the partial rotational excitation cross sections for transitions between the ground and lowest three excited states for collisions between He and DF at an energy (c.m.) of 0.05 eV. The general behavior of the partial cross sections closely resembles that of He-HF. In fact, the arguments we made about the general shape and relative ordering of the partial cross sections for He-HF apply equally well to the He-DF system since the potential energy surfaces are identical and the ratios of the ground state wave number to those of the excited states are in the same relative order [i.e., \( k_0/k_1 < k_0/k_2 < k_0/k_3 \)]. However, compared to the He-HF system the partial cross sections for the transitions (0→2) and (0→3) are larger in magnitude relative to the partial cross section for the transition (0→1). Since the coupling matrix elements are the same for the two systems, the explanation for the comparatively larger cross sections for the transitions (0→2) and (0→3) must lie in the reduced spacing of the DF energy levels. The excited levels of DF lie lower in energy (relative to the
Fig. 14  Partial rotational excitation cross sections at $E = 0.05$ eV for He-DF: transitions from the ground state.
ground state) than the corresponding levels of HF (see Fig. 10), and therefore, the differences between the wave numbers associated with the excited states of DF are smaller than those associated with the excited states of HF. In the distorted wave approximation, the smaller the difference in the values of the wave numbers associated with the initial and final states, the more constructively their corresponding wave functions interfere in the integral in Eq. (2.43b) and the larger the resulting cross section. Therefore, the partial cross sections for He-DF are larger than the corresponding cross sections for He-HF. Since the rotational energy increases approximately as the square of the rotational angular momentum \( j \), the energy difference between the third excited states \( (j = 3) \) of HF and DF is greater than that between the lowest excited states \( (j = 1) \) of the two molecules. We therefore expect the cross section for the transition \( (0\rightarrow3) \) to be affected the most by the change in the level spacing. Thus, the rotational excitation cross sections for DF compared with those of HF should increase in magnitude most for the transition \( (0\rightarrow3) \) and least for the transition \( (0\rightarrow1) \). This is exactly the behavior we observe in comparing Figs. 14 and 11.

In Fig. 15, we present the partial rotational excitation cross sections for transitions \( (1\rightarrow2) \), \( (1\rightarrow3) \) and \( (2\rightarrow3) \) for collisions between He and DF at
Fig. 15 Partial rotational excitation cross sections at $E = 0.05$ eV for He-DF: excited state transitions.
<table>
<thead>
<tr>
<th>J</th>
<th>σ_J^{(0-1)} CCC</th>
<th>σ_J^{(0-1)} JZCS</th>
<th>σ_J^{(0-2)} CCC</th>
<th>σ_J^{(0-2)} JZCS</th>
<th>σ_J^{(0-3)} CCC</th>
<th>σ_J^{(0-3)} JZCS</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.194</td>
<td>0.193</td>
<td>0.104</td>
<td>0.105</td>
<td>0.056</td>
<td>0.058</td>
</tr>
<tr>
<td>8</td>
<td>0.353</td>
<td>0.350</td>
<td>0.175</td>
<td>0.176</td>
<td>0.100</td>
<td>0.104</td>
</tr>
<tr>
<td>12</td>
<td>0.465</td>
<td>0.463</td>
<td>0.196</td>
<td>0.197</td>
<td>0.125</td>
<td>0.133</td>
</tr>
<tr>
<td>16</td>
<td>0.469</td>
<td>0.469</td>
<td>0.147</td>
<td>0.146</td>
<td>0.118</td>
<td>0.121</td>
</tr>
<tr>
<td>20</td>
<td>0.297</td>
<td>0.299</td>
<td>0.050</td>
<td>0.049</td>
<td>0.078</td>
<td>0.058</td>
</tr>
<tr>
<td>24</td>
<td>0.054</td>
<td>0.051</td>
<td>0.004</td>
<td>0.003</td>
<td>0.025</td>
<td>0.007</td>
</tr>
</tbody>
</table>

All cross sections in units of a_0^2. The scattering parameters are: E = 0.05 eV, μ = 6168.96, the basis is (0-4), the starting value is 3.0 a_0, R_max = 20.0 a_0, Δ = 0.01 a_0, the rotational constant is given in Table 3. The interaction surface is that of He-HF given by Table 1 with R_0 = 5.0 a_0 and m = 6. The CCCC cross sections include contributions from both odd and even parities, and the JZCS cross sections include contributions for m_j ≤ 2.
Table 11. Comparison JZCS and CCCC Partial Cross Sections: He-DF

<table>
<thead>
<tr>
<th>J</th>
<th>$\sigma^J(1\rightarrow 2)$</th>
<th>$\sigma^J(1\rightarrow 3)$</th>
<th>$\sigma^J(2\rightarrow 3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CCCC</td>
<td>JZCS</td>
<td>CCCC</td>
</tr>
<tr>
<td>4</td>
<td>0.173</td>
<td>0.172</td>
<td>0.075</td>
</tr>
<tr>
<td>8</td>
<td>0.313</td>
<td>0.313</td>
<td>0.122</td>
</tr>
<tr>
<td>12</td>
<td>0.406</td>
<td>0.410</td>
<td>0.130</td>
</tr>
<tr>
<td>16</td>
<td>0.389</td>
<td>0.403</td>
<td>0.090</td>
</tr>
<tr>
<td>20</td>
<td>0.226</td>
<td>0.237</td>
<td>0.031</td>
</tr>
</tbody>
</table>

* All cross sections in units of $a_0^2$. The scattering and potential parameters are the same as those of Table 10. The incident energy relative to the following states is: 0.05 eV ($j = 0$), 0.0473 eV ($j = 1$), 0.0418 eV ($j = 2$), and 0.0336 eV ($j = 3$).
E = 0.05 eV. The relative ordering can be explained by arguments similar to those used for the He-HF system; the increased importance of certain of these cross sections can be understood through arguments similar to those presented in this subsection.

We have also performed calculations of the partial rotational excitation cross sections for collisions between He and DF in the $j_z$-conserving coupled state approximation. In Tables 10 and 11, we compare the results of calculations in the CCCC and JZCS formulations at an energy of 0.05 eV. The good agreement between the two sets of cross sections indicates that for this intermediate coupling case, the coupling matrix elements of the JZCS formulation between states are effectively modeling the coupling matrix elements in the CCCC formulation between channels. We also observe the trend toward larger differences in the partial cross sections of the two formulations for transitions involving the higher excited states.

Finally, in Table 12, we present the total rotational excitation cross sections as a function of energy calculated in the CCCC formulation. The total cross sections were calculated in the same manner as those for He-HF by summing the partial cross sections obtained from calculations and graphical extrapolation. The rise in the total cross sections with increasing energy can be explained along the same lines of argument as with the He-HF system. Again, we
<table>
<thead>
<tr>
<th>$E$ (ev)</th>
<th>$\sigma^J(0-1)$</th>
<th>$\sigma^J(0-2)$</th>
<th>$\sigma^J(0-3)$</th>
<th>$\sigma^J(1-2)$</th>
<th>$\sigma^J(1-3)$</th>
<th>$\sigma^J(2-3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>5.3</td>
<td>1.2</td>
<td>0.8</td>
<td>4.2</td>
<td>0.6</td>
<td>2.5</td>
</tr>
<tr>
<td>0.05</td>
<td>7.5</td>
<td>2.8</td>
<td>2.0</td>
<td>6.3</td>
<td>1.8</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The potential and scattering parameters are the same as those for Table 10. All cross sections were calculated in the CCCC formulation. The incident energy with respect to the ground rotational state $(j = 0)$ is given by $E$. The incident energy relative to the excited states can be found by subtracting from $E$ the following rotor level energies: 0.00273 eV for $j = 1$, 0.00819 eV for $j = 2$, and 0.0164 eV for $j = 3$. 
note the importance of transitions to the higher excited states and emphasize the need to include these excited state transitions in model studies of such systems as lasers.

