Quantum mechanical reactive scattering for three-dimensional atom plus diatom systems. I. Theory*

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A method is presented for accurately solving the Schrödinger equation for the reactive collision of an atom with a diatomic molecule in three dimensions on a single Born–Oppenheimer potential energy surface. The Schrödinger equation is first expressed in body-fixed coordinates. The wavefunction is then expanded in a set of vibration–rotation functions, and the resulting coupled equations are integrated in each of the three arrangement channel regions to generate primitive solutions. Next, these are smoothly matched to each other on three matching surfaces which appropriately separate the arrangement channel regions. The resulting matched solutions are linearly combined to generate wavefunctions which satisfy the reactance and scattering matrix boundary conditions, from which the corresponding **R** and **S** matrices are obtained. The scattering amplitudes in the helicity representation are easily calculated from the body fixed **S** matrices, and from these scattering amplitudes several types of differential and integral cross sections are obtained. Simplifications arising from the use of parity symmetry to decouple the coupled-channel equations, the matching procedures and the asymptotic analysis are discussed in detail. Relations between certain important angular momentum operators in body-fixed coordinate systems are derived and the asymptotic solutions to the body-fixed Schrödinger equation are analyzed extensively. Application of this formalism to the three-dimensional $H+H_2$ reaction is considered including the use of arrangement channel permutation symmetry, even–odd rotational decoupling and postantisymmetrization. The range of applicability and limitations of the method are discussed.

I. INTRODUCTION

One of the most important goals of chemical dynamics is the accurate calculation of cross sections for reactive bimolecular collisions. Such calculations can be used to develop and test approximate reaction dynamic theories and statistical theories, to advance our understanding of dynamical processes governing reactive collisions, and to interpret, analyze, and make predictions concerning the results of experiments.

In recent years, a number of attempts have been made to solve this problem accurately (i.e., quantum mechanically) for the simplest possible such chemical reaction, the collision of an atom with a diatomic molecule on a single electronically adiabatic potential energy surface. One of the major difficulties in achieving this goal in the past has been the absence of computationally efficient procedures for obtaining accurate solutions to the Schrödinger equation for reactive collisions. For the simple case in which the three atoms are confined to move on a space-fixed straight line, adequately accurate and efficient methods have been developed within the last several years and applied to a variety of systems.[1–13] However, when the collinearity restriction is eliminated, the problem becomes more difficult, especially when the atom is permitted to react with either end of the diatom. To tackle such noncollinear problems, several different techniques have been proposed and to a certain extent tested. Baer and Kouri[14] have developed an integral equation method and have applied it to a simple three-dimensional model atom plus diatom system in which reaction with only one end is permitted. Saxon and Light, and Altenberger-Siczek and Light,[15] have investigated the coplanar $H+H_2$ reaction using a coupled-equation (i.e., close-coupling) procedure which ignored closed vibrational channels, while Wyatt and co-workers[16] have developed a somewhat different coupled-equation procedure in which closed channels are included and for which the use of hindered rotor basis functions leads to simple bifurcation properties. Quite recently, Elkowitz and Wyatt[16a] have applied this procedure to the three-dimensional $H+H_2$ reaction. Wolken and Karplus[17] have applied an integrodifferential equation method proposed by Miller[18] to 3D $H+H_2$ using a one-vibrational-basis-function approximation.

In a previous paper[19] (hereafter referred to as Paper I) we described a method for accurately solving the Schrödinger equation for reactions of the type $A+BC \rightarrow AB+C$ or $AC+B$ on a single electronic potential energy surface with the restriction that the motions of the three atoms be constrained to lie in a single space-fixed plane. An extensive application of this method to the planar $H+H_2$ exchange reaction has now been made.[20,21] The present paper describes an extension of this method to three-dimensional atom–diatom collisions. It yields a computationally practical procedure for accurately calculating reaction cross sections for many atom–diatom chemical reactions. A number of additional concepts not present in the planar problem are introduced, and the simplifications occurring in an application to three-dimensional $H+H_2$ are discussed. Preliminary results of an application of this method to the $H+H_2$ reaction on a realistic potential surface have recently been published,[22] providing the first fully converged quantum mechanical cross sections for a chemical reaction. The extension of these calculations to energies above the threshold for vibrational excitation has lead to the discovery of an internal excitation resonance[23] for that reaction, a phenomenon whose experimental detection may be an important tool in the characterization of reactive potential energy surfaces. A more complete description of these results for $H+H_2$ follows.[24]

The method utilizes a coupled-channel (i.e., close-coupling) propagation technique to generate complete sets of solutions in each of the three arrangement channel regions of configuration space, followed by a "matching procedure" in which the solutions are smoothly matched to one another on a set of three appropriately chosen surfaces which separate these three regions. The scattering matrices, amplitudes, and cross sections are then determined by analyzing the asymptotic behavior of these matched solutions. As thus formulated, the method is similar in spirit to the corresponding planar theory described in Paper I and, for this reason, many of the concepts presented in that paper and which carry into the three-dimensional world without modification will only be summarized briefly. There are, however, some aspects which are different, most notably in the matching procedure, and these will be discussed in detail. In addition, the concepts of angular momentum coupling, of body- and space-fixed coordinate systems, and of parity symmetry decoupling will be developed thoroughly as their utilization is of great importance to the three-dimensional method.

In Sec. II we discuss the body-fixed partial wave Schrödinger equation along with angular momentum coupling and the division of configuration space into arrangement channel regions. The fully coupled Schrödinger equation for the four different internal configuration space regions of each arrangement channel region is discussed in Sec. III and the matching procedure is described in Sec. IV. In Sec. V. the body-fixed R and S matrices are defined and their relationships to the helicity representation scattering amplitudes and cross sections are derived. In Sec. VI we discuss the limitations of the method and its possible generalizations. In each section, where appropriate, the simplifications pertinent to the $H + H_2$ exchange reaction are indicated. Appendix A outlines the derivation of the body-fixed Schrödinger equation and indicates relationships between several important angular momentum operators. Appendix B includes a discussion of parity symmetry and the simplifications in the method which may be gained by explicitly including it.

II. THE BODY-FIXED ROTATIONALLY COUPLED SCHRÖDINGER EQUATION

A. Separation of internal configuration space into arrangement channel regions

We consider the three-dimensional collision of an atom A with a diatomic molecule BC and, in parallel, the B plus CA and C plus AB collisions. A convenient procedure for specifying the locations of A ($\equiv A_\alpha$), B ($\equiv A_\beta$), and C ($\equiv A_\gamma$) in the center of mass system is depicted in Fig. 1. $\bar{R}_\alpha$ is the vector from the center of mass of BC to A, and $\bar{r}_\alpha$ is the B to C internuclear vector. As $|\bar{R}_\alpha| \to \infty$, with $|\bar{r}_\alpha|$ remaining finite, we obtain the separated A + BC arrangement channel (denoted by the symbol α). The vectors $\bar{R}_\beta$, $\bar{r}_\beta$ and $\bar{R}_\gamma$, $\bar{r}_\gamma$ are defined analogously for the arrangement channels β (B + AC) and γ (C + AB), respectively. Note that the arrangement of the vectors in Fig. 1 is cyclic in the indices $\alpha\beta\gamma$. We let $\lambda\nu\kappa$ represent any one of the cyclic permutations

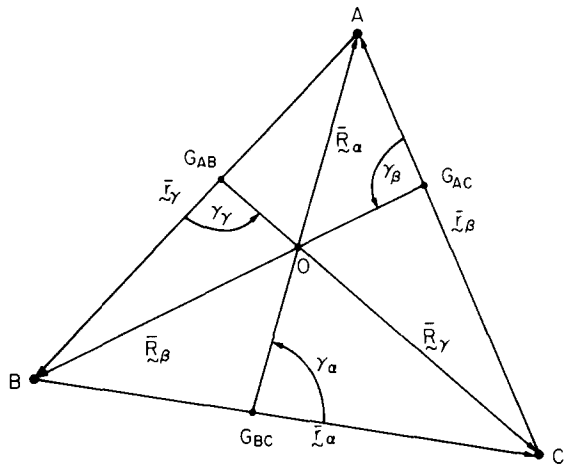

FIG. 1. Vectors used to specify the location of the three atoms A, B, and C relative to the center of mass O. G_{BC}, G_{AC}, and G_{AB} denote the locations of the centers of mass of the diatoms BC, AC, and AB, respectively. The vectors $\bar{R}_\alpha$, $\bar{r}_\alpha$, $\bar{R}_\beta$, $\bar{r}_\beta$, $\bar{R}_\gamma$, $\bar{r}_\gamma$ are defined in text.

$\alpha\beta\gamma$, $\beta\gamma\alpha$, and $\gamma\alpha\beta$, and define the vectors $\bar{R}_\lambda$, $\bar{r}_\lambda$, $\bar{R}_\nu$, $\bar{r}_\nu$, and $\bar{R}_\kappa$, $\bar{r}_\kappa$ accordingly. We also introduce the scaled variables $\mathbf{R}_\lambda$, $\mathbf{r}_\lambda$ which are related to $\bar{R}_\lambda$, $\bar{r}_\lambda$ by

$$\mathbf{r}_\lambda = a_\lambda^{-1}\bar{r}_\lambda \,, \tag{2.1a}$$

$$\mathbf{R}_\lambda = a_\lambda \bar{r}_\lambda \,, \tag{2.1b}$$

where

$$a_\lambda = (\mu_{\lambda,\nu\kappa}/\mu_{\nu\kappa})^{1/4} \,, \tag{2.2a}$$

and $\mu_{\lambda,\nu\kappa}$ and $\mu_{\nu\kappa}$ are the reduced masses corresponding to $\bar{R}_\lambda$ and $\bar{r}_\lambda$ motion, respectively:

$$\mu_{\lambda,\nu\kappa} = m_\lambda(m_\nu + m_\kappa)/(m_\lambda + m_\nu + m_\kappa) \,, \tag{2.2b}$$

$$\mu_{\nu\kappa} = m_\nu m_\kappa/(m_\nu + m_\kappa) \,. \tag{2.2c}$$

This notation is identical to that used in Paper I and is dictated by the considerable mathematical convenience associated with using scaled variables.[25–27]

We are interested in solving the six-dimensional Schrödinger equation for the motion of the three nuclei, on a single electronically adiabatic potential energy surface, obtained after the motion of the center of mass of the system is removed. The surface (in the absence of external fields) is a function of only three appropriately chosen variables which specify the internal configuration of the system. A convenient representation of this potential V is afforded by the use of the variables R_λ, r_λ, and γ_λ ($\lambda = \alpha, \beta,$ or γ), where γ_λ is the angle between R_λ and r_λ defined by

$$\gamma_\lambda = \cos^{-1}\frac{\mathbf{R}_\lambda \cdot \mathbf{r}_\lambda}{|\mathbf{R}_\lambda||\mathbf{r}_\lambda|} \qquad 0 \le \gamma_\lambda \le \pi \tag{2.3}$$

in terms of which $V = V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$. As was discussed in Paper I (Sec. III. A), the variables $\mathbf{R}_\lambda$, $\mathbf{r}_\lambda$ are useful for describing the triatomic motions only for configurations in which R_λ is significantly larger than, say, R_ν or R_κ. This is most easily understood by representing V^λ in terms of variables $\zeta = (r_\lambda^2 + R_\lambda^2)^{1/2}$ [which, as shown in Eq. (A6) of Paper I is independent of λ], $\omega_\lambda = 2\tan^{-1}(r_\lambda/R_\lambda)$ (in the 0 to π range), and γ_λ. The properties of such

a representation have been discussed elsewhere,[28] the most important one being that a change from polar coordinates ζ, ω_λ, γ_λ to ζ, ω_ν, γ_ν rotates the map of V without distorting it. For the Porter–Karplus H_3 surface, this representation of V is given in Fig. 2 of Paper I and discussed in Sec. III. A of that paper. However, the range of γ_ν in the 3D case if 0 to π rather than the 0 to 2π of the 2D case. From that figure one can see that the three-dimensional internal configuration space is naturally divided into arrangement channel region subspaces, labeled by the indices $\lambda = \alpha, \beta, \gamma$. In region λ, for large ζ, R_λ is approximately equal to Z_λ and r_λ is approximately half of the distance of the point $P(\zeta, \omega_\lambda, \gamma_\lambda)$ to the Z_λ axis. Therefore, in that region, R_λ, r_λ, γ_λ are the "natural" variables for describing the translational, vibrational, and rotational motions, respectively, of the three atoms, but these same variables are both awkward and inefficient for representing the corresponding motions in arrangement channels ν and κ. As a result, we will use R_λ, r_λ, γ_λ in region λ only. Associated to these, we will pick a set of three additional external variables (which specify the orientation of the instantaneous three-atom triangle with respect to a laboratory system) which will also be different for different arrangement channel regions. Accordingly, our procedure for solving the Schrödinger equation involves first the generation of solutions in each of the three arrangement channel regions $\lambda = \alpha, \beta, \gamma$ in separate calculations using variables appropriate to each region. This is followed by a matching procedure which yields a set of smooth and continuous solutions throughout all of configuration space. To complete the problem, we need to linearly combine these "primitive" solutions to generate ones which satisfy the desired asymptotic boundary conditions.

The procedure thus outlined is general and can be applied to any nondissociative reactive system, but in any specific application, we must specify the boundaries (in internal configuration space) of the three arrangement channel regions. As was discussed in Sec. III. A of Paper I, the choice of boundary surfaces is primarily determined by the nature of the potential surface, but for $H + H_2$ and many other reactive systems, a very useful separation is obtained by the use of the three half-planes $\pi_{\nu\lambda}$, $\pi_{\kappa\nu}$, and $\pi_{\lambda\kappa}$ of Fig. 2 of I and defined by Eq. (3. 2) of that paper. They are limited by and intersect on the OY_λ axis. $\pi_{\nu\lambda}$ makes an angle $\beta_{\nu\lambda}$ (in the 0 to $\pi/2$ range) with the $OY_\lambda Z_\lambda$ plane given by

$$\cos\beta_{\nu\lambda} = \left(\frac{m_\nu m_\lambda}{(m_\lambda + m_\kappa)(m_\nu + m_\kappa)}\right)^{1/2}, \tag{2.4a}$$

$$\sin\beta_{\nu\lambda} = \left(\frac{m_\kappa M}{(m_\lambda + m_\kappa)(m_\nu + m_\kappa)}\right)^{1/2}, \tag{2.4b}$$

where

$$M = m_\lambda + m_\nu + m_\kappa . \tag{2.5}$$

Analogous expressions are valid for the angles between $\pi_{\kappa\nu}$ and $OY_\lambda Z_\nu$ and between $\pi_{\lambda\kappa}$ and $OY_\lambda Z_\kappa$. These $\pi_{\nu\lambda}$ surfaces ($\nu\lambda = \alpha\beta, \beta\gamma, \gamma\alpha$), hereafter called the matching surfaces, are analogous to those used in Paper I, and their properties are described in great detail in Appendix A of that paper. They are of great importance in the matching procedure of Sec. IV, and the method of solution of the Schrödinger equation in each arrangement channel region must include a procedure for determining the wavefunction of these surfaces. The remainder of this section will be concerned with the rotationally coupled Schrödinger equations for each arrangement channel region.

B. Partial wave analysis

In the system of coordinates specified by the index λ, the Schrödinger equation for the motions of the three nuclei is

$$\left(-\frac{\hbar^2}{2\mu_{\lambda,\nu\kappa}}\nabla^2_{\bar{R}_\lambda} - \frac{\hbar^2}{2\mu_{\nu\kappa}}\nabla^2_{\bar{r}_\lambda} + V^\lambda(\bar{r}_\lambda, \bar{R}_\lambda, \gamma_\lambda) - E\right)\Psi^\lambda(\bar{r}_\lambda, \bar{R}_\lambda) = 0, \tag{2.6}$$

where $\nabla^2_{\bar{R}_\lambda}$ and $\nabla^2_{\bar{r}_\lambda}$ are the appropriate Laplacian operators, and E is the total energy excluding that associated with the motion of the center of mass. Upon introduction of the scaled coordinates of Eq. (2. 1), Eq. (2. 6) is converted to

$$\left(-\frac{\hbar^2}{2\mu}(\nabla^2_{\bar{R}_\lambda} + \nabla^2_{\bar{r}_\lambda}) + V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) - E\right)\Psi^\lambda(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = 0 , \tag{2.7}$$

where the reduced mass μ is given by

$$\mu = (\mu_{\lambda,\nu\kappa}\,\mu_{\nu\kappa})^{1/2} = [m_\lambda m_\nu m_\kappa/(m_\lambda + m_\nu + m_\kappa)]^{1/2} \tag{2.8}$$

and is independent of the choice of arrangement channel.

We now introduce the space fixed coordinate system $Oxyz$ (Fig. 2) centered on the center of mass O of the triatom system and whose axes are constantly parallel to the axes of a laboratory-fixed system of coordinates. In $Oxyz$ the polar and azimuthal angles of $\mathbf{R}_\lambda$ and $\mathbf{r}_\lambda$ are θ_λ, ϕ_λ and $\theta_{r_\lambda}, \phi_{r_\lambda}$, respectively. By expressing the Laplacian operators in Eq. (2. 7) in terms of R_λ, r_λ and these angles, the Schrödinger equation can be rewritten

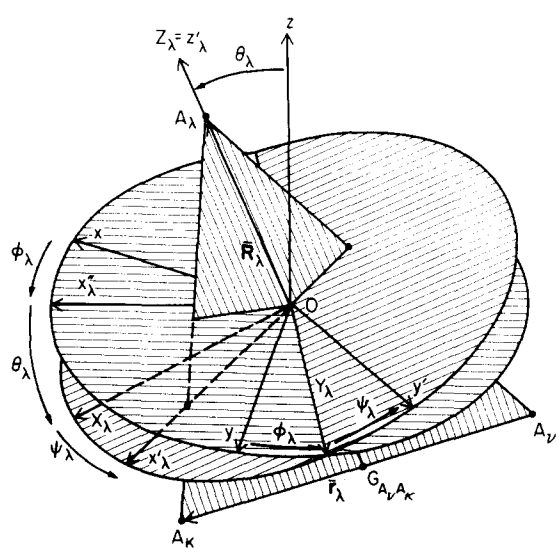

FIG. 2. Space-fixed coordinate system Oxyz and body-fixed systems $OX_\lambda Y_\lambda Z_\lambda$ and $Ox'_\lambda y' z'_\lambda$ (Sec. IIB). The origin O of this figure is the same as that of Fig. 1.

as

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{R_\lambda}\frac{\partial^2}{\partial R_\lambda^2}R_\lambda+\frac{1}{r_\lambda}\frac{\partial^2}{\partial r_\lambda^2}r_\lambda\right)+\frac{j_\lambda^2}{2\mu r_\lambda^2}+\frac{l_\lambda^2}{2\mu R_\lambda^2}+V^\lambda(r_\lambda,R_\lambda,\gamma_\lambda)-E\right]\Psi^\lambda(\mathbf{r}_\lambda,\mathbf{R}_\lambda)=0\ , \qquad (2.9)$$

where $\mathbf{l}_\lambda$ and $\mathbf{j}_\lambda$ are the usual orbital and rotational angular momentum operators expressed in the spherical coordinates $\theta_\lambda, \phi_\lambda$ and $\theta_{r_\lambda}, \phi_{r_\lambda}$ and are given in Appendix A. The total angular momentum operator J is the vector sum of $\mathbf{l}_\lambda$ and $\mathbf{j}_\lambda$,

$$\mathbf{J}=\mathbf{l}_\lambda+\mathbf{j}_\lambda\ , \qquad (2.10)$$

and is independent of arrangement channel.

The operators $\mathbf{J}^2$ and J_z (the z component of J) commute with each other and with the Hamiltonian H. In the partial wave analysis procedure, we expand $\Psi^\lambda(\mathbf{r}_\lambda,\mathbf{R}_\lambda)$ in terms of simultaneous eigenfunctions $\Psi^\lambda_{JM}(\mathbf{r}_\lambda,\mathbf{R}_\lambda)$ of $\mathbf{J}^2$, J_z, and H with eigenvalues $\hbar^2J(J+1)$, $\hbar M$, and E, respectively:

$$\Psi^\lambda(\mathbf{r}_\lambda,\mathbf{R}_\lambda)=\sum_{J=0}^{\infty}\sum_{M=-J}^{J}C^\lambda_{JM}\Psi^\lambda_{JM}(\mathbf{r}_\lambda,\mathbf{R}_\lambda)\ . \qquad (2.11)$$

The Ψ^λ_{JM} still satisfy Eq. (2.9).

C. The body-fixed Schrödinger equation

In the standard space-fixed theory (as formulated, for example, by Arthurs and Dalgarno[29]), one now expands Ψ^λ_{JM} in terms of a set of simulataneous eigenfunctions of $\mathbf{J}^2$, J_z, $\mathbf{l}_\lambda^2$, and $\mathbf{j}_\lambda^2$, thereby obtaining a set of coupled equations in the quantum numbers j_λ and l_λ. This derivation is summarized in Appendix A. A more convenient and computationally efficient procedure for our purposes is to transform to a system of body-fixed coordinates. These coordinate systems were applied to quantum mechanical problems long ago by Hirschfelder and Wigner[30] and have been discussed extensively by Curtiss, Hirschfelder, and Adler[31] and more recently by Pack,[32] and much of the present development will follow that of Pack. In a fully converged calculation, both the body-fixed and space-fixed formalisms lead to the same number of coupled equations and, for fully converged nonreactive atom diatom calculations, they may be implemented with comparable ease. However, body-fixed coordinate systems lead to an approximate decoupling of certain degrees of freedom which is not naturally present in the space-fixed analysis and which is useful in the development of approximate theories. More important, the body-fixed analysis leads to both computational and conceptual simplifications in the matching procedure, thus providing a considerable advantage in reactive scattering calculations over the corresponding space-fixed theory.

We now introduce the two different body fixed coordinate systems $OX_\lambda Y_\lambda Z_\lambda$ and $Ox'_\lambda y' z'_\lambda$ (see Fig. 2) as follows: (1) $OX_\lambda Y_\lambda Z_\lambda$ (not to be confused with the internal configuration space coordinate system $OX_\lambda Y_\lambda Z_\lambda$ of Fig. 2 of Paper I) is obtained from $Oxyz$ by rotating through the Euler angles[33] $\alpha=\phi_\lambda$, $\beta=\theta_\lambda$, $\gamma=0$ so that the resulting Z_λ axis points along the $\mathbf{R}_\lambda$ direction and the Y_λ axis lies in the xy plane; (2) $Ox'_\lambda y' z'_\lambda$ is obtained from $OX_\lambda Y_\lambda Z_\lambda$ by rotating it counterclockwise about OZ_λ ($\equiv Oz'_\lambda$) by an angle ψ_λ (in the 0 to 2π range) so as to bring Ox'_λ into the $\mathbf{R}_\lambda, \mathbf{r}_\lambda$ plane and Oy' (which is independent of λ) perpendicular to it and oriented in the direction of $\mathbf{R}_\lambda \times \mathbf{r}_\lambda$:

$$\hat{\mathbf{y}}'=\frac{\mathbf{R}_\lambda\times\mathbf{r}_\lambda}{|\mathbf{R}_\lambda\times\mathbf{r}_\lambda|}\ . \qquad (2.12)$$

The Euler angles which rotate $Oxyz$ into $Ox'_\lambda y' z'_\lambda$ are therefore $\alpha=\phi_\lambda$, $\beta=\theta_\lambda$, $\gamma=\psi_\lambda$. In either of the body-fixed coordinate systems $OX_\lambda Y_\lambda Z_\lambda$ or $Ox'_\lambda y' z'_\lambda$ the variables used to describe the system are $r_\lambda, R_\lambda, \phi_\lambda, \theta_\lambda, \psi_\lambda, \gamma_\lambda$. As seen from Fig. 2, ψ_λ is the counterclockwise angle from OY_λ to Oy' or from OX_λ to Ox'_λ as viewed from the positive OZ_λ axis. Since OY_λ is perpendicular to the $OX_\lambda Z_\lambda$ plane and therefore the $\mathbf{R}_\lambda$, Oz plane, and Oy' is perpendicular to the $\mathbf{R}_\lambda, \mathbf{r}_\lambda$ plane, we conclude that ψ_λ is the angle between these last two planes. This can also be seen by noticing that the plane containing the three axes OX_λ, Ox'_λ, and OY_λ is perpendicular to the $\mathbf{R}_\lambda$ vector and intersects the $\mathbf{R}_\lambda, Oz$ and $\mathbf{R}_\lambda, \mathbf{r}_\lambda$ planes along the OX_λ and Ox'_λ axes, respectively. Therefore, the angle ψ_λ between these two axes is equal to the angle between those two planes. A motion in which $R_\lambda, \phi_\lambda, \theta_\lambda, r_\lambda$, and γ_λ are kept constant but ψ_λ varies is a "tumbling" (i.e., rigid rotation) of the triatomic system around the $\mathbf{R}_\lambda$ vector, and for this reason the ψ_λ angle will be called the tumbling angle. In what follows we will find it most convenient to use the coordinate system $OX_\lambda Y_\lambda Z_\lambda$ for deriving the coupled form of the Schrödinger equation and $Ox'_\lambda y' z'_\lambda$ in developing the matching procedure. The procedure for expressing the operators $\mathbf{j}_\lambda^2$ and $\mathbf{l}_\lambda^2$ of Eq. (2.9) in variables $\phi_\lambda, \theta_\lambda, \psi_\lambda, \gamma_\lambda$ is described in Appendix A.

We now expand Ψ^λ_{JM} in terms of the elements of the Wigner rotation matrix $\mathbf{D}$ (α,β,γ) as follows[32]:

$$\Psi^\lambda_{JM}(\mathbf{r}_\lambda,\mathbf{R}_\lambda)=\sum_{\Omega_\lambda=-J}^{J}D^J_{M\Omega_\lambda}(\phi_\lambda,\theta_\lambda,0)\Psi^\lambda_{J\Omega_\lambda}(r_\lambda,R_\lambda,\gamma_\lambda,\psi_\lambda)\ . \qquad (2.13)$$

The notation used for the matrix elements is that of Davydov.[33] $\Psi^\lambda_{J\Omega_\lambda}$ is called a body-fixed wavefunction. The quantum number Ω_λ in Eq. (2.13) specifies the component of the total angular momentum J around $\mathbf{R}_\lambda$ or, equivalently, OZ_λ. The component of $\mathbf{l}_\lambda$ (the angular momentum conjugate to $\mathbf{R}_\lambda$) around this axis vanishes and therefore Ω_λ also specifies the Z_λ component of the rotational angular momentum $\mathbf{j}_\lambda$ in the body-fixed frame. The equality of J_{Z_λ} and $j_{\lambda Z_\lambda}$ is verified independently in Table I (which is described in Appendix A). We will refer to either J_{Z_λ} or $j_{\lambda Z_\lambda}$ as the tumbling angular momentum (since it describes the tumbling of the triatom around $\mathbf{R}_\lambda$) and Ω_λ as the tumbling quantum number in arrangement channel λ.

