Infinite order sudden approximation for reactive scattering. I. Basic $I$-labeled formulation

V. Khare$^a$

Departments of Chemistry and Physics, University of Houston, Houston, Texas 77004

D. J. Kouri$^b$

Institute for Advanced Studies, Hebrew University of Jerusalem, Mt. Scopus Campus, Jerusalem, Israel

M. Baer$^c$

Department of Theoretical Physics and Applied Mathematics, Soreq Nuclear Research Center, Yavne, Israel and Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel

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An infinite order sudden (IOS) treatment of reactive scattering is developed taking into account recent results of nonreactive collision studies on the importance of $I$-labeling, nonconservation of helicity, and transformation properties of sudden approximation wave functions. The present IOS method should be sufficiently simple to apply to a number of chemically interesting atom–diatom reactions. Such applications are currently in progress.

I. INTRODUCTION

During the last decade, a number of approaches to reactive scattering have been proposed and evaluated in order to treat accurately atom–diatom collision processes in three physical dimensions (3D). $^1$–$^8$ The simplest real system on which to test these procedures is $H + H_2$. Although the method of Baer and Kouri$^1$ was the first to be used in obtaining fully converged and complete cross sections for a model 3D reactive collision, subsequently the method of Kuppermann, Schatz, and Baer$^4$ (KSB) and Kuppermann and Schatz$^5$ (KS), that of Elkowitz and Wyatt, $^8$ and more recently that of Walker et al.$^{16}$ have been used to calculate complete integral reactive cross sections for the real $H + H_2$ system (without approximating certain partial wave contributions, etc.). The status of reactive collisions of $H + H_2$ has recently been reviewed by Truhlar and Wyatt. $^b$ Besides the intrinsically interesting numerical results obtained, it has been made quite clear by these studies that accurate approximations are essential in order for theoretical studies of more interesting heavier systems to be done.

So far as quantum mechanical approximations are concerned, based on nonreactive inelastic scattering studies, the most promising appear to be those based on sudden approximations, especially the centrifugal

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$^b$J. S. Guggenheim Foundation Fellow 1978–79. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Permanent address: Departments of Chemistry and Physics, University of Houston, Houston, Texas 77004.

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ations and asymptotic conditions directly from the corresponding exact CC equations by use of closure approximations.

In Sec. II, we begin by motivating our particular approach and viewpoint to a reactive IOS approximation. In Sec. III, we present a brief summary of the body-frame close coupling formalism of KSB and SK and indicate in what ways our present space frame approach departs from their work. This provides the basic starting point for deriving our IOS approximation. Then, in Sec. IV, we derive the basic differential equations of our IOS approximation, obtaining them directly from the space frame close coupling equations of the preceding section. In Sec. V, we address the problem of numerically integrating the IOS equations. In Sec. VI, we deal with the question of identification of the effective orbital angular momentum quantum number \( l \) that appears in the CS part of the IOS. Next, in Sec. VII, we discuss the IOS matching conditions used in smoothly joining the IOS solutions between various regions of configuration space. Also, in Sec. VII, we derive some additional simplifications for the matching equations and asymptotic conditions. In Sec. VIII, we present the analysis of the IOS \( R \) matrix in order to illustrate its behavior in the coordinate representation. This makes clearer the relationship between the IOS expressions and exact expressions for the more usual coupled representation \( R \) matrix in terms of the coordinate representation \( R \) matrix. In Sec. IX, we discuss how one may generalize the present initial \( I \)-labeled IOS theory to other \( I \) choices. Finally, in Sec. X, we present our conclusions.