3) He-HCl Collisions

In this subsection, we present and discuss the results of calculations of rotational excitation cross sections for excitations of the lowest few rotor levels of hydrogen chloride (HCl) by collisions with ground-state helium atoms. The He-HCl interaction surface (see Fig. 9) exhibits a strong anisotropy, with the expansion coefficient $v_3$ being somewhat larger and the other important non-spherical terms $v_1$, $v_2$, and $v_4$ being somewhat smaller than the spherical term $v_0$ over much of the short-range region (0 to $\sim 6.0\ a_0$). This strong anisotropy provides strong coupling between the scattering channels. The rotational spectrum of HCl is similar to that of DF (see Fig. 10) since the moments of inertia of the two molecules are approximately equal. The study of collisions of He with HF, DF, and HCl provide the opportunity to compare respectively two systems with the same coupling matrix elements but with different rotational spectra (viz. HF and DF) and two systems with different coupling matrix elements but with approximately the same rotational spectra (viz. DF and HCl). We have already discussed the former cases in subsection 2), and we shall consider the
latter case in detail in this subsection. We discuss first the behavior of the partial rotational cross sections at several energies and then the energy dependence of the total rotational cross sections.

In Fig. 16, we present the partial rotational excitation cross sections for transitions between the ground and lowest two excited states for collisions between He and HCl at an energy of 0.015 eV. Since the radial expansion coefficients \( v_1 \) and \( v_2 \) are approximately equal in magnitude and the ratios of the wave numbers exhibit the relationship \( k_0/k_1 < k_0/k_2 \), the relative ordering of the cross sections can be explained by arguments similar to those of subsections 1) and 2). However, unlike the previous cases, the partial cross section for the transition (0-1) has a strong secondary maximum.\(^{12}\) This behavior is due to quantum mechanical interference between the various channel wave functions. We discuss this example to emphasize our earlier caveat that although simple models can give a rather good qualitative description of the scattering processes, there are certain effects which arise from the complicated interplay of the various coupled channels and are difficult to model in a simple fashion. We can gain some insight into these effects by noting that the partial cross sections for large values of \( J \) are determined mainly by the attractive long-range potential energy since the large repulsive
Fig. 16  Partial rotational excitation cross sections at $E = 0.015$ eV for He-HCl: transitions from the ground state.
centrifugal barrier prevents the incident atom from deeply penetrating the short-range region.\textsuperscript{13} On the other hand, due to the small magnitude of the centrifugal barrier for small values of $J$, the partial cross sections at such $J$ values are determined by the repulsive short-range interaction surface. The effect of a repulsive (attractive) potential is to push the scattered wave function out (in) so that the nodes of the scattered wave function lie exterior (interior) to those of the unscattered function. For intermediate $J$ values, the partial cross sections are determined by both the long- and short-range contributions to the interaction surface. The influence of one region on the wave function can be cancelled by that of the other, leading to a minimum in the partial cross section.\textsuperscript{8}

In Fig. 17, we display the partial cross sections for transitions between the ground and lowest three excited rotor states for collisions between He and HCl at an energy of 0.025 eV. Since the rotational spectrums of DF and HCl are similar, the greater magnitude of the cross section $\sigma^J(0\rightarrow 3)$ for He-HCl compared to He-DF can be viewed in the distorted wave approximation as arising from the relatively larger radial expansion coefficient $v_3$ of the He-HCl surface. Since the $v_3$ coefficient is larger than either $v_1$ or $v_2$ over most of the short-range region (see Fig. 9), we might expect the cross section
Fig. 17 Partial rotational excitation cross sections at $E = 0.025$ eV for He-HCl: transitions from the ground state.
$\sigma^J_{(0-3)}$ to be even larger compared to those for the transitions (0-1) and (0-2) than it appears in Fig. 17. However, the decrease in the size of the Percival-Seaton coefficients for increasing rotational angular momentum and the greater difference between the ground and higher excited-state wave numbers tend to oppose this trend. The competition between these effects leads to the ordering of the partial cross sections observed in Fig. 17.

We also performed calculations of the rotational excitation cross sections for collisions between He and HCl in the JZCS formulation. The results of these calculations are given in Table 13 for an energy of 0.025 eV. Although the agreement between the partial cross sections determined in these two formulations is good, the JZCS cross sections are not as accurate as in the case of He-HF. Kouri and McGuire\textsuperscript{14} have shown that for the strongly coupled Li$^+$-H$_2$ system a choice of $(J-j)(J-j+1)$ for the constant of the centrifugal term of Eq. (3.19') rather than $J(J+1)$ leads to much better agreement between the JZCS and CCCC cross sections. We have calculated cross sections for the He-HCl system in the JZCS formulation for both choices of centrifugal constant and have found that the choice of $J(J+1)$ gives cross sections in better agreement with CCCC results. The system He-HCl represents an intermediate case between the weakly coupled He-HF system and the strongly coupled Li$^+$-H$_2$ system. Like the
Table 13. Comparison CCCC and JZCS Partial Cross Sections:

He-HCl²

<table>
<thead>
<tr>
<th>J</th>
<th>(\sigma^J(0-1)) CCCC</th>
<th>(\sigma^J(0-1)) JZCS</th>
<th>(\sigma^J(0-2)) CCCC</th>
<th>(\sigma^J(0-2)) JZCS</th>
<th>(\sigma^J(0-3)) CCCC</th>
<th>(\sigma^J(0-3)) JZCS</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.0263</td>
<td>0.256</td>
<td>0.158</td>
<td>0.164</td>
<td>0.128</td>
<td>0.142</td>
</tr>
<tr>
<td>8</td>
<td>0.479</td>
<td>0.462</td>
<td>0.229</td>
<td>0.231</td>
<td>0.201</td>
<td>0.215</td>
</tr>
<tr>
<td>12</td>
<td>0.596</td>
<td>0.581</td>
<td>0.200</td>
<td>0.194</td>
<td>0.197</td>
<td>0.170</td>
</tr>
<tr>
<td>16</td>
<td>0.430</td>
<td>0.428</td>
<td>0.089</td>
<td>0.102</td>
<td>0.102</td>
<td>0.023</td>
</tr>
<tr>
<td>20</td>
<td>0.040</td>
<td>0.033</td>
<td>0.008</td>
<td>0.013</td>
<td>0.005</td>
<td>--</td>
</tr>
</tbody>
</table>

² All cross sections are in units of \(a_0^2\). The scattering parameters are as follows: \(E = 0.025\) eV, \(\mu = 6609.6\), the starting radius is \(3.0\ a_0\), \(R_{\text{max}} = 20.0\ a_0\), \(\Delta = 0.01\ a_0\), the basis is \((0-4)\), and the rotation constant is given in Table 3. The long- and short-range potential energy surfaces are given in Table 1, and the total surface is determined by \(R = 5.0\ a_0\) and \(m = 12\). The CCCC cross sections include contributions from both even and odd parities, and the JZCS cross sections include contributions for \(m_j \leq 2\).
latter system, one of the anisotropic radial expansion coefficients for the He-HCl surface is larger than the spherical term; however, like the former system, the terms of smaller magnitude, \( v_1, v_2, \) and \( v_4 \), also play important roles in the coupling. These properties, together with the fact that the Li\(^+\)-H\(_2\) system is coupled by much larger long-range terms, suggest that a choice of centrifugal constant for the He-HCl system similar to that of the He-HF system is more appropriate. As in the case of HF and DF, we observe that the JZCS partial cross sections are in better agreement with the CCCC results for transitions involving the lower excited states. The cross section \( \sigma^J(0\rightarrow3) \) provides an interesting example. While the JZCS method overestimates the partial cross section at small values of \( J \) and underestimates it at large values of \( J \), the resulting total cross section \( \sigma(0\rightarrow3) \) is within five percent of the total cross section calculated in the CCCC formulation. This good agreement indicates that the JZCS method might be used to calculate accurate total cross sections for systems resembling He-HCl.