As outlined in Appendix A, substitution of Eq. (2.13) into Eq. (2.9) yields the following set of Ω_λ-coupled equations for the $\Psi^\lambda_{J\Omega_\lambda}(r_\lambda,R_\lambda,\gamma_\lambda,\psi_\lambda)$:

$$H^{J\lambda}_{\Omega_\lambda,\Omega_\lambda}\Psi^\lambda_{J\Omega_\lambda}+H^{J\lambda}_{\Omega_\lambda,\Omega_\lambda+1}\Psi^\lambda_{J,\Omega_\lambda+1}+H^{J\lambda}_{\Omega_\lambda,\Omega_\lambda-1}\Psi^\lambda_{J,\Omega_\lambda-1}=E\Psi^\lambda_{J\Omega_\lambda}\ . \qquad (2.14)$$

The $H^{J\lambda}_{\Omega_\lambda,\Omega'_\lambda}$ can be considered as the elements of a tridiagonal Hamiltonian operator matrix $\mathbf{H}^{J\lambda}(r_\lambda,R_\lambda,\gamma_\lambda,\psi_\lambda)$ whose diagonal and off-diagonal elements are defined, respectively, by

TABLE I. Angular momentum operators in space-fixed and body-fixed coordinate systems. [a]

$Oxyz$	$OX_\lambda Y_\lambda Z_\lambda$	$Ox'_\lambda y' z'_\lambda$
$J_x = -i\hbar\left(-\cos\phi\cot\theta\frac{\partial}{\partial\phi} - \sin\phi\frac{\partial}{\partial\theta} + \frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\psi}\right)$	$J_{X_\lambda} = -i\hbar\left(-\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} + \cos\theta\frac{\partial}{\partial\psi}\right)$	$J_{x'_\lambda} = -i\hbar\left(-\frac{\cos\psi}{\sin\theta}\frac{\partial}{\partial\phi} + \sin\psi\frac{\partial}{\partial\theta} + \cot\theta\cos\psi\frac{\partial}{\partial\psi}\right)$
$J_y = -i\hbar\left(-\sin\phi\cot\theta\frac{\partial}{\partial\phi} + \cos\phi\frac{\partial}{\partial\theta} + \frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\psi}\right)$	$J_{Y_\lambda} = -i\hbar\frac{\partial}{\partial\theta}$	$J_{y'} = -i\hbar\left(\frac{\sin\psi}{\sin\theta}\frac{\partial}{\partial\phi} + \cos\psi\frac{\partial}{\partial\theta} - \cot\theta\sin\psi\frac{\partial}{\partial\psi}\right)$
$J_z = -i\hbar\frac{\partial}{\partial\phi}$	$J_{Z_\lambda} = -i\hbar\frac{\partial}{\partial\psi}$	$J_{z'_\lambda} = -i\hbar\frac{\partial}{\partial\psi}$
$j_{\lambda x} = -i\hbar\left[\cos\phi\sin\theta + \sin\phi\sin\psi\cot\gamma - \cos\phi\cos\theta\cos\psi\cot\gamma\right)\frac{\partial}{\partial\psi} - (\sin\phi\cos\psi + \cos\phi\cos\theta\sin\psi)\frac{\partial}{\partial\gamma}\right]$	$j_{\lambda X_\lambda} = -i\hbar\left(-\cos\psi\cot\gamma\frac{\partial}{\partial\psi} - \sin\psi\frac{\partial}{\partial\gamma}\right)$	$j_{\lambda x'_\lambda} = -i\hbar\left(-\cot\gamma\frac{\partial}{\partial\psi}\right)$
$j_{\lambda y} = -i\hbar\left[(\sin\phi\sin\theta - \cos\phi\sin\psi\cot\gamma - \sin\phi\cos\theta\cos\psi\cot\gamma)\frac{\partial}{\partial\psi} + (\cos\phi\cos\psi - \sin\phi\cos\theta\sin\psi)\frac{\partial}{\partial\gamma}\right]$	$j_{\lambda Y_\lambda} = -i\hbar\left(-\sin\psi\cot\gamma\frac{\partial}{\partial\psi} + \cos\psi\frac{\partial}{\partial\gamma}\right)$	$j_{\lambda y'} = -i\hbar\frac{\partial}{\partial\gamma}$
$j_{\lambda z} = -i\hbar\left[(\cos\theta + \sin\theta\cos\psi\cot\gamma)\frac{\partial}{\partial\psi} + \sin\theta\sin\psi\frac{\partial}{\partial\gamma}\right]$	$j_{\lambda Z_\lambda} = -i\hbar\frac{\partial}{\partial\psi}$	$j_{\lambda z'_\lambda} = i\hbar\frac{\partial}{\partial\psi}$
$J^2 = J_x^2 + J_y^2 + J_z^2 = -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial\psi^2}\right) - \frac{2\cos\theta}{\sin^2\theta}\frac{\partial^2}{\partial\phi\partial\psi}\right]$	$J^2 = J_{X_\lambda}^2 + J_{Y_\lambda}^2 + J_{Z_\lambda}^2 - i\hbar\cot\theta J_{Y_\lambda}$	$J^2 = J_{x'_\lambda}^2 + J_{y'}^2 + J_{z'_\lambda}^2$
$j_\lambda^2 = j_{\lambda x}^2 + j_{\lambda y}^2 + j_{\lambda z}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\gamma^2} + \cot\gamma\frac{\partial}{\partial\gamma} + \frac{1}{\sin^2\gamma}\frac{\partial^2}{\partial\psi^2}\right)$	$j_\lambda^2 = j_{\lambda X_\lambda}^2 + j_{\lambda Y_\lambda}^2 + j_{\lambda Z_\lambda}^2$	$j_\lambda^2 = j_{\lambda x'_\lambda}^2 + j_{\lambda y'}^2 + j_{\lambda z'_\lambda}^2 - i\hbar\cot\gamma\, j_{\lambda y'}$
$\mathbf{j}_\lambda\cdot\mathbf{J} = j_{\lambda z}J_z + j_{\lambda x}J_x + j_{\lambda y}J_y = -\hbar^2\left[\frac{\cos\psi\cot\gamma}{\sin\theta}\frac{\partial^2}{\partial\psi\partial\phi} + \frac{\sin\psi}{\sin\theta}\frac{\partial^2}{\partial\gamma\partial\phi} - \sin\psi\cot\theta\frac{\partial^2}{\partial\psi\partial\gamma} - \sin\psi\cot\gamma\frac{\partial^2}{\partial\psi\partial\theta} + \cos\psi\frac{\partial^2}{\partial\gamma\partial\theta} + (1 - \cos\psi\cot\gamma\cot\theta)\frac{\partial^2}{\partial\psi^2}\right]$	$\mathbf{j}_\lambda\cdot\mathbf{J} = j_{\lambda Z_\lambda}J_{Z_\lambda} + j_{\lambda X_\lambda}J_{X_\lambda} + j_{\lambda Y_\lambda}J_{Y_\lambda}$	$\mathbf{j}_\lambda\cdot\mathbf{J} = j_{\lambda z'_\lambda}J_{z'_\lambda} + j_{\lambda x'_\lambda}J_{x'_\lambda} + j_{\lambda y'}J_{y'} - i\hbar\cot\gamma J_{y'}$

[a] The subscript λ has been omitted from the symbols θ, ϕ, γ, ψ. The expressions for J^2, j_λ^2, and $\mathbf{j}_\lambda\cdot\mathbf{J}$ in terms of θ, ϕ, γ, ψ are independent of coordinate system.

$$H^{J\lambda}_{\Omega_\lambda,\Omega_\lambda} = -\frac{\hbar^2}{2\mu}\left(\frac{1}{r_\lambda}\frac{\partial^2}{\partial r_\lambda^2}r_\lambda + \frac{1}{R_\lambda}\frac{\partial^2}{\partial R_\lambda^2}R_\lambda\right) + \frac{\mathbf{j}_\lambda^2}{2\mu r_\lambda^2} + \frac{1}{2\mu R_\lambda^2}[J(J+1)\hbar^2 - 2\Omega_\lambda\hbar j_{\lambda Z_\lambda} + j_\lambda^2] + V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) \tag{2.15}$$

and

$$H^{J\lambda}_{\Omega_\lambda,\Omega_\lambda\pm1} = -\frac{\hbar}{2\mu R_\lambda^2}\sqrt{J(J+1) - \Omega_\lambda(\Omega_\lambda\pm1)}\, j_\lambda^\mp . \tag{2.16}$$

The $j_\lambda^\mp$ are the lowering (−) and raising (+) operators of the rotational angular momentum $\mathbf{j}_\lambda$ in the body-fixed $OX_\lambda Y_\lambda Z_\lambda$ coordinate system. The $1/2\mu R_\lambda^2$ term in Eq. (2.15) results directly from the $\mathbf{j}_\lambda^2/2\mu R_\lambda^2$ term in Eq. (2.9). Defining Ψ_J^λ as the $(2\Omega_\lambda+1)$-dimensional column vector whose elements are the $\Psi^\lambda_{J\Omega_\lambda}$, Eq. (2.14) can be put in the matrix form

$$\mathbf{H}^{J\lambda}\Psi_J^\lambda = E\Psi_J^\lambda . \tag{2.17}$$

Equations (2.14) or (2.17) are the body-fixed partial wave Schrödinger equation. Equation (2.14) is identical to the corresponding result of Pack[32] and indicates that the kinetic energy operator is no longer diagonal in the body-fixed representation and is the sole mechanism which couples different tumbling quantum numbers Ω_λ.

The potential coupling is diagonal in Ω_λ and is responsible for coupling between states of different vibration–rotation quantum numbers $v_\lambda j_\lambda$, as indicated later in Eq. (3.16) and its counterparts for the strong interaction and matching regions. This separation of kinematic and potential coupling is of prime importance in the development of approximate decoupling procedures, as will be discussed in the next section.

D. The rotationally coupled Schrödinger equation; tumbling-decoupling approximations

We now expand the body-fixed wavefunctions $\Psi^\lambda_{J\Omega_\lambda}$ in terms of the spherical harmonics $Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda,\psi_\lambda)$ which, as discussed in Appendix A, are the simultaneous eigenfunctions of $\mathbf{j}_\lambda^2$ and $j_{\lambda z_\lambda}$:

$$\Psi^\lambda_{J\Omega_\lambda}(r_\lambda,R_\lambda,\gamma_\lambda,\psi_\lambda)=\sum_{j_\lambda=|\Omega_\lambda|}^{\infty} Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda,\psi_\lambda)w^\lambda_{Jj_\lambda\Omega_\lambda}(r_\lambda,R_\lambda)\qquad \Omega_\lambda=-J,\,-J+1,\,\ldots,\,J;\quad J=0,1,2,\ldots \tag{2.18}$$

If we substitute this into Eq. (2.14), multiply throughout by $Y^*_{j'_\lambda\Omega'_\lambda}(\gamma_\lambda,\psi_\lambda)$ and integrate over γ_λ and ψ_λ (using the solid angle volume element $\sin\gamma_\lambda\,d\gamma_\lambda d\psi_\lambda$), and finally interchange the primed and unprimed quantum numbers, it becomes a Schrödinger equation in the two scaled distances r_λ, R_λ:

$$(t^{J\lambda j_\lambda}_{\Omega_\lambda\Omega_\lambda}-E)\,w^\lambda_{Jj_\lambda\Omega_\lambda}(r_\lambda,R_\lambda)+\sum_{j'_\lambda=|\Omega_\lambda|}^{\infty} V^{\lambda\Omega_\lambda}_{j_\lambda j'_\lambda}\,w^\lambda_{Jj'_\lambda\Omega_\lambda}(r_\lambda,R_\lambda)+t^{J\lambda j_\lambda}_{\Omega_\lambda,\Omega_\lambda+1}w^\lambda_{Jj_\lambda,\Omega_\lambda+1}(r_\lambda,R_\lambda)+t^{J\lambda j_\lambda}_{\Omega_\lambda,\Omega_\lambda-1}w^\lambda_{Jj_\lambda,\Omega_\lambda-1}(r_\lambda,R_\lambda)=0$$

$$J=0,1,2,\ldots;\quad \Omega_\lambda=-J,\,-J+1,\,\ldots,\,J;\quad j_\lambda=|\Omega_\lambda|,\,|\Omega_\lambda|+1,\,\ldots, \tag{2.19}$$

where

$$t^{J\lambda j_\lambda}_{\Omega_\lambda\Omega_\lambda}=-\frac{\hbar^2}{2\mu}\left(\frac{1}{R_\lambda}\frac{\partial^2}{\partial R_\lambda^2}R_\lambda+\frac{1}{r_\lambda}\frac{\partial^2}{\partial r_\lambda^2}r_\lambda\right)+\frac{j_\lambda(j_\lambda+1)\hbar^2}{2\mu r_\lambda^2}+\frac{\hbar^2}{2\mu R_\lambda^2}[J(J+1)-2\Omega_\lambda^2+j_\lambda(j_\lambda+1)]\,, \tag{2.20}$$

$$t^{J\lambda j_\lambda}_{\Omega_\lambda,\Omega_\lambda\pm1}=-\frac{\hbar^2}{2\mu R_\lambda^2}\xi_\pm(J,\Omega_\lambda)\xi_\pm(j_\lambda,\Omega_\lambda)\,, \tag{2.21}$$

$$\xi_\pm(J,\Omega_\lambda)=[J(J+1)-\Omega_\lambda(\Omega_\lambda\pm1)]^{1/2}\qquad |\Omega_\lambda|\le J\,, \tag{2.22}$$

and

$$V^{\lambda\Omega_\lambda}_{j_\lambda j'_\lambda}(r_\lambda,R_\lambda)=\langle j_\lambda\Omega_\lambda|\,V^\lambda(r_\lambda,R_\lambda,\gamma_\lambda)\,|j'_\lambda\Omega_\lambda\rangle\,, \tag{2.23}$$

Equation (2.19) is the three-dimensional generalization of an analogous equation for collinear and coplanar[19] reactions. None of the four angular coordinates $\theta_\lambda, \phi_\lambda, \gamma_\lambda, \psi_\lambda$ appear in it, with only the two scaled distances r_λ, R_λ remaining. In the collinear case, none of the angular momentum quantum numbers J, Ω_λ, or j_λ appear, and we have only one such equation. For systems confined to a space-fixed plane, Ω_λ does not appear (or it can be considered to have the fixed value zero) since the system does not tumble, and there is therefore no Ω_λ coupling. In that case, j_λ assumes all integer values, including negative ones, and there is one set of j_λ-coupled equations for each J. In the present three-dimensional case, there is both j_λ and Ω_λ coupling, but still no J coupling. Let us consider a kinetic energy matrix $\mathbf{t}^{J\lambda}(r_\lambda,R_\lambda)$ (which includes the centrifugal potential terms) and a potential energy matrix $\mathbf{V}^\lambda(r_\lambda,R_\lambda)$ whose rows and columns are scanned by the indices j_λ,Ω_λ and $j'_\lambda,\Omega'_\lambda$, respectively. They are defined by

$$(\mathbf{t}^{J\lambda})^{j'_\lambda\Omega'_\lambda}_{j_\lambda\Omega_\lambda}=\delta_{j_\lambda j'_\lambda}\sum_{i=-1}^{1}\delta_{\Omega_\lambda,\Omega'_\lambda-i}\,t^{J\lambda j_\lambda}_{\Omega_\lambda,\Omega_\lambda+i} \tag{2.24}$$

and

$$(\mathbf{V}^\lambda)^{j'_\lambda\Omega'_\lambda}_{j_\lambda\Omega_\lambda}=\delta_{\Omega_\lambda\Omega'_\lambda}V^{\lambda\Omega}_{j_\lambda j'_\lambda}\,, \tag{2.25}$$

respectively, where the several t and V were defined by Eqs. (2.20)–(2.23). It can be seen that $\mathbf{t}^{J\lambda}$ is diagonal in j_λ (and tridiagonal in Ω_λ) whereas $\mathbf{V}^\lambda$ is diagonal in Ω_λ. Defining $\mathbf{w}^\lambda_J(r_\lambda,R_\lambda)$ as the column vector whose elements, scanned by $j_\lambda\Omega_\lambda$, are the functions $w^\lambda_{Jj_\lambda\Omega_\lambda}(r_\lambda,R_\lambda)$ Eq. (2.19) can be rewritten as

$$(\mathbf{t}^{J\lambda}+\mathbf{V}^\lambda)\mathbf{w}^\lambda_J=E\mathbf{w}^\lambda_J\,. \tag{2.26}$$

Equation (2.26) shows clearly that the potential coupling is diagonal in Ω_λ. This, along with the weakness of the centrifugal coupling (due to the terms in $\mathbf{t}^{J\lambda}$ of angular origin) for small J and j_λ has lead to the development of fairly accurate tumbling–decoupling approximations by several workers[32,34,35] in studies of nonreactive atom–diatom scattering. In such procedures, the $t^{J\lambda j_\lambda}_{\Omega_\lambda,\Omega_\lambda\pm1}$ terms in Eqs. (2.19) and (2.24) are neglected, thereby making Eq. (2.26) be diagonal in Ω_λ. In addition, the $\hbar^2/2\mu R_\lambda^2$ term in Eq. (2.20) [which arises from the $\mathbf{l}_\lambda^2$ term in Eq. (2.9)] is usually replaced by an approximate expression. Pack[32] replaces it by $\hbar^2J(J+1)/2\mu R_\lambda^2$, and McGuire and Kouri[34] by $\hbar^2 l_\lambda(l_\lambda+1)/2\mu R_\lambda^2$, where l_λ is the orbital angular momentum quantum number in the space-fixed system of coordinates.[36] Such additional approximations are unnecessary to produce Ω_λ decoupling and may furthermore introduce additional errors without significant computational simplification; we suggest that they should be omitted. For the case of reactive scattering, an Ω_λ decoupling requires neglect of the $t^{J\lambda j_\lambda}_{\Omega_\lambda,\Omega_\lambda\pm1}$ in Eq. (2.19) for each arrangement channel region $\lambda=\alpha,\beta,\gamma$. The exact matching procedure described in Sec. III may be retained, or be replaced by approximate ones which retain the spirit of Ω_λ decoupling. In a separate paper

we will present some results of an application of some of these possible procedures to 3D reactive scattering.

The elements of the potential coupling matrix of Eqs. (2.23) and (2.26) may be conveniently calculated by expanding the potential $V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$ in a series of Legendre polynomials

$$V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) = \sum_{k=0}^{\infty} V_k^\lambda(r_\lambda, R_\lambda) P_k(\cos\gamma_\lambda) \tag{2.27}$$

which, when substituted into Eq. (2.23), leads to[32]

$$V^{\lambda\Omega_\lambda}_{j_\lambda j'_\lambda}(r_\lambda, R_\lambda) = \sum_{k=0}^{\infty} \left(\frac{2j_\lambda+1}{2j'_\lambda+1}\right)^{1/2} C(j_\lambda k j'_\lambda; \Omega_\lambda 0 \Omega_\lambda) \, C(j_\lambda k j'_\lambda; 000) V_k^\lambda(r_\lambda, R_\lambda) \, , \tag{2.28}$$

where the Clebsch–Gordan coefficients C are expressed in the notation of Rose.[37] For collisions of an atom with a homonuclear diatomic molecule (as in $H+H_2$), the only nonzero terms in Eq. (2.27) occur for even k [since $V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$ is symmetric about $\gamma_\lambda = \pi/2$]. Since[38]

$$C(j_\lambda k j'_\lambda; 000) = 0 \quad \text{for } j_\lambda + k + j'_\lambda = \text{odd}, \tag{2.29}$$

we see that $\mathbf{V}^\lambda$ does not couple even with odd rotational states. Use of this decoupling in reducing the necessary calculations for reactions like $H+H_2$ was discussed in Paper I for the planar case, and most of the simplifications described there are valid for 3D collisions as well. Note that Eq. (2.28) involves a single sum over products of Clebsch–Gordan coefficients, a substantial simplification over the corresponding space-fixed expansion which requires 6-j symbols[32]

Let us now define a new function $F^\lambda_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda)$ by

$$F^\lambda_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda) = R_\lambda r_\lambda w^\lambda_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda) \, . \tag{2.30}$$

Substitution of this into Eq. (2.19) leads to

$$(\bar{t}^{J\lambda j_\lambda}_{\Omega_\lambda \Omega_\lambda} - E) F^\lambda_{J j_\lambda \Omega_\lambda} + \sum_{j'_\lambda} V^{\lambda\Omega_\lambda}_{j_\lambda j'_\lambda} F^\lambda_{J j'_\lambda \Omega_\lambda} + t^{J\lambda j_\lambda}_{\Omega_\lambda, \Omega_\lambda+1} F^\lambda_{J j_\lambda, \Omega_\lambda+1} + t^{J\lambda j_\lambda}_{\Omega_\lambda, \Omega_\lambda-1} F^\lambda_{J j_\lambda, \Omega_\lambda-1} = 0 \tag{2.31}$$

where

$$\bar{t}^{J\lambda j_\lambda}_{\Omega_\lambda \Omega_\lambda} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial R_\lambda^2} + \frac{\partial^2}{\partial r_\lambda^2}\right) + \frac{j_\lambda(j_\lambda+1)\hbar^2}{2\mu r_\lambda^2} + \frac{\hbar^2}{2\mu R_\lambda^2}[J(J+1) - 2\Omega_\lambda^2 + j_\lambda(j_\lambda+1)] \, , \tag{2.32}$$

and the remaining quantities are defined by Eqs. (2.21)–(2.23). In matrix form, Eq. (2.31) can be written as

$$(\bar{\mathbf{t}}^{J\lambda} + \mathbf{V}^\lambda)\mathbf{F}^\lambda_J = E\mathbf{F}^\lambda_J \, , \tag{2.33}$$

where $\bar{\mathbf{t}}^{J\lambda}$ is defined similarly to $\mathbf{t}^{J\lambda}$ and $\mathbf{F}^\lambda_J$ similarly to $\mathbf{w}^\lambda_J$. Equations (2.31) and (2.33) are called the body-fixed rotationally coupled Schrödinger equation.

III. THE INTEGRATION IN ARRANGEMENT CHANNEL REGION λ

A. Division of r_λ, R_λ configuration space into regions

To solve Eq. (2.31) or (2.33) we expand the wavefunction $F^\lambda_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda)$ in terms of a set of one-variable

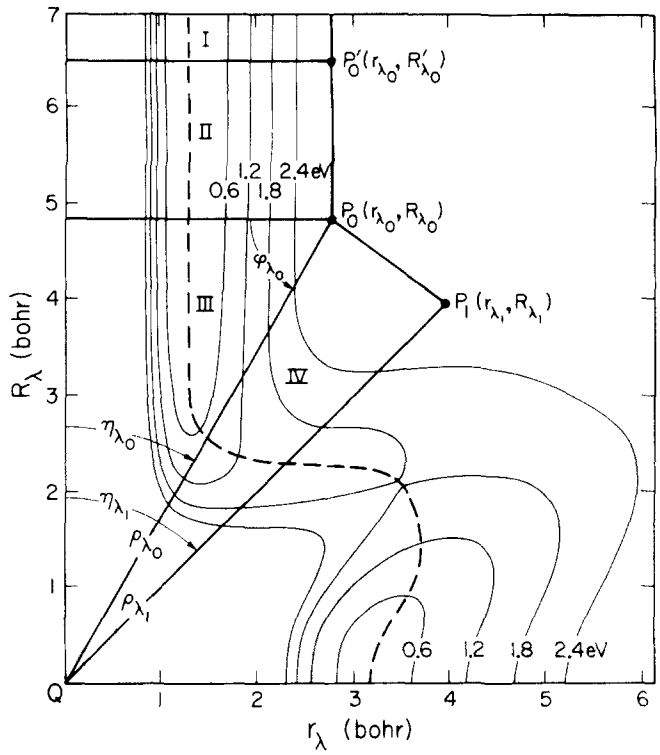

FIG. 3. Division of the $\mathbf{R}_\lambda$, $\mathbf{r}_\lambda$ space into four regions, I, II, III, and IV. The contours are equipotentials of the matrix element $V^\lambda_0(r_\lambda, R_\lambda)$ [see Eq. (2.27)] in eV for the Porter–Karplus $H+H_2$ potential energy function. The dashed line is the line of steepest ascents for V^λ_0. The locations of the points P'_0, P_0, and P_1 are discussed in Sec. III. A of the text. Q is the origin of this space.

pseudovibrational functions which locally span the r_λ, R_λ configuration space along cuts which are approximately perpendicular to a conveniently defined reaction coordinate. The resulting expansion coefficients satisfy ordinary coupled differential equations which must be numerically integrated through the arrangement channel region λ to generate a set of solutions to the Schrödinger equation in that region. In order to obtain an efficient representation of the pseudovibrational motion everywhere, we must change both coordinate systems and basis sets frequently during this propagation. This may be done in many different ways depending on the boundaries of the arrangement channel regions and the shape of the potential energy surface in these regions. For the $H+H_2$ reaction, and most others for which the choice of matching surfaces is given by Eq. (3.2) of Paper I, a convenient procedure consists of dividing the r_λ, R_λ configuration space into four areas called regions, as depicted in Fig. 3. For reference contours of the potential matrix element $V_0(r_\lambda, R_\lambda)$ of Eq. (2.27) for the H_3 Porter–Karplus surface[39] are plotted on the same figure. The regions are denoted as follows: I—asymptotic region; II—weak interaction region; III—strong interaction region; and IV—matching region. The boundary points P'_0, P_0, and P_1 are required to lie in the high-energy plateau region corresponding to dissociation of the triatomic system into A+B+C (i.e., large r_λ and R_λ), in positions which are primarily determined by certain geometrical criteria. These are

described in detail in Sec. III.C of Paper I and are unchanged in the present application. Within each region, we choose a set of orthogonal coordinates which efficiently describe the local vibrational and translational motion. The choice of these coordinates is also the same as in Sec. III.C of Paper I.

B. The coupled Schrödinger equation in the propagation variable

We now consider the solution of Eq. (2.31) in each of the four regions in arrangement channel region λ. Much of this treatment is completely analogous to the corresponding coplanar theory (Sec. III. D of Paper I), and that paper should be consulted for a more detailed explanation of the concepts involved.