II. MOTIVATING THE IOS APPROXIMATION

A solution to the reactive scattering problem can be gotten in any of a variety of possible representations. It is well known\(^5,6)\) that, in reactive CC calculations, it is convenient to solve for the wave function in a body fixed formulation because this is most appropriate for matching solutions of the Schrödinger equation between various arrangements. One thus obtains an \( R \) matrix with elements \( R^\ell(\nu v, j j' \Omega) \), where \( \nu, j \) denote specific molecular arrangements, \( \nu \) represents the vibrational quantum number of the molecule in arrangement \( \nu \), \( j \) represents the rotational angular momentum quantum number of the \( \nu \) arrangement molecule, and \( \Omega \) is the projection of total angular momentum along the \( \nu \)-arrangement \( z \) axis (which in the body frame is equal to the projection of the \( \nu \)-rotor angular momentum along the \( \nu \)-arrangement \( z \) axis). Other possible representations are the coupled space fixed representation with \( R \)-matrix element \( R(\nu v, j j' \Omega) \) and the uncoupled space fixed representation with \( R \)-matrix element \( R(\nu v, m j \Omega, j j' \Omega) \). Here, \( I_\nu \) is the orbital angular momentum quantum number for arrangement \( \nu \), \( m \) is the projection along a single space fixed \( z \) axis of the orbital angular momentum in arrangement \( \nu \), and \( s \) is the projection of the \( \nu \)-arrangement rotor angular momentum along the \( \nu \)-arrangement \( z \) axis. These \( R \)-matrix elements are related by the well known transformations\(^32)\):

\[
R^\ell(\nu v, j j' \Omega) = \sum_{I_\nu} \frac{\sqrt{2I_\nu + 1}(2I_\nu + 1)}{(2J + 1)} \langle I_\nu | j j' \Omega | I_\nu \rangle R^\ell(\nu v, j j' \Omega)
\]

and

\[
R(\nu v, j j' \Omega) = \sum_{I_\nu} \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
\]

and the corresponding inverse relations.

Alternatively, one may consider the coordinate representation \( R \)-matrix elements. The angular quantum numbers can be chosen either as four space fixed angular coordinates \((\theta, \phi, \theta_r, \phi_r)\) or as three Euler angles \((\phi_1, \theta_1, \phi_1)\) and the relative internal angle \( \gamma_1 \). Here, \( \theta \) and \( \phi \) are angles of relative motion and \( \theta_r \) and \( \phi_r \) are rotor angles. The coordinate representation \( R \)-matrix element is related to \( R(\nu v, m j s \Omega, j j' \Omega) \) by

\[
R_{\nu v}(\theta, \phi, \theta_r, \phi_r) Y_{\ell m}(\theta, \phi) = \sum_{I_\nu} Y_{\ell m}(\theta_1, \phi_1) Y_{\ell m}(\theta, \phi)
\]

\[
\times \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
\]

\[
R(\nu v, j j' \Omega) = \sum_{I_\nu} \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
\]

where clearly the spherical harmonics are the elements of the unitary transformation from the \( \theta, \phi \) representation to the \( I, m \) representation, i.e., \( Y_{\ell m}(\theta, \phi) \) equals \( \langle I_\nu m | \ell m \rangle \). Now, employing Eqs. (1) and (2) and the transformation properties of the spherical harmonics, we obtain an expression in terms of Euler angles \( \Lambda = \{(\phi_1, \theta_1, \phi_1)\} \) and the internal angle \( \gamma_1 \) given by

\[
R_{\nu v}(\Lambda, \gamma_1) = \sum_{I_\nu} D_{\ell^\nu \nu}^{\gamma_1} \langle I_\nu \gamma_1 \rangle Y_{\ell m}(\theta, \phi)
\]

\[
\times \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
\]

\[
R_{\nu v}(\Lambda, \gamma_1) = \sum_{I_\nu} D_{\ell^\nu \nu}^{\gamma_1} \langle I_\nu \gamma_1 \rangle Y_{\ell m}(\theta, \phi)
\]

\[
\times \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
\]

\[
R(\nu v, j j' \Omega) = \sum_{I_\nu} \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
\]

\[
R(\nu v, j j' \Omega) = \sum_{I_\nu} \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
\]

At this point, we notice that, as a consequence of rotational invariance, the \( M \) summation in Eq. (4) may be done and the result is

\[
R_{\nu v}(\Lambda, \gamma_1) = \sum_{I_\nu} D_{\ell^\nu \nu}^{\gamma_1} \langle I_\nu \gamma_1 \rangle Y_{\ell m}(\theta, \phi)
\]

\[
\times \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
\]

\[
R_{\nu v}(\Lambda, \gamma_1) = \sum_{I_\nu} D_{\ell^\nu \nu}^{\gamma_1} \langle I_\nu \gamma_1 \rangle Y_{\ell m}(\theta, \phi)
\]

\[
\times \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
\]

\[
R(\nu v, j j' \Omega) = \sum_{I_\nu} \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
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R(\nu v, j j' \Omega) = \sum_{I_\nu} \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
\]