Finally, the total rotational excitation cross sections as a function of energy are given in Table 14. The behavior of the various total cross sections can be explained by arguments similar to those given for the other systems. The larger magnitude of the total cross sections
Table 14. Total Rotational Excitation Cross Sections vs Energy: He-HC₅H₄

<table>
<thead>
<tr>
<th>E (ev)</th>
<th>$\sigma^J(0\rightarrow1)$</th>
<th>$\sigma^J(0\rightarrow2)$</th>
<th>$\sigma^J(0\rightarrow3)$</th>
<th>$\sigma^J(1\rightarrow2)$</th>
<th>$\sigma^J(1\rightarrow3)$</th>
<th>$\sigma^J(2\rightarrow3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a₀²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.015</td>
<td>6.3</td>
<td>1.3</td>
<td>--</td>
<td>7.6</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.025</td>
<td>7.2</td>
<td>2.9</td>
<td>2.6</td>
<td>10.1</td>
<td>1.8</td>
<td>7.6</td>
</tr>
<tr>
<td>0.050</td>
<td>8.3</td>
<td>6.5</td>
<td>5.0</td>
<td>11.4</td>
<td>4.6</td>
<td>12.2</td>
</tr>
</tbody>
</table>

The potential and scattering parameters are the same as those for Table 13 except that a basis (0-5) is used at E = 0.05 eV. Unless otherwise indicated, total cross sections were calculated in the CCCC formulation. The incident energy with respect to the ground rotational state (j = 0) is given by E. The incident energy relative to the excited states can be found by subtracting from E the following rotor level energies: 0.0027 eV for j = 1, 0.0079 eV for j = 2, and 0.0158 eV for j = 3.

a All total cross sections for the transitions (1→2), (1→3), and (2→3) were calculated by the JZCS method.

b All total cross sections at E = 0.05 eV were calculated in the JZCS formulation.
for He-HCl as compared with He-HF is due mainly to the stronger coupling provided by the Hd-HCl interaction surface.

4) He-DCl Collisions

The results of calculations of rotational excitation cross sections for excitations of the lowest three rotor levels of DCl by collisions with ground state He atoms are discussed in this subsection. The interaction surface for He-DCl is the same as that for He-HCl (see Fig. 9). The surface is strongly anisotropic and therefore provides for strong coupling between the channels. The energy levels of DCl are more closely spaced than those of HCl, giving them the smallest separation of the four hydride systems considered in this thesis. We are interested in the effects of this smaller separation on the cross sections for excitations of DCl as compared with those for HCl. As before, we first discuss the behavior of the partial cross sections at a particular energy and then treat the energy dependence of the total rotational excitation cross sections.

In Fig. 18, we display the partial rotational excitation cross sections for transitions between the ground and lowest three excited states at an energy (c.m.) of 0.015 eV. We note that the cross section for the transition (0-3) is larger than that for the transition (0-1) for small values of J (J < 16). The closer spacing of
Fig. 18 Partial rotational excitation cross sections at $E = 0.015$ eV for $\text{He-DCl}$: transitions from the ground state.
the wave numbers associated with the excited states of
DCl differ in magnitude by less than those associated
with the corresponding excited states of HCl [e.g., at
$E = 0.025$ eV, $k_0/k_3$ is equal to $1.48$ for DCl and to $2.70$
for HCl]. The smaller difference between the excited
state wave numbers leads to less destructive interference
and therefore to the integral in Eq. (2.43b) being less
sensitive to the level spacing. Thus, for the case of
DCl, the ordering of the cross sections is mainly deter-
mined by the relative size of the coupling matrix elements.
We have already argued in subsection 3) that for the inter-
action surface of He-HCl, the matrix elements for the
transition (0-3) are larger than those for the transition
(0-1). We therefore expect from an argument based on the
distorted wave approximation that the partial cross sec-
tion $\sigma^J(0-3)$ is larger than $\sigma^J(0-1)$. We observe a double
maximum in the partial cross sections $\sigma^J(0-1)$ and $\sigma^J(0-2)$.
The origin of these secondary peaks can be understood in
terms of interference effects between the scattering chan-
nels. Because of this second peak, the total cross sec-
tion $\sigma(0-1)$ is approximately equal to $\sigma(0-3)$. Thus,
the relative ordering of the partial cross sections for
He-DCl can be understood in terms of the relative size
of the radial expansion coefficients of the interaction
surface and the spacing of the rotor levels.
Table 15. Comparison JZCS and CCC Partial Cross Sections: He-DCJ

<table>
<thead>
<tr>
<th>J</th>
<th>$\sigma^J_{(0-1)}$ (CCCC)</th>
<th>$\sigma^J_{(0-1)}$ (JZCS)</th>
<th>$\sigma^J_{(0-2)}$ (CCCC)</th>
<th>$\sigma^J_{(0-2)}$ (JZCS)</th>
<th>$\sigma^J_{(0-3)}$ (CCCC)</th>
<th>$\sigma^J_{(0-3)}$ (JZCS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.289</td>
<td>0.279</td>
<td>0.149</td>
<td>0.154</td>
<td>0.340</td>
<td>0.367</td>
</tr>
<tr>
<td>6</td>
<td>0.387</td>
<td>0.374</td>
<td>0.176</td>
<td>0.178</td>
<td>0.456</td>
<td>0.499</td>
</tr>
<tr>
<td>8</td>
<td>0.439</td>
<td>0.428</td>
<td>0.167</td>
<td>0.165</td>
<td>0.516</td>
<td>0.586</td>
</tr>
<tr>
<td>10</td>
<td>0.420</td>
<td>0.405</td>
<td>0.127</td>
<td>0.122</td>
<td>0.499</td>
<td>0.573</td>
</tr>
<tr>
<td>12</td>
<td>0.306</td>
<td>0.286</td>
<td>0.074</td>
<td>0.062</td>
<td>0.409</td>
<td>0.398</td>
</tr>
<tr>
<td>14</td>
<td>0.119</td>
<td>0.102</td>
<td>0.024</td>
<td>0.021</td>
<td>0.268</td>
<td>0.124</td>
</tr>
<tr>
<td>16</td>
<td>1.22(-4)</td>
<td>1.08(-3)</td>
<td>4.31(-3)</td>
<td>1.30(-3)</td>
<td>0.102</td>
<td>0.009</td>
</tr>
<tr>
<td>18</td>
<td>0.129</td>
<td>0.179</td>
<td>0.021</td>
<td>0.004</td>
<td>0.010</td>
<td>--</td>
</tr>
<tr>
<td>20</td>
<td>0.262</td>
<td>0.294</td>
<td>0.035</td>
<td>0.007</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>22</td>
<td>0.158</td>
<td>0.155</td>
<td>0.018</td>
<td>0.003</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>24</td>
<td>0.062</td>
<td>0.059</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>26</td>
<td>0.024</td>
<td>0.022</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

All cross sections are in units of $a_0^2$. The scattering parameters are as follows: $E = 0.015$ eV, $\mu = 6627.5$, the starting radius is $3.0 \ a_0$, $R_{\text{max}} = 20.0 \ a_0$, $\Delta = 0.01 \ a_0$, the basis is (0-4), and the rotation constant is given in Table 3. The potential parameters are those of He-HCl given in Table 1 with $R_p = 5.0 \ a_0$ and $m = 12$. All cross sections calculated by the CCC formulation include contributions from both even and odd parities. The cross sections in the JZCS formulation include all contributions for $m_j \leq 2$. 
Table 16. Comparison JZCS and CCCC Partial Cross Sections: He-DC<sub>x</sub> 

<table>
<thead>
<tr>
<th>J</th>
<th>( \sigma^J(1\rightarrow2) )</th>
<th>( \sigma^J(1\rightarrow3) )</th>
<th>( \sigma^J(2\rightarrow3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CCCC</td>
<td>JZCS</td>
<td>CCCC</td>
</tr>
<tr>
<td>4</td>
<td>0.487</td>
<td>0.487</td>
<td>0.137</td>
</tr>
<tr>
<td>8</td>
<td>0.744</td>
<td>0.767</td>
<td>0.149</td>
</tr>
<tr>
<td>12</td>
<td>0.561</td>
<td>0.607</td>
<td>0.068</td>
</tr>
<tr>
<td>16</td>
<td>0.109</td>
<td>0.113</td>
<td>0.007</td>
</tr>
<tr>
<td>20</td>
<td>0.091</td>
<td>0.051</td>
<td>--</td>
</tr>
<tr>
<td>24</td>
<td>0.002</td>
<td>0.014</td>
<td>--</td>
</tr>
</tbody>
</table>

* All cross sections are in units of \( a_o^2 \). The scattering and potential parameters are the same as those of Table 15. The incident energies relative to the following rotor states are: 0.015 (j = 0), 0.0137 (j = 1), 0.011 eV (j = 2), and 0.0069 eV (j = 3).
We have also calculated rotational excitation cross sections for He-DC\& in the JZCS formulation. In Tables 15 and 16 we compare the partial cross sections calculated in the CCCC and JZCS formulations at an energy (c.m.) of 0.015 eV. Although the agreement between the two sets of partial cross sections is good, the differences for DC\& are greater than those encountered in the other three systems. The greater differences probably arise from the greater effective coupling in the He-DC\& system due to its closer spaced energy levels and strongly anisotropic interaction surface. In Fig. 19 we compare the partial cross sections $\sigma^J(0-3)$ calculated in the CCCC and JZCS formulations. The JZCS method tends to overestimate the partial cross section at small $J$ values ($J < 12$) and underestimate it at large $J$ values. However, the total cross sections $\sigma(0-3)$ calculated from these two curves agree to within better than one percent [$\sigma(0-3)$ is equal to 5.6 $a_0^2$ for JZCS and to 5.7 $a_0^2$ for CCCC]. Thus, the total excitation cross sections calculated in the CCCC and JZCS can be in better agreement than the corresponding partial cross sections from which the total cross sections are calculated.