1. *The asymptotic region*

The coordinates for this region are r_λ, R_λ. In terms of these, the potential function $V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$ becomes the isolated diatomic potential $v^\lambda(r_\lambda)$ since the boundaries of the asymptotic region are chosen[19] so that in it the potential has assumed its asymptotic form. We now expand the wavefunction $F^\lambda_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda)$ of Eq. (2.31) in terms of the eigenfunctions $\phi^{\lambda(a)}_{v_\lambda j_\lambda}(r_\lambda)$ of the vibrational Hamiltonian:

$$F^{\lambda(a)}_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda) = \sum_{v_\lambda} g^{\lambda(a)}_{J v_\lambda j_\lambda \Omega_\lambda}(R_\lambda)\, \phi^{\lambda(a)}_{v_\lambda j_\lambda}(r_\lambda), \tag{3.1}$$

where the (a) refers to asymptotic region, and the $\phi^{\lambda(a)}_{v_\lambda j_\lambda}$ are vibrational basis functions which satisfy

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr_\lambda^2} + \frac{j_\lambda(j_\lambda+1)\hbar^2}{2\mu r_\lambda^2} + v^\lambda(r_\lambda)\right)\phi^{\lambda(a)}_{v_\lambda j_\lambda}(r_\lambda) = \epsilon^{\lambda(a)}_{v_\lambda j_\lambda}\, \phi^{\lambda(a)}_{v_\lambda j_\lambda}(r_\lambda) \tag{3.2}$$

with boundary conditions

$$\phi^{\lambda(a)}_{v_\lambda j_\lambda}(r_{\lambda_0}) = \phi^{\lambda(a)}_{v_\lambda j_\lambda}(0) = 0. \tag{3.3}$$

$\epsilon^{\lambda(a)}_{v_\lambda j_\lambda}$ is the asymptotic diatomic vibration–rotation energy, and $r_\lambda^{-1}\phi^{\lambda(a)}_{v_\lambda j_\lambda}(r_\lambda)$, except for a normalization constant, is the radial part of the corresponding diatomic eigenfunction. Substituting Eq. (3.1) into Eq. (2.31), using Eq. (3.2), multiplying by $\phi^{\lambda(a)}_{v'_\lambda j'_\lambda}(r_\lambda)$, integrating over r_λ, and replacing v'_λ by v_λ, we obtain the Schrödinger equation for translational R_λ motion in the asymptotic region:

$$\left(\frac{d^2}{dR_\lambda^2} - \frac{1}{R_\lambda^2}[J(J+1) - 2\Omega_\lambda^2 + j_\lambda(j_\lambda+1)] + k^{\lambda(a)2}_{v_\lambda j_\lambda}\right) g^{\lambda(a)}_{J v_\lambda j_\lambda \Omega_\lambda}(R_\lambda)$$
$$+ \frac{1}{R_\lambda^2}[\xi_+(J,\Omega_\lambda)\xi_+(j_\lambda,\Omega_\lambda) g^{\lambda(a)}_{J v_\lambda j_\lambda, \Omega_\lambda+1}(R_\lambda)$$
$$+ \xi_-(J,\Omega_\lambda)\xi_-(j_\lambda,\Omega_\lambda) g^{\lambda(a)}_{J v_\lambda j_\lambda, \Omega_\lambda-1}] = 0, \tag{3.4}$$

where

$$k^{\lambda(a)2}_{v_\lambda j_\lambda} = \frac{2\mu}{\hbar^2}(E - \epsilon^{\lambda(a)}_{v_\lambda j_\lambda}). \tag{3.5}$$

Note that while no vibrational or rotational coupling exists in Eq. (3.4), the kinetic energy coupling between g's of different Ω_λ persists in this asymptotic region, decreasing only as R_λ^{-2} (rather than exponentially or as R_λ^{-6} as is often the case with potential coupling). Of course, as $R_\lambda \to \infty$ (the "far" asymptotic region), Eqs. (3.4) completely uncouple and the $g^{\lambda(a)}_{J v_\lambda j_\lambda \Omega_\lambda}$ become solutions to

$$\left(\frac{d^2}{dR_\lambda^2} + k^{\lambda(a)2}_{v_\lambda j_\lambda}\right) g^{\lambda(a)}_{J v_\lambda j_\lambda \Omega_\lambda}(R_\lambda) = 0, \tag{3.6}$$

which are simply linear combinations of $\exp(\pm i k^{\lambda(a)}_{v_\lambda j_\lambda} R_\lambda)$ for open channels ($E > \epsilon^{\lambda(a)}_{v_\lambda j_\lambda}$) and $\exp(\pm |k^{\lambda(a)}_{v_\lambda j_\lambda}| R_\lambda)$ for closed ones ($E < \epsilon^{\lambda(a)}_{v_\lambda j_\lambda}$). Equation (3.4) may be solved analytically either by diagonalizing the Hamiltonian in that equation or by realizing that the corresponding space-fixed Schrödinger equation is already diagonal,[29] and thus its solutions may be linearly combined to satisfy Eq. (3.4).[35] The solutions of the space-fixed Schrödinger equation for open channels are related to the regular and irregular spherical Bessel functions $j_{l_\lambda}(k^{\lambda(a)}_{v_\lambda j_\lambda} R_\lambda)$ and $y_{l_\lambda}(k^{\lambda(a)}_{v_\lambda j_\lambda} R_\lambda)$,[29] where l_λ is the orbital angular momentum quantum number. The corresponding body-fixed solutions are found by equating Eqs. (A5) and (A13) of Appendix A and using Eq. (A14) to solve for the body-fixed coefficients $w^\lambda_{J j_\lambda \Omega_\lambda}$. Since Eqs. (2.30) and (3.1) apply equally to space-fixed and body-fixed solutions, we can immediately write the asymptotic body-fixed solutions for open channels as linear combinations of the regular and irregular solutions

$$g^{\lambda(a)}_{J v_\lambda j_\lambda \Omega_\lambda}(R_\lambda) = k^{\lambda(a)}_{v_\lambda j_\lambda} R_\lambda \left(\frac{2J+1}{4\pi}\right)^{1/2} (-1)^{j_\lambda - \Omega_\lambda}$$
$$\times \sum_{l_\lambda} C(J j_\lambda l_\lambda;\ \Omega_\lambda - \Omega_\lambda 0) \begin{pmatrix} j_{l_\lambda}(k^{\lambda(a)}_{v_\lambda j_\lambda} R_\lambda) \\ y_{l_\lambda}(k^{\lambda(a)}_{v_\lambda j_\lambda} R_\lambda) \end{pmatrix}$$
$$(E > \epsilon^{\lambda(a)}_{v_\lambda j_\lambda}), \tag{3.7}$$

where the upper (lower) term in the large parentheses refers to the regular (irregular) solution. The use of Eq. (3.6) in formulating the asymptotic R and S matrix boundary conditions will be discussed in Sec. V. A. For closed channels, the body-fixed solution is still of the form in Eq. (3.7) but with the spherical Bessel functions j_{l_λ} and y_{l_λ} replaced by the modified spherical Bessel functions $i_{l_\lambda}(|k^{\lambda(a)}_{v_\lambda j_\lambda}| R_\lambda)$ and $k_{l_\lambda}(|k^{\lambda(a)}_{v_\lambda j_\lambda}| R_\lambda)$.[40]

Let us now introduce a matrix notation for the Schrödinger equation [Eq. (3.4)]. We consider the $g^{\lambda(a)}_{J v_\lambda j_\lambda \Omega_\lambda}$ as elements of a column vector $\mathbf{g}^{\lambda(a)}_J$ whose elements are labeled by the indices $v_\lambda j_\lambda \Omega_\lambda$, which are assumed to scan a total of N values (in a truncated coupled-channel expansion). This vector represents one of $2N$ possible linearly independent solutions of Eq. (3.4). These $2N$ solutions which form $2N$ column vectors can be assembled into two matrices of dimension $N \times N$ which we label as $\mathbf{g}^{\lambda(a)+}_J$ and $\mathbf{g}^{\lambda(a)-}_J$, where a set of indices $v'_\lambda j'_\lambda \Omega'_\lambda$ analogous to the row indices explained above is associated with each column.[41] The labels $\pm$ are in general arbitrary, but may be chosen to distinguigh the solutions generated in the propagation from Region I–IV (labeled plus) and from IV–I (labeled minus). Both propagations are necessary to generate all $2N$ solutions (we get N from the propagation in each direction). Using this notation, Eq. (3.4) may be written as

$$\frac{d^2 \mathbf{g}^{\lambda(a)\pm}_J}{dR_\lambda^2} = \mathbf{U}^{\lambda(a)}_J(R_\lambda)\mathbf{g}^{\lambda(a)\pm}_J, \tag{3.8}$$

where

$$\mathbf{U}_J^{\lambda(a)} = -\mathbf{K}^{\lambda(a)2} + \mathbf{U}_J^{c\lambda(a)} , \tag{3.9}$$

$$(\mathbf{K}^{\lambda(a)2})_{t_\lambda}^{t'_\lambda} = \delta_{t_\lambda}^{t'_\lambda} k_{v_\lambda j_\lambda}^{\lambda(a)2} , \tag{3.10}$$

$$(\mathbf{U}_J^{c\lambda(a)})_{t_\lambda}^{t'_\lambda} = \frac{\delta_{v_\lambda j_\lambda}^{v'_\lambda j'_\lambda}}{R_\lambda^2} \{\delta_{\Omega_\lambda,\Omega'_\lambda}[J(J+1) - 2\Omega_\lambda^2 + j_\lambda(j_\lambda+1)] - \delta_{\Omega_\lambda+1,\Omega'_\lambda}\xi_+(J,\Omega_\lambda)\xi_+(j_\lambda,\Omega_\lambda) - \delta_{\Omega_\lambda-1,\Omega'_\lambda}\xi_-(J,\Omega_\lambda)\xi_-(j_\lambda,\Omega_\lambda)\} . \tag{3.11}$$

The symbol t_λ stands for the set of indices $v_\lambda j_\lambda \Omega_\lambda$ and the subscripts and superscripts on a matrix element designate its row and column, respectively. The $\mathbf{U}_J^{c\lambda(a)}$ matrix arises from the $1/R_\lambda^2$ centrifugal terms. Equation (3.8) is the full coupled propagation equation for the asymptotic region I.

2. The weak interaction region

In this region we still use the variables r_λ and R_λ to represent vibrational and translational motion, but the potential $V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$ is now dependent on R_λ and γ_λ as well as r_λ, so we no longer use the asymptotic vibrational eigenfunctions of Eqs. (3.1) and (3.2) to expand the wavefunction. Since it may be desirable to change vibrational basis functions several times within Region II, we subdivide that region into $n_{\rm II}^\lambda$ subregions separated by lines of constant R_λ at

$$R_\lambda = R'_{\lambda_0},\ R'_{\lambda_1},\ \ldots,\ R'_{\lambda_{n_{\rm II}^\lambda}} = R_{\lambda_0} .$$

The range of R_λ for the ith subregion is $R'_{\lambda_{i-1}} \le R_\lambda \le R'_{\lambda_i}$ and we choose the expansion basis functions for that subregion to be the eigenfunctions of a reference potential $V_{\rm ref}^\lambda(r_\lambda; R_{\lambda_i}^0)$ at a point $R_{\lambda_i}^0$ belonging to the subregion (such as the midpoint). The reference potential $V_{\rm ref}^\lambda(r_\lambda; R_\lambda)$ is in general arbitrary provided that a complete vibration–rotation expansion is used, but an efficient representation of the vibrational motions can greatly reduce the number of closed channels required for such completeness. Examples of reference potentials are the $V_0^\lambda(r_\lambda, R_\lambda)$ of Eq. (2.27) and the exact potential $V^\lambda(r_\lambda, R_\lambda, \bar\gamma_\lambda)$ at fixed $\bar\gamma_\lambda$. Once a reference potential is chosen, the vibrational basis functions for subregion i may be determined by solving

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr_\lambda^2} + \frac{j_\lambda(j_\lambda+1)\hbar^2}{2\mu r_\lambda^2} + V_{\rm ref}(r_\lambda; R_{\lambda_i}^0)\right)\phi_{v_\lambda j_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda_i}^0) = \epsilon_{v_\lambda j_\lambda}^{\lambda(w)}(R_{\lambda_i}^0)\phi_{v_\lambda j_\lambda}^{\lambda(w)} \tag{3.12}$$

subject to boundary conditions analogous to Eq. (3.3) where the superscript (w) indicates weak interaction region. We now expand the wavefunction $F_{J j_\lambda \Omega_\lambda}^\lambda$ in terms of these basis functions,

$$F_{J j_\lambda \Omega_\lambda}^{\lambda(w)\pm}(r_\lambda, R_\lambda) = \sum_{v_\lambda} g_{J v_\lambda j_\lambda \Omega_\lambda}^{\lambda(w)\pm}(R_\lambda; R_{\lambda_i}^0)\phi_{v_\lambda j_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda_i}^0) . \tag{3.13}$$

Substituting this into Eq. (2.31), using Eq. (3.12) to simplify, then multiplying by $\phi_{v'_\lambda j'_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda_i}^0)$ and integrating over r_λ, we obtain the following coupled differential equations (in the matrix notation of Sec. III.B.1):

$$\frac{d^2\mathbf{g}_J^{\lambda(w)\pm}}{dR_\lambda^2} = \mathbf{U}_J^{\lambda(w)}(R_\lambda; R_{\lambda_i}^0)\mathbf{g}_J^{\lambda(w)\pm} , \tag{3.14}$$

where

$$\mathbf{U}_J^{\lambda(w)} = -\mathbf{K}^{\lambda(w)2} + \mathbf{U}_J^{c\lambda(w)} + \mathbf{U}_p^{\lambda(w)} . \tag{3.15}$$

The matrices $\mathbf{K}^{\lambda(w)2}$ and $\mathbf{U}_J^{c\lambda(w)}$ are given by Eqs. (3.10) and (3.11) with the superscript (w) substituted for (a), while the J-independent potential coupling potential matrix $\mathbf{U}_p^{\lambda(w)}$ is given by

$$(\mathbf{U}_p^{\lambda(w)})_{t_\lambda}^{t'_\lambda} = \frac{2\mu}{\hbar^2}\delta_{\Omega_\lambda\Omega'_\lambda}\int \phi_{v_\lambda j_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda_i}^0) \times [V_{j_\lambda j'_\lambda}^{\lambda\Omega_\lambda}(r_\lambda, R_\lambda) - V_{\rm ref}(r_\lambda; R_{\lambda_i}^0)]\phi_{v'_\lambda j'_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda_i}^0)\, dr_\lambda = \langle t_\lambda | V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) - V_{\rm ref}^\lambda(r_\lambda; R_{\lambda_i}^0) | t'_\lambda \rangle , \tag{3.16}$$

where t_λ was defined after Eq. (3.11) and the γ_λ integral is performed as indicated in Eq. (2.23). Equation (3.16) clearly shows that this potential energy matrix is diagonal in Ω_λ but couples states of different vibration–rotation quantum numbers $v_\lambda j_\lambda$, as stated at the end of Sec. II.B. Equation (3.14) must now be integrated (as described in Sec. III.C) through each subregion i of Region II. At the boundary between two subregions (say, i and $i+1$), a vibrational basis set change is performed. If one makes both $\Psi_{J\Omega_\lambda}^\lambda$ and its derivative with respect to R_λ continuous at this boundary $R_\lambda = R'_{\lambda_i}$, the following relations between the "g" coefficients in two adjacent subregions are obtained:

$$\mathbf{g}_J^{\lambda(w)\pm}(R'_{\lambda_i}; R_{\lambda_{i+1}}^0) = \mathbf{S}_i^{\lambda(w)}\mathbf{g}_J^{\lambda(w)\pm}(R'_{\lambda_i}; R_{\lambda_i}^0) , \tag{3.17a}$$

$$\frac{d\mathbf{g}_J^{\lambda(w)\pm}(R'_{\lambda_i}; R_{\lambda_{i+1}}^0)}{dR_\lambda} = \mathbf{S}_i^{\lambda(w)}\frac{d\mathbf{g}_J^{\lambda(w)\pm}(R'_{\lambda_i}; R_{\lambda_i}^0)}{dR_\lambda} \tag{3.17b}$$

where the overlap matrix $\mathbf{S}_i^{\lambda(w)}$ is given by

$$[\mathbf{S}_i^{\lambda(w)}]_{t_\lambda}^{t'_\lambda} = \delta_{j_\lambda\Omega_\lambda}^{j'_\lambda\Omega'_\lambda}\langle\phi_{v_\lambda j_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda_{i+1}}^0) | \phi_{v'_\lambda j'_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda_i}^0)\rangle . \tag{3.18}$$

As discussed in Paper I (Sec. III.D), $\mathbf{S}_i^{\lambda(w)}$ should be orthogonal for a complete vibrational expansion. For a truncated expansion, as required by practical considerations, $\mathbf{S}_i^{\lambda(w)}$ must be nearly orthogonal in order for us to obtain scattering matrices which satisfy conservation of flux (see Sec. V) to an acceptable degree of accuracy. The transformation between Regions I and II is accomplished by setting $i=0$ in Eqs. (3.17) and interpreting $R_{\lambda_0}^0$ to mean R'_{λ_0} (Fig. 3) and $\phi_{v_\lambda j_\lambda}^{\lambda(w)}(r_\lambda; R_{\lambda_0}^0)$ to mean $\phi_{v_\lambda j_\lambda}^{\lambda(a)}(r_\lambda)$.

3. The strong interaction region

In this region we use the polar coordinates ρ_λ, φ_λ of Eq. (3.16) of I and regard φ_λ as the propagation variable. Before we can expand the wavefunction in terms of a set of pseudovibrational eigenfunctions in the variable ρ_λ, we must first transform Eq. (2.31) to these polar coordinates. The only important change in this transformation occurs in $\bar t_{\Omega_\lambda\Omega_\lambda}^{J\lambda j_\lambda}$ [of Eq. (2.32)], which becomes

$$\bar t_{\Omega_\lambda\Omega_\lambda}^{J\lambda j_\lambda} = -\frac{\hbar^2}{2\mu}\left(\frac{1}{\rho_\lambda}\frac{\partial}{\partial\rho_\lambda}\rho_\lambda\frac{\partial}{\partial\rho_\lambda} + \frac{1}{\rho_\lambda^2}\frac{\partial^2}{\partial\varphi_\lambda^2}\right) + \frac{j_\lambda(j_\lambda+1)\hbar^2}{2\mu(r_{\lambda_0} - \rho_\lambda\cos\varphi_\lambda)^2}$$

$$+\frac{\hbar^2[J(J+1)-2\Omega_\lambda^2+j_\lambda(j_\lambda+1)]}{2\mu(R_{\lambda_0}-\rho_\lambda\sin\varphi_\lambda)^2}\ . \tag{3.19}$$

As for Region II, we divide Region III into $n_{\rm III}^\lambda$ subregions bounded by lines of constant

$$\varphi_\lambda(=\varphi'_{\lambda_1},\varphi'_{\lambda_2},\ \ldots,\varphi'_{\lambda_{n_{\rm III}^\lambda}}=\varphi_{\lambda_0})\ .$$

We choose our vibrational basis set to satisfy

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{d\rho_\lambda^2}+V_{\rm ref}^\lambda(\rho_\lambda;\varphi_{\lambda_i}^0)\right)\phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda;\varphi_{\lambda_i}^0)=\epsilon_{v_\lambda}^{\lambda(s)}(\varphi_{\lambda_i}^0)\phi_{v_\lambda}^{\lambda(s)} \tag{3.20}$$

with boundary conditions analogous to Eq. (3.3). $\varphi_{\lambda_i}^0$ is generally a point within the ith subregion and the reference potential has been re-expressed in the polar coordinates ρ_λ, φ_λ so that it has the shape of a diatomic potential as a function of ρ_λ for a given $\varphi_{\lambda_i}^0$ within Region III (see Fig. 3). The superscript (s) in Eq. (3.20) refers to strong interaction region. Note that the centrifugal term appearing in Eqs. (3.2) and (3.12) has been omitted. [It has been transferred to Eq. (3.26) below.] This results in a vibrational function $\phi_{v_\lambda}^{\lambda(s)}$ independent of j_λ, which simplifies the matching procedure (Sec. IV) and should not seriously slow down the rate of convergence of the vibrational expansion. If we now expand $F_{Jj_\lambda\Omega_\lambda}^\lambda$ in terms of these $\phi_{v_\lambda}^{\lambda(s)}$,

$$F_{Jj_\lambda\Omega_\lambda}^{\lambda(s)\pm}(\rho_\lambda,\varphi_\lambda)=\rho_\lambda^{-1/2}\sum_{v_\lambda}g_{v_\lambda j_\lambda\Omega_\lambda}^{\lambda(s)\pm}(\varphi_\lambda;\varphi_{\lambda_i}^0)\phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda;\phi_{\lambda_i}^0)\ , \tag{3.21}$$

we obtain the following matrix equation:

$$\frac{d^2\mathbf{g}_J^{\lambda(s)\pm}}{d\varphi_\lambda^2}=\overline{\mathbf{U}}_J^{\lambda(s)}(\varphi_\lambda;\varphi_{\lambda_i}^0)\mathbf{g}_J^{\lambda(s)\pm}\ , \tag{3.22}$$

where

$$\overline{\mathbf{U}}_J^{\lambda(s)}=\boldsymbol{\rho}_\lambda^2(\varphi_{\lambda_i}^0)\mathbf{U}_J^{\lambda(s)}(\varphi_\lambda;\varphi_{\lambda_i}^0) \tag{3.23}$$

and

$$\mathbf{U}_J^{\lambda(s)}(\varphi_\lambda;\varphi_{\lambda_i}^0)=-\mathbf{K}^{\lambda(s)^2}+\mathbf{U}_J^{c\lambda(s)}+\mathbf{U}_p^{\lambda(s)}\ . \tag{3.24}$$

The matrix $\boldsymbol{\rho}_\lambda^2$ (whose elements have the physical dimension of the square of a length) is given by

$$[\rho_\lambda^2(\varphi_{\lambda_i}^0)]_{t_\lambda}^{t'_\lambda}=\delta_{j_\lambda\Omega_\lambda}^{j'_\lambda\Omega'_\lambda}\langle v_\lambda|\rho_\lambda^2|v'_\lambda\rangle\ , \tag{3.25}$$

while the centrifugal coupling matrix $\mathbf{U}_J^{c\lambda(s)}$ is

$$[\mathbf{U}_J^{c\lambda(s)}(\varphi_\lambda;\varphi_{\lambda_i}^0)]_{t_\lambda}^{t'_\lambda}=\delta_{j_\lambda\Omega_\lambda}^{j'_\lambda\Omega'_\lambda}\left[\langle v_\lambda|\left(-\frac{1}{4\rho_\lambda^2}+\frac{J(J+1)-2\Omega_\lambda^2+j_\lambda(j_\lambda+1)}{(R_{\lambda_0}-\rho_\lambda\sin\varphi_\lambda)^2}+\frac{j_\lambda(j_\lambda+1)}{(r_{\lambda_0}-\rho_\lambda\cos\varphi_\lambda)^2}\right)|v'_\lambda\rangle\right.$$
$$\left.-\delta_{j_\lambda j'_\lambda}\langle v_\lambda|\frac{1}{(R_{\lambda_0}-\rho_\lambda\sin\varphi_\lambda)^2}|v'_\lambda\rangle[\delta_{\Omega_\lambda+1,\Omega'_\lambda}\xi_+(J,\Omega_\lambda)\xi_+(j_\lambda,\Omega_\lambda)+\delta_{\Omega_\lambda-1,\Omega'_\lambda}\xi_-(J,\Omega_\lambda)\xi_-(j_\lambda,\Omega_\lambda)]\right]\ . \tag{3.26}$$

The matrices $\mathbf{K}^{\lambda(s)^2}$ and $\mathbf{U}_p^{\lambda(s)}$ are given by equations analogous to Eqs. (3.10) and (3.16) with superscripts and coordinates appropriate to the strong interaction region substituted where necessary. Note that the centrifugal coupling [Eq. (3.26) is no longer diagonal in v_λ. The effective potential matrix $\overline{U}_J^{\lambda(s)}$ is not symmetric in this region but rather is equal to the product of two symmetric matrices [Eq. (3.23)], one of which $(\boldsymbol{\rho}_\lambda^2)$ is the matrix representation of a positive definite operator. The nonsymmetric nature of $\overline{\mathbf{U}}_J^{\lambda(s)}$ complicates the integration of Eq. (3.22), and a way of handling this problem was described in Paper I (Sec. III.E and Appendix B).

To solve the Schrödinger equation in Region III, we need to propagate the solution of Eq. (3.22) through each subregion of that region, relating solutions in adjacent subregions by equations analogous to Eqs. (3.17) and (3.18). To relate the solutions at the boundary of Regions II and III, we use the following formula [which is derived in a manner analogous to Eq. (3.17)]:

$$\mathbf{g}_J^{\lambda(s)\pm}(\varphi_\lambda=0;\varphi_{\lambda_1}^0)=\boldsymbol{\rho}_\lambda^{1/2}\mathbf{g}_J^{\lambda(w)\pm}(R_{\lambda_0};R_{\lambda_{n_{\rm II}^\lambda}}^0)\ , \tag{3.27a}$$

$$d\mathbf{g}_J^{\lambda(s)\pm}(\varphi_\lambda=0;\varphi_{\lambda_1}^0)/d\varphi_\lambda=-\boldsymbol{\rho}_\lambda^{3/2}[d\mathbf{g}_J^{\lambda(w)\pm}(R_{\lambda_0};R_{\lambda_{n_{\rm II}^\lambda}}^0)/dR_\lambda]\ , \tag{3.27b}$$

where

$$[\boldsymbol{\rho}_\lambda^b]_{t_\lambda}^{t'_\lambda}=\delta_{j_\lambda\Omega_\lambda}^{j'_\lambda\Omega'_\lambda}\langle\phi_{v_\lambda}^{\lambda(s)}(\rho_\lambda;\varphi_{\lambda_1}^0)|\rho_\lambda^b|\phi_{v'_\lambda j'_\lambda}^{\lambda(w)}(r_{\lambda_0}-\rho_\lambda;R_{\lambda_{n_{\rm II}^\lambda}}^0)\rangle\qquad b=\tfrac{1}{2},\tfrac{3}{2}\ . \tag{3.28}$$

4. The matching region

The polar coordinates ζ, η_λ of Eq. (3.17) of I are used in Region IV with η_λ acting as the propagation variable. Upon transformation of Eq. (2.31) to these coordinates, the operator $\overline{t}_{\Omega_\lambda',\Omega_\lambda}^{J\lambda j_\lambda}$ of Eq. (2.32) becomes

$$\overline{t}_{\Omega_\lambda\Omega_\lambda'}^{J\lambda j_\lambda}=-\frac{\hbar^2}{2\mu}\left(\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\zeta\frac{\partial}{\partial\zeta}+\frac{1}{\zeta^2}\frac{\partial^2}{\partial\eta_\lambda^2}\right)+\frac{\hbar^2 j_\lambda(j_\lambda+1)}{2\mu\zeta^2\sin^2\eta_\lambda}+\frac{\hbar^2[J(J+1)-2\Omega_\lambda^2+j_\lambda(j_\lambda+1)]}{2\mu\zeta^2\cos^2\eta_\lambda}\ . \tag{3.29}$$

In analogy with Region III, Region IV is divided into $n_{\rm IV}^\lambda$ subregions by lines of constant η_λ, with the vibrational eigenfunctions of each subregion satisfying an equation analogous to (3.20):

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{d\zeta^2}+V_{\rm ref}(\zeta;\eta_{\lambda_i}^0)\right)\phi_{v_\lambda}^{\lambda(m)}(\zeta;\eta_{\lambda_i}^0)=\epsilon_{v_\lambda}^{\lambda(m)}(\eta_{\lambda_i}^0)\phi_{v_\lambda}^{\lambda(m)}\ , \tag{3.30}$$

where the superscript (m) denotes matching region. Writing

$$F^{\lambda(m)\pm}_{J j_\lambda \Omega_\lambda}(\zeta,\ \eta_\lambda) = \zeta^{-1/2} \sum_{v_\lambda} g^{\lambda(m)\pm}_{J v_\lambda j_\lambda \Omega_\lambda}(\eta_\lambda;\ \eta^0_{\lambda_i})\, \phi^{\lambda(m)}_{v_\lambda}(\zeta;\ \eta^0_{\lambda_i})\ , \tag{3.31}$$

the counterpart of Eq. (3.22) becomes

$$\frac{d^2}{d\eta_\lambda^2}\ \mathbf{g}^{\lambda(m)\pm}_J = \overline{\mathbf{U}}^{\lambda(m)}_J(\eta_\lambda;\ \eta^0_{\lambda_i})\mathbf{g}^{\lambda(m)\pm}_J\ , \tag{3.32}$$

where

$$\overline{\mathbf{U}}^{\lambda(m)}_J = \boldsymbol{\zeta}^2(\eta^0_{\lambda_i})\mathbf{U}^{\lambda(m)}_J(\eta_\lambda;\ \eta^0_{\lambda_i}) \tag{3.33}$$

and

$$\mathbf{U}^{\lambda(m)}_J(\eta_\lambda;\ \eta^0_{\lambda_i}) = -\mathbf{K}^{\lambda(m)^2} + \mathbf{U}^{c\lambda(m)}_J + \mathbf{U}^{\lambda(m)}_p\ . \tag{3.34}$$

The matrix $\boldsymbol{\zeta}^2(\eta^0_{\lambda_i})$ is defined analogously to ρ^2_λ of Eq. (3.25) with ζ substituted for ρ_λ. The matrices $\mathbf{K}^{\lambda(m)^2}$ and $\mathbf{U}^{\lambda(m)}_p$ are given by equations similar to Eqs. (3.10) and (3.16), respectively, with the superscript (m) inserted and the appropriate coordinate changes made. The centrifugal coupling matrix $\mathbf{U}^{c\lambda(m)}_J$ is given by

$$\begin{aligned}[\mathbf{U}^{c\lambda(m)}_J(\eta_\lambda;\ \eta^0_{\lambda_i})]^{t'_\lambda}_{t_\lambda} = \langle v_\lambda | \zeta^{-2} | v'_\lambda \rangle \{ & \delta^{j'_\lambda \Omega'_\lambda}_{j_\lambda \Omega_\lambda} \{ -\tfrac{1}{4} + [J(J+1) - 2\Omega^2_\lambda + j_\lambda(j_\lambda+1)]/\cos^2\eta_\lambda + j_\lambda(j_\lambda+1)/\sin^2\eta_\lambda \} \\ & - \delta_{j_\lambda, j'_\lambda}[\delta_{\Omega_\lambda+1, \Omega'_\lambda}\, \xi_+(J,\ \Omega_\lambda)\xi_+(j_\lambda,\ \Omega_\lambda) \\ & + \delta_{\Omega_\lambda-1, \Omega'_\lambda}\, \xi_-(J,\ \Omega_\lambda)\xi_-(j_\lambda,\ \Omega_\lambda)]/\cos^2\eta_\lambda\ .\end{aligned} \tag{3.35}$$

To solve the Schrödinger equation in Region IV, one must integrate Eq. (3.32) through each subregion, relating solutions in adjacent subregions by equations analogous to Eqs. (3.17) and (3.18). The transformation between Regions III and IV is accomplished by equations analogous to Eqs. (3.27a) and (3.27b) (with a plus rather than a minus sign in the right hand side of the latter) and the matrix $\boldsymbol{\zeta}^b$ substituted for ρ^b_λ, where

$$[\boldsymbol{\zeta}^b]^{t'_\lambda}_{t_\lambda} = \delta^{j'_\lambda \Omega'_\lambda}_{j_\lambda \Omega_\lambda} \left\langle \phi^{\lambda(m)}_{v_\lambda}(\zeta,\ \eta^0_{\lambda_1}) \middle| \left(\frac{\zeta}{\rho_{\lambda_0} - \zeta}\right)^b \middle| \phi^{\lambda(s)}_{v_\lambda}\left(\rho_{\lambda_0} - \zeta;\ \varphi^0_{\lambda_{n^\lambda_{II}}}\right) \right\rangle \qquad b = \tfrac{1}{2},\ \tfrac{3}{2}\ . \tag{3.36}$$

with ρ_{λ_0} defined in Fig. 3.