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\]

\[
R(\nu v, j j' \Omega) = \sum_{I_\nu} \langle I_\nu | m j s \Omega | I_\nu \rangle J(\nu v, m j \Omega, j j' \Omega)
\]
where

\[ R_{J\lambda M_{1}J^{*}0_{1}}(\gamma_{1}, \gamma_{0}) = \sum_{J^{\prime}M_{1}^{\prime}} Y_{J^{\prime}M_{1}^{\prime}}(\gamma_{0}, 0) R^{J^{\prime}}(\lambda_{J^{\prime}J}, M_{1}^{\prime}J^{\prime}M_{1}) Y_{J^{\prime}M_{1}^{\prime}}^{*}(\gamma_{1}, 0). \]  

(8)

Thus, rotational invariance does not imply that \( R_{J\lambda M_{1}J^{*}0_{1}}(\gamma_{1}, \gamma_{0}) \) is independent of the Euler angles but rather that it depends only upon the relative Euler angles \( \gamma_{1}, \gamma_{0} \). Using this property in Eq. (6), or equivalently by inverting Eq. (8), we obtain the exact relationship

\[ R^{J}(\lambda_{J^{*}J}, M_{1}^{\prime}J^{\prime}M_{1}) = 4\pi \int Y_{J^{\prime}M_{1}^{\prime}}^{*}(\gamma_{0}, 0) R_{J\lambda M_{1}J^{*}0_{1}}(\gamma_{1}, \gamma_{0}) \times Y_{J^{\prime}M_{1}^{\prime}}(\gamma_{0}, 0) d(\cos \gamma_{0}) d(\cos \gamma_{1}), \]  

(9)

where \( R_{J\lambda M_{1}J^{*}0_{1}}(\gamma_{1}, \gamma_{0}) \) is related to \( R_{J\lambda M_{1}J^{*}0_{1}}(\lambda, \gamma_{1}, \lambda, \gamma_{0}) \) by [cf. Eq. (7)]

\[ R_{J\lambda M_{1}J^{*}0_{1}}(\lambda, \gamma_{1}, \lambda, \gamma_{0}) = \int D_{\lambda J^{*}}^{\lambda}(\hat{\Lambda}_{\lambda}) R_{J\lambda M_{1}J^{*}0_{1}}(\lambda, \gamma_{1}, \lambda, \gamma_{0}) d\hat{\Lambda}_{\lambda}, \]  

(10)

and

\[ \hat{\Lambda}_{\lambda} = \Lambda_{\lambda}^{0} \Lambda_{\lambda}. \]  

(11)

Thus, the exact BF \( R \)-matrix elements may be obtained from a knowledge of \( R_{J\lambda M_{1}J^{*}0_{1}}(\gamma_{1}, \gamma_{0}) \). These in turn may be obtained by solving the Schrödinger equation in the coordinate representation and suitably integrating out the radial dependence. We now remark that the exact relation given in Eq. (9) is reminiscent of IOS approximate treatments of nonreactive scattering.16

In the latter, the approximate treatment effectively yields a \( \gamma \)-dependent \( R \) matrix such that the final result may be expressed in terms of integration over only one \( \gamma \) value. We shall come back to this point later (Sec. VI).

Now, in our approach to a reactive scattering IOS approximation, we shall follow the procedure used in earlier accurate CC studies.4,5 Each of the three arrangement channels will be treated separately and independently. Complete sets of solutions (satisfying arbitrary asymptotic conditions) are to be smoothly matched among one another on appropriate boundary surfaces separating the various arrangement channels. However, one essential difficulty is encountered. In the exact CC treatment, the final \( R \) matrices are independent of the specific surface chosen on which to carry out the matching. This may not be the case in the IOS. In particular, this can occur if one insists on decoupling the matching equations with respect to the \( \gamma \) angle in each arrangement. Since this is a very desirable simplification, it requires some care. From Eq. (9), one sees that, in order to calculate the \( R \) matrix in the representation commonly called the body frame (BF), one first must generate the reduced coordinate representation \( R \)-matrix elements \( R_{J\lambda M_{1}J^{*}0_{1}}(\gamma_{1}, \gamma_{0}) \), which of course vary with \( \gamma_{1} \) and \( \gamma_{0} \).