Finally, the energy dependence of the total rotational excitation cross sections for He-DC\& are given in Table 17. These cross sections exhibit the same general behavior as a function of energy as those of the other
Fig. 19 Comparison of partial cross sections $\sigma^J(0-3)$ at $E = 0.015$ eV for He-DCl calculated in the CCCC (solid line) and JZCS (dashed line) formulations.
Table 17. Total Rotational Excitation Cross Sections
vs Energy: He-DC<x>

<table>
<thead>
<tr>
<th>E (eV)</th>
<th>σ^J(0→1)</th>
<th>σ^J(0→2)</th>
<th>σ^J(0→3)</th>
<th>σ^J(1→2)</th>
<th>σ^J(1→3)</th>
<th>σ^J(2→3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>5.1</td>
<td>1.8</td>
<td>5.7</td>
<td>8.3</td>
<td>1.5</td>
<td>5.8</td>
</tr>
<tr>
<td>0.025</td>
<td>6.8</td>
<td>3.8</td>
<td>8.1</td>
<td>9.5</td>
<td>3.0</td>
<td>8.5</td>
</tr>
<tr>
<td>0.050^a</td>
<td>6.9</td>
<td>7.7</td>
<td>9.3</td>
<td>10.1</td>
<td>5.8</td>
<td>11.1</td>
</tr>
</tbody>
</table>

^ The potential and scattering parameters are the same as those of Table 15 except the basis (0-5) is used at E = 0.025 eV and the basis (0-7) at E = 0.050 eV. The incident energy relative to the ground rotational state (J = 0) is given by E. The incident energy relative to the excited states can be found by subtracting from E the following rotor level energies: 0.0013 eV for J = 1, 0.0040 eV for j = 2, and 0.0081 eV for j = 3.

^a All cross sections were calculated in the CCCC formulation except those at 0.050 eV which were obtained by the JZCS method.
hydride systems, and the explanation of this behavior is similar to that present in the other subsections.

In this section, we have presented the results of calculations of the partial and total rotational excitation cross sections in both the CCCC and JZCS formulations for collisions between ground state helium atoms and four diatomic hydrides. We have discussed these results in terms of simple models which emphasize the important features of the scattering processes. By comparing the cross sections of one system with the corresponding cross sections of another system, we have discovered certain trends in the cross sections which arise from changes in the interaction surfaces and spacings between the rotor levels. Finally, we have compared calculations of cross sections in the JZCS and CCCC formulations and found that the JZCS method provides a rapid, economic technique for calculating accurate total rotational excitation cross sections for the hydride systems under discussion.

The task of filling up the blanks I'd rather leave to you. The Mikado
Appendix A: Numerical Solution of a Set of Coupled Equations

A set of $N$ coupled differential equations of the form of Eq. (2.12') has a general numerical solution matrix $\mathbf{Y}(R)$ of dimension $N$. Each column vector represents one of the $N$ solutions which consists of a set of $N$ radial wave functions $\{Y_{\gamma'}(R) | \gamma' = 1, \ldots, N\}$. We have used $\mathbf{Y}$ to denote the solution rather than $u$ since numerical solutions of Eq. (2.12') need not, in fact generally do not, satisfy the asymptotic boundary conditions of Eq. (2.19). A numerical technique does not exist to start a solution to a set of coupled equations and guarantee a particular asymptotic behavior. From the choice of initial conditions, we can, however, guarantee that the solution vectors are linearly independent. Any general solution to Eq. (2.12') can then be constructed as a superposition of the linearly independent vector solutions as

$$
\begin{bmatrix}
Y_{\gamma 1} \\
u_{\gamma N} \\
\vdots \\
u_{\gamma 1} \\
u_{\gamma N}
\end{bmatrix} = \sum_{\sigma=1}^{N} a_{\sigma} 
\begin{bmatrix}
Y_{\gamma 1}^{\sigma} \\
\vdots \\
Y_{\gamma N}^{\sigma}
\end{bmatrix}.
$$

(A.1)

Thus, the proper scattering asymptotic solutions $\mathbf{u}$ can be obtained by forming the proper linear combination of the numerical solution vectors of $\mathbf{Y}$. The coefficients $\{a_{\sigma}\}$ can be trapped by forcing the asymptotic form of $\mathbf{u}$ on the
superposition of Eq. (A.1). In this manner, we obtain scattering wave functions with the proper asymptotic behavior from the numerical solutions of Eq. (2.12').
Appendix B. The Symmetric Top Wave Functions

In deriving the expressions for the angular integrals for the matrix elements of Chapter 2, we have used a particular choice for the rotational wave functions of a symmetric top rigid rotor and thus a particular convention for the rotation or D-matrices. We have selected the rotor wave functions of Brink and Satchler (Ref. 5, Ch. 2) which are expressed in terms of the D-matrices of Rose (Ref. 4, Ch. 2) as

\[
\psi_{j}^{m_{j}m_{k}}(\alpha\beta\gamma) = \left(\frac{2j+1}{8\pi^{2}}\right)^{\frac{1}{2}} D_{m_{j}m_{k}}^{j}(\alpha\beta\gamma), \quad (B.1)
\]

where \((\alpha\beta\gamma)\) are the Euler angles, \(j\) is the total rotational angular momentum, and \(m_{j}\) and \(m_{k}\) are the projections of \(j\) along the space-fixed and body-fixed z-axes respectively. The properties of the D-matrices are taken from Rose. For example, the angular integral for three D-matrices, which is used in evaluating the term \(I_{1}\) in Chapter 2, is given by

\[
\sum_{\mu_{1}} \sum_{\mu_{2}} \sum_{\mu_{3}} D_{\mu_{3}m_{3}}^{j_{3}}(\alpha\beta\gamma) D_{\mu_{2}m_{2}}^{j_{2}}(\alpha\beta\gamma) D_{\mu_{1}m_{1}}^{j_{1}}(\alpha\beta\gamma) d\alpha \sin \beta \; d\beta \; d\gamma
\]

\[
= \frac{8\pi^{2}}{2j_{3}+1} \; C(j_{1}j_{2}j_{3};m_{1}m_{2}m_{3})C(j_{1}j_{2}j_{3};\mu_{1}\mu_{2}\mu_{3}) \quad (B.2)
\]

\[
\times \; \delta_{\mu_{1}+\mu_{2},\mu_{3}} \; \delta_{m_{1}+m_{2},m_{3}}.
\]

In addition to those of Brink and Satchler, the symmetric top wave functions of Davydov (Ref. 2, Ch. 2) and Edmonds
(Ref. 10, Ch. 2) are commonly used. The symmetric top wave functions \( \psi_{m_j m_k}^j \) in terms of the D-matrices of Davydov \( \bar{D}_{m_j m_k}^j (\alpha \beta \gamma) \) and Edmonds \( D_{m_j m_k}^j (\alpha \beta \gamma) \) have the form

\[
\psi_{m_j m_k}^j (\alpha \beta \gamma) = \left( \frac{2j+1}{8\pi^2} \right)^{\frac{1}{2}} \begin{bmatrix}
\bar{D}_{m_j m_k}^j (\alpha \beta \gamma) \\
D_{m_j m_k}^j (\alpha \beta \gamma) (-1)^{m_k - m_j}
\end{bmatrix}.
\] (B.3)

Substituting either of these wave functions into Eq. (2.13) and using the corresponding properties of the D-matrices given by either Davydov or Edmonds, we can derive the same general expression for the matrix element \( U_{\gamma}^{\prime\prime} \), as is given in Eq. (2.17).
Appendix C. Linear Independence of Numerical Solutions

For an N-channel problem, the column vectors of \( \mathbf{u}(r) \) represent N-linearly independent solutions to the coupled set of differential equations. Such linear independence in the numerical solution can be guaranteed initially by a proper choice of starting boundary conditions. However, many times difficulties arise in trying to maintain this condition at each successive point. This is especially true in problems involving barrier penetration. Within the barrier, the solution must be exponentially increasing from the origin to the classical turning point. This exponential growth, especially in cases where channels initiate this rapid growth at different points, many times destroys the numerical linear independence of the solution vectors. Thus, a procedure which would force the solution vectors to be linearly independent at a particular point would be most desirable.