C. Integration of the Schrödinger equation

We generate the solution $\mathbf{g}^{\lambda+}_J$ and its derivative with respect to the propagation variable by choosing at $R_\lambda = R'_{\lambda 0}$ (Fig. 3) arbitrary initial values for these two matrices and integrating numerically Eqs. (3.8), (3.14), (3.22), and (3.32) from the beginning of Region II to the end of Region IV. The solution $\mathbf{g}^{\lambda-}_J$ and its derivative are determined by integrating the same equations from the end of Region IV to the beginning of Region II. Any appropriate numerical procedure may be used to solve these coupled ordinary second order differential equations. A particular one which is well suited to such equations and which we used is the Gordon method.[42] More particulars of this procedure are described in Paper I (Sec. III. E).

For the $H + H_2$ reaction, the coupled equations need only be solved in one of the three equivalent arrangement channels. Reactions of the type $A + B_2$ involving two identical atoms will require two such integrations, and reactions with three different atoms will require three. For arrangement channels for which the target is homonuclear, Eq. (2.29) implies zero potential coupling between odd and even rotational states. Since all kinetic energy coupling is diagonal in j_λ in all four regions, our matrix differential equations may be decoupled into two separate ones for the even and odd rotational states with a consequent savings in computation time. Both must be integrated before the matching, which mixes these two sets of solutions, is performed.

Any chemical reaction displays in addition parity (i.e., inversion through the center of mass) symmetry, as shown for triatomic systems in Appendix B. Although the body-fixed wavefunctions obtained from Eqs. (2.13), (2.18), (2.30), and either (3.1), (3.13), (3.21), or (3.31) are not eigenfunctions of the parity operator, they may be linearly combined to yield solutions which are, and this transformation to the "parity representation" results in a partial decoupling of Eqs. (3.8), (3.14), (3.22), and (3.32) into two sets, one for even and one for odd parity. A description of this transformation and other consequences of the parity operation are given in Appendix B. By using parity eigenfunctions, the integration in each arrangement channel is done in two separate steps (four for homonuclear targets). Since the transformation between arrangement channels preserves parity (as shown in Appendix B), the matching procedure also can be done separately for solutions of each parity, as can the calculation of the reactance and scattering matrices. The final plane wave solution is not, however, an eigenfunction of the parity operator, and as a result the calculation of scattering amplitudes requires a transformation back to the body-fixed representation of the previous two sections. The enormous reduction in computation time more than outweighs the additional work involved in this transformation. Appendix B describes this in more detail.

IV. THE MATCHING

A. The λ to ν transformation

At the completion of the integrations in each of the three arrangement channel regions, one has solutions

to the Schrödinger equation which span all of configuration space but which are neither smooth nor continuous at the internal configuration space boundaries of these regions. In this section we describe the procedure for linearly combining these solutions so as to produce a smooth matching at those boundaries. This procedure will also include the transformation from λ to ν coordinates (appropriate for arrangement channels λ and ν, respectively), a transformation which is both conceptually and numerically facilitated by the use of body-fixed coordinates. Our analysis will focus primarily on the behavior of the wavefunction in the vicinity of the half-plane matching surfaces defined in Eq. (3.2) of I.

Equations describing the λ to ν transformation have been derived for coplanar reactions in Appendix A of Paper I, and most of these expressions are still valid in 3D. However, some angles which span a range of 2π in 2D become polar angles in 3D (with a range of π), so some care is required in making the analogy. The basic equations which govern the transformation are given by[19]

$$\begin{pmatrix} \mathbf{R}_\nu \\ \mathbf{r}_\nu \end{pmatrix} = \begin{pmatrix} \cos\alpha_{\nu\lambda} & -\sin\alpha_{\nu\lambda} \\ \sin\alpha_{\nu\lambda} & \cos\alpha_{\nu\lambda} \end{pmatrix} \begin{pmatrix} \mathbf{R}_\lambda \\ \mathbf{r}_\lambda \end{pmatrix} , \tag{4.1}$$

where $\alpha_{\nu\lambda}$ is the angle between $\pi/2$ and π defined by

$$\alpha_{\nu\lambda} = \pi - \beta_{\nu\lambda} , \tag{4.2}$$

$\beta_{\nu\lambda}$ having been given by Eqs. (2.4). Equation (4.1) may be easily derived from Fig. 1 and Eq. (2.1). By taking the scalar products $\mathbf{R}_\nu \cdot \mathbf{R}_\nu$, $\mathbf{r}_\nu \cdot \mathbf{r}_\nu$, and $\mathbf{R}_\nu \cdot \mathbf{r}_\nu$ and using Eqs. (4.1) and (2.3), we find the following expressions for the R_λ, r_λ, $\gamma_\lambda \rightarrow R_\nu$, r_ν, γ_ν transformation:

$$R_\nu^2 = \cos^2\alpha_{\nu\lambda} R_\lambda^2 + \sin^2\alpha_{\nu\lambda} r_\lambda^2 - \sin 2\alpha_{\nu\lambda} \cos\gamma_\lambda r_\lambda R_\lambda , \tag{4.3}$$

$$r_\nu^2 = \sin^2\alpha_{\nu\lambda} R_\lambda^2 + \cos^2\alpha_{\nu\lambda} r_\lambda^2 + \sin 2\alpha_{\nu\lambda} \cos\gamma_\lambda r_\lambda R_\lambda , \tag{4.4}$$

$$\cos\gamma_\nu = (R_\nu r_\nu)^{-1}[\tfrac{1}{2}(R_\lambda^2 - r_\lambda^2)\sin 2\alpha_{\nu\lambda} + R_\lambda r_\lambda \cos 2\alpha_{\nu\lambda} \cos\gamma_\lambda] . \tag{4.5}$$

Equations (4.3) and (4.4) may be combined to yield

$$R_\nu^2 + r_\nu^2 = R_\lambda^2 + r_\lambda^2 \tag{4.6}$$

which, together with Eq. (3.17) of I proves the invariance of ζ to arrangement channel. Also of use in our analysis below is the polar angle $\Delta_{\nu\lambda}$ (in the 0 to π range) between $\mathbf{R}_\lambda$ and $\mathbf{R}_\nu$ which is determined by

$$\cos\Delta_{\nu\lambda} = \frac{\mathbf{R}_\nu \cdot \mathbf{R}_\lambda}{R_\nu R_\lambda} = \cos\alpha_{\nu\lambda} \frac{R_\lambda}{R_\nu} - \sin\alpha_{\nu\lambda} \cos\gamma_\lambda \frac{r_\lambda}{R_\nu} . \tag{4.7}$$

We now examine the consequences of Eqs. (4.3)–(4.7) on the matching surface $\pi_{\nu\lambda}$. Combining Eq. (3.2a) of I with Eq. (4.6) gives

$$R_\lambda = R_\nu , \tag{4.8}$$

and this equation together with Eqs. (3.2a) of I and (4.3) leads to

$$R_\lambda / r_\lambda = -\cot\alpha_{\nu\lambda} \cos\gamma_\lambda + (1 + \cot^2\alpha_{\nu\lambda} \cos^2\gamma_\lambda)^{1/2} , \tag{4.9}$$

which is the equation of the matching surface $\pi_{\nu\lambda}$ in R_λ, r_λ, γ_λ coordinates. If Eqs. (4.8) and (4.9) and Eq. (3.2) of I are now substituted into Eq. (4.5), we find

$$\cos\gamma_\nu = -\cos\gamma_\lambda ,$$

and since γ_λ and γ_ν are in the range 0 to π we conclude that on $\pi_{\nu\lambda}$

$$\gamma_\nu = \pi - \gamma_\lambda . \tag{4.10}$$

Equations (4.7)–(4.9) and Eq. (3.2) of I may be combined to yield

$$\cos\Delta_{\nu\lambda} = \cos\alpha_{\nu\lambda} - \sin\alpha_{\nu\lambda} \cos\gamma_\lambda [\cot\alpha_{\nu\lambda} \cos\gamma_\lambda + (1 + \cot^2\alpha_{\nu\lambda} \cos^2\gamma_\lambda)^{1/2}] , \tag{4.11}$$

which implies that on $\pi_{\nu\lambda}$ the angle $\Delta_{\nu\lambda}$ is a function of γ_λ only.

It will also be useful to convert from R_λ, r_λ to the polar coordinates ζ, η_λ [of Eqs. (3.17) of Paper I]. First, from Eqs. (3.17) of Paper I and (4.8), we have

$$\eta_\lambda = \eta_\nu \quad \text{on } \pi_{\nu\lambda} \tag{4.12}$$

and, after some manipulation, Eq. (4.9) becomes

$$\cot 2\eta_\lambda = -\cot\alpha_{\nu\lambda} \cos\gamma_\lambda \quad \text{on } \pi_{\nu\lambda} , \tag{4.13}$$

which is the equation of $\pi_{\nu\lambda}$ in ζ, η_λ, γ_λ coordinates. Since $\eta_\lambda = \tan^{-1}(r_\lambda / R_\lambda)$ and is in the 0 to $\pi/2$ range, we conclude that

$$\eta_\lambda = \tfrac{1}{2}\omega_\lambda , \tag{4.14}$$

where ω_λ was defined after Eq. (2.3). Therefore, Eq. (4.13) is equivalent to

$$\cot\omega_\lambda = -\cot\alpha_{\nu\lambda} \cos\gamma_\lambda , \tag{4.15}$$

which is the equation of the $\pi_{\nu\lambda}$ half-plane of Fig. 2 of I in the polar coordinates ζ, ω_λ, γ_λ. Finally, Eq. (4.11) may be re-expressed in η_λ, γ_λ coordinates as

$$\cos\Delta_{\nu\lambda} = \cos\alpha_{\nu\lambda} - \sin\alpha_{\nu\lambda} \cos\gamma_\lambda \tan\eta_\lambda . \tag{4.16}$$

We now consider the transformation from the body-fixed coordinate system $Ox'_\lambda y' z'_\lambda$ (Fig. 2) to $Ox'_\nu y' z'_\nu$. Both systems have the same y' axis (which is perpendicular to the three-atom plane), and from Eq. (4.7) and Fig. 2 it can easily be shown that this coordinate transformation is a clockwise rotation about Oy' by $\Delta_{\nu\lambda}$.

Let us determine the effect of the $(\mathbf{R}_\lambda, \mathbf{r}_\lambda) \rightarrow (\mathbf{R}_\nu, \mathbf{r}_\nu)$ transformation on the wavefunctions. The complete body-fixed wavefunction, as obtained from Eqs. (2.13), (2.18), and (2.30) is

$$\Psi_{JM} = \sum_{j_\lambda \Omega_\lambda} D^J_{M\Omega_\lambda}(\phi_\lambda, \theta_\lambda, 0)\, Y_{j_\lambda \Omega_\lambda}(\gamma_\lambda, \psi_\lambda) \frac{F^\lambda_{Jj_\lambda\Omega_\lambda}(r_\lambda, R_\lambda)}{r_\lambda R_\lambda}$$
$$= \frac{1}{\sqrt{2\pi}} \sum_{\Omega_\lambda} D^J_{M\Omega_\lambda}(\phi_\lambda, \theta_\lambda, \psi_\lambda) \chi^\lambda_{J\Omega_\lambda}(r_\lambda, R_\lambda, \gamma_\lambda) , \tag{4.17}$$

where, from Eq. (A3),

$$\chi^\lambda_{J\Omega_\lambda} = \sum_{j_\lambda = |\Omega_\lambda|}^{\infty} \frac{\mathcal{P}^{\Omega_\lambda}_{j_\lambda}(\cos\gamma_\lambda) F^\lambda_{Jj_\lambda\Omega_\lambda}(r_\lambda, R_\lambda)}{r_\lambda R_\lambda} . \tag{4.18}$$

In the second line of Eq. (4.17), the $\exp i\Omega_\lambda \psi_\lambda$ part of $Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda, \psi_\lambda)$ has been incorporated into the rotation matrix $D^J_{M\Omega_\lambda}$ which trivially converts Ψ_{JM} from the

$OX_\lambda Y_\lambda Z_\lambda$ to the $Ox'_\lambda y' z'_\lambda$ coordinate system. If Ψ_{JM} is fully matched (i.e., a smoothly continuous solution of the Schrödinger equation), it may be expressed in the $Ox'_\nu y' z'_\nu$ coordinate system in an analogous way:

$$\Psi_{JM} = \frac{1}{\sqrt{2\pi}} \sum_{\Omega_\nu} D^J_{M\Omega_\nu}(\phi_\nu, \theta_\nu, \psi_\nu)\chi^\nu_{J\Omega_\nu}(r_\nu, R_\nu, \gamma_\nu) . \tag{4.19}$$

We now define Ψ_J, $\chi^\lambda_J(r_\lambda, R_\lambda, \gamma_\lambda)$, and $\chi^\nu_J(r_\nu, R_\nu, \gamma_\nu)$ as the $(2J+1)$-dimensional column vectors whose components are, respectively, the Ψ_{JM}, $\chi^\lambda_{J\Omega_\lambda}$, and $\chi^\nu_{J\Omega_\nu}$, where each one of the indices M, Ω_λ, and Ω_ν assumes the values (top to bottom) $J, J-1, \ldots, -J$. In matrix notation, Eqs. (4.17) and (4.19) can be written as

$$\Psi_J = \frac{1}{\sqrt{2\pi}} \mathbf{D}^J(\phi_\lambda, \theta_\lambda, \psi_\lambda)\chi^\lambda_J(r_\lambda, R_\lambda, \gamma_\lambda)$$

$$= \frac{1}{\sqrt{2\pi}} \mathbf{D}^J(\phi_\nu, \theta_\nu, \psi_\nu)\chi^\nu_J(r_\nu, R_\nu, \gamma_\nu) ,$$

from which one gets

$$\chi^\lambda_J = \mathbf{D}^{J-1}(\phi_\lambda, \theta_\lambda, \psi_\lambda)\mathbf{D}^J(\phi_\nu, \theta_\nu, \psi_\nu)\chi^\nu_J . \tag{4.20}$$

The $Oxyz \to Ox'_\lambda y' z'_\lambda$ transformation, which is a rotation defined by the Euler angles ϕ_λ, θ_λ, ψ_λ, can be accomplished through a sequence of two rotations, the $Oxyz \to Ox'_\nu y' z'_\nu$ one (Euler angles ϕ_ν, θ_ν, ψ_ν) followed by $Ox'_\nu y' z'_\nu \to Ox'_\nu y' z'_\nu$ (Euler angles 0, $\Delta_{\nu\lambda}$, 0). From this results the relation $\mathbf{D}^J(\phi_\nu, \theta_\nu, \psi_\nu) = \mathbf{D}^J(\phi_\lambda, \theta_\lambda, \psi_\lambda)\mathbf{d}^J(\Delta_{\nu\lambda})$, where $\mathbf{d}^J(\Delta_{\nu\lambda}) = \mathbf{D}^J(0, \Delta_{\nu\lambda}, 0)$. Since the $\mathbf{D}^J$ are unitary and $\mathbf{d}^J$ is in addition real, we get from Eq. (4.20)

$$\chi^\lambda_J = [\mathbf{d}^J(\Delta_{\nu\lambda})]^{-1}\chi^J_\nu = \tilde{\mathbf{d}}^J(\Delta_{\nu\lambda})\chi^J_\nu ,$$

and therefore, in the notation of Davydov,[33]

$$\chi^\lambda_{J\Omega_\lambda} = \sum_{\Omega_\nu} d^J_{\Omega_\nu\Omega_\lambda}(\Delta_{\nu\lambda})\chi^\nu_{J\Omega_\nu} . \tag{4.21}$$

This equation relating the matched solutions χ^λ and χ^ν is valid for any internal configuration of the triatom (i.e., is not restricted to those configurations corresponding to the $\pi_{\nu\lambda}$ matching surface).

B. Projection of the wavefunction onto the matching surface basis functions

In this section we consider the evaluation of the unmatched wavefunctions and normal derivatives obtained from the integrations in both channels λ and ν on the matching surface $\pi_{\nu\lambda}$, and their expansion in a set of functions $B^{\nu\lambda}_{\nu\lambda j\lambda\Omega\lambda}(\xi, \gamma_\lambda)$ which span that surface. The complete, unmatched wavefunction in the $Ox'_\lambda y' z'_\lambda$ coordinate system in Region IV of internal configuration space (subregion i) is [from Eqs. (4.17), (4.18), and (3.31)]

$$\Psi^{\lambda t'^{\pm}_\lambda}_{JM} = \frac{1}{\sqrt{2\pi}} \sum_{\Omega_\lambda} D^J_{M\Omega_\lambda}(\phi_\lambda, \theta_\lambda, \psi_\lambda)\bar{\chi}^{\lambda t'^{\pm}_\lambda}_{J\Omega_\lambda}(\xi, \eta_\lambda, \gamma_\lambda) , \tag{4.22}$$

where

$$\bar{\chi}^{\lambda t'^{\pm}_\lambda}_{J\Omega_\lambda} = \sum_{v_\lambda j_\lambda} \frac{2\mathcal{P}^{\Omega_\lambda}_{j_\lambda}(\cos\gamma_\lambda)\,\phi^\lambda_{v_\lambda}(\xi; \eta^0_{\lambda t'_\lambda})\, g^{\lambda t'^{\pm}_\lambda}_{Jv_\lambda j_\lambda\Omega_\lambda}(\eta_\lambda; \eta^0_{\lambda t'_\lambda})}{\xi^{5/2}\sin 2\eta_\lambda} . \tag{4.23}$$

Here we have dropped the superscript (m), as it will be implicit throughout this section, but we have included the labels $t'^{\pm}_\lambda \equiv (v'_\lambda j'_\lambda \Omega'_\lambda \pm)$ to denote the $2N$ linearly independent solutions obtained (from an N coupled-channel calculation). Equation (4.23) may be evaluated on $\pi_{\nu\lambda}$ by using Eq. (4.13) to relate η_λ and γ_λ. Since $0 \leq \gamma_\lambda \leq \pi/2$ on $\pi_{\nu\lambda}$, we find that η_λ must lie between $\eta_{\lambda_0} = (\pi - \alpha_{\nu\lambda})/2$ and $\eta_{\lambda_1} = \pi/4$ to satisfy Eq. (4.13). In order to evaluate Eq. (4.23) over this range of η_λ, it is convenient to change to a common set of vibrational basis functions $\phi^\lambda_{v_\lambda}(\xi)$ for all subregions i. This is accomplished by transformations analogous to Eq. (3.17) and (3.18), with the result that

$$\bar{\chi}^{\lambda t'^{\pm}_\lambda}_{J\Omega_\lambda} = 2\xi^{-5/2}(\sin 2\eta_\lambda)^{-1}\Phi^{\lambda t'^{\pm}_\lambda}_{J\Omega_\lambda} , \tag{4.24}$$

where

$$\Phi^{\lambda t'^{\pm}_\lambda}_{J\Omega_\lambda} = \sum_{v_\lambda j_\lambda} \mathcal{P}^{\Omega_\lambda}_{j_\lambda}(\cos\gamma_\lambda)\phi^\lambda_{v_\lambda}(\xi)\, g^{\lambda t'^{\pm}_\lambda}_{Jv_\lambda j_\lambda\Omega_\lambda}(\eta_\lambda) . \tag{4.25}$$

To insure a smooth matching, we must also consider the derivative of $\bar{\chi}$ normal to $\pi_{\nu\lambda}$ (other derivatives are possible) for points on this plane. Expressions for this normal derivative operator were derived in Paper I (Appendix A), where it was found that

$$\frac{\partial}{\partial n_{\nu\lambda}} = \frac{1}{\xi}\frac{\sin\alpha_{\nu\lambda}}{\sin\omega_\lambda}\left(\frac{\partial}{\partial\omega_\lambda} + \cot\alpha_{\nu\lambda}\sin\gamma_\lambda\frac{\partial}{\partial\gamma_\lambda}\right)$$

$$= \frac{1}{\xi}\frac{\sin\alpha_{\nu\lambda}}{\sin 2\eta_\lambda}\left(\frac{1}{2}\frac{\partial}{\partial\eta_\lambda} + \cot\alpha_{\nu\lambda}\sin\gamma_\lambda\frac{\partial}{\partial\gamma_\lambda}\right)$$

$$= -\frac{1}{\xi}\frac{\sin\alpha_{\nu\lambda}}{\sin 2\eta_\lambda}\left(\frac{1}{2}\frac{\partial}{\partial\eta_\nu} - \cot\alpha_{\nu\lambda}\sin\gamma_\lambda\frac{\partial}{\partial\gamma_\nu}\right) . \tag{4.26}$$

Applying this operator to Eq. (4.23), and evaluating the result on $\pi_{\nu\lambda}$, we find

$$\frac{\partial\bar{\chi}^{\lambda t'^{\pm}_\lambda}_{J\Omega_\lambda}}{\partial n_{\nu\lambda}} = \frac{2\sin\alpha_{\nu\lambda}}{\xi^{7/2}\sin^2 2\eta_\lambda}\Phi'^{\lambda t'^{\pm}_\lambda}_{J\Omega_\lambda} , \tag{4.27}$$

where

$$\Phi'^{\lambda t'^{\pm}_\lambda}_{J\Omega_\lambda} = \sum_{v_\lambda j_\lambda}\phi^\lambda_{v_\lambda}(\xi)\, G'^{\lambda t'^{\pm}_\lambda}_{Jv_\lambda j_\lambda\Omega_\lambda} \tag{4.28}$$

and

$$G'^{\lambda t'^{\pm}_\lambda}_{Jv_\lambda j_\lambda\Omega_\lambda} = \tfrac{1}{2}\mathcal{P}^{\Omega_\lambda}_{j_\lambda}(\cos\gamma_\lambda)\frac{dg^{\lambda t'^{\pm}_\lambda}_{Jv_\lambda j_\lambda\Omega_\lambda}[\eta_\lambda(\gamma_\lambda)]}{d\eta_\lambda} - \cot\alpha_{\nu\lambda}$$

$$\times g^{\lambda t'^{\pm}_\lambda}_{Jv_\lambda j_\lambda\Omega_\lambda}(\eta_\lambda(\gamma_\lambda))\left[j_\lambda\cos\gamma_\lambda\mathcal{P}^{\Omega_\lambda}_{j_\lambda}(\cos\gamma_\lambda) - \left(\frac{2j_\lambda+1}{2j_\lambda+3}\right)^{1/2}[(j_\lambda+1)^2 - \Omega_\lambda^2]^{1/2}\mathcal{P}^{\Omega_\lambda}_{j_\lambda+1}(\cos\gamma_\lambda)\right] . \tag{4.29}$$

In deriving Eq. (4.29), the use has been made of Eq. (A2) and certain recursion relations between the associated Legendre polynomials.[38]

We now wish to expand Eqs. (4.25) and (4.28) on the matching surface in terms of a set of functions $B^{\nu\lambda}_{v_\lambda j_\lambda\Omega_\lambda} \times(\xi, \gamma_\lambda)$ which are orthonormal and complete on it. (We choose ξ and γ_λ to be the independent variables which scan $\pi_{\nu\lambda}$.) The $B^{\nu\lambda}_{v_\lambda j_\lambda\Omega_\lambda}$ are given by

$$B^{\nu\lambda}_{v_\lambda j_\lambda\Omega_\lambda}(\xi, \gamma_\lambda) = \phi^\lambda_{v_\lambda}(\xi)A^{\nu\lambda}_{j\Omega\Omega_\lambda}(\gamma_\lambda) , \tag{4.30}$$

where the $\phi_{v_\lambda}^{\lambda}$'s are those of Eq. (4.25) and the $A_{j_\lambda\Omega_\lambda}^{\nu\lambda}$ are a set of rotational functions which must be orthonormal (with weight function $\sin\gamma_\lambda$) and complete on the domain $0 \leq \gamma_\lambda \leq \pi/2$. The reason for this choice of the domain of γ_λ is analogous to that used for the coplanar matching in Paper I (Sec. IV A). An important consequence of this procedure is that the number of functions $B_{v_\lambda j_\lambda \Omega_\lambda}^{\nu\lambda}$ used to expand the wavefunction of Eq. (4.25) for each v_λ, Ω_λ must be less than the number of vibration rotation basis functions $\phi_{v_\lambda}(\xi)\mathcal{P}_{j_\lambda}^{\Omega_\lambda}(\cos\gamma_\lambda)$ in that equation. For many reactions, including $H+H_2$, the number of $B_{v_\lambda j_\lambda \Omega_\lambda}^{\nu\lambda}$'s should be half the number of vibration–rotation basis functions, and we shall use this number in the discussion below. This would imply that the number of j_λ's for each v_λ, Ω_λ used in the close coupling expansion must be even. An example of how this might be done would be to use a complete set of Ω_λ's for each j_λ within a given vibrational manifold, except for the case $j_\lambda = j_{\lambda_{\max}}$. For this case (as long as $J \geq j_{\lambda_{\max}}$) one uses $\Omega_\lambda = j_{\lambda_{\max}} - 1,\ j_{\lambda_{\max}} - 3, \ldots, -j_{\lambda_{\max}} + 1$. For $J < j_{\lambda_{\max}}$, we use the same procedure and then eliminate those Ω_λ for which $|\Omega_\lambda| > J$. Other choices are possible, but this particular set of quantum numbers is useful because it leads, for $j_\lambda = j_{\lambda_{\max}}$, to an asymptotic uncoupling of those terms in Eq. (2.31) which are not diagonal in Ω_λ, and this allows us to solve for the asymptotic behavior of these partially truncated solutions in a simple way.[43] Whatever the choice, this restriction on the method is seldom a serious limitation because it only affects the highest rotational state j_λ for each v_λ, Ω_λ, and this channel is usually closed in a converged treatment. An example of a choice of $A_{j_\lambda\Omega_\lambda}^{\nu\lambda}$ which is real and orthonormal over the 0 to $\pi/2$ range (weighted by $\sin\gamma_\lambda$) is

$$A_{j_\lambda\Omega_\lambda}^{\nu\lambda}(\gamma_\lambda) = \begin{cases} \sqrt{2}\,\mathcal{P}_{j_\lambda}^{\Omega_\lambda}(\cos\gamma_\lambda) & \text{for } j_\lambda + \Omega_\lambda = \text{odd} \\ 0 \quad \text{for } j_\lambda + \Omega_\lambda = \text{even} \,. \end{cases} \tag{4.31}$$

This choice is very appropriate for expanding the γ_λ-dependent part of Eq. (4.25) for a collinearly dominated reaction such as $H+H_2$ because these $A_{j_\lambda\Omega_\lambda}^{\nu\lambda}$ vanish at $\gamma_\lambda = \pi/2$ (where the interaction potential on the matching surface is high and the wavefunction very small) and are most effective in representing the wavefunction near $\gamma_\lambda = 0$ (where the potential is low). Other choices for the $A_{j_\lambda\Omega_\lambda}^{\nu\lambda}$ may be made in analogy with those discussed for the planar problem in Paper I.