In what follows, we will see that the \( I \)-labeled IOS leads to an approximate \( R_{J\lambda M_{1}J^{*}0_{1}}(\gamma_{1}, \gamma_{0}) \) that is also nonlocal in \( \gamma_{1} \) and \( \gamma_{0} \). This is in contrast to a \( J \)-labeled IOS which yields an \( R \) matrix that is diagonal in \( \Omega_{1} \) and \( \Omega_{0} \), and local in \( \gamma_{1} \) and \( \gamma_{0} \) (cf. Sec. VI). However, in the initial \( I \)-labeled theory, all the dynamical information in \( R_{J\lambda M_{1}J^{*}0_{1}}(\gamma_{1}, \gamma_{0}) \) comes from a certain \( R(\gamma_{1}) \) [cf. Eq. (106)]

that depends only upon \( \gamma_{1} \) and also depends upon the matching surface \( \pi_{k} \). It will be rigorously shown that this quantity \( R(\gamma_{1}) \) is obtained by matching the solution in the \( \lambda \) channel at \( \gamma_{1} \) with that in the \( \nu \) channel at \( \gamma_{0} \), where \( \gamma_{1} \) and \( \gamma_{0} \) are related according to the matching surface. Thus, for instance, in the case of the surface

\[ \gamma_{\nu} = \gamma_{\lambda}, \]  

(12)

where \( \gamma_{\nu} \) and \( \gamma_{\lambda} \) are mass-scaled interatomic distances in the \( \lambda \) and \( \nu \) arrangement channels, we match the solutions for

\[ \gamma_{\nu} = \pi_{k} - \gamma_{\lambda}. \]  

(13)

One possible way to circumvent the dependence of \( R(\gamma_{1}) \) on the matching surface without losing the simplifications due to the IOS approximation is to perform the matching with respect to a set of surfaces of the form

\[ \gamma_{\nu} = B_{\lambda} \gamma_{\lambda}, \]  

(14)

where \( B_{\lambda} \) is a parameter. For a given \( \gamma_{1} \), each value of \( B_{\lambda} \) produces a particular \( \gamma_{\nu} \) and consequently a corresponding reduced \( R \) matrix \( R(\gamma_{1}, \gamma_{\nu}) \) and therefore, by varying \( B_{\lambda} \), one can produce values of \( R(\gamma_{1}, \gamma_{\nu}) \) at the grid of \( \gamma_{1}, \gamma_{\nu} \) required to calculate the integral in Eq. (9).

In the next sections, we discuss the IOS approach to reactions along lines similar to the exact CC treatment as formulated by KSB and by SK, except we shall replace their \( \gamma_{\nu} = \gamma_{\lambda} \) surface by \( \gamma_{\nu} = B_{\lambda} \gamma_{\lambda} \) and we shall work within a space fixed formalism.

### III. AN EXACT FORMULATION OF REACTIVE CC EQUATIONS

In this section, we briefly discuss an exact formulation of reactive scattering. A solution to the reactive scattering problem may be obtained by solving the Schrödinger equation in each arrangement channel and matching the resulting wave functions on a matching surface. The \( R \) matrix is then obtained by demanding that proper asymptotic conditions be satisfied.

The dynamics in a given arrangement channel is described by a set of coordinates in the center of mass system shown in Fig. 1. Thus, \( R_{\alpha} \) and \( r_{\alpha} \) are the collision vector and diatomic separation vector, respectively, for arrangement channel \( \alpha \) defining the configuration \( A + BC \). \( \gamma_{\nu} \) and \( \gamma_{\nu} \) are the potential in channel \( \alpha \), i.e., \( V(\gamma_{\nu}, R_{\alpha}, \gamma_{\nu}) \), depends upon \( \gamma_{\nu} \) and \( R_{\alpha} \) and \( \gamma_{\nu} \) and \( R_{\alpha} \).