We recall from matrix theory that any non-singular matrix \( \mathbf{u} \) can be decomposed into a product of upper \( \mathbf{R} \) and lower \( \mathbf{L} \) triangular matrices as

\[
\mathbf{u} = \mathbf{R} \cdot \mathbf{L} = \begin{bmatrix}
1 & a \\
1 & 1 \\
0 & 1
\end{bmatrix} \cdot \begin{bmatrix}
c_{11} & 0 \\
c_{22} & c_{nn}
\end{bmatrix}
\]

The columns of matrix \( \mathbf{R} \) form a set of linearly independent vectors. To see this we write
\[
\alpha = \alpha_1 \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix} + \alpha_2 \begin{bmatrix} a_{12} \\ 1 \\ \vdots \\ 0 \end{bmatrix} + \ldots + \alpha_n \begin{bmatrix} a_{1n} \\ 0 \\ \vdots \\ 1 \end{bmatrix}.
\]

Now, the column vectors are linearly independent if and only if the equation \(\alpha = 0\) is only satisfied by the solution \([\alpha_i = 0]_{i=1,n}\). Multiplying and adding rows, we find

\[
\begin{bmatrix}
\alpha_1 + \alpha_2 a_{12} + \ldots & \alpha_n a_{1n} \\
0 + \alpha_2 a_{22} + \ldots & \alpha_n a_{2n} \\
\vdots & \vdots \\
0 + \ldots + \alpha_{n-1} a_{n-1,n-2} & \alpha_n a_{n-1,n} \\
0 & 0 & \ldots & + \alpha_n a_{nn}
\end{bmatrix} = 0 .
\]

The equation represented by the last row is

\[
\alpha_n a_{nn} = 0 .
\]

Since \(a_{nn} \neq 0\); this implies that \(\alpha_n = 0\). By substituting this into the next row, we find that \(\alpha_{n-1} = 0\). Continuing this process leads to the solution \([\alpha_1 = \alpha_2 \ldots = \alpha_n = 0]\). Therefore, the column vectors of \(\mathbb{R}\) form a set of linearly independent solutions.

In replacing \(u\) with \(R\) at a particular point in the integration, we must be careful to adjust all affected quantities. This generally means we have to perform a
transformation on all quantities that depend on \( u \). For example, the integrals \( I^1 \) and \( I^2 \) must be properly replaced by their transformed values. We can see how this is accomplished by considering the following case. If the wave function is replaced by its upper triangular form at \( r_i \), then

\[
u(r_i) = R(r_i) \cdot \mathbb{L}(r_i) = G^1(r_i) \cdot O^{22}(r_{i-1}) - G^2(r_i) \cdot O^{11}(r_{i-1}) ,
\]
or

\[
R(r_i) = G^1(r_i) \cdot [O^{22}(r_{i-1}) \cdot \mathbb{L}^{-1}(r_i)] - G^2(r_i) \cdot [O^{11}(r_{i-1}) \cdot \mathbb{L}^{-1}(r_i)]
= G^1(r_i) \cdot N^{22}(r_{i-1}) - G^2(r_i) \cdot N^{11}(r_{i-1}) ,
\]

such that

\[
N^{i,j}(r_{i-1}) = O^{i,j}(r_{i-1}) \cdot \mathbb{L}^{-1}(r_i) ; \quad j = 1 \text{ or } 2.
\]

The value of the integral at \( r_i \) may then be obtained as

\[
N^{i,j}(r_i) = G^j(r_i) \cdot U(r_i) \cdot R(r_i) w_i + N^{i,j}(r_{i-1}) ;
\]

however, since \( R = u \cdot \mathbb{L}^{-1} \)

\[
N^{i,j}(r_i) = G^j(r_i) \cdot \mathbb{L}(r_i) \cdot U(r_i) \cdot \mathbb{L}^{-1}(r_i)
+ O^{i,j}(r_{i-1}) \cdot \mathbb{L}^{-1}(r_i),
\]
or

\[
N^{i,j}(r_i) = O^{i,j}(r_i) \cdot \mathbb{L}^{-1}(r_i) .
\]
In this manner, linear independence of the solution vectors may be forced at each point in the solution. Using $R(r_i)$ for $u^O(r_i)$ and $N_{r_j}(r_i)$ for $I_j^j(r_i)$ in Eq. (4.35a), we can continue the integration of the solution by the algorithm of Eq. (4.36).

Before leaving this section, we wish to make two additional points. First, the stabilization procedure cannot generate a wave function matrix $\Psi$ of linearly independent solutions from a matrix that is already singular (i.e., whose solutions are linearly dependent). We recall that starting conditions can be chosen to give initially linearly independent solutions. The stabilization technique is then applied often enough to prevent the solution matrix from becoming singular. Second, since the solutions in the region inside a potential barrier behave as locally closed channels, we expect the stabilization technique to be important in systems with globally closed channels. Further discussion of the stabilization procedure is given by Adams, Smith, and Hayes [J. Chem. Phys. 61, 2183 (1974)] and White and Hayes [J. Chem. Phys. 57, 2985 (1972) and Chem. Phys. Lett. 14, 98 (1972)].
Appendix D. Method of Pseudopotentials

In this appendix, we present a brief outline of the method of pseudopotentials. We follow rather closely the development of Phillips and Klienman (Ref. 6a, Ch. 5) and confine our discussion to one-electron systems which are described by a Hamiltonian

$$H = T + V,$$

where $T$ is the kinetic energy operator and $V$ is the potential energy experienced by the electron. We assume that $H$ has a set of bound eigenfunctions $\{\varphi_c(r)\}$, called core wave function, which satisfy the relations

$$H \varphi_c(r) = E_c \varphi_c(r)$$

$$\varphi_c(r) \rightarrow 0 \quad (r \rightarrow \infty).$$

The region of space in which the core wave function has its largest magnitude is defined as the core region. We now seek a solution $\psi_n(r)$ which is an eigenfunction of $H$ such that

$$H \psi_n(r) = E_n \psi_n(r), \quad E_n > E_c,$$

and which is orthogonal to the core wave functions as

$$\langle \varphi_c | \psi_n \rangle = 0.$$

The "valence" wave function $\psi_n(r)$ can represent either a
bound or scattering solution. We wish to incorporate the orthogonality condition of Eq. (D.3) directly into the wave equation. We begin by constructing a solution of Eq. (D.2) of the form

$$\psi_n(r) = \varphi_n(r) + \sum_c a_{nc} \varphi_c(r), \quad (D.4)$$

where the sum varies over all core wave functions. From the orthogonality condition, we have that

$$a_{nc} = -\langle \varphi_c | \varphi_n \rangle,$$

and that

$$\psi_n(r) = \varphi_n(r) - \sum_c \langle \varphi_c | \varphi_n \rangle \varphi_c(r). \quad (D.4')$$

We can determine the form of the pseudo-wave function \( \varphi_n(r) \) by substituting Eq. (D.4') into Eq. (D.2). The resulting equation is given by

$$(H + V_p)\varphi_n(r) = E_n \varphi_n(r), \quad (D.5)$$

with

$$V_p \varphi_n = -\sum_c (E_c - E_n) \langle \varphi_c | \varphi_n \rangle \varphi_c(r). \quad (D.6)$$

The pseudopotential is given by \( V_p \) and the effective potential \( V_{\text{eff}} \) by \( (V_p + V) \). The valence wave function is determined by solving Eq. (D.5) for \( \varphi_n(r) \) and substituting the result into Eq. (D.4'). Since the pseudopotential depends on \( \varphi_n(r) \), the wave equation (D.5) must be solved self-consistently. We have thus replaced a formulation in terms
of an unmodified Hamiltonian, $H$, and constrained wave
function $\psi_n$ by an equivalent formulation in terms of a
modified Hamiltonian $(H+V_p)$ and unconstrained wave func-
tion $\phi_n$.