We now expand Eqs. (4.25) and (4.28) in terms of the $B_{v_\lambda j_\lambda \Omega_\lambda}^{\nu\lambda}$, obtaining

$$\Phi_{J\Omega_\lambda}^{\lambda t_\lambda^{\pm}} = \sum_{v_\lambda j_\lambda} h_{Jv_\lambda j_\lambda \Omega_\lambda}^{\lambda t_\lambda^{\pm}} B_{v_\lambda j_\lambda \Omega_\lambda}^{\nu\lambda}(\xi, \gamma_\lambda) \,, \tag{4.32}$$

$$\Phi'^{\lambda t_\lambda^{\pm}}_{J\Omega_\lambda} = \sum_{v_\lambda j_\lambda} h'^{\lambda t_\lambda^{\pm}}_{Jv_\lambda j_\lambda \Omega_\lambda} B_{v_\lambda j_\lambda \Omega_\lambda}^{\nu\lambda}(\xi, \gamma_\lambda) \,, \tag{4.33}$$

$$h_{Jv_\lambda j_\lambda \Omega_\lambda}^{\lambda t_\lambda^{\pm}} = \sum_{j_\lambda''} \int_0^{\pi/2} A_{j_\lambda\Omega_\lambda}^{\nu\lambda}(\gamma_\lambda) \mathcal{P}_{j_\lambda''}^{\Omega_\lambda}(\cos\gamma_\lambda) \times g_{Jv_\lambda j_\lambda'' \Omega_\lambda}^{\lambda t_\lambda^{\pm}}[\eta_\lambda(\gamma_\lambda)] \sin\gamma_\lambda \, d\gamma_\lambda \,, \tag{4.34}$$

and

$$h'^{\lambda t_\lambda^{\pm}}_{Jv_\lambda j_\lambda \Omega_\lambda} = \sum_{j_\lambda''} \int_0^{\pi/2} A_{j_\lambda\Omega_\lambda}^{\nu\lambda}(\gamma_\lambda) G'^{\lambda t_\lambda^{\pm}}_{Jv_\lambda j_\lambda'' \Omega_\lambda}(\gamma_\lambda) \sin\gamma_\lambda \, d\gamma_\lambda \,, \tag{4.35}$$

where Eq. (4.29) is to be used in evaluating Eq. (4.35). Note that the row (lower) indices $v_\lambda j_\lambda \Omega_\lambda$ in Eqs. (4.32)–(4.35) can assume only $N/2$ values (from the discussion above), whereas the column (upper) indices $v_\lambda' j_\lambda' \Omega_\lambda'$ (implied in t_λ') scan N values. This means that the matrices $\mathbf{h}_J^{\lambda}$ and $\mathbf{h}_J'^{\lambda}$ have dimensions $N/2 \times N$.

We now consider the expansion of the wavefunction $\bar{\chi}_{J\Omega_\nu}^{\nu t_\nu^{\pm}}$ obtained from the integration in arrangement channel region ν on $\pi_{\nu\lambda}$ in a manner analogous to that for $\bar{\chi}_{J\Omega_\lambda}^{\lambda t_\lambda^{\pm}}$. The expressions for the wavefunctions are given by Eqs. (4.24) and (4.25) with ν replacing λ everywhere. To find the normal derivatives, the rightmost side of Eq. (4.26) is used. The resulting expression is given by Eqs. (4.27) and (4.28) with ν replaced by λ and with the function $G'^{\nu t_\nu^{\pm}}_{Jv_\nu j_\nu \Omega_\nu}$ given by

$$G'^{\nu t_\nu^{\pm}}_{Jv_\nu j_\nu \Omega_\nu} = -(-1)^{j_\nu - \Omega_\nu} \Big\{ \tfrac{1}{2} \mathcal{P}_{j_\nu}^{\Omega_\nu}(\cos\gamma_\lambda) \frac{dg^{\nu t_\nu^{\pm}}_{Jv_\nu j_\nu \Omega_\nu}[\eta_\nu(\gamma_\lambda)]}{d\eta_\nu} - \cot\alpha_{\nu\lambda} g^{\nu t_\nu^{\pm}}_{Jv_\nu j_\nu \Omega_\nu}[\eta_\nu(\gamma_\lambda)] \Big[j_\nu \cos\gamma_\lambda \mathcal{P}_{j_\nu}^{\Omega_\nu}(\cos\gamma_\lambda) - \left(\frac{2j_\nu+1}{2j_\nu+3}\right)^{1/2} [(j_\nu+1)^2 - \Omega_\nu^2]^{1/2} \mathcal{P}_{j_\nu+1}^{\Omega_\nu}(\cos\gamma_\lambda) \Big] \Big\} \,. \tag{4.36}$$

Note that Eq. (4.10) has been used in Eq. (4.36) [along with the property $\mathcal{P}_j^m(-x) = (-1)^{j+m}\mathcal{P}_j^m(x)$] to express all quantities in terms of γ_λ. The relation between η_ν and γ_λ on $\pi_{\nu\lambda}$ is obtained from Eqs. (4.12) and (4.13).

The expansions analogous to Eqs. (4.32) and (4.33) are given by

$$\Phi_{J\Omega_\nu}^{\nu t_\nu^{\pm}} = \sum_{v_\nu j_\nu} f^{\nu t_\nu^{\pm}}_{Jv_\nu j_\nu \Omega_\nu} B_{v_\nu j_\nu \Omega_\nu}^{\lambda\nu}(\xi, \gamma_\lambda) \,, \tag{4.37}$$

$$\Phi'^{\nu t_\nu^{\pm}}_{J\Omega_\nu} = \sum_{v_\nu j_\nu} f'^{\nu t_\nu^{\pm}}_{Jv_\nu j_\nu \Omega_\nu} B_{v_\nu j_\nu \Omega_\nu}^{\lambda\nu}(\xi, \gamma_\lambda) \,, \tag{4.38}$$

where $B^{\lambda\nu}$ differs from $B^{\nu\lambda}$ by the use, in Eq. (4.30), of ϕ^{ν} instead of ϕ^{λ}. This approach is slightly different from the one followed previously,[19] in which the basis functions used to expand the Φ_J^{λ} and Φ_J^{ν} were the same. For homonuclear targets, this difference disappears. The f and f' are given by

$$f^{\nu t_\nu^{\pm}}_{Jv_\nu j_\nu \Omega_\nu} = \sum_{j_\nu''} (-1)^{j_\nu'' - \Omega_\nu} \int_0^{\pi/2} A_{j_\nu\Omega_\nu}^{\nu\lambda}(\gamma_\lambda) \mathcal{P}_{j_\nu''}^{\Omega_\nu}(\cos\gamma_\lambda) \times g^{\nu t_\nu^{\pm}}_{Jv_\nu j_\nu'' \Omega_\nu}[\eta_\nu(\gamma_\lambda)] \sin\gamma_\lambda \, d\gamma_\lambda \,, \tag{4.39}$$

$$f'^{\nu t_\nu^{\pm}}_{Jv_\nu j_\nu \Omega_\nu} = \sum_{j_\nu''} \int_0^{\pi/2} A_{j_\nu\Omega_\nu}^{\nu\lambda}(\gamma_\lambda) G'^{\nu t_\nu^{\pm}}_{Jv_\nu j_\nu'' \Omega_\nu}(\gamma_\lambda) \sin\gamma_\lambda \, d\gamma_\lambda \,, \tag{4.40}$$

with Eq. (4.36) being used to evaluate Eq. (4.40). All expansions are made in terms of the coordinate γ_λ to facilitate later manipulations.

For atom plus homonuclear diatom collisions, the coefficients $f^{\lambda t_\lambda^{\pm}}_{Jv_\lambda j_\lambda \Omega_\lambda}$ obtained by matching on the $\pi_{\lambda\kappa}$ plan can be related to the $h^{\lambda t_\lambda^{\pm}}_{Jv_\lambda j_\lambda \Omega_\lambda}$ of the $\pi_{\nu\lambda}$ plane matching by noting in Eq. (4.39) (with λ substituted for ν and κ for λ) that $g^{\lambda t_\lambda^{\pm}}_{Jv_\lambda j_\lambda'' \Omega_\lambda} = 0$[44] for $j_\lambda'' - j_\lambda' = \text{odd}$ and therefore that $(-1)^{j_\lambda''} = (-1)^{j_\lambda'}$ for the nonvanishing terms. For

collisions with a homonuclear diatom, $m_\nu = m_\kappa$ so $\beta_{\lambda\kappa} = \beta_{\nu\lambda}$ [from Eq. (2.4)], and the mathematical expressions analogous to Eqs. (4.12)–(4.16) for $\pi_{\lambda\kappa}$ are identical to those equations. Therefore, from Eqs. (4.34) and (4.39) (transformed to $\pi_{\lambda\kappa}$), we have

$$f^{\lambda t'^{\pm}_{\lambda}}_{Jv_\lambda j_\lambda \Omega_\lambda} = (-1)^{j'_\lambda - \Omega_\lambda} h^{\lambda t'^{\pm}_{\lambda}}_{Jv_\lambda j_\lambda \Omega_\lambda} \quad . \tag{4.41}$$

By similar arguments for the derivative equations, Eqs. (4.35) and (4.4), using Eqs. (4.29) and (4.36), we find

$$f'^{\lambda t'^{\pm}_{\lambda}}_{Jv_\lambda j_\lambda \Omega_\lambda} = -(-1)^{j'_\lambda - \Omega_\lambda} h'^{\lambda t'^{\pm}_{\lambda}}_{Jv_\lambda j_\lambda \Omega_\lambda} \quad . \tag{4.42}$$

C. The matching equations

We now wish to find the appropriate linear combinations of the $\bar{\chi}$'s and $\partial\bar{\chi}/\partial n_{\nu\lambda}$'s of Eqs. (4.24) and (4.27) in channels λ and ν which give smoothly matched solutions χ and $\partial\chi/\partial n_{\nu\lambda}$ satisfying Eq. (4.20) and its normal derivative counterpart, both evaluated on $\pi_{\nu\lambda}$. Accordingly, we write

$$\chi^{(i)t}_{\lambda J\Omega_\lambda} = \sum_{t'_\lambda} (\bar{\chi}^{\lambda t'^{+}_{\lambda}}_{J\Omega_\lambda} C^{(i)t+}_{J\lambda t'_\lambda} + \bar{\chi}^{\lambda t'^{-}_{\lambda}}_{J\Omega_\lambda} C^{(i)t-}_{J\lambda t'_\lambda}) \quad , \tag{4.43}$$

where the coefficients $C_{J\lambda}$ in Eq. (4.43) are to be determined by evaluating Eq. (4.20) and its normal derivative on $\pi_{\nu\lambda}$, and analogous equations on $\pi_{\kappa\nu}$ and $\pi_{\lambda\kappa}$. The indices $(i)t \equiv (i)vj\Omega$ denote different linearly independent matched solutions, with t assuming N values and $i = 1$, 2, or 3 for a total of $3N$ solutions. This is equal to the number of linearly independent scattering solutions possible, as was discussed in Paper I (Sec. IV B). The normal derivative of Eq. (4.43) is

$$\frac{\partial \chi^{(i)t}_{\lambda J\Omega_\lambda}}{\partial n_{\nu\lambda}} = \sum_{t'_\lambda} \left(\frac{\partial \bar{\chi}^{\lambda t'^{+}_{\lambda}}_{J\Omega_\lambda}}{\partial n_{\nu\lambda}} C^{(i)t+}_{J\lambda t'_\lambda} + \frac{\partial \bar{\chi}^{\lambda t'^{-}_{\lambda}}_{J\Omega_\lambda}}{\partial n_{\nu\lambda}} C^{(i)t-}_{J\lambda t'_\lambda} \right) \quad . \tag{4.44}$$

The normal derivative of Eq. (4.20) is in general a complicated quantity, but for the particular choice of matching surface specified by Eq. (2.5a), we have the important relation[19]

$$\left(\frac{\partial \Delta_{\nu\lambda}}{\partial n_{\nu\lambda}} \right)_{\text{on } \pi_{\nu\lambda}} = 0 \quad , \tag{4.45}$$

which implies

$$\frac{\partial \chi^{(i)t}_{\lambda J\Omega_\lambda}}{\partial n_{\nu\lambda}} = \sum_{\Omega_\nu} d^J_{\Omega_\nu \Omega_\lambda}(\Delta_{\nu\lambda}) \frac{\partial \chi^{(i)t}_{\nu J\Omega_\nu}}{\partial n_{\nu\lambda}} \quad . \tag{4.46}$$

Let us now substitute Eq. (4.43) and its counterpart for channel ν into Eq. (4.20), as well as (4.44) and its ν counterpart into (4.46), utilizing Eqs. (4.24) and (4.27) (and their ν counterparts) along with Eq. (4.12). We obtain

$$\sum_{t'_\lambda} (\Phi^{\lambda t'^{+}_{\lambda}}_{J\Omega_\lambda} C^{(i)t+}_{J\lambda t'_\lambda} + \Phi^{\lambda t'^{-}_{\lambda}}_{J\Omega_\lambda} C^{(i)t-}_{J\lambda t'_\lambda})$$

$$= \sum_{\Omega_\nu} d^J_{\Omega_\nu \Omega_\lambda}(\Delta_{\nu\lambda}) \sum_{t'_\nu} (\Phi^{\nu t'^{+}_{\nu}}_{J\Omega_\nu} C^{(i)t+}_{J\nu t'_\nu} + \Phi^{\nu t'^{-}_{\nu}}_{J\Omega_\nu} C^{(i)t-}_{J\nu t'_\nu}) \quad , \tag{4.47}$$

with a similar equation involving Φ' resulting from the matching of the normal derivatives. If we now substitute Eqs. (4.32) and (4.37) into Eq. (4.47), multiply the resulting expression by the $B^{\nu\lambda}_{v_\lambda j_\lambda \Omega_\lambda}$ [defined by Eq. (4.30)], and integrate it using the orthonormality properties of these $B^{\nu\lambda}$, we obtain

$$\sum_{t'_\lambda} (h^{\lambda t'^{+}_{\lambda}}_{Jv_\lambda j_\lambda \Omega_\lambda} C^{(i)t+}_{J\lambda t'_\lambda} + h^{\lambda t'^{-}_{\lambda}}_{Jv_\lambda j_\lambda \Omega_\lambda} C^{(i)t-}_{J\lambda t'_\lambda})$$

$$= \sum_{v_\nu j_\nu \Omega_\nu} (s^J_{\nu\lambda})^{v_\nu j_\nu \Omega_\nu}_{v_\lambda j_\lambda \Omega_\lambda} \sum_{t'_\nu} (f^{\nu t'^{+}_{\nu}}_{Jv_\nu j_\nu \Omega_\nu} C^{(i)t+}_{J\nu t'_\nu} + f^{\nu t'^{-}_{\nu}}_{Jv_\nu j_\nu \Omega_\nu} C^{(i)t-}_{J\nu t'_\nu}) \quad . \tag{4.48}$$

An analogous equation results for the derivatives with h' and f' substituted for h and f. The $(s^J_{\nu\lambda})^{v_\nu j_\nu \Omega_\nu}_{v_\lambda j_\lambda \Omega_\lambda}$ are the elements of an "arrangement channel transformation" matrix $\mathbf{s}^J_{\nu\lambda}$ and are defined by

$$(s^J_{\nu\lambda})^{v_\nu j_\nu \Omega_\nu}_{v_\lambda j_\lambda \Omega_\lambda} = S^{\lambda\nu}_{v_\lambda v_\nu} \int_0^{\pi/2} A^{\nu\lambda}_{j_\lambda \Omega_\lambda}(\gamma_\lambda) \, d^J_{\Omega_\nu \Omega_\lambda}[\Delta_{\nu\lambda}(\gamma_\lambda)]$$

$$\times A^{\nu\lambda}_{j_\nu \Omega_\nu}(\gamma_\lambda) \sin\gamma_\lambda \, d\gamma_\lambda \quad , \tag{4.49}$$

where

$$S^{\lambda\nu}_{v_\lambda v_\nu} = \int_0^\infty \phi^\lambda_{v_\lambda}(\zeta) \, \phi^\nu_{v_\nu}(\zeta) \, d\zeta \quad . \tag{4.50}$$

As shown in Appendix C, $\mathbf{s}^J_{\nu\lambda}$ is a real orthogonal matrix as long as the $A^{\nu\lambda}_{j_\lambda \Omega_\lambda}(\gamma_\lambda)$ of Eq. (4.30) form a complete set of orthonormal functions which span the γ_λ space, and the $\phi^\lambda_{v_\lambda}(\zeta)$ and $\phi^\nu_{v_\nu}(\zeta)$ form two sets of orthonormal functions which span the ζ space and are related by a real orthogonal transformation. Let us now write Eq. (4.48) as a matrix equation by regarding the h, f, and C appearing there as the elements of matrices, obtaining

$$\mathbf{h}^{\lambda+}_J \mathbf{C}^{(i)+}_{J\lambda} + \mathbf{h}^{\lambda-}_J \mathbf{C}^{(i)-}_{J\lambda} = \mathbf{s}^J_{\nu\lambda} (\mathbf{f}^{\nu+}_J \mathbf{C}^{(i)+}_{J\nu} + \mathbf{f}^{\nu-}_J \mathbf{C}^{(i)-}_{J\nu}) \quad . \tag{4.51}$$

According to the arguments of the previous section, the matrices $\mathbf{h}^{\lambda\pm}_J$ and $\mathbf{f}^{\nu\pm}_J$ have dimensions $N/2 \times N$, while the $\mathbf{s}^J_{\nu\lambda}$ are $N/2 \times N/2$ and the $\mathbf{C}$'s are $N \times N$ matrices. The corresponding derivative equation is obtained from Eq. (4.51) by substituting $\mathbf{h}'$ and $\mathbf{f}'$ for $\mathbf{h}$ and $\mathbf{f}$. We can combine function and derivative equations into a single matrix equation involving only $N \times N$ matrices by defining the augmented $N \times N$ matrices $\hat{\mathbf{h}}^{\lambda\pm}_J$, $\hat{\mathbf{f}}^{\nu\pm}_J$, and $\hat{\mathbf{s}}^J_{\nu\lambda}$ as

$$\hat{\mathbf{h}}^{\lambda\pm}_J = \begin{pmatrix} \mathbf{h}^{\lambda\pm}_J \\ \mathbf{h}'^{\lambda\pm}_J \end{pmatrix} \quad , \tag{4.52}$$

$$\hat{\mathbf{f}}^{\nu\pm}_J = \begin{pmatrix} \mathbf{f}^{\nu\pm}_J \\ \mathbf{f}'^{\nu\pm}_J \end{pmatrix} \quad , \tag{4.53}$$

$$\hat{\mathbf{s}}^J_{\nu\lambda} = \begin{pmatrix} \mathbf{s}^J_{\nu\lambda} & \mathbf{0} \\ \mathbf{0} & \mathbf{s}^J_{\nu\lambda} \end{pmatrix} \quad , \tag{4.54}$$

where $\mathbf{0}$ is an $N/2 \times N/2$ null matrix. The resulting smooth matching equation on $\pi_{\nu\lambda}$ is

$$\hat{\mathbf{h}}^{\lambda+}_J \mathbf{C}^{(i)+}_{J\lambda} + \hat{\mathbf{h}}^{\lambda-}_J \mathbf{C}^{(i)-}_{J\lambda} = \hat{\mathbf{s}}^J_{\nu\lambda} (\hat{\mathbf{f}}^{\nu+}_J \mathbf{C}^{(i)+}_{J\nu} + \hat{\mathbf{f}}^{\nu-}_J \mathbf{C}^{(i)-}_{J\nu}) \quad . \tag{4.55}$$

Following the same arguments as were used in Paper I (Sec. IV.B), we now combine Eq. (4.55) and its counterparts on $\pi_{\kappa\nu}$ and $\pi_{\lambda\kappa}$ into a single $3N \times 3N$ equation which can then be solved for the coefficients $\mathbf{C}^\pm_J$ which determine the matched solutions. The final result is

$$\mathbf{C}^+_J (\mathbf{C}^-_J)^{-1} = -(\mathbf{N}^+_J)^{-1} \mathbf{N}^-_J \quad , \tag{4.56}$$

where

$$\mathbf{N}_J^{\pm} = \begin{pmatrix} \hat{\mathbf{h}}_J^{\lambda\pm} & -\hat{\mathbf{s}}_{\nu\lambda}^J \hat{\mathbf{f}}_J^{\nu\pm} & \mathbf{0} \\ \mathbf{0} & \hat{\mathbf{h}}_J^{\nu\pm} & -\hat{\mathbf{s}}_{\kappa\nu}^J \hat{\mathbf{f}}_J^{\kappa\nu} \\ -\hat{\mathbf{s}}_{\lambda\kappa}^J \hat{\mathbf{f}}_J^{\lambda\pm} & \mathbf{0} & \hat{\mathbf{h}}_J^{\kappa\pm} \end{pmatrix} \tag{4.57}$$

and

$$\mathbf{C}_J^{\pm} = \begin{pmatrix} \mathbf{C}_{J\lambda}^{(1)\pm} & \mathbf{C}_{J\lambda}^{(2)\pm} & \mathbf{C}_{J\lambda}^{(3)\pm} \\ \mathbf{C}_{J\nu}^{(1)\pm} & \mathbf{C}_{J\nu}^{(2)\pm} & \mathbf{C}_{J\nu}^{(3)\pm} \\ \mathbf{C}_{J\kappa}^{(1)\pm} & \mathbf{C}_{J\kappa}^{(2)\pm} & \mathbf{C}_{J\kappa}^{(3)\pm} \end{pmatrix} . \tag{4.58}$$

$\mathbf{0}$ here represents an $N\times N$ matrix of zeros.

Equation (4.56) can now be used in conjunction with the asymptotic analysis of the next section to determine the $3N\times 3N$ coefficient matrices $\mathbf{C}_J^{\pm}$ which will provide wavefunctions which are both smooth and continuous everywhere and which also satisfy the proper scattering boundary conditions. Note that our procedure for matching simultaneously combines the primitive solutions in channels λ, ν, and κ to yield solutions which are smoothly continuous throughout all of configuration space. This contrasts with the analogous procedures of Wyatt and co-workers[16] and of Light and co-workers,[15] which seem not to include the coupling between channels ν and κ (here represented by the $\pi_{\kappa\nu}$ matching equation) explicitly when dealing with collisions originating in channel λ. They may have included such coupling implicitly by utilizing the symmetry of the H_3 system. However, if A_ν and A_κ are different atoms, we believe that the $\nu-\kappa$ coupling must be included explicitly.

V. ASYMPTOTIC ANALYSIS

A. The reactance and scattering matrices

In this section we define the reactance and scattering solutions and relate these to the matched solutions of the previous section so as to complete the determination of the coefficient matrices $\mathbf{C}_J^{\pm}$ and also the reactance and scattering matrices $\mathbf{R}_J$ and $\mathbf{S}_J$. In Paper I we proved that the $\mathbf{R}$ and $\mathbf{S}$ matrices (which are physically dimensionless) can be equivalently defined in the scaled variables $\mathbf{r}_\lambda$, $\mathbf{R}_\lambda$ or in the "physical" ones $\bar{\mathbf{r}}_\lambda$, $\bar{\mathbf{R}}_\lambda$. Here, for simplicity, we use the scaled coordinates in all definitions except that of the scattering amplitudes of Sec. V.B.

If we use Eqs. (2.13), (2.18), (2.30), and (3.1) to express the matched wavefunction [of Eqs. (4.17), (4.18), and (4.43)] in the asymptotic region of each arrangement channel, we find

$$\Psi_{JM}^{(i)t} \sim \sum_\lambda \sum_{t_\lambda} D_{M\Omega_\lambda}^J(\phi_\lambda, \theta_\lambda, 0)\, Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda, \psi_\lambda) \times \frac{\phi_{v_\lambda j_\lambda}^\lambda(r_\lambda)}{r_\lambda R_\lambda}\, e_{\lambda J t_\lambda}^{(i)t}(R_\lambda) , \tag{5.1}$$

where

$$e_{\lambda J t_\lambda}^{(i)t} = \sum_{t_\lambda'} \left(g_{J t_\lambda}^{\lambda t_\lambda +} C_{J\lambda t_\lambda'}^{(i)t+} + g_{J t_\lambda}^{\lambda t_\lambda -} C_{J\lambda t_\lambda'}^{(i)t-} \right) . \tag{5.2}$$

Here we have dropped the superscript (a) which denotes the asymptotic region as it will be implicit throughout Sec. V. The sum over arrangement channels serves as a convenient notation for expressing the asymptotic wavefunction in all three arrangement channels simultaneously and is made possible by the fact that asymptotically there is no overlap between the separated atom plus diatom wavefunctions in different arrangement channels. An equation analogous to Eq. (5.1) for the derivative $(1/R_\lambda)(\partial/\partial R_\lambda) R_\lambda \Psi_{JM}^{(i)t}$ can be obtained by replacing $g_{J t_\lambda}^{\lambda t_\lambda' \pm}$ by $dg_{J t_\lambda}^{\lambda t_\lambda' \pm}/dR_\lambda$ in Eq. (5.2).