The Schrödinger equation in arrangement channel \( \alpha \)
has the form

$$
\left[ -\frac{\hbar^2}{2\mu_{C}} \nabla_k^2 + \frac{\hbar^2}{2\mu_{B}} \nabla_x^2 + V(r_x, R, \gamma) - E \right] \psi_k(r_x, R) = 0,
$$

(15)

where \((\lambda \nu k)\) is a cyclic permutation of \((\alpha \beta \gamma)\). In the above equation, \(\mu_{C}\) is the reduced mass of atom C with respect to atom B and \(\mu_{B,\alpha,\beta,\gamma}\) is that of atom A with respect to the molecule BC. This may be put in a more symmetric form by making the transformation\(^{1,5}\)

$$
R_\alpha = a_\alpha R_x, \tag{16}
$$

$$
r_\alpha = a_\alpha^2 r_x, \tag{17}
$$

where

$$
a_\alpha = \left(\mu_{B,\alpha,\beta,\gamma}/\mu_{C}\right)^{1/4}. \tag{18}
$$

This transformation leaves \(\gamma\) unchanged. The above transformation holds for all channels, as \(\lambda \nu k\) are all cyclic combinations of \(\alpha, \beta,\) and \(\gamma\).

In terms of reduced coordinates, the Schrödinger equation becomes

$$
\left[ -\frac{\hbar^2}{2\mu} \left( \nabla^2_{R_\alpha} + \nabla^2_{r_\alpha} \right) + V(r_\alpha, R, \gamma) - E \right] \psi_{\alpha}(r_\alpha, R) = 0, \tag{19}
$$

where the scaled reduced mass is given by

$$
\mu = [m_a m_b m_c]/(m_a + m_b + m_c)^{1/2}. \tag{20}
$$

The total angular momentum and total z component of angular momentum operators \(J^2\) and \(J_z\) commute with the Hamiltonian and are therefore constants of the motion. The total wave function may therefore be expanded in terms of eigenfunctions of \(J^2\) and \(J_z\) with eigenvalues \(\hbar^2 J(J+1)\) and \(\hbar M\), respectively. We thus have the partial wave expansion of the total wave function

$$
\psi_{\alpha}(r_\alpha, R) = \sum_{J, M} \sum_{\alpha} C^{J, M}_{\alpha} \psi^{J,M}_{\alpha}(r_\alpha, R), \tag{21}
$$

where \(\psi^{J,M}_{\alpha}(r_\alpha, R)\) satisfies Eq. (19).

A. Schrödinger equation in body fixed coordinates

From the viewpoint of exact computations, it is most convenient to solve the reactive collision problem in terms of a set of body fixed (BF) coordinates,\(^{4,5}\) where the \(z\) axis in each arrangement channel is oriented along the collision vector \(R_x\). This is so mainly because the matching equations are most conveniently expressed in terms of BF coordinates.

It is well known\(^{4,5,8,4}\) that \(\psi^{J,M}_{\alpha}\) may be expressed in terms of body fixed wave functions as

$$
\psi^{J,M}_{\alpha}(r_\alpha, R) = \sum_{\alpha} \sqrt{\frac{2J+1}{4\pi}} D_{J,M}^{\alpha} \psi^{J,M}_{\alpha}(\phi_\alpha, \theta_\alpha, \theta), \tag{22}
$$

where the quantum numbers \(M\) and \(\Omega\) are the projections of the total angular momentum along the space fixed and the body fixed \(z\) axes, respectively.

Substitution of the above expansion (22) into the Schrödinger equation (19) gives the well known BF equation for \(\psi^{J,M}_{\alpha}\)\(^{4,5,8,4}\):

$$
H_{\alpha\alpha}^{J,M} \phi^{J,M}_{\alpha}(r_\alpha, R) + H_{\alpha\alpha}^{J,M} \psi^{J,M}_{\alpha}(r_\alpha, R) + H_{\alpha\alpha}^{J,M} \psi^{J,M}_{\alpha}(r_\alpha, R) = E \psi^{J,M}_{\alpha}, \tag{23}
$$

where

$$
H_{\alpha\alpha}^{J,M} = -\frac{\hbar^2}{2\mu} \left( \frac{1}{\gamma_\alpha} \gamma_\alpha \gamma_\alpha + \frac{1}{R_\alpha} \gamma_\alpha \gamma_\alpha + \frac{1}{2\mu} \gamma_\alpha \gamma_\alpha \right) + \frac{1}{2\mu} \gamma_\alpha \gamma_\alpha \gamma_\alpha + \frac{1}{2\mu} \gamma_\alpha \gamma_\alpha \gamma_\alpha + V(r_\alpha, R, \gamma) \tag{24}
$$

and

$$
H_{\alpha\alpha}^{J,M} = -\frac{\hbar^2}{2\mu} \sqrt{j(j+1) - \Omega_\alpha (\Omega_\alpha + 1)} \gamma_\alpha. \tag{25}
$$