The pseudopotential $V_p$ and pseudo-wave function
$\phi_n$ have the following interesting properties: 1) the
pseudopotential is non-local and energy dependent;
2) the pseudopotential is generally repulsive, and
3) the pseudo-wave function is smooth in the region where
the core wave functions are large. The first property
is a direct consequence of Eq. (D.6). In actual calcula-
tions, the pseudopotential is generally approximated by
a local potential $\tilde{V}_p$ that is independent of energy. This
choice is not unique; however, a skillful choice of the
approximate pseudopotential $\tilde{V}_p$ results in a substantial
simplification, since the constrained Eqs. (D.2) and (D.3)
are then replaced by a single particle equation of the
form of Eq. (D.5) with $V_p$ replaced by $\tilde{V}_p$. The second
property is more difficult to demonstrate, but can be
shown from variational arguments (see Ref. 6g, Ch. 5).
The repulsive nature of the pseudopotential is a conse-
quence of the inclusion of the orthogonality condition in
the wave equation (D.6). The orthogonality condition of
Eq. (D.3) implies that the probability of finding the
particle described by $\psi_n(r)$ in the core region is small.
We may therefore think of the particle as being excluded
or "repelled" from the core region. Since in the pseudo-potential method the orthogonality condition is directly incorporated within $V_p$, we somehow expect the pseudopotential to exhibit this exclusion of the valence electron. The repulsive nature of $V_p$ does indeed introduce such an exclusion. For electron-atom collisions, the orthogonality condition (D.3) is a consequence of the Pauli principle, and therefore this exchange effect is included in the resulting pseudopotential. The third property also arises from the orthogonality condition. Since the valence wave function must be orthogonal to each core wave function, the valence wave function must develop a sufficient number of nodes in the core region. Thus, the "kinetic energy" of the valence electron is correspondingly large in the core region. In the pseudopotential method, the orthogonality condition is incorporated into the valence wave function through the second term in Eq. (D.4). The pseudo-wave function is thus free of this condition and is generally quite smooth in the core region. The pseudopotential that appears in the equation for $\bar{\Phi}_n$ must therefore to some extent implicitly incorporate this large "kinetic energy." Thus, the effective potential $(V+V_p)$ contains contributions not only from the electrostatic potential but also from the orthogonality condition and kinetic energy effects. For the scattering case, the asymptotic form of the pseudo-wave function must equal that of the valence wave function since the
bound core states must go to zero (see Eq. (D.4')).
Therefore, the scattering phase shifts must also be the
same. The term $V_{\text{eff}}$ thus represents the effective scat-
tering potential for the electron.
Appendix E. Molecular Wave Functions

For an N-electron molecule the total wave function \( \Psi \) is a function of the coordinates of each molecular electron with

\[
\Psi = \psi(\mathbf{x}_1, \ldots, \mathbf{x}_N).
\]  

(E.1)

The probability \( \rho(\mathbf{x}_1, \ldots, \mathbf{x}_N) \) of finding an electron at each of the positions \( \mathbf{x}_1 \) to \( \mathbf{x}_N \) is given by

\[
\rho(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \langle \psi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N) | \psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \rangle.
\]

(E.2)

The probability \( \rho(\mathbf{x}_1) \) of finding an electron at \( \mathbf{x}_1 \) regardless of the position of all the remaining electrons is found by integrating Eq. (E.2) over the spaces of all but one of the electrons as

\[
\rho(\mathbf{x}_1) = \int \ldots \int d\mathbf{x}_2 d\mathbf{x}_3 \ldots d\mathbf{x}_N \rho(\mathbf{x}_1, \ldots, \mathbf{x}_N).
\]

(E.3)

The quantity \( \rho(\mathbf{x}) \) is termed a single-electron probability density.

The Hartree-Fock wave function for an N-electron closed shell diatomic molecule is given by a single Slater determinant of the form

\[
\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \ldots & \phi_1(\mathbf{x}_N) \\ \vdots & \ddots & \vdots \\ \phi_N(\mathbf{x}_1) & \ldots & \phi_N(\mathbf{x}_N) \end{vmatrix},
\]

(E.4)
where $\phi_i(x_j)$ is the $i^{th}$ molecular spin orbital. The wave function is normalized and anti-symmetric. The molecular spin-orbitals consist of a spatial part, $\psi_i$, and a spin part as

$$\phi_i(x_j) = \psi_i(x_j) \{ \alpha_i, \beta_i \} ,$$  \hspace{1cm} (E.5)

where $\alpha_i (\beta_i)$ corresponds to spin up (down). The spatial part of the molecular orbital is usually expanded in terms of atomic orbitals centered on the molecular nuclei.

For a diatomic molecule with nuclei A and B at distances $R_A$ and $R_B$ respectively from the molecular center of mass (CM), the spatial molecular orbital can be written as

$$\psi_i(x_j) = \sum_{p=1}^{N_A} C_p^{(A)} \chi_{n_p}^{(A)} (x_A) + \sum_{p'=1}^{N_B} C_p^{(B)} \chi_{n_p}^{(B)} (x_B) ,$$  \hspace{1cm} (E.6)

where $N_A$ and $N_B$ are the number of atomic basis functions on atoms A and B respectively, $\chi_{n_p}^{(A)} (x_A)$ is the atomic orbital of symmetry $\lambda$ centered on atom $A$, $C_p^{(A)}$ is the linear expansion coefficient of the $p^{th}$ atomic orbital of atom $A$ and is determined from the Hartree-Fock self-consistent field calculation, $x_j$ is the vector position of the $j^{th}$ electron with respect to the molecular CM, and $x_\alpha$ to the vector position ($x_j - x_\alpha$) of the $j^{th}$ electron with respect to the $\alpha$ atomic center. The atomic basis functions must be of the same reflection symmetry as the molecular orbital. The most common choices for the basis functions
are Slater-type orbitals (STO) and gaussian-type orbitals (GTO). The Slater-type atomic orbitals have the form

\[ \chi_{npn_p \lambda p \mu p}^{\alpha \lambda} = (2 \zeta_p)^{n_p + \frac{1}{2}} (2n_p!)^{-\frac{1}{2}} r_p^{-\frac{1}{2}} \]

\[ \times \exp[-\zeta_p r_p] y_{npn_p \lambda p \mu p}^{\alpha \lambda} (\theta_{\alpha}, \phi_{\alpha}) , \]

(E.7)

where \((r_{\alpha}, \theta_{\alpha}, \phi_{\alpha})\) is the position of the electron with respect to coordinate axes centered on the atom \(\alpha\), \(\zeta_p\) is a nonlinear parameter usually determined from an electronic structure calculation for the atom \(\alpha\), \((n_p, \lambda_p, \mu_p)\) are the principal, orbital and magnetic quantum numbers of the atomic orbital. Since the atomic orbitals must have the same symmetry as the molecular orbital with respect to reflection, the magnetic quantum numbers for all atomic orbitals forming a particular molecular orbital must be equal. The parameters \(\zeta_p\) and \(C_p\) are found by a Hartree-Fock electronic structure calculation and can generally be found in the literature.