The reactance and scattering body-fixed solutions are defined to have the asymptotic form

$$\Psi_{JM}^{\lambda' t_\lambda'}[R \text{ or } S] \underset{R_{\alpha\gamma}, R_{\beta\gamma}, R_\nu \to \infty}{\sim} \sum_\lambda \sum_{t_\lambda} D_{M\Omega_\lambda}^J(\phi_\lambda, \theta_\lambda, 0)\, Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda, \psi_\lambda) \frac{\phi_{v_\lambda j_\lambda}^\lambda(r_\lambda)}{r_\lambda R_\lambda}\, b_{\lambda J t_\lambda}^{\lambda' t_\lambda'}[R \text{ or } S] , \tag{5.3}$$

where, in the far asymptotic region [in which both potential coupling and the centrifugal coupling of Eq. (3.4) have become negligible], we have, for the R solution,

$$b_{\lambda J t_\lambda}^{\lambda' t_\lambda'}[R] = (|V_{v_\lambda j_\lambda}^\lambda|)^{-1/2} \begin{cases} \sin[k_{v_\lambda j_\lambda}^\lambda R_\lambda - (J+j_\lambda)\tfrac{1}{2}\pi]\, \delta_{\lambda t_\lambda}^{\lambda' t_\lambda'} \\ +\cos[k_{v_\lambda j_\lambda}^\lambda R_\lambda - (J+j_\lambda)\tfrac{1}{2}\pi]\, R_{J\lambda' v_\lambda' j_\lambda' \Omega_\lambda'}^{\lambda v_\lambda j_\lambda \Omega_\lambda} & \text{(open channels)} \\ \exp(|k_{v_\lambda j_\lambda}^\lambda| R_\lambda)\, \delta_{\lambda t_\lambda}^{\lambda' t_\lambda'} - \exp(-|k_{v_\lambda j_\lambda}^\lambda| R_\lambda)\, R_{J\lambda' v_\lambda' j_\lambda' \Omega_\lambda'}^{\lambda v_\lambda j_\lambda \Omega_\lambda} & \text{(closed channels)} , \end{cases} \tag{5.4}$$

and, for the S solution,[32]

$$b_{\lambda J t_\lambda}^{\lambda' t_\lambda'}[S] = (|V_{v_\lambda j_\lambda}^\lambda|)^{-1/2} \begin{cases} \exp\{-i[k_{v_\lambda j_\lambda}^\lambda R_\lambda - (J+j_\lambda)\tfrac{1}{2}\pi]\}\, \delta_{\lambda t_\lambda}^{\lambda' t_\lambda'} \\ -\exp\{i[k_{v_\lambda j_\lambda}^\lambda R_\lambda - (J+j_\lambda)\tfrac{1}{2}\pi]\}\, S_{J\lambda' v_\lambda' j_\lambda' \Omega_\lambda'}^{\lambda v_\lambda j_\lambda \Omega_\lambda} & \text{(open channels)} \\ \exp(|k_{v_\lambda j_\lambda}^\lambda| R_\lambda)\, \delta_{\lambda t_\lambda}^{\lambda' t_\lambda'} - \exp(-|k_{v_\lambda j_\lambda}^\lambda| R_\lambda)\, S_{J\lambda' v_\lambda' j_\lambda' \Omega_\lambda'}^{\lambda v_\lambda j_\lambda \Omega_\lambda} & \text{(closed channels)} . \end{cases} \tag{5.5}$$

$V^{\lambda}_{v_\lambda j_\lambda}$ is the velocity (in scaled variables) and is related to the wave number of Eq. (3.5) by

$$V^{\lambda}_{v_\lambda j_\lambda} = \hbar k^{\lambda}_{v_\lambda j_\lambda}/\mu \quad . \tag{5.6}$$

The primed variables $v'_\lambda j'_\lambda \Omega'_\lambda$ in Eqs. (5.4) and (5.5) define the reagent state in the λ' arrangement channel. (Note our use of the abbreviation $\lambda' t'_\lambda \equiv \lambda' t'_{\lambda'}$.) $\mathbf{R}_J$ and $\mathbf{S}_J$ are the partial wave reactance and scattering matrices and, for exact solutions of the Schrödinger equation, they are symmetric.[45] Note that $-\Omega'_\lambda$ rather than Ω'_λ appears in the definition of $\mathbf{R}_J$ and $\mathbf{S}_J$. This choice allows the open channel part of the scattering matrix to become the identity matrix in the limit of zero interaction potential (as will be evident from the partial wave expression for the scattering amplitude in Sec. V.B). The phase factors $i^{\pm(J+j_\lambda)}$ appearing in Eqs. (5.4) and (5.5) are arbitrary but will prove convenient later on. The open-channel subblocks of $\mathbf{R}_J$ and $\mathbf{S}_J$ are labeled $\mathbf{R}^0_J$ and $\mathbf{S}^0_J$, and from Eqs. (5.4) and (5.5), one can easily show[46] that

$$\mathbf{S}^0_J = (\mathbf{I} + i\mathbf{R}^0_J)(\mathbf{I} - i\mathbf{R}^0_J)^{-1} \quad , \tag{5.7}$$

where $\mathbf{I}$ is the identity matrix, and that the closed channel parts of $\mathbf{R}_J$ and $\mathbf{S}_J$ are identical. In addition to being symmetric, $\mathbf{R}^0_J$ is real and $\mathbf{S}^0_J$ is unitary. From the unitarity of $\mathbf{S}^0_J$ one can prove flux conservation, and microscopic reversibility results from its symmetry.[45]

In an actual calculation, we wish to use the R and S solutions of the Schrödinger equation at a finite R_λ for which the potential coupling has become negligible but the centrifugal coupling in Eq. (3.4) has not. These solutions can be obtained by taking the appropriate linear combinations of space-fixed Bessel functions as was done in Eq. (3.7) so that the far asymptotic behavior in Eqs. (5.3) and (5.4) is obtained in that limit. In other words, as soon as potential coupling has become negligible (but not the centrifugal one), the b in Eq. (5.3) can be written according to Eq. (3.7) as

$$b^{\lambda' t'_\lambda}_{\lambda J t_\lambda}[R] = (|V^{\lambda}_{v_\lambda j_\lambda}|)^{-1/2} \sum_{\lambda'' t''_\lambda} \{ I^{\lambda'' t''_\lambda}_{J\lambda t_\lambda}[R]\delta^{\lambda' t'_\lambda}_{\lambda'' t''_\lambda} + O^{\lambda'' t''_\lambda}_{J\lambda t_\lambda}[R] R^{\lambda'' t''_\lambda}_{J\lambda' v'_\lambda j'_\lambda - \Omega'_\lambda} \} \ , \tag{5.8}$$

$$b^{\lambda' t'_\lambda}_{\lambda J t_\lambda}[S] = (|V^{\lambda}_{v_\lambda j_\lambda}|)^{-1/2} \sum_{\lambda'' t''_\lambda} \{ I^{\lambda'' t''_\lambda}_{J\lambda t_\lambda}[S]\delta^{\lambda' t'_\lambda}_{\lambda'' t''_\lambda} - O^{\lambda'' t''_\lambda}_{J\lambda t_\lambda}[S] S^{\lambda'' t''_\lambda}_{J\lambda' v'_\lambda j'_\lambda - \Omega'_\lambda} \} \ , \tag{5.9}$$

where, for both R and S matrix solutions,

$$\begin{pmatrix} I_J \\ O_J \end{pmatrix}^{\lambda' t'_\lambda}_{\lambda t_\lambda} = \delta^{\lambda' v'_\lambda j'_\lambda}_{\lambda v_\lambda j_\lambda} (-1)^{\Omega'_\lambda - \Omega_\lambda} \sum_{l_\lambda} C(Jj_\lambda l_\lambda; \Omega'_\lambda, -\Omega'_\lambda, 0)\, C(Jj_\lambda l_\lambda; \Omega_\lambda, -\Omega_\lambda, 0) \begin{pmatrix} \mathcal{I}_{Jv_\lambda j_\lambda l_\lambda} \\ \mathcal{O}_{Jv_\lambda j_\lambda l_\lambda} \end{pmatrix} \ . \tag{5.10}$$

For the R solution,

$$\mathcal{I}_{Jv_\lambda j_\lambda l_\lambda}[R] = |k_{v_\lambda j_\lambda}|R_\lambda \begin{cases} y_{l_\lambda}(k^{\lambda}_{v_\lambda j_\lambda}R_\lambda)\sin[(J+j_\lambda-l_\lambda)\tfrac{1}{2}\pi] + j_{l_\lambda}(k^{\lambda}_{v_\lambda j_\lambda}R_\lambda)\cos[(J+j_\lambda-l_\lambda)\tfrac{1}{2}\pi] & \text{(open channels)} \\ 2i_{l_\lambda}(|k^{\lambda}_{v_\lambda j_\lambda}|R_\lambda) & \text{(closed channels)} \ , \end{cases} \tag{5.11a}$$

$$\mathcal{O}_{Jv_\lambda j_\lambda l_\lambda}[R] = |k^{\lambda}_{v_\lambda j_\lambda}|R_\lambda \begin{cases} -y_{l_\lambda}(k^{\lambda}_{v_\lambda j_\lambda}R_\lambda)\cos[(J+j_\lambda-l_\lambda)\tfrac{1}{2}\pi] + j_{l_\lambda}(k^{\lambda}_{v_\lambda j_\lambda}R_\lambda)\sin[(J+j_\lambda-l_\lambda)\tfrac{1}{2}\pi] & \text{(open channels)} \\ k_{l_\lambda}(|k^{\lambda}_{v_\lambda j_\lambda}|R_\lambda) & \text{(closed channels)} \ , \end{cases} \tag{5.11b}$$

while, for the S solution,

$$\mathcal{I}_{Jv_\lambda j_\lambda l_\lambda}[S] = |k^{\lambda}_{v_\lambda j_\lambda}|R_\lambda \begin{cases} \exp[i(J+j_\lambda-l_\lambda)\tfrac{1}{2}\pi]\, h^{(-)}_{l_\lambda}(k^{\lambda}_{v_\lambda j_\lambda}R_\lambda) & \text{(open channels)} \\ 2i_{l_\lambda}(|k^{\lambda}_{v_\lambda j_\lambda}|R_\lambda) & \text{(closed channels)} \ , \end{cases} \tag{5.12a}$$

$$\mathcal{O}_{Jv_\lambda j_\lambda l_\lambda}[S] = |k^{\lambda}_{v_\lambda j_\lambda}|R_\lambda \begin{cases} \exp[-i(J+j_\lambda-l_\lambda)\tfrac{1}{2}\pi]\, h^{(+)}_{l_\lambda}(k^{\lambda}_{v_\lambda j_\lambda}R_\lambda) & \text{(open channels)} \\ k_{l_\lambda}(|k^{\lambda}_{v_\lambda j_\lambda}|R_\lambda) & \text{(closed channels)} \ , \end{cases} \tag{5.12b}$$

where

$$h^{(\pm)}_{l_\lambda} = -y_{l_\lambda} \pm i j_{l_\lambda} \ , \tag{5.13}$$

and y_{l_λ}, j_{l_λ}, i_{l_λ}, and k_{l_λ} are the spherical Bessel functions of Sec. III. B. 1. To show that Eqs. (5.8) and (5.9) do indeed reduce, respectively, to Eqs. (5.4) and (5.5) in the far asymptotic limit, one simply uses the asymptotic form of these Bessel functions at large values of the argument $|k^{\lambda(a)}_{v_\lambda j_\lambda}|R_\lambda$.[38,40] We may use Eq. (A14) to relate the usual space-fixed $\mathbf{S}$ matrix $\hat{\mathbf{S}}_J$ to the body-fixed $\mathbf{S}_J$. We obtain the R_λ-independent unitary transformation

$$\hat{\mathbf{S}}_J = \mathcal{J}^\dagger \mathbf{S}_J \mathcal{J} \ , \tag{5.14}$$

where

$$(\mathcal{J})^{\lambda' v'_\lambda j'_\lambda l'_\lambda}_{\lambda v_\lambda j_\lambda \Omega_\lambda} = \delta^{\lambda' v'_\lambda j'_\lambda}_{\lambda v_\lambda j_\lambda} C(J j_\lambda l'_\lambda; \Omega_\lambda, -\Omega_\lambda, 0) i^{l'_\lambda - j_\lambda} (-1)^{\Omega_\lambda} . \tag{5.15}$$

In order to obtain $\mathbf{R}_J$, we generate an R solution of the Schrödinger equation satisfying the asymptotic conditions of Eqs. (5.3) or (5.8) by taking linear combinations of the matched solutions $\Psi^{(i)t}_{JM}$ of Eq. (5.1):

$$\Psi^{\lambda' t'_\lambda}_{JM}[R] = \sum_{(i)t} \Psi^{(i)t}_{JM} Q^{J\lambda' t'_\lambda}_{(i)t} . \tag{5.16}$$

As in Paper I, we are free to choose $Q^{\lambda' t'_\lambda}_{(i)t} = \delta^{\lambda' t'_\lambda}_{(i)t}$ and require the $\mathbf{C}^{\pm}_J$ matrices to provide for us those linear combinations of the primitive solutions satisfying both the matching condition [Eq. (4.56)] and the asymptotic conditions. If we substitute Eqs. (5.1)–(5.3) and (5.8) into Eq. (5.16) and express everything in matrix notation (involving matrices of dimension $3N\times 3N$), we get

$$\mathbf{V}^{-1/2}(\mathbf{I}_J[R] + \mathbf{O}_J[R]\,\bar{\mathbf{R}}_J)(\mathbf{C}^-_J)^{-1} = \mathbf{g}^+_J \mathbf{C}^+_J (\mathbf{C}^-_J)^{-1} + \mathbf{g}^-_J , \tag{5.17}$$

where $\bar{\mathbf{R}}_J$ is related to $\mathbf{R}_J$ of Eq. (5.8) by

$$(\bar{\mathbf{R}}_J)^{\lambda' v'_\lambda j'_\lambda \Omega'_\lambda}_{\lambda v_\lambda j_\lambda \Omega_\lambda} = (\mathbf{R}_J)^{\lambda v_\lambda j_\lambda \Omega_\lambda}_{\lambda' v'_\lambda j'_\lambda - \Omega'_\lambda} \tag{5.18}$$

and

$$(\mathbf{V})^{\lambda' t'_\lambda}_{\lambda t_\lambda} = |V^\lambda_{v_\lambda j_\lambda}|\,\delta^{\lambda' t'_\lambda}_{\lambda t_\lambda} . \tag{5.19}$$

Note that the $(\mathbf{g}_J)^{\lambda' t'_\lambda \pm}_{\lambda t_\lambda}$ in Eq. (5.17) is identical to $\delta_{\lambda\lambda'}$ times the $g^{\lambda' t'_\lambda \pm}_{J t_\lambda}$ of Eq. (5.2). An equation analogous to Eq. (5.17) for the derivative $R_\lambda^{-1}(\partial/\partial R_\lambda)R_\lambda \Psi^{\lambda' t'_\lambda}_{JM}$ is easily shown to be

$$\mathbf{V}^{-1/2}(\mathbf{I}'_J[R] + \mathbf{O}'_J[R]\,\bar{\mathbf{R}}_J)(\mathbf{C}^-_J)^{-1} = \mathbf{g}'^+_J \mathbf{C}^+_J (\mathbf{C}^-_J)^{-1} + \mathbf{g}'^-_J , \tag{5.20}$$

where prime denotes differentiation with respect to R_λ. The quantity $\mathbf{C}^+_J(\mathbf{C}^-_J)^{-1}$ is given by Eq. (4.56). Equations (5.17) and (5.20) therefore provide two simultaneous linear matrix equations in the two unknown matrices $(\mathbf{C}^-_J)^{-1}$ and $\bar{\mathbf{R}}_J$. Eliminating the former from these two equations and using Eq. (4.56), we get

$$\begin{aligned}\bar{\mathbf{R}}_J = -\mathbf{V}^{1/2}\mathbf{W}^{-1}\{&(\mathbf{I}'_J[R]\mathbf{g}^+_J - \mathbf{I}_J[R]\mathbf{g}'^+_J)(\mathbf{N}^+_J)^{-1}\mathbf{N}^-_J - (\mathbf{I}'_J[R]\mathbf{g}^-_J \\ &- \mathbf{I}_J[R]\mathbf{g}'^-_J)\}\{(\mathbf{O}'_J[R]\mathbf{g}^+_J - \mathbf{O}_J[R]\mathbf{g}'^+_J) \\ &\times (\mathbf{N}^+_J)^{-1}\mathbf{N}^-_J - (\mathbf{O}'_J[R]\mathbf{g}^-_J - \mathbf{O}_J[R]\mathbf{g}'^-_J)\}^{-1}\mathbf{W}\mathbf{V}^{-1/2} .\end{aligned} \tag{5.21}$$

Here

$$\mathbf{W} = \mathbf{O}'[R]\mathbf{I}[R] - \mathbf{I}'_J[R]\,\mathbf{O}_J[R] \tag{5.22}$$

is a Wronskian matrix which, as can be seen by inspection of Eqs. (5.10) and (5.11), is diagonal and constant, i.e., independent of R_λ. The right-hand side of Eq. (5.21) involves real matrices which are obtained directly from the integration and matching steps of the calculation. Therefore, $\bar{\mathbf{R}}_J$ and $\mathbf{R}_J$ are real, as expected.

With $\bar{\mathbf{R}}_J$ and hence $\mathbf{R}_J$ determined, we use Eq. (5.7) to calculate $\mathbf{S}^0_J$, which in turn can be related to the scattering amplitude by the formulas of the next section. In addition, the scattering matrix is related to the probability of transition from initial arrangement channel λ and quantum state $v_\lambda j_\lambda \Omega_\lambda$ to final channel λ' and state $v'_\lambda j'_\lambda \Omega'_\lambda$ by[47]

$$P^{\lambda' v'_\lambda j'_\lambda \Omega'_\lambda}_{J\lambda v_\lambda j_\lambda \Omega_\lambda} = |S^{0\lambda' v'_\lambda j'_\lambda \Omega'_\lambda}_{J\lambda v_\lambda j_\lambda \Omega_\lambda}|^2 . \tag{5.23}$$

[In the rest of this paper, lower (upper) indices, which refer to the initial (final) state, will be unprimed (primed).] The scattering matrix may also be related to the opacity function as discussed in the next section.

B. Scattering amplitudes and cross sections

We now define the scattered plane wave solution and relate it to the scattering solution of the previous section so as to express the scattering amplitude in terms of the open parts of the partial wave scattering matrices. Our analysis will be done using the helicity representation[48] in which the axis of quantization of the incoming and outgoing rotational states is chosen to coincide with the direction of the incident and final wave vectors respectively. The helicity formalism is very closely related to the use of body-fixed coordinate systems of the type described in Sec. II.B and leads to a particularly simple relation between the helicity scattering amplitudes and body-fixed $\mathbf{S}$ matrices.

We define the helicity representation scattered plane wave solution by

$$\begin{aligned}\bar{\Psi}^{\lambda \hat{t}_\lambda}[P] \sim &\exp[i\bar{k}^\lambda_{v_\lambda j_\lambda}(\bar{\mathbf{R}}_\lambda)_z]\frac{\bar{\phi}^\lambda_{v_\lambda j_\lambda}(\bar{r}_\lambda)}{\bar{r}_\lambda} Y_{j_\lambda m_{j_\lambda}}(\theta_{r_\lambda}\phi_{r_\lambda}) \\ &+ \sum_{\lambda' \hat{t}'_\lambda} \frac{\exp(i\bar{k}^{\lambda'}_{v'_\lambda j'_\lambda}\bar{R}_{\lambda'})}{\bar{R}'_\lambda}\frac{\bar{\phi}^{\lambda'}_{v'_\lambda j'_\lambda}(\bar{r}'_\lambda)}{\bar{r}'_\lambda} \\ &\times Y_{j'_\lambda m'_{j_\lambda}}(\gamma_{\lambda'}, \psi_{\lambda'})\bar{f}^{\lambda' \hat{t}'_\lambda}_{\lambda \hat{t}_\lambda}(\theta_{\lambda'}, \phi_{\lambda'}),\end{aligned} \tag{5.24}$$

where the sum over final states includes both open and closed channels. For closed-channel solutions (which we shall ignore below), $\bar{k}^\lambda_{v_\lambda j_\lambda}$ is pure imaginary, so $\exp(i\bar{k}^\lambda_{v_\lambda j_\lambda}\bar{R}_\lambda)$ decreases exponentially. Note that the physical coordinates $\bar{\mathbf{R}}_\lambda$, $\bar{r}_\lambda$ and wave numbers $\bar{k}^\lambda_{v_\lambda j_\lambda} = a_\lambda k^\lambda_{v_\lambda j_\lambda}$ have been used in Eq. (5.24). In addition, we have introduced the global index $\hat{t}$ to denote the quantum numbers vjm_j. (We will relate m_j to Ω and hence $\hat{t}$ to t below.) For simplicity, the space-fixed z axis has been chosen to be in the direction of the incident wave vector. It then follows (by inspection of Fig. 2) that the space-fixed and body-fixed z axes will point in opposite directions initially (i.e., for $(\bar{\mathbf{R}}_\lambda)_z \to -\infty$). The outgoing body-fixed z'_λ axis points in the same direction as the outgoing wave vector, thus allowing us to use $Y_{j'_\lambda m'_{j_\lambda}}(\gamma'_\lambda, \psi'_\lambda)$ instead of $Y_{j'_\lambda m'_{j_\lambda}}(\theta_{r'_\lambda}, \phi_{r'_\lambda})$ in the summation appearing in Eq. (5.24).

The differential scattering cross section is defined as the ratio of the outgoing radial flux per unit solid angle to the incoming plane wave flux and, from Eq. (5.24), is related to the scattering amplitude $\bar{f}$ by

$$\sigma^{\lambda' \hat{t}'_\lambda}_{\lambda \hat{t}_\lambda} = \frac{\bar{V}^{\lambda'}_{v'_\lambda j'_\lambda}}{\bar{V}^\lambda_{v_\lambda j_\lambda}} |\bar{f}^{\lambda' \hat{t}'_\lambda}_{\lambda \hat{t}_\lambda}|^2 \tag{5.25}$$

for $\lambda v_\lambda j_\lambda m_{j_\lambda}$ and $\lambda' v'_\lambda j'_\lambda m'_{j_\lambda}$ representing open final and initial channels, respectively. Here $\bar{V}^\lambda_{v_\lambda j_\lambda}$ is the physical velocity

$$\bar{V}^\lambda_{v_\lambda j_\lambda} = \frac{1}{a_\lambda} V^\lambda_{v_\lambda j_\lambda} = \left(\frac{2(E - \epsilon^\lambda_{v_\lambda j_\lambda})}{\mu_{\lambda, \nu_\kappa}}\right)^{1/2} . \tag{5.26}$$

In order to relate $\bar{f}$ to the scattering matrices, it is desirable to first define a scattering solution analogous to Eq. (5.24) in terms of the scaled coordinates of Eq. (2.1). This is easily done by removing the "bars" on all symbols containing them in Eq. (5.24). By comparing the plane wave parts, we see that the resulting $\Psi^{\lambda\hat{t}_\lambda}[P]$ is proportional to $\bar{\Psi}^{\lambda\hat{t}_\lambda}[P]$ with a proportionality constant $a_\lambda^{3/2}$. Comparison of the outgoing wave parts of Ψ and $\bar{\Psi}$ then yields

$$\bar{f}_{\lambda\hat{t}_\lambda}^{\lambda'\hat{t}'_\lambda} = a_\lambda^{-1} f_{\lambda\hat{t}_\lambda}^{\lambda'\hat{t}'_\lambda}\left(\frac{a'_\lambda}{a_\lambda}\right)^{1/2}, \tag{5.27}$$

which will be useful below.

One now expands the plane wave part of $\Psi^{\lambda\hat{t}_\lambda}[P]$ in terms of a series of products of Legendre polynomials $P_{l_\lambda}(\cos\theta_\lambda)$ times spherical Bessel functions $j_{l_\lambda}(k^\lambda_{v_\lambda j_\lambda}R_\lambda)$, takes the asymptotic limit ($R_\lambda \to \infty$), and converts the result to the body-fixed variables $r_\lambda\gamma_\lambda\psi_\lambda$ and $R_\lambda\theta_\lambda\phi_\lambda$ following the procedure outlined by Pack,[32] obtaining

$$\exp[ik^\lambda_{v_\lambda j_\lambda}(\mathbf{R}_\lambda)_z]\left(\frac{\phi^\lambda_{v_\lambda j_\lambda}(r_\lambda)}{r_\lambda}\right)Y_{j_\lambda m_{j_\lambda}}(\theta_{r_\lambda},\phi_{r_\lambda}) \sim \frac{1}{2k^\lambda_{v_\lambda j_\lambda}R_\lambda}\left(\frac{\phi^\lambda_{v_\lambda j_\lambda}(r_\lambda)}{r_\lambda}\right)\sum_{JM\Omega_\lambda}\delta_{Mm_{j_\lambda}}D^J_{M\Omega_\lambda}(\phi_\lambda,\theta_\lambda,0)$$

$$\times Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda,\psi_\lambda)(2J+1)\,i^{J+j_\lambda+1}\left(\exp\{-i[k^\lambda_{v_\lambda j_\lambda}R_\lambda-(J+j_\lambda)\tfrac{1}{2}\pi]\}\delta_{M,-\Omega_\lambda}-\exp\{i[k^\lambda_{v_\lambda j_\lambda}R_\lambda-(J+j_\lambda)\tfrac{1}{2}\pi]\}\delta_{M\Omega_\lambda}\right). \tag{5.28}$$

In analogy to Eq. (2.11), the scattered plane wave solution $\Psi^{\lambda v_\lambda j_\lambda m_{j_\lambda}}[P]$ may be expanded in terms of the scattering solutions $\Psi^{\lambda v_\lambda j_\lambda\Omega_\lambda}[S]$ as

$$\Psi^{\lambda v_\lambda j_\lambda m_{j_\lambda}}[P] = \sum_{JM\Omega_\lambda} C^{\lambda v_\lambda j_\lambda m_{j_\lambda}\Omega_\lambda}_{JM}\Psi^{\lambda v_\lambda j_\lambda\Omega_\lambda}_{JM}[S]. \tag{5.29}$$

Using Eq. (5.28) to express $\Psi[P]$ in terms of body-fixed quantities, Eqs. (5.3) and (5.5) for the asymptotic form of $\Psi^{\lambda\hat{t}_\lambda}_{JM}[S]$, and equating coefficients of the incoming spherical wave parts, one finds

$$C^{\lambda v_\lambda j_\lambda m_{j_\lambda}\Omega_\lambda}_{JM} = \delta_{M,-\Omega_\lambda}\delta_{Mm_{j_\lambda}}\left(\frac{\hbar}{\mu}\right)^{1/2}\frac{2J+1}{2}\,i^{J+j_\lambda+1}. \tag{5.30}$$

This shows that the only value of Ω_λ contributing to the right-hand side of Eq. (5.29) is $\Omega_\lambda = -m_j$, which relates $\hat{t}_\lambda \equiv v_\lambda j_\lambda m_{j_\lambda}$ and $t_\lambda \equiv v_\lambda j_\lambda\Omega_\lambda$ for the reagent states. If we now equate coefficients of outgoing spherical wave parts and use Eq. (5.30) to simplify the result, we get

$$f_{\lambda\hat{t}_\lambda}^{\lambda'\hat{t}'_\lambda} = \left(\frac{V^\lambda_{v_\lambda j_\lambda}}{V^{\lambda'}_{v'_\lambda j'_\lambda}}\right)^{1/2}\frac{e^{im'_{j_\lambda}\phi_{\lambda'}}}{2k^\lambda_{v_\lambda j_\lambda}}\,i^{j_\lambda-j'_\lambda+1}\sum_{J=0}^{\infty}(2J+1)d^J_{m_{j_\lambda}m'_{j_\lambda}}(\theta_{\lambda'})T^{\lambda'\hat{t}'_\lambda}_{J\lambda\hat{t}_\lambda}, \tag{5.31}$$

where

$$\mathbf{T}_J = \mathbf{I} - \mathbf{S}^0_J \tag{5.32}$$

is the transition matrix,[32] and $m'_{j_\lambda} = \Omega'_\lambda$ for the product states so that $\hat{t}'_\lambda$ and t'_λ are identical. Equation (5.31) shows that the helicity amplitude and body-fixed scattering matrix are related by a single sum reminiscent of the analogous result for potential scattering. This illustrates one of the primary advantages of the use of helicity amplitudes in conjunction with body-fixed coordinates such as those depicted in Fig. 2. Combining Eqs. (5.31) and (5.27), and using Eq. (5.26) and its counterpart for the wave numbers $\bar{k}^\lambda_{v_\lambda j_\lambda}$ and $k^\lambda_{v_\lambda j_\lambda}$, we find that the physical scattering amplitude $\bar{f}^{\lambda'\hat{t}'_\lambda}_{\lambda\hat{t}_\lambda}$ is given by an expression identical to Eq. (5.31) with all velocities and wave numbers "barred." Substituting this into Eq. (5.25), we find

$$\sigma^{\lambda'\hat{t}'_\lambda}_{\lambda\hat{t}_\lambda}(\theta_{\lambda'}) = \frac{1}{4\bar{k}^{\lambda 2}_{v_\lambda j_\lambda}}\left|\sum_{J=0}^{\infty}(2J+1)d^J_{m_{j_\lambda}m'_{j_\lambda}}(\theta_{\lambda'})T^{\lambda'\hat{t}'_\lambda}_{J\lambda\hat{t}_\lambda}\right|^2, \tag{5.33}$$

which demonstrates that the differential cross section is independent of $\phi_{\lambda'}$.[49] Using the properties $d^J_{m'm}(0) = \delta_{m'm}$ and $d^J_{m'm}(\pi) = (-1)^{J+m}\delta_{m',-m}$ [derivable directly from the definition of $d^J_{m'm}(\beta)$], we get from Eq. (5.33)

$$\sigma^{\lambda'\hat{t}'_\lambda}_{\lambda\hat{t}_\lambda}(0) = \delta_{m'_{j_\lambda}m_{j_\lambda}}\frac{1}{4\bar{k}^{\lambda 2}_{v_\lambda j_\lambda}}\left|\sum_{J=0}^{\infty}(2J+1)T^{\lambda'\hat{t}'_\lambda}_{J\lambda\hat{t}_\lambda}\right|^2$$

and

$$\sigma^{\lambda'\hat{t}'_\lambda}_{\lambda\hat{t}_\lambda}(\pi) = \delta_{m'_{j_\lambda},-m_{j_\lambda}}\frac{1}{4\bar{k}^{\lambda 2}_{v_\lambda j_\lambda}}\left|\sum_{J=0}^{\infty}(-1)^J(2J+1)T^{\lambda'\hat{t}'_\lambda}_{J\lambda\hat{t}_\lambda}\right|^2,$$

which show that for $m'_{j_\lambda} \neq m_{j_\lambda}$, $\sigma^{\lambda'\hat{t}'_\lambda}_{\lambda\hat{t}_\lambda}(0)$ vanishes, and for $m'_{j_\lambda} \neq -m_{j_\lambda}$, $\sigma^{\lambda'\hat{t}'_\lambda}_{\lambda\hat{t}_\lambda}(\pi)$ vanishes. These are rigorous selection rules for forward and backward scattering related to the conservation of J_z.[24]

The integral cross section $Q^{\lambda'\hat{t}'_\lambda}_{\lambda\hat{t}_\lambda}$ is obtained by integrating Eq. (5.33) over $\theta_{\lambda'}$ and $\phi_{\lambda'}$, and using the orthonormality property of the d^J functions.[33] This yields the remarkably simple expression

$$Q^{\lambda'\hat{t}'_\lambda}_{\lambda\hat{t}_\lambda} = \frac{\pi}{\bar{k}^{\lambda 2}_{v_\lambda j_\lambda}}\sum_{J=0}^{\infty}(2J+1)\left|T^{\lambda'\hat{t}'_\lambda}_{J\lambda\hat{t}_\lambda}\right|^2. \tag{5.34}$$

Both $\sigma^{\lambda'\hat{t}'_\lambda}_{\lambda\hat{t}_\lambda}$ and $Q^{\lambda'\hat{t}'_\lambda}_{\lambda\hat{t}_\lambda}$ may be averaged over initial m_{j_λ} and summed over final m'_{j_λ} to give the degeneracy-averaged quantities $\sigma^{\lambda' v'_\lambda j'_\lambda}_{\lambda v_\lambda j_\lambda}$ and $Q^{\lambda' v'_\lambda j'_\lambda}_{\lambda v_\lambda j_\lambda}$, respectively. The latter of these two can be written as[32]

$$Q^{\lambda' v'_\lambda j'_\lambda}_{\lambda v_\lambda j_\lambda} = \frac{\pi}{\bar{k}^{\lambda 2}_{v_\lambda j_\lambda}}\sum_{J=0}^{\infty}(2J+1)P^{v'_\lambda j'_\lambda}_{Jv_\lambda j_\lambda}, \tag{5.35}$$

where the opacity function P_J is

$$P^{v'_\lambda j'_\lambda}_{Jv_\lambda j_\lambda} = (2j_\lambda+1)^{-1}\sum_{m_{j_\lambda}}\sum_{m'_{j_\lambda}}P^{\lambda'\hat{t}'_\lambda}_{J\lambda\hat{t}_\lambda}, \tag{5.36}$$

and the ranges of the sums are $|m_{j_\lambda}| \leq \min(j_\lambda, J)$ and $|m'_{j_\lambda}| \leq \min(j'_\lambda, J)$.