In order to solve the above equation, we expand \(\psi^{J,M}_{\alpha}\) in terms of the spherical harmonics \(Y_{\alpha,\beta}(r_\alpha, \phi_\alpha)\) as follows:

$$
\psi^{J,M}_{\alpha}(r_\alpha, R, \gamma) = \sum_{j, \Omega} \sum_{M} (1/r_\alpha R_\alpha) Y_{j,M}(r_\alpha, \phi_\alpha) F_{j,M}(r_\alpha, R_\alpha). \tag{26}
$$

It then follows from Eq. (23) that \(F_{j,M}(r_\alpha, R_\alpha)\) satisfies the set of coupled equations\(^{3}\)

$$
\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r_\alpha^2} + \frac{\delta^2}{\partial R_\alpha^2} \right) + \frac{\hbar^2}{2\mu} \gamma_\alpha \gamma_\alpha + \frac{1}{2\mu} \gamma_\alpha \gamma_\alpha \right] F_{j,M}(r_\alpha, R_\alpha) + \sum_{j', \Omega'} V_{j,M}^{j', \Omega'} F_{j', \Omega'}(r_\alpha, R_\alpha) = 0, \tag{27}
$$

where

$$
\sum_{j', \Omega'} V_{j,M}^{j', \Omega'} = \frac{\hbar^2}{2\mu} (j(j+1) - \Omega_\alpha (\Omega_\alpha + 1)), \tag{28}
$$

and

$$
\sum_{j', \Omega'} J_{j,M}^{j', \Omega'} = -\frac{\hbar^2}{2\mu} \sum_{j'} \xi(j, \Omega) \xi(j', \Omega), \tag{29}
$$

with

$$
\xi(j, \Omega) = [j(j+1) - \Omega (\Omega + 1)]^{1/2}, \quad |\Omega| \leq J. \tag{30}
$$

The potential matrix elements in Eq. (27) are diagonal in \(\Omega\) and are given by

$$
V_{j,M}^{j', \Omega'}(r_\alpha, R_\alpha) = 2\pi \int_{0}^{\pi} Y_{j,M}(\gamma, 0) V(\gamma, R_\alpha, \gamma) Y_{j', \Omega'}^*(\gamma, 0) \sin \gamma d\gamma, \tag{31}
$$

which gives a result which is independent of \(J\).

Integration of Eq. (27) is done by first expanding \(F\) in terms of a set of single variable pseudovibrational functions. The resulting expansion coefficients satisfy a set of coupled differential equations with respect to some propagation coordinate. The choice of these coordinates has been described in great detail,\(^{4,1}\) and will be discussed further later in this work. In the present IOS approach, we shall employ a close coupled space fixed formulation, which we believe is more convenient for introducing an \(l\)-labeled infinite order sudden approximation. We now describe it.

B. Coupled space fixed formulation of the Schrödinger equation

The integration within a given channel may alternatively be done for space fixed radial functions, and body
fixed functions can then be constructed from these for the purpose of interchannel matching. Although this procedure is somewhat roundabout for the exact calculations, for the purpose of developing an \(l\)-labeled IOS, it is more convenient. Therefore, we shall now describe the space fixed formalism.