As an example of the application of the above formulae, we consider the boron hydride (BH) molecule calculations of Cade and Huo (see Ref. 18, Ch. 5). BH is a diatomic molecule with the boron located a distance of 0.19 \(a_0\) and the hydrogen a distance of 2.14 \(a_0\) from the CM respectively. The 1\(\sigma\) molecular orbital of BH has four atomic STO's centered on the H and twelve STO's on the B. Cade and Huo define the coordinate systems on the atomic centers to
have their z-axes pointing toward each other and lying along the molecular symmetry (figure) axis. We wish to evaluate the \(1\sigma\) wave function at a point \(P\) located at coordinates \((r, \theta, \phi)\) with respect to a coordinate system fixed at the CM whose z-axis points along the symmetry axis in the direction of the H atom (see figure).

\[
|\mathbf{r}_H|^2 = r_H^2 = R_H^2 + r^2 - 2R_Hr \cos \theta
\]

\[
|\mathbf{r}_B|^2 = r_B^2 = R_B^2 + r^2 + 2R_Br \cos \theta
\]

\[
\theta_H = \cos^{-1}\left[\frac{(R_H^2 + r_H^2 - r^2)}{2R_Hr_H}\right]
\]

\[
\theta_B = \cos^{-1}\left[\frac{(R_B^2 + r_B^2 - r^2)}{2R_Br_B}\right]
\]

\[
\phi_H = \phi_B = \phi .
\]
Since there is no standard convention as to the orientation of the various coordinate systems, one should be careful to use the convention of the paper from which the wave function parameters are obtained. All STO's on the H atom are evaluated at \((r_H, \theta_H, \phi)\) and all STO's on the B atom are evaluated at \((r_B, \theta_B, \phi)\). With this in mind, we simplify the STO notation by repressing the coordinates and explicitly representing the nonlinear atomic parameter \(\zeta_p\) as

\[ \chi_{n_p l_p m_p}^{(\zeta_p)} \rightarrow \chi_{n_p}^{\alpha} \chi_{n_p}^{\beta} \chi_{n_p}^{\gamma} (\zeta_p). \]

Using this convention, we write the 1\(\sigma\) orbital wave function of BH as

\[ \psi_{1\sigma}^{BH} = 0.000524 \chi_{100}^H (1.18274) - 0.00098 \chi_{100}^H (2.90014) \]

\[ - 0.00159 \chi_{200}^H (1.98224) + 0.00077 \chi_{210}^H (1.69999) \]

\[ + 0.90962 \chi_{100}^B (3.91385) + 0.17036 \chi_{100}^B (7.32757) \]

\[ + \ldots + 0.0035 \chi_{320}^B (1.86930) \]

\[ - 0.00018 \chi_{430}^B (1.25224). \]

Similar expressions are obtained for the 2\(\sigma\) and 3\(\sigma\) orbitals. The one-electron probability density for a Hartree-Fock wave function is given by

\[ p(\xi) = \sum_{i=1}^{N_o} n_i \psi_i^*(\xi) \psi_i(\xi), \quad (E.8) \]

where \(N_o\) is the number of molecular orbitals and \(n_i\) is the
number of electrons occupying the $i^{th}$ orbital. Since BH has a configuration $1\sigma^2 2\sigma^2 3\sigma^2$, the probability density becomes

$$
\rho_{BH}(\xi) = 2\psi_1^*(\xi) \cdot \psi_1(\xi) + 2\psi_2^*(\xi) \cdot \psi_2(\xi) + 2\psi_3^*(\xi) \cdot \psi_3(\xi).
$$
Appendix F. Radial Expansion Coefficients: e-He Effective Potential

The radial expansion coefficients \( \overline{v}_\ell (r, R) \) of the effective interaction potential energy \( V_{\text{eff}} \) between an electron and tightly bound atom of the form

\[
V_{\text{eff}}(s) = \begin{cases} 
-\frac{2}{s} e^{-as} + b e^{-s^2/2\sigma^2} & s \leq r_c \\
0 & s > r_c,
\end{cases} \tag{F.1}
\]

are given by the integral

\[
\overline{v}_\ell (r, R) = \frac{(2\ell + 1)}{2} \int_0^{\psi_o} V_{\text{eff}}(s) P_\ell (\cos \psi) \sin \psi \, d\psi, \tag{F.2}
\]

where the geometry is given by Fig. 4 and \( s^2 = r^2 + R^2 - 2rr\cos \psi \). We have truncated the effective potential at a critical radius, \( r_c \), in order to remove certain polarization effects which will be included in the long-range potential. The integration in Eq. (F.2) runs from 0 to the critical angle \( \psi_o \), given by

\[
\psi_o = \cos^{-1} \left[ \frac{r^2 + R^2 - r_c^2}{2rr} \right], \tag{F.3}
\]

instead of from 0 to \( \pi \), since the effective potential vanishes for all angles greater than \( \psi_o \).

We treat the exponential and gaussian parts of Eq. (F.1) separately as

\[
\overline{v}_\ell (r, R) = \overline{v}_\ell^E (r, R) + \overline{v}_\ell^G (r, R) \tag{F.4}
\]
with

$$
\tilde{v}_E(r,R) = -(2\ell+1) \int_0^{\psi_0} \exp(-as)s^{-1} P_\ell(\cos \psi) \sin \psi \, d\psi
$$

$$
\tilde{v}_G(r,R) = \frac{(2\ell+1)}{2} \int_0^{\psi_0} e^{-(r^2+R^2)/2\sigma^2} \exp(\frac{rR \cos \psi}{\sigma}) P_\ell(\cos \psi) \sin \psi \, d\psi.
$$

Changing the variable in Eq. (F.5b) as

$$
u = \frac{rR \cos \psi}{\sigma^2},$$

we find that

$$
\tilde{v}_G(r,R) = -\frac{(2\ell+1)}{2} \frac{b_0^2}{rr} e^{-(r^2+R^2)/2\sigma^2} \int_0^{\psi_0} \frac{rR \cos \psi}{\sigma^2} \exp(u) P_\ell\left(\frac{\sigma^2 u}{rR}\right) \, du.
$$

The Legendre polynomials have the general form

$$
P_\ell(x) = \sum_{m=0}^{\ell} a_{\ell} x^m,
$$

where $a_{\ell}$ is the coefficient of the $m$th power of the independent variable $x$. For example, the Legendre polynomial of second order, $P_2$, has the form

$$
P_2(x) = \frac{3}{2} x^2 - \frac{1}{2},
$$

with the coefficients given by
\[ a_0^2 = -\frac{1}{2}, \quad a_1^2 = 0, \quad a_2^2 = \frac{3}{2}. \]

Substituting Eq. (F.6') into Eq. (F.6) and making the definition \( \alpha = rR/\sigma^2 \), we find

\[ \tilde{V}_L^G(r,R) = (2\lambda+1) \frac{b}{\alpha} \exp[-(r^2+R^2/2\sigma^2)] \sum_{m=0}^{\lambda} \alpha^m \frac{\lambda}{m} I_m, \]

where

\[ I_m = -\frac{1}{\alpha} \int_{0}^{\alpha \cos \psi_0} (\frac{u}{\alpha})^m \exp(u) \, du. \]  \hspace{1cm} (F.7')

The integral can be evaluated by parts to give

\[ I_m = -\frac{1}{2} \left[ \exp(\alpha \cos \psi_0) \cos^m \psi_0 - \exp(\alpha) \right] - \frac{m}{\alpha} I_{m-1}. \]  \hspace{1cm} (F.8)

We have thus established a recursion relation for generating the integrals \( I_m \). We can start the recursion relation with the simplest integral \( I_0 \) which has the form

\[ I_0 = \frac{1}{2} \left[ \exp(\alpha R/\sigma^2) - \exp(\alpha \cos \psi_0 (\sigma^2)) \right]. \]

Using the integrals \( I_m \) in Eq. (F.7) with the appropriate Legendre polynomial coefficients \( \alpha^m \), we can derive an exact analytical expression for the gaussian contribution to the effective interaction potential \( V_{\text{eff}} \).

The exponential contribution \( \tilde{V}_L(r) \) can be determined directly without having to evaluate the integral in Eq. (F.5a). From Eq. (B.100) in Appendix B of Messiah [Quantum Mechanics (Wiley, New York, 1968), vol. I], we find
\[ \exp(-as)/s = ia \sum_{\ell} (2\ell+1) j_{\ell}(iar_\leq) h_{\ell}^{(+)}(iar_\geq) P_{\ell}(\cos \vartheta), \] 

where \( j_{\ell} \) and \( h_{\ell}^{(+)} \) are the spherical bessel function and hankel function respectively and \( r_\leq \) and \( r_\geq \) are defined such that

\[ r_\leq = \min(r,R) \]
\[ r_\geq = \max(r,R). \]

Making a direct identification with the Legendre expansion of \( V_{\text{eff}} \), we write

\[ \bar{V}^E_{\ell}(r,R) = -2ai(2\ell+1) j_{\ell}(iar_\leq) h_{\ell}^{(+)}(iar_\geq). \] 

From Eqs. (F.10) and (F.7), we can generate the radial expansion coefficient of the effective potential by using Eq. (F.4).
References

Chapter 1.


Chapter 2.


5 We use the symmetric top wave functions of D. M. Brink and G. R. Satchler, Angular Momentum, 2nd ed. (Oxford, 1968) which are given in terms of the D-matrices of Rose (Ref. 4).