In an application to the $H + H_2$ reaction, the number of different distinguishable atom scattering amplitudes and cross sections may be greatly reduced by considering the symmetries involved. This was done in Paper I and the derivations are essentially unchanged in 3D. First, the scattering amplitudes are invariant to a cyclic permutation of arrangement channel indices so that (suppressing the $\hat{t}_\lambda, \hat{t}'_\lambda$) $f^\lambda_\lambda = f^\nu_\nu = f^\kappa_\kappa$, $f^\nu_\lambda = f^\kappa_\nu = f^\lambda_\kappa$, and $f^\lambda_\nu = f^\nu_\kappa = f^\kappa_\lambda$. Second, f^κ_λ and f^ν_λ are related by[19]

$$f^{\kappa v' j' m'_j}_{\lambda v j m_j} = (-1)^{j+j'} f^{\nu v' j' m'_j}_{\lambda v j m_j} \tag{5.37}$$

and the nonreactive f^{λ}_{λ} satisfy

$$f^{\lambda v' j' m'_j}_{\lambda v j m_j} = 0 \quad \text{if } j - j' = \text{odd}. \tag{5.38}$$

These statements imply that f^{λ}_{λ} and f^{ν}_{λ} are the only distinct scattering amplitudes and that many components of f^{λ}_{λ} are zero. These symmetry relations also apply to the scattering matrix $\mathbf{S}_J$ so that the entire distinguishable-atom cross section calculation can be considerably streamlined. It should be mentioned that although the cyclic permutational symmetry is built into the calculation if the integration is done in only one of the three equivalent arrangement channel regions, Eqs. (5.37) and (5.38) will only hold rigorously if $\mathbf{s}^{J}_{\nu\lambda}$ defined by Eq. (4.49) is orthogonal, and this will only be the case if the matching surface basis functions given by Eq. (4.30) form a sufficiently complete set. This provides a test of convergence of the method as long as the symmetries of Eqs. (5.37) and (5.38) are not built in to the calculation.

To convert these distinguishable-atom scattering amplitudes into the corresponding indistinguishable ones when two or three of the atoms are identical, the standard technique of postantisymmetrization[50] may be used. Application to $H + H_2$ was given in Paper I and is unchanged in the three-dimensional treatment. In the notation of this paper we obtain the following expressions for the antisymmetrized differential cross sections:

(a) para → para ($j, j' =$ even):

$$\sigma^{p\hat{t}'}_{p\hat{t}} = \frac{\bar{V}_{v'j'}}{\bar{V}_{vj}} \left| \bar{f}^{\lambda\hat{t}'}_{\lambda\hat{t}} - \bar{f}^{\nu\hat{t}'}_{\lambda\hat{t}} \right|^2, \tag{5.39a}$$

(b) para → ortho ($j =$ even, $j' =$ odd):

$$\sigma^{o\hat{t}'}_{p\hat{t}} = 3 \frac{\bar{V}_{v'j'}}{\bar{V}_{vj}} \left| \bar{f}^{\nu\hat{t}'}_{\lambda\hat{t}} \right|^2, \tag{5.39b}$$

(c) ortho → para ($j =$ odd, $j' =$ even):

$$\sigma^{p\hat{t}'}_{o\hat{t}} = \frac{\bar{V}_{v'j'}}{\bar{V}_{vj}} \left| \bar{f}^{\nu\hat{t}'}_{\lambda\hat{t}} \right|^2, \tag{5.39c}$$

(d) ortho → ortho ($j, j' =$ odd):

$$\sigma^{o\hat{t}'}_{o\hat{t}} = \frac{\bar{V}_{v'j'}}{\bar{V}_{vj}} \left(\left| \bar{f}^{\lambda\hat{t}'}_{\lambda\hat{t}} + \bar{f}^{\nu\hat{t}'}_{\lambda\hat{t}} \right|^2 + 2 \left| \bar{f}^{\nu\hat{t}'}_{\lambda\hat{t}} \right|^2 \right), \tag{5.39d}$$

where Eqs. (5.27) and (5.31) are to be used in evaluating Eqs. (5.39). The expressions for the antisymmetrized integral reaction cross sections are

(a) para → para:

$$Q^{p\hat{t}'}_{p\hat{t}} = \frac{\pi}{\bar{k}^2_{vj}} \sum_J (2J+1) \left| \delta^{\hat{t}'}_{\hat{t}} - S^{0\lambda\hat{t}'}_{J\lambda\hat{t}} + S^{0\nu\hat{t}'}_{J\lambda\hat{t}} \right|^2, \tag{5.40a}$$

(b) para → ortho:

$$Q^{o\hat{t}'}_{p\hat{t}} = 3 \frac{\pi}{\bar{k}^2_{vj}} \sum_J (2J+1) \left| S^{0\nu\hat{t}'}_{J\lambda\hat{t}} \right|^2, \tag{5.40b}$$

(c) ortho → para:

$$Q^{p\hat{t}'}_{o\hat{t}} = \frac{\pi}{\bar{k}^2_{vj}} \sum_J (2J+1) \left| S^{0\nu\hat{t}'}_{J\lambda\hat{t}} \right|^2, \tag{5.40c}$$

(d) ortho → ortho:

$$Q^{o\hat{t}'}_{o\hat{t}} = \frac{\pi}{\bar{k}^2_{vj}} \sum_J (2J+1) \left(\left| \delta^{\hat{t}'}_{\hat{t}} - S^{0\lambda\hat{t}'}_{J\lambda\hat{t}} - S^{0\nu\hat{t}'}_{J\lambda\hat{t}} \right|^2 + 2 \left| S^{0\nu t'}_{J\lambda t} \right|^2 \right). \tag{5.40d}$$

As was pointed out in Sec. III. C, parity symmetry may be used in both the integration and matching procedures for any chemical reaction to reduce the number of states coupled in these stages of the calculation. One may also define parity scattering matrices, but the plane wave solution of Eq. (5.24) does not have parity symmetry so that these two decoupled parity S matrices must be recoupled before performing the calculation of the scattering amplitude in Eq. (5.31). This procedure is outlined in Appendix B.

VI. DISCUSSION

The method we have outlined in Secs. II–V has a number of limitations or restrictions which we shall now analyze. First, we have considered the reactive collision of an atom with a diatomic molecule on a single electronically adiabatic potential energy surface. The extension to multisurface reactions is straightforward and would follow the general format previously developed for collinear reactions.[51] All three reactive arrangement channels are assumed to be energetically accessible and the diatom in each arrangement channel is assumed to be in a $^1\Sigma$ electronic state. A straightforward modification of the matching procedure which simplifies it appropriately is required for single reaction path systems (for which one of the three arrangement channels is closed). This was discussed in Paper I. For diatoms having electronic states other than $^1\Sigma$ (such as $^1\Lambda$ with $\Lambda \neq 0$), the rotational states $Y_{j_\lambda m_{j_\lambda}}(\theta_{r_\lambda}, \phi_{r_\lambda})$ must be modified[33] to $D^{j_\lambda}_{m_{j_\lambda}\Lambda}(\theta_{r_\lambda}, \phi_{r_\lambda}, 0)$ and electronic–vibration–rotation coupling must be considered, but the basic integration and matching procedures are unchanged. One basic restriction of the method is its inability to treat dissociative or break-up channels. This is not a serious limitation for many important chemical reactions at thermal energies. A procedure for treating both dissociative and reactive collisions is currently being developed in this laboratory.

The integration procedure outlined in Sec. III may be applied to any reaction for which the criteria of the preceding paragraph apply, but the matching procedure (and hence the choice of coordinate system in the matching region) is strongly dependent on our choice of matching surfaces [Eq. (2.3) of I]. Other choices will require significant modifications in the details of Sec. IV, although the basic concepts involved in matching will still be applicable. The matching surfaces considered in Eqs. (2.3) of I should be useful for many chemical reactions but may not always be ideal for obtaining rapidly convergent coupled-channel expansions. In particular, if the reaction has a low barrier for $\gamma_\lambda = \pi/2$ configurations, the expansion of the wavefunction in terms of matching surface basis functions $T^{\nu\lambda}$ (Sec. IV. B) may be slowly convergent. Conversely, too strong an anisotropy favoring collinear reactions over perpendicular ones leads to an ill-conditioned coupled-equation problem. These and related restrictions on

the matching surfaces were outlined in Paper I.

The asymptotic analysis of Sec. V is quite general and should be applicable to those chemical reactions which fit the criteria of the first paragraph of this section. The antisymmetrized results presented in Sec. V are only applicable to a collision system of three identical spin $\frac{1}{2}$ particles. Other combinations of identical particles and spins may be treated by postantisymmetrization procedures analogous to that in Appendix D of Paper I.

The final criterion regarding the applicability of the method is computational efficiency. The large number of open rotational channels present in any 3D atom–diatom system makes the application of any coupled-channel method a large computational project. Much effort has, however, been spent in designing the method so that a minimum number of such channels are needed for convergence of the results. We therefore feel that this method should provide a computationally feasible procedure for studying simple chemical reactions. The first application of this procedure (to 3D $H+H_2$)[24] supports this statement.

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APPENDIX A: ANGULAR MOMENTUM OPERATORS AND THE SCHRÖDINGER EQUATION IN SPACE-FIXED AND BODY-FIXED COORDINATE SYSTEMS

In this Appendix we will establish the relations between the rotational and total angular momentum operators in the space-fixed and body-fixed coordinate systems defined in Sec. II. B and Fig. 2.

We first consider the space-fixed coordinate system $Oxyz$. In terms of the variables ϕ_{r_λ}, θ_{r_λ}, ϕ_λ, and θ_λ (Sec. II. B), the various components of the rotational ($\mathbf{j}_\lambda$) and orbital ($\mathbf{l}_\lambda$) angular momentum operators are given by the usual spherical polar coordinate expressions

$$j_{\lambda z} = -i\hbar \frac{\partial}{\partial \phi_{r_\lambda}}, \tag{A1a}$$

$$j_{\lambda x} = -i\hbar \left(-\cos\phi_{r_\lambda} \cot\theta_{r_\lambda} \frac{\partial}{\partial \phi_{r_\lambda}} - \sin\phi_{r_\lambda} \frac{\partial}{\partial \theta_{r_\lambda}} \right), \tag{A1b}$$

$$j_{\lambda y} = -i\hbar \left(-\sin\phi_{r_\lambda} \cot\theta_{r_\lambda} \frac{\partial}{\partial \phi_{r_\lambda}} + \cos\phi_{r_\lambda} \frac{\partial}{\partial \theta_{r_\lambda}} \right), \tag{A1c}$$

and similar expressions for the components of $\mathbf{l}_\lambda$ with ϕ_λ, θ_λ substituted for ϕ_{r_λ}, θ_{r_λ}. Expressions for the components of $\mathbf{J}$ are trivially obtained by the addition $\mathbf{J} = \mathbf{l}_\lambda + \mathbf{j}_\lambda$. The eigenfunctions of the operators j_λ^2 and l_λ^2 appearing in Eq. (2.9) (and also of $j_{\lambda z}$ and $l_{\lambda z}$) are the spherical harmonics $Y_{j_\lambda m_{j_\lambda}}(\theta_{r_\lambda}, \phi_{r_\lambda})$ and $Y_{l_\lambda m_{l_\lambda}}(\theta_\lambda, \phi_\lambda)$. For notational convenience we shall define the modified associated Legendre function $\Phi_j^{m_j}$ by

$$\Phi_j^{m_j}(\cos\theta) = P_j^{|m_j|}(\cos\theta) \left(\frac{(j-|m_j|)!}{(j+|m_j|)!} \frac{2j+1}{2} \right)^{1/2} \times \begin{cases} (-1)^{m_j} & m_j > 0 \\ 1 & m_j \le 0 \end{cases}, \tag{A2}$$

where $P_j^{|m_j|}$ is the usual associated Legendre function. The spherical harmonic Y_{jm_j} is expressed in terms of $\Phi_j^{m_j}$ by

$$Y_{jm_j}(\theta, \phi) = \frac{e^{im_j\phi}}{\sqrt{2\pi}} \Phi_j^{m_j}(\cos\theta). \tag{A3}$$

In the space-fixed formalism of Arthurs and Dalgarno,[29] the full wavefunction is expanded in terms of a set of functions $\mathcal{Y}_{l_\lambda j_\lambda}^{JM}(\theta_\lambda, \phi_\lambda; \theta_{r_\lambda}, \phi_{r_\lambda})$ which are simultaneous eigenfunctions of J^2, J_z, l_λ^2, and j_λ^2. These $\mathcal{Y}_{l_\lambda j_\lambda}^{JM}$ are related to the $Y_{j_\lambda m_{j_\lambda}}$ and $Y_{l_\lambda m_{l_\lambda}}$ via

$$\mathcal{Y}_{l_\lambda j_\lambda}^{JM}(\theta_\lambda, \phi_\lambda; \theta_{r_\lambda}, \phi_{r_\lambda}) = \sum_{m_{j_\lambda} m_{l_\lambda}} C(j_\lambda l_\lambda J; m_{j_\lambda} m_{l_\lambda} M) \times Y_{j_\lambda m_{j_\lambda}}(\theta_{r_\lambda}, \phi_{r_\lambda}) Y_{l_\lambda m_{l_\lambda}}(\theta_\lambda, \phi_\lambda), \tag{A4}$$

where the notation of Rose[37] is used for the Clebsch–Gordan coefficients C. The full space-fixed wavefunction is then written as

$$\Psi_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = \sum_{l_\lambda j_\lambda} \mathcal{Y}_{l_\lambda j_\lambda}^{JM}(\theta_\lambda, \phi_\lambda; \theta_{r_\lambda}, \phi_{r_\lambda}) G_{j_\lambda l_\lambda}^{JM}(r_\lambda, R_\lambda), \tag{A5}$$

and the space-fixed coupled Schrödinger equation for $G_{j_\lambda l_\lambda}^{JM}$ is[29]

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{1}{R_\lambda} \frac{\partial^2}{\partial R_\lambda^2} R_\lambda + \frac{1}{r_\lambda} \frac{\partial^2}{\partial r_\lambda^2} r_\lambda \right) + \frac{j_\lambda(j_\lambda+1)\hbar^2}{2\mu r_\lambda^2} + \frac{l_\lambda(l_\lambda+1)\hbar^2}{2\mu R_\lambda^2} - E \right] G_{j_\lambda l_\lambda}^{JM} + \sum_{j'_\lambda l'_\lambda} \langle l_\lambda j_\lambda | V | l'_\lambda j'_\lambda \rangle G_{j'_\lambda l'_\lambda}^{JM} = 0 . \tag{A6}$$

We now consider the transformation to the body-fixed coordinate systems $OX_\lambda Y_\lambda Z_\lambda$ and $Ox'_\lambda y' z'_\lambda$ of Sec. II B. A convenient representation of angular momentum operators in these coordinate systems involves choosing the operators $\mathbf{J}$ and $\mathbf{j}_\lambda$ as independent and expressing the $\mathbf{l}_\lambda^2$ of Eq. (2.9) by the expansion

$$\mathbf{l}_\lambda^2 = |\mathbf{J} - \mathbf{j}_\lambda|^2 = \mathbf{J}^2 + \mathbf{j}_\lambda^2 - (\mathbf{J}\cdot\mathbf{j}_\lambda + \mathbf{j}_\lambda \cdot \mathbf{J}) . \tag{A7}$$

To convert the operators $\mathbf{j}_\lambda$ and $\mathbf{J}$, and thus the Hamiltonian of Eq. (2.9), to the body-fixed systems requires first a change from the variables $\theta_\lambda \phi_\lambda \theta_{r_\lambda} \phi_{r_\lambda}$ to $\theta_\lambda \phi_\lambda \gamma_\lambda \psi_\lambda$ as defined in Sec. II.B, followed by successive rotations of the components of the operators. These rotational transformations may be accomplished by using the general expression[52]

$$J_{k'} = R(\alpha\beta\gamma)^{-1} J_k R(\alpha\beta\gamma) , \tag{A8}$$

where J_k refers to the kth component of any angular momentum operator $\mathbf{J}$ in an initial system and

$$R(\alpha\beta\gamma) = e^{i\gamma J_z/\hbar} e^{i\beta J_y/\hbar} e^{i\alpha J_z/\hbar}. \tag{A9}$$

$J_{k'}$ refers to the k'th component of $\mathbf{J}$ in a transformed coordinate system which is obtained through rotations by Euler angles $\alpha\beta\gamma$ from the initial system. One important point to note in the application of Eq. (A8) to the body-fixed coordinate systems $OX_\lambda Y_\lambda Z_\lambda$ or $Ox'_\lambda y' z'_\lambda$ is that the components J_k and $(j_\lambda)_k$ of the operators $\mathbf{J}$

and $\mathbf{j}_\lambda$ will in general operate upon one or more of the Euler angles ϕ_λ, θ_λ, and ψ_λ of the transformations, and thus great care must be taken with the order of the operators. In Table I we express the resulting components of the operators J and $\mathbf{j}_\lambda$ as well as various combinations thereof in terms of the variables $\theta_\lambda \phi_\lambda \gamma_\lambda \psi_\lambda$ in the three coordinate systems $Oxyz$, $OX_\lambda Y_\lambda Z_\lambda$, and $Ox'_\lambda y' z'_\lambda$. Some of the relations in that table have been given previously by Vezzetti and Rubinow,[53] Morse and Feshbach,[54] and Curtiss, Hirschfelder, and Adler.[31]

One very useful point to notice about $j_{\lambda X_\lambda}$, $j_{\lambda Y_\lambda}$, and $j_{\lambda Z_\lambda}$ is that their expressions in terms of γ_λ, ψ_λ in Table I have the same functional form as the corresponding $j_{\lambda x}$, $j_{\lambda y}$, and $j_{\lambda z}$ in Eqs. (A1). This implies that the rotational angular momentum eigenfunctions in the $X_\lambda Y_\lambda Z_\lambda$ coordinate system will simply be the spherical harmonics $Y_{j_\lambda \Omega_\lambda}(\gamma_\lambda, \psi_\lambda)$ where, as is explained in Sec. II. B, Ω_λ is the quantum number associated with $j_{\lambda z_\lambda}$.

In terms of the coordinate system $OX_\lambda Y_\lambda Z_\lambda$, the Hamiltonian of Eq. (2.9) may be written as

$$H = -\frac{\hbar^2}{2\mu}\left(\frac{1}{R_\lambda}\frac{\partial^2}{\partial R_\lambda^2} R_\lambda + \frac{1}{r_\lambda}\frac{\partial^2}{\partial r_\lambda^2} r_\lambda\right) + \frac{\mathbf{j}_\lambda^2}{2\mu r_\lambda^2} + \frac{1}{2\mu R_\lambda^2}\left[\mathbf{J}^2 + \mathbf{j}_\lambda^2 - 2j_{\lambda z_\lambda} J_{z_\lambda} - (j_\lambda^- J^+ + j_\lambda^+ J^-)\right] + V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda), \tag{A10}$$

where the raising and lowering operators are defined in terms of the X_λ and Y_λ components of J and $\mathbf{j}_\lambda$ in the usual way.[37] In order to express the Schrödinger equation in $OX_\lambda Y_\lambda Z_\lambda$ coordinates, we rotate the wavefunction according to Eq. (2.13). Substituting this expression, along with Eq. (A10) into Eq. (2.9), and using the normal raising and lowering properties of the rotation matrix,[33] i.e.,

$$J^\pm D^J_{M\Omega_\lambda} = \hbar\left[J(J+1) - \Omega_\lambda(\Omega_\lambda \mp 1)\right]^{1/2} D^J_{M\Omega_\lambda \mp 1} \tag{A11}$$

(where the $\pm$ components refer to the body-fixed system), we obtain the following coupled equations for the $\Psi^\lambda_{J\Omega_\lambda}$:

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{R_\lambda}\frac{\partial^2}{\partial R_\lambda^2} R_\lambda + \frac{1}{r_\lambda}\frac{\partial^2}{\partial r_\lambda^2} r_\lambda\right) + \frac{\mathbf{j}_\lambda^2}{2\mu r_\lambda^2} + \frac{1}{2\mu R_\lambda^2}\left[J(J+1)\hbar^2 + \mathbf{j}_\lambda^2 - 2\hbar\Omega_\lambda j_{\lambda z_\lambda}\right] + V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) - E\right]$$

$$\times \Psi^\lambda_{J\Omega_\lambda} - \frac{\hbar}{2\mu R_\lambda^2}\left[J(J+1) - \Omega_\lambda(\Omega_\lambda+1)\right]^{1/2} j_\lambda^- \Psi^\lambda_{J,\Omega_\lambda+1} - \frac{\hbar}{2\mu R_\lambda^2}\left[J(J+1) - \Omega_\lambda(\Omega_\lambda-1)\right]^{1/2} j_\lambda^+ \Psi^\lambda_{J,\Omega_\lambda-1} = 0. \tag{A12}$$

Since the rotational eigenfunctions in the $OX_\lambda Y_\lambda Z_\lambda$ coordinate system are the $Y_{j_\lambda \Omega_\lambda}(\gamma_\lambda, \psi_\lambda)$, the rotationally coupled body-fixed solutions analogous to Eq. (A5) are given by

$$\Psi_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = \sum_{j_\lambda \Omega_\lambda} D^J_{M\Omega_\lambda}(\phi_\lambda, \theta_\lambda, 0)\, Y_{j_\lambda \Omega_\lambda}(\gamma_\lambda, \psi_\lambda) w^\lambda_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda), \tag{A13}$$

which is a combination of Eqs. (2.18) and (2.13). The body-fixed and space-fixed representations may be related by using the equality

$$D^J_{M\Omega_\lambda}(\phi_\lambda, \theta_\lambda, 0)\, Y_{j_\lambda \Omega_\lambda}(\gamma_\lambda, \psi_\lambda) = \left(\frac{4\pi}{2J+1}\right)^{1/2} \sum_{l_\lambda} (-1)^{j_\lambda - \Omega_\lambda}\, C(J j_\lambda l_\lambda; \Omega_\lambda - \Omega_\lambda 0)\, \mathcal{Y}^{JM}_{j_\lambda l_\lambda}(\theta_\lambda \phi_\lambda; \theta_{r_\lambda} \phi_{r_\lambda}). \tag{A14}$$

Equation (A14) is of great utility in the asymptotic analysis of Sec. V. A.

APPENDIX B: PARITY DECOUPLING

In this Appendix we consider the decoupling that occurs when eigenfunctions of the parity (or inversion) operator $\hat{\mathcal{I}}$ are used in the coupled-channel expansion. This operator inverts all atoms through the system's center of mass. For the three-particle system we are considering,

$$\hat{\mathcal{I}}\Psi(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = \Psi(-\mathbf{r}_\lambda, -\mathbf{R}_\lambda), \tag{B1}$$

where Ψ is any wavefunction describing the system, $\hat{\mathcal{I}}$ commutes with $\nabla^2_{\mathbf{R}_\lambda}$ and $\nabla^2_{\mathbf{r}_\lambda}$. In addition, the internal configuration of the system before and after inversion is the same and consequently the potential energy is not changed by the parity operation. We conclude that $\hat{\mathcal{I}}$ commutes with the Hamiltonian in Eq. (2.7) for any triatomic system.

If we express $\mathbf{R}_\lambda$ and $\mathbf{r}_\lambda$ in body-fixed variables, we find that

$$\hat{\mathcal{I}}\Psi(r_\lambda, \gamma_\lambda, \psi_\lambda, R_\lambda, \theta_\lambda, \phi_\lambda) = \Psi(r_\lambda, \gamma_\lambda, \pi - \psi_\lambda, R_\lambda, \pi - \theta_\lambda, \pi + \phi_\lambda). \tag{B2}$$

The body-fixed wavefunction we are considering is given, from Eqs. (2.13), (2.18), (2.30), and (3.1), by

$$\Psi_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = \sum_{v_\lambda j_\lambda \Omega_\lambda} D^J_{M\Omega_\lambda}(\phi_\lambda, \theta_\lambda, 0)\, \Upsilon_{j_\lambda \Omega_\lambda}(\gamma_\lambda, \psi_\lambda) \times \frac{\phi^\lambda_{v_\lambda j_\lambda}(r_\lambda)}{r_\lambda R_\lambda}\, g^\lambda_{J v_\lambda j_\lambda \Omega_\lambda}(R_\lambda). \tag{B3}$$

Since $\hat{\mathcal{I}}$ leaves γ_λ and the scalars R_λ and r_λ unchanged, all derivations of this Appendix are independent of which of the four regions of each arrangement channel region we are concerned with, so we shall omit any explicit reference to them, using the general form for Ψ_{JM} in Region I or II and dropping the superscript (a) or (w) in the ϕ^λ vibrational basis functions. Let us now apply $\hat{\mathcal{I}}$

to Eq. (B3), using the relations[33] $D^J_{M\Omega_\lambda}(\phi_\lambda+\pi,\ \pi-\theta_\lambda,\ 0) = (-1)^J \times D^J_{M,-\Omega_\lambda}(\phi_\lambda, \theta_\lambda, 0)$ and $Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda,\ \pi-\psi_\lambda) = Y_{j_\lambda,-\Omega_\lambda} \times(\gamma_\lambda, \psi_\lambda)$. By changing the sign of Ω_λ in Eq. (B3) and remembering that its summation limits in that equation are invariant with respect to a sign change, we find

$$\hat{\mathcal{J}}\Psi_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = (-1)^J \sum_{v_\lambda j_\lambda \Omega_\lambda} D^J_{M\Omega_\lambda}(\phi_\lambda, \theta_\lambda, 0)\, Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda, \psi_\lambda) \times \frac{\phi^\lambda_{v_\lambda j_\lambda}(r_\lambda)}{r_\lambda R_\lambda}\, g^\lambda_{Jv_\lambda j_\lambda,-\Omega_\lambda}(R_\lambda)\,. \tag{B4}$$

The $-\Omega_\lambda$ index of g^λ in the right-hand side of this equation indicates that Ψ^λ_{JM} is not an eigenfunction of the parity operator $\hat{\mathcal{J}}$ unless $J=0$ (since Ω must equal zero as well in that case). Since $\hat{\mathcal{J}}$ commutes with the Hamiltonian, we should be able to linearly combine the Ψ_{JM}'s so as to produce simultaneous eigenfunctions of $\hat{\mathcal{J}}$ and H. Let us consider the linear combinations

$$\bar{\Psi}^\pm_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = \frac{1}{\sqrt{2}}\left\{\Psi_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) \pm (-1)^J \Psi_{JM}(-\mathbf{r}_\lambda, -\mathbf{R}_\lambda)\right\}. \tag{B5}$$

By substituting Eqs. (B3) and (B4) in Eq. (B5) and rearranging the result, we find that

$$\bar{\Psi}^\pm_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = \sum_{v_\lambda j_\lambda \Omega_\lambda} D^J_{M\Omega_\lambda}(\phi_\lambda, \theta_\lambda, 0)\, Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda, \psi_\lambda) \frac{\phi^\lambda_{v_\lambda j_\lambda}(r_\lambda)}{r_\lambda R_\lambda} \times \begin{pmatrix} \frac{1}{\sqrt{2}}\left(g^\lambda_{Jv_\lambda j_\lambda\Omega_\lambda} + g_{Jv_\lambda j_\lambda,-\Omega_\lambda}\right) \\ \frac{1}{\sqrt{2}}\left(g_{Jv_\lambda j_\lambda\Omega_\lambda} - g_{Jv_\lambda j_\lambda,-\Omega_\lambda}\right) \end{pmatrix}, \tag{B6}$$

where the upper term in the large parentheses refers to the plus solution and the lower to the minus solution. From Eq. (B4), it should be apparent that

$$\hat{\mathcal{J}}\bar{\Psi}^\pm_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = \pm(-1)^J \bar{\Psi}^\pm_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda). \tag{B7}$$

Since the basis functions $D^J_{M\Omega_\lambda} Y_{j_\lambda\Omega_\lambda}\phi^\lambda_{v_\lambda j_\lambda}$ in Eq. (B6) are the same as those in Eq. (B3), the equations of Secs. II–IV may be converted to the corresponding ones involving parity solutions by simply linearly combining the g's according to the expression in braces in Eq. (B6). To facilitate this, we define a new function $\bar{g}$ via[55]

$$\bar{g}^\lambda_{Jv_\lambda j_\lambda\Omega_\lambda}(R_\lambda) = \begin{cases} \frac{1}{\sqrt{2}}\left(g^\lambda_{Jv_\lambda j_\lambda\Omega_\lambda} + g^\lambda_{Jv_\lambda j_\lambda,-\Omega_\lambda}\right) & \text{for } \Omega_\lambda > 0 \\ g^\lambda_{Jv_\lambda j_\lambda\Omega_\lambda} & \text{for } \Omega_\lambda = 0 \\ \frac{1}{\sqrt{2}}\left(-g^\lambda_{Jv_\lambda j_\lambda\Omega_\lambda} + g^\lambda_{Jv_\lambda j_\lambda,-\Omega_\lambda}\right) & \text{for } \Omega_\lambda < 0, \end{cases} \tag{B8}$$

or in the matrix notation of Sec. III.A,

$$\bar{\mathbf{g}}^\lambda_J(R_\lambda) = \mathcal{Q}_\lambda\, \mathbf{g}^\lambda_J(R_\lambda), \tag{B9}$$

where the orthogonal matrix $\mathcal{Q}_\lambda$ is given by

$$(\mathcal{Q}_\lambda)^{v'_\lambda j'_\lambda \Omega'_\lambda}_{v_\lambda j_\lambda \Omega_\lambda} = \delta^{v'_\lambda j'_\lambda}_{v_\lambda j_\lambda} \begin{cases} \frac{1}{\sqrt{2}}\left(\delta_{\Omega_\lambda\Omega'_\lambda} + \delta_{\Omega_\lambda,-\Omega'_\lambda}\right) & \text{for } \Omega_\lambda > 0 \\ \delta_{\Omega_\lambda\Omega'_\lambda} & \text{for } \Omega_\lambda = 0 \\ \frac{1}{\sqrt{2}}\left(-\delta_{\Omega_\lambda\Omega'_\lambda} + \delta_{\Omega_\lambda,-\Omega'_\lambda}\right) & \text{for } \Omega_\lambda < 0. \end{cases} \tag{B10}$$

If we include initial conditions of the proper symmetry to form the matrix $\bar{\mathbf{g}}^\lambda_J$, we find that

$$\bar{\mathbf{g}}^\lambda_J(R_\lambda) = \mathcal{Q}_\lambda \mathbf{g}^\lambda_J(R_\lambda)\tilde{\mathcal{Q}}_\lambda\,. \tag{B11}$$

To convert the equations of Sec. III to the corresponding expressions involving parity solutions, we need only to use Eq. (B11) to transform them into expressions for $\bar{\mathbf{g}}^\lambda_J$ rather than $\mathbf{g}^\lambda_J$. For example, the fully coupled Schrödinger equation [Eq. (3.14)] becomes

$$\frac{d^2\bar{\mathbf{g}}^{\lambda\pm}_J}{dR^2_\lambda} = \bar{\mathbf{U}}^\lambda_J\, \bar{\mathbf{g}}^{\lambda\pm}_J\,, \tag{B12}$$

where

$$\bar{\mathbf{U}}^\lambda_J = \mathcal{Q}_\lambda \mathbf{U}^\lambda_J \tilde{\mathcal{Q}}_\lambda\,. \tag{B13}$$

$\bar{\mathbf{U}}^\lambda_J$ is identical to $\mathbf{U}^\lambda_J$ in all terms of Eq. (3.15) except those off-diagonal in Ω_λ (i.e., in $\mathbf{U}^{c\lambda}_J$). From Eqs. (3.11) and (B10), we find that

$$(\bar{\mathbf{U}}^{c\lambda}_J)^{v'_\lambda j'_\lambda}_{v_\lambda j_\lambda} = \delta^{v'_\lambda j'_\lambda}_{v_\lambda j_\lambda}/R^2_\lambda \left\{\delta_{\Omega_\lambda\Omega'_\lambda}\left[J(J+1) - 2\Omega^2_\lambda + j_\lambda(j_\lambda+1)\right] - a_{\Omega_\lambda}\delta_{\Omega_\lambda+1,\Omega'_\lambda}\, \xi_+(J, \Omega_\lambda)\, \xi_+(j_\lambda, \Omega_\lambda) - b_{\Omega_\lambda}\delta_{\Omega_\lambda-1,\Omega'_\lambda}\, \xi_-(J, \Omega_\lambda)\, \xi_-(j_\lambda, \Omega_\lambda)\right\}, \tag{B14}$$

where

$$a_{\Omega_\lambda} = \begin{cases} 1 & \text{for } \Omega_\lambda \geq 1 \text{ and } \Omega_\lambda < -1 \\ \sqrt{2} & \text{for } \Omega_\lambda = 0 \\ 0 & \text{for } \Omega_\lambda = -1 \end{cases} \tag{B15}$$

and

$$b_{\Omega_\lambda} = \begin{cases} 1 & \text{for } \Omega_\lambda > 1 \text{ and } \Omega_\lambda \leq -1 \\ \sqrt{2} & \text{for } \Omega_\lambda = 1 \\ 0 & \text{for } \Omega_\lambda = 0\,. \end{cases} \tag{B16}$$

An examination of the structure of $\bar{\mathbf{U}}^{c\lambda}_J$ indicates that it contains no elements which couple states whose Ω_λ is positive or zero to those whose Ω_λ is negative. Since only $\bar{\mathbf{U}}^{c\lambda}_J$ provides off-diagonal Ω_λ coupling in Eq. (B12), we see that our coupled Schrödinger equations have been separated into two uncoupled sets—those with $\Omega_\lambda \geq 0$ [of parity $(-1)^J$] and those with $\Omega_\lambda < 0$ [parity $-(-1)^J$]. This uncoupling is preserved throughout the integration in a given arrangement channel region since the only Ω_λ-dependent coupling appearing anywhere in this process occurs in centrifugal terms analogous to those of Eq. (B14). Thus by constructing parity eigenfunctions, we can separate our integration problem into two smaller ones [each of which can be further separated into two parts for homonuclear targets (Sec. III.C)].

Parity is also preserved in the matching procedure because, as can be seen by inspection of Fig. 1, the parity operation is invariant to which arrangement channel coordinate system one is considering. This means that solutions of the same parity symmetry but expressed in different arrangement channel coordinates should be related to each other by a transformation which does not mix in solutions of the opposite parity. To prove this, we must first transform the coefficient matrices $\mathbf{h}^\lambda_J$, $\mathbf{h}'^\lambda_J$, $\mathbf{f}^\nu_J$, and $\mathbf{f}'^\nu_J$ of Sec. IV.B to the representation involving parity eigenfunctions. This requires a transformation similar to Eq. (B11),

$$\bar{\mathbf{h}}^{\lambda}_{J} = \mathcal{Q}'_{\nu\lambda}\,\mathbf{h}^{\lambda}_{J}\,\tilde{\mathcal{Q}}_{\lambda}\,, \tag{B17}$$

where $\mathcal{Q}'_{\nu\lambda}$ is an $N/2\times N/2$ matrix (N = total number of solutions of both parities) whose precise mathematical form is identical to $\mathcal{Q}_{\lambda}$ in Eq. (B10), but whose actual structure is different because the set of indices $v_\lambda j_\lambda$ involving the matching surface basis functions of Eq. (4.30) will assume only half the number of values that the asymptotic solutions do (as discussed in Sec. IV. C). Note that we still right multiply $\mathbf{h}^{\lambda}_{J}$ by $\mathcal{Q}_{\lambda}$ in Eq. (B17) because right multiplication corresponds to linearly combining different initial conditions, and the number of these is always N. By writing equations analogous to Eq. (B17) for $\mathbf{h}'^{\lambda}_{J}$, $\mathbf{f}^{\nu}_{J}$, and $\mathbf{f}'^{\nu}_{J}$, substituting these into Eq. (4.55) [using Eqs. (4.52)–(4.54) and simplifying, we obtain

$$\hat{\bar{\mathbf{h}}}^{\lambda+}_{J}\bar{\mathbf{C}}^{(i)+}_{\lambda J} + \hat{\bar{\mathbf{h}}}^{\lambda-}_{J}\bar{\mathbf{C}}^{(i)-}_{\lambda J} = \bar{\mathbf{s}}^{J}_{\nu\lambda}\{\hat{\bar{\mathbf{f}}}^{\nu+}_{J}\bar{\mathbf{C}}^{(i)+}_{\nu J} + \hat{\bar{\mathbf{f}}}^{\nu-}_{J}\bar{\mathbf{C}}^{(i)-}_{\nu J}\}\,, \tag{B18}$$

where the circumflex symbol implies definitions analogous to Eqs. (4.52)–(4.54) for barred (i.e., parity) quantities, and

$$\bar{\mathbf{s}}^{J}_{\nu\lambda} = \mathcal{Q}'_{\nu\lambda}\,\mathbf{s}^{J}_{\nu\lambda}\,\tilde{\mathcal{Q}}'_{\nu\lambda}\,. \tag{B19}$$

From Eq. (4.49) we can rewrite $\bar{\mathbf{s}}^{J}_{\nu\lambda}$ as

$$(\bar{\mathbf{s}}^{J}_{\nu\lambda})^{v_\nu j_\nu \Omega_\nu}_{v_\lambda j_\lambda \Omega_\lambda} = S^{\lambda\nu}_{v_\lambda v_\nu}\int A^{\nu\lambda}_{j_\lambda\Omega_\lambda}(\gamma_\lambda)$$

$$\times A^{\nu\lambda}_{j_\nu\Omega_\nu}(\gamma_\lambda)\begin{Bmatrix}(d^{J}_{\Omega_\nu\Omega_\lambda} + d^{J}_{\Omega_\nu,-\Omega_\lambda})\\ (d^{J}_{\Omega_\nu\Omega_\lambda} - d^{J}_{\Omega_\nu,-\Omega_\lambda})\end{Bmatrix} f_{\Omega_\lambda\Omega_\nu}\sin\gamma_\lambda d\gamma_\lambda\,, \tag{B20}$$

where

$$f_{\Omega_\lambda\Omega_\nu} = \begin{cases} 1/\sqrt{2} & \text{for } \Omega_\lambda = 0 \text{ or } \Omega_\nu = 0\\ 1/2 & \text{for } \Omega_\lambda = \Omega_\nu = 0\\ 1 & \text{for } \Omega_\lambda\times\Omega_\nu > 0\\ 0 & \text{for } \Omega_\lambda\times\Omega_\nu < 0\,, \end{cases} \tag{B21}$$

and the upper term in the braces is used for $\Omega_\lambda, \Omega_\nu \geq 0$ and the lower term for $\Omega_\lambda, \Omega_\nu < 0$. It should be evident from Eq. (B21) that $\bar{\mathbf{s}}^{J}_{\nu\lambda}$ does not couple terms of different parity nor does any part of Eq. (B18); this implies that the matching procedure can be done separately for solutions of each parity. It should also be noted that for a complete set of matching surface functions, the two subblocks of $\bar{\mathbf{s}}^{J}_{\nu\lambda}$ corresponding to solutions of different parity are separately orthogonal.

A convenient procedure for extracting the asymptotic information from the matched solutions involves first a calculation of reactance and scattering matrices which are defined in terms of parity eigenfunctions. This is followed by a coupling transformation in which the positive and negative parity $\mathbf{S}_J$ matrices are combined to yield the body-fixed $\mathbf{S}_J$ matrix of Eq. (5.5). From that point onward the formulas of Sec. V.B must be used, since the plane wave scattering solution is not an eigenfunction of $\hat{\mathcal{J}}$ [as seen by inspection of Eq. (5.24)]. The parity scattering and reactance matrix solutions are defined by equations identical in form to Eqs. (5.4) and (5.5), or to Eqs. (5.8) and (5.9), but the incoming and outgoing solutions $\mathbf{I}_J$ and $\mathbf{O}_J$ of Eq. (5.10) must be parity eigenfunctions and hence satisfy Eq. (B12) asymptotically. One can find these solutions by actually diagonalizing the asymptotic Hamiltonian obtained from Eq. (B12), or by performing transformations analogous to Eq. (B11) on $\mathbf{I}_J$ and $\mathbf{O}_J$. Both procedures lead to expressions for $\mathbf{I}_J$ and $\mathbf{O}_J$ identical to Eq. (5.10) except for the following two changes:

(a) the sum over l_λ in that equation includes only those l_λ of the same parity as is specified by the signs of Ω_λ and Ω'_λ appearing in that equation. (The only nonzero terms will always involve Ω_λ and Ω'_λ of the same signs.) In other words, when $\Omega_\lambda, \Omega'_\lambda \geq 0$, $l_\lambda = J + j_\lambda, J + j_\lambda - 2, \cdots, |J - j_\lambda|$ and when $\Omega_\lambda, \Omega'_\lambda < 0$, $l_\lambda = J + j_\lambda - 1, \cdots, |J - j_\lambda| + 1$.

(b) Equation (5.10) is to be multiplied by $\bar{f}_{\Omega_\lambda\Omega'_\lambda}$, where

$$\bar{f}_{\Omega_\lambda\Omega_\nu} = \begin{cases} \sqrt{2} & \text{for } \Omega_\lambda = 0 \text{ or } \Omega_\nu = 0\\ 1 & \text{for } \Omega_\lambda = \Omega_\nu = 0\\ 2 & \text{for } \Omega_\lambda\times\Omega_\nu > 0\\ 0 & \text{for } \Omega_\lambda\times\Omega_\nu < 0\,. \end{cases} \tag{B22}$$

This form of $\bar{f}_{\Omega_\lambda\Omega_\nu}$ leads to block diagonal $\mathbf{I}_J$ and $\mathbf{O}_J$ matrices, thus decoupling the reactance and scattering matrix analysis for solutions of different parities.

When these expressions for $\mathbf{I}_J$ and $\mathbf{O}_J$ are substituted into Eq. (5.21) along with the parity expressions for $\mathbf{g}^{\pm}_{J}$, $\mathbf{g}'^{\pm}_{J}$, and $\mathbf{C}^{\pm}_{J}$, the correct parity reactance matrix $\bar{\mathbf{R}}'_J$ [analogous to $\bar{\mathbf{R}}'_J$ of Eq. (5.18)] is obtained (where we consider $\bar{\mathbf{R}}'_J$ to contain the even and odd parity reactance matrices as separate subblocks). This may be subsequently converted to $\bar{\mathbf{S}}'_J$ via an equation analogous to Eq. (5.7) and the remark which follows it. The rows and columns of the parity scattering matrix may then be rearranged to form the body-fixed scattering matrix $\bar{\mathbf{S}}_J$ via

$$\bar{\mathbf{S}}_J = \tilde{\mathcal{Q}}\bar{\mathbf{S}}'_J\mathcal{Q}\,, \tag{B23}$$

where the $3N\times 3N$ matrix $\mathcal{Q}$ is obtained from the $N\times N$ matrices $\mathcal{Q}_\lambda$, $\mathcal{Q}_\nu$, $\mathcal{Q}_\kappa$ [whose definitions are analogous to Eq. (B10)], by

$$\mathcal{Q} = \begin{pmatrix} \mathcal{Q}_\lambda & \mathbf{0} & \mathbf{0}\\ \mathbf{0} & \mathcal{Q}_\nu & \mathbf{0}\\ \mathbf{0} & \mathbf{0} & \mathcal{Q}_\kappa \end{pmatrix} \tag{B24}$$

in which $\mathbf{0}$ is an $N\times N$ matrix of zeros. Finally, the body-fixed scattering matrix $\mathbf{S}_J$ used to calculate the scattering amplitudes according to Eqs. (5.31) and (5.32) is obtained from $\bar{\mathbf{S}}_J$ by

$$(\mathbf{S}_J)^{\lambda' v'_\lambda j'_\lambda \Omega'_\lambda}_{\lambda v_\lambda j_\lambda \Omega_\lambda} = (\bar{\mathbf{S}}_J)^{\lambda v_\lambda j_\lambda \Omega_\lambda}_{\lambda' v'_\lambda j'_\lambda, -\Omega'_\lambda}\,. \tag{B25}$$

It should be noted that the decoupling of the integration and matching procedures described above to generate parity eigenfunctions is completely general, not depending on an identicity between any of the three atoms A, B, C comprising the system. This results in an appreciable saving of computer time when implementing this calculational procedure.

APPENDIX C: ORTHOGONAL NATURE OF THE ARRANGEMENT CHANNEL TRANSFORMATION MATRIX $\mathbf{s}^J_{\nu\lambda}$

In this Appendix we show that the arrangement channel transformation matrix $\mathbf{s}^J_{\nu\lambda}$ defined by Eq. (4.49) is real orthogonal under certain conditions which are easily satisfied.

The definition of $d^J_{\Omega_\nu\Omega_\lambda}$ appearing in Eq. (4.49) is

$$d^J_{\Omega_\nu\Omega_\lambda}(\Delta_{\nu\lambda}) = \langle J\Omega_\lambda \,|\, \exp\left(\frac{i}{\hbar}\Delta_{\nu\lambda} J_{y'}\right) \,|\, J\Omega_\nu\rangle , \tag{C1}$$

where $|J\Omega_\nu\rangle$ and $|J\Omega_\lambda\rangle$ are simultaneous orthonormal eigenfunctions of J^2 and $J_{z'_\lambda}$ in coordinate system $Ox'_\lambda y' z'_\lambda$, having eigenvalues J, Ω_ν and J, Ω_λ, respectively; they are functions of θ_λ, ϕ_λ, and ψ_λ and the integration implied by the angular brackets is performed over these three angles with weighing function $\sin\theta_\lambda$. Replacing Eqs. (C1), (4.30), and (4.50) into Eq. (4.49) furnishes

$$(s^J_{\nu\lambda})^{v_\nu j_\nu\Omega_\nu}_{v_\lambda j_\lambda\Omega_\lambda} = \langle v_\lambda \,|\, v_\nu\rangle \langle J j_\lambda\Omega_\lambda| \exp\left(\frac{i}{\hbar}\Delta_{\nu\lambda} J_{y'}\right) |\, J j_\nu\Omega_\nu\rangle , \tag{C2}$$

where

$$|\, J j_\nu\Omega_\nu\rangle = A^{\nu\lambda}_{j_\nu\Omega_\nu}(\gamma_\lambda)\,|\, J\Omega_\nu\rangle , \tag{C3}$$

$$\langle J j_\lambda\Omega_\lambda \,| = A^{\nu\lambda}_{j_\lambda\Omega_\lambda}(\gamma_\lambda)\langle J\Omega_\lambda \,| ,$$

$$|\, v_\nu\rangle = \phi^\nu_{v_\nu}(\xi), \tag{C4}$$

$$\langle v_\lambda \,| = \phi^{\lambda *}_{v_\lambda}(\xi) .$$

The integration implied in $\langle v_\lambda \,|\, v_\nu\rangle$ is over ξ, and the other integration in Eq. (C2) is over the independent variables γ_λ, θ_λ, ϕ_λ, ψ_λ with weighing function $\sin\gamma_\lambda \sin\theta_\lambda$. As long as they form a complete orthonormal set of functions in γ_λ space, the $|J j_\nu\Omega_\nu\rangle$ form a complete orthonormal set in γ_λ, θ_λ, ϕ_λ, ψ_λ space, and Eq. (C2) can be written as

$$\mathbf{s}^J_{\nu\lambda} = \mathbf{S}^{\lambda\nu} \otimes \exp\left(\frac{i}{\hbar}\,\mathbf{\Delta}^J_{\nu\lambda}\right), \tag{C5}$$

where

$$(\Delta^J_{\nu\lambda})^{j_\nu\Omega_\nu}_{j_\lambda\Omega_\lambda} = \langle J j_\lambda\Omega_\lambda \,|\, \Delta_{\nu\lambda} J_{y'} \,|\, J j_\nu\Omega_\nu\rangle \tag{C6}$$

and

$$(S^{\lambda\nu})^{v_\nu}_{v_\lambda} = \langle v_\lambda \,|\, v_\nu\rangle = S^{\lambda\nu}_{v_\lambda v_\nu} , \tag{C7}$$

the $S^{\lambda\nu}_{v_\lambda v_\nu}$ being given by Eq. (4.50) and the $\otimes$ in Eq. (C5) representing a direct product of the two matrices appearing in its right-hand side. The elements of $\exp[(i/\hbar)\,\mathbf{\Delta}^J_{\nu\lambda}]$ are equal to the integral over γ_λ in the right-hand side of Eq. (4.49) and are therefore real if the functions $A^{\nu\lambda}_{j_\lambda\Omega_\lambda}(\gamma_\lambda)$ are real. It is convenient to use the notation $|j_\nu\Omega_\nu\rangle \equiv A^{\nu\lambda}_{j_\nu\Omega_\nu}(\gamma_\lambda)$ and $\langle j_\lambda\Omega_\lambda| \equiv A^{\nu\lambda *}_{j_\lambda\Omega_\lambda}(\gamma_\lambda)$, in terms of which we can write

$$|\, J j_\nu\Omega_\nu\rangle = |\, j_\nu\Omega_\nu\rangle |\, J\Omega_\nu\rangle$$

and

$$\langle J j_\lambda\Omega_\lambda \,| = \langle J\Omega_\lambda \,|\, \langle j_\lambda\Omega_\lambda \,| .$$

Since on the matching surface $\pi_{\nu\lambda}$, $\Delta_{\nu\lambda}$ is a function of γ_λ only [see Eq. (4.11)] and $J_{y'}$ operates on variables θ_λ, ϕ_λ, ψ_λ only, Eq. (C6) can be written as

$$(\Delta^J_{\nu\lambda})^{j_\nu\Omega_\nu}_{j_\lambda\Omega_\lambda} = \langle j_\lambda\Omega_\lambda \,|\, \Delta_{\nu\lambda}(\gamma_\lambda) \,|\, j_\nu\Omega_\nu\rangle \langle J\Omega_\lambda \,|\, J_{y'} \,|\, J\Omega_\nu\rangle . \tag{C8}$$

Each of the two matrices represented by the factors in the right-hand side of this equation is Hermitian and therefore

$$[(\Delta^J_{\nu\lambda})^{j_\lambda\Omega_\lambda}_{j_\nu\Omega_\nu}]^* = (\Delta^J_{\nu\lambda})^{j_\nu\Omega_\nu}_{j_\lambda\Omega_\lambda} ,$$

from which we conclude that $\mathbf{\Delta}^J_{\nu\lambda}$ is Hermitian and that $\exp[(i/\hbar)\,\mathbf{\Delta}^J_{\nu\lambda}]$ is unitary. If the $\phi^\lambda_{v_\lambda}(\xi)$ and $\phi^\nu_{v_\nu}(\xi)$ are separately complete sets of orthonormal functions which span the ξ space, their overlap matrix $\mathbf{S}^{\nu\lambda}$ is also unitary. $\mathbf{s}^J_{\nu\lambda}$ then is the direct product of two unitary matrices and therefore is unitary. Furthermore, if $\mathbf{S}^{\nu\lambda}$ is in addition real [as will be the case if, for example, the $\phi^\lambda_{v_\lambda}(\xi)$ and $\phi^\nu_{v_\nu}(\xi)$ are real], and the $A^{\nu\lambda}_{j_\lambda\Omega_\lambda}$ are also real, so is $\mathbf{s}^J_{\nu\lambda}$, as can be seen by inspection of the right-hand side of Eq. (4.49). We conclude that if $\phi^\lambda_{v_\lambda}(\xi)$ and $\phi^\nu_{v_\nu}(\xi)$ are two complete sets of orthonormal functions which span the ξ space and are related by a real orthogonal transformation, and if $A^{\nu\lambda}_{j_\lambda\Omega_\lambda}(\gamma_\lambda)$ is a complete set of real orthonormal functions which span the γ_λ space, then the arrangement channel transformation matrix $\mathbf{s}^J_{\nu\lambda}$ is real and orthogonal. These conditions are satisfied by the $A^{\nu\lambda}_{j_\lambda\Omega_\lambda}(\gamma_\lambda)$ of Eq. (4.31), the $\phi^\lambda_{v_\lambda}(\xi)$ vibrational basis functions appearing in Eqs. (4.25) and (4.28), and the analogous functions $\phi^\nu_{v_\nu}(\xi)$ for arrangement channel ν.

If Eq. (C5) is used to evaluate $\mathbf{s}^J_{\nu\lambda}$, the second factor in the right-hand side of Eq. (C8) can be calculated using the explicit expression[33]

$$\langle J\Omega_\lambda \,|\, J_{y'} \,|\, J\Omega_\nu\rangle = \frac{1}{2}\frac{\hbar}{i}\{[(J-\Omega_\lambda)(J+\Omega_\lambda+1)]^{1/2}\delta_{\Omega_\lambda,\Omega_\nu-1} - [(J+\Omega_\lambda)(J-\Omega_\lambda+1)]^{1/2}\delta_{\Omega_\lambda,\Omega_\nu+1}\} . \tag{C9}$$

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