7. We represent a matrix $A$ by a bar under the letter as $\bar{A}$.


11. There are $2j+1$ channels for each rotor state $(j m_k \nu)$ only if $J \geq j$. For $J < j$ the number of channels is less than $2j+1$.


Chapter 3


7We use the form of Eq. (2.20) appropriate to a linear rigid rotor with $\alpha = j$ and the set $(jm_k)$ replaced by $j$.


12aIn a recent paper, D. Secrest [J. Chem. Phys. 62, 710 (1975)] has derived the same form of the total rotational excited cross section as Kouri and McGuire [see Eqs. (3.22) and (3.23)] without the assumption of equivalence of the SF and RA wave functions. The differential cross
sections, however, have a different form in the two approaches.

D. J. Kouri and P. McGuire (in press). For the strongly coupled system Li\(^{+}\)-H\(_{2}\), the authors find that a constant expression of the form \((J-j)(J-j+1)\) gives better results than that of Eq. (3.19').

Chapter 4.


The integral equations formalism applied to electron-atom scattering is described in the articles in Ref. 1 by R.J.W. Henry and that by Knirk and Hayes. The application to electron-molecule scattering is described in W. N. Sams, L. Frommhold, and D. J. Kouri, *Phys. Rev.* A6, 1070 (1971).

We are especially interested in atom-linear molecule scattering, in which case the matrix elements $U_{\gamma'}^{\gamma''}$ are given by Eq. (2.32).


This notation is explained in the discussion of Eqs. (2.19).

The inverse of a matrix $\mathbf{A}$ is denoted by $\mathbf{A}^{-1}$.

The basis which converges the cross sections at small J values will usually serve over the entire domain of J values which make non-negligible contributions to the total cross section. However, for large values of J, a smaller basis may suffice for convergence of the partial cross sections. For cross sections that have contributions over a large domain of J values, several choices of basis may be desirable and more economical. This point is addressed in the article by T. P. Tsien, G. A. Parker, and R. T. Pack, *J. Chem. Phys.* 59, 5373 (1973).

Chapter 5.


3 A good discussion of this effect is given in Ref. 1b, pp. 483–485.


This expansion is only valid for the cylindrically symmetric $\Sigma$ state of a molecule.

9 M. Abramowitz and A. Stegun, Handbook of Mathematical Functions (NBS, Washington, 1964), Ch. 25.

10 A. Ralston and H. F. Wilf, eds., Mathematical Methods for Digital Computers (Wiley, New York, 1960), vol. 1. The cubic spline method fits a cubic polynomial between the mesh points such that the fit is smooth over the whole mesh.


14 A review of polarizability calculations is given by
17 See Ref. 4 and references therein.
    and b) 647 (1967).
19 F. Smith, Physics of Electronic and Atomic Collisions,
   VII ICPEAC (North Holland, Amsterdam, 1972).
21 C. F. Bender, private communication. The results of
   this RHF surface calculation appear in Table 2a.
   Phys. 57, 3421 (1972).
24 The Bender surface is evaluated at values of $R$ of 2.5,
   3.0, and 4.0 $a_0$, while the Lischka surface is given for
   values of $R$ greater than 4.8 $a_0$.
25 Margenau and Kestner, op. cit., p. 72.
   (1967).


Chapter 6

1 All collision energies refer to relative motion in a space-fixed (SF) reference frame whose origin is at the center-of-mass of the atom-molecule system.

2 The bessel functions which determine the Green's function of Eq. (4.9) are numerically evaluated by two complimentary
techniques. If the argument, kr, is greater than the order \( \ell \), the bessel functions are evaluated by the standard recursion relations. However, if kr is less than \( \ell \), the bessel functions are evaluated by the iterative technique of Snow which is outlined in Abramowitz and Stegun (Ref. 11, Chp. 4).

3a) The expression \((0-j_{\text{max}})\) denotes the rotor basis in which all rotor states with values of \( j \) between 0 and \( j_{\text{max}} \) are included.

b) The stabilization procedure is outlined in Appendix C. The code INEQJZ also needs the maximum value of \( m_j \) to be considered.

4The potential energy surface used in all He-H\(_2\) calculations is that of C. S. Roberts, Phys. Rev. 131, 209 (1963).


6N. F. Lane, private communication.


W. A. Lester and J. Schaeffer, *J. Chem. Phys.* 59, 3676 (1973); the partial cross sections of Table 5 were kindly supplied by Dr. Lester.

The distorted wave approximation gives poor results for the He-H₂ system for energies greater than 0.25 eV. Since the He-HF system is more strongly coupled than He-H₂, we expect the distorted wave cross sections to be in error even at lower energies.

The partial cross sections for the transitions (0-1) and (0-2) also exhibit secondary maxima for the systems He-HF and He-DF. However, the magnitudes of these maxima are so small compared to the primary peaks in the cross sections that they do not appear on the graphs.


Epilogue

In this thesis, we have developed the formalism for inelastic atom-molecule collisions and presented the results of calculations for rotational excitation of four diatomic hydrides by collisions with helium atoms. We have, in this development, reviewed the close-coupling coupled-channel formulation of the scattering equations in space-fixed and rotating-atom frames and the various approximations to this coupling scheme such as the distorted wave and \( j_z \)-conserving coupled-states methods. In addition, we have developed a technique for calculating approximate potential-energy surfaces for interactions between closed-shell atom-atom and atom-molecule systems. Rotational excitation cross sections for collisions between helium and the diatomic hydrides: HF, DF, HCl, and DCl were calculated by the coupled channel and coupled states methods. Simple models were employed to qualitatively explain the behavior of the cross sections as a function of energy, total angular momentum (J), and target molecule.

This research project has derived its motivation from three basic considerations. First, we sought to calculate rotational excitation cross sections which would have applications to a number of fields, such as laser physics. This goal lead us to refine our numerical codes, to carefully test convergence criteria, and to compare
the approximate methods for generating potential energy surfaces and cross sections against more accurate methods. Taking into account the uncertainties in the various potential parameters, we judge the accuracy of the cross sections to be within fifty percent of the exact results. Second, we have attempted to develop and investigate various approximation procedures for calculating cross sections and potential energy surfaces. We have employed these methods not only for their efficiency but also for the insight that they provide into the functionings of more complicated techniques. We have observed the ability of a simple additive approach to produce potential energy surfaces in good agreement with Hartree-Fock and configuration interaction methods and the ability of a scattering formulation based on coupled states to adequately approximate the more complex couplings between channels. We have also drawn from the distorted wave approximation to explain the behavior of the partial rotational excitation cross sections. Third and most important, we have discovered and explained trends in the cross sections between different hydride systems. Although the current models used to explain these trends are simple, they do account for changes in such features as the relative orderings of the rotational excitation cross sections as the potential energy surfaces and spacings between the rotational levels are varied. The number of hydride systems investigated was small; however,
the cases investigated are probably sufficient to allow us to predict from the general features of the potential energy surface and rotational spectrum the qualitative behavior of the rotational excitation cross sections for a new hydride system. In summary, our goal has been not only to calculate accurate cross sections which have practical applications to model studies of macroscopic systems such as lasers but also to better understand the complicated features of inelastic scattering processes through the use of models and approximation techniques.

We hope to extend this research into a number of areas. First, using the same formalism and numerical codes, we intend to calculate the rotational excitation cross sections for collisions between other closed-shell hydrides and helium. We are especially interested in boron hydride since it provides an example of a very strongly coupled system (He-BH). The cross sections for other hydrides will also allow us to test our simple qualitative models and possibly to develop a more quantitative model to explain the various trends. Second, additional study of the approximation methods is needed. The criteria under which the use of the $j_z$-conserving coupled state method is valid are not clear at present. A more detailed study based on a simple model system in which various parameters can be systematically adjusted as well as a more thorough formal study are needed. A more extensive investigation of the
effective potential method is also in order. The method seems to work well for the interaction of a small, tightly bound atom and a closed-shell molecule. In this sense, the method compliments the statistical Gordon-Kim procedure. Further applications to other closed-shell systems are necessary before any bold claims can be made for this method. Third, the integral equations technique for solving a set of coupled equations can be applied to a large variety of systems. We are at present collaborating with others in applying the method to calculate cross sections for fine structure transitions in collisions of excited and ground state neon atoms and for rotational and vibrational excitation in electron-molecule collisions. Finally, we hope to investigate in greater detail the possibility of using frame transformations to simplify the calculation of cross sections for heavy particle systems.