The body fixed functions \(F_{\ell' \ell m l}^{(2)}\) defined in Eq. (26) are related to space fixed functions \(F_{\ell' \ell m}^{(2)}(r_a, R_a)\) via

\[
F_{\ell' \ell m}^{(2)}(r_a, R_a) = \sum_{n_{l' \ell' m'}} \left( \frac{2l' + 1}{2j' + 1} \right)^{1/2} \times \langle \ell' m', 0 \mid j'_{l' m'} \mid J_{l' m'} \rangle F_{\ell' \ell m'}^{(2)}(r_a, R_a)
\]

or equivalently

\[
F_{\ell' \ell m}^{(2)}(r_a, R_a) = \sum_{n_{l' \ell' m'}} \left( \frac{2l' + 1}{2j' + 1} \right)^{1/2} \times \langle \ell' m', 0 \mid j'_{l' m'} \mid J_{l' m'} \rangle F_{\ell' \ell m'}^{(2)}(r_a, R_a)
\]

Substitution of Eq. (33) into (27) gives the set of coupled differential equations

\[
\begin{align*}
\left[ \frac{\partial^2}{\partial R_a^2} + \frac{2 \mu}{\hbar^2} \frac{\partial^2}{\partial l_a^2} \right] + 2 \mu E / \hbar^2 - \frac{\ell'_{l' m'} + 1}{R_a^2} - \frac{j'_{l' m'} (j'_{l' m'} + 1)}{r_a^2} \right] F_{\ell' \ell m}^{(2)}(r_a, R_a) \\
= \frac{2 \mu}{\hbar^2} \sum_{\ell' m'} \langle \ell' m' \mid V' \mid j'_{l' m'} \rangle F_{\ell' \ell m}^{(2)}(r_a, R_a),
\end{align*}
\]

where now the kinetic energy operator is completely diagonal and independent of \(J\). The potential matrix on the other hand contains more coupling than in the BF case and is given by

\[
\langle \ell' m' \mid V' \mid j'_{l' m'} \rangle = \sum_{n_{l' \ell' m'}} \frac{\sqrt{2l'_{l' m'} (2j'_{l' m'} + 1)}}{(2j'_{l' m'} + 1)} \langle \ell' m' 0 \mid j'_{l' m'} \mid J_{l' m'} \rangle 2\pi \int_0^\infty Y^*_{l_a m_a}(r_a, 0) V(r_a, R_a, \gamma_a) \\
\times Y_{l' m'}(r_a, 0) \sin\gamma_a d\gamma_a.
\]

We note that it now depends on \(J\).

Thus, instead of solving Eq. (27) for \(F_{\ell' \ell m}^{(2)}\) with a given set of initial conditions, one may solve Eq. (34) for \(F_{\ell' \ell m}^{(2)}\) with corresponding boundary conditions [also related by Eq. (32)], and obtain \(F_{\ell' \ell m}^{(2)}\) by using Eq. (33). The two procedures give identical results in exact calculations with comparable ease in computation. We emphasize here that, for the purpose of matching, one still constructs the body fixed functions, in terms of which the matching equations are most conveniently written. We now turn to derive the \(l\)-labeled IOS approximation.

IV. THE \(l\)-LABELED IOS FOR REACTIVE SCATTERING

In the IOS, we treat the centrifugal terms in Eqs. (27) and (34) in an approximate manner. Although entirely equivalent from the point of view of exact computations, there is a significant difference between the Eqs. (27) and (34) for the purpose of introducing the IOS. In Eq. (27), one is naturally led to a \(J\)-labeled IOS, whereas Eq. (34) allows for either an \(l\)-labeled or a \(J\)-labeled IOS, as both these indices explicitly enter the differential equations. It has recently been shown that the \(J\)-labeled IOS for nonreactive problems leads to some important fundamental difficulties. In particular, it leads to \(\Delta n\) transitions in the limit where the potential becomes spherically symmetric. The \(l\)-labeled IOS, on the other hand, becomes exact in this limit. In this section, we develop an \(l\)-labeled IOS for reactive scattering starting from Eq. (34).

For this purpose, we first make the transformation

\[
F_{\ell' \ell m}^{(2)}(r_a, R_a, \gamma_a) = \sum_{n_{l' \ell' m'}} \sqrt{\frac{2l'_{l' m'} + 1}{2j'_{l' m'} + 1}} \langle \ell' m', 0 \mid j'_{l' m'} \mid J_{l' m'} \rangle Y^*_{l_a m_a}(r_a, \gamma_a) \\
\times Y_{J_{l' m'}}(r_a, 0) F_{\ell' \ell m}^{(2)}(r_a, R_a),
\]

and conversely

\[
F_{\ell' \ell m}^{(2)}(r_a, R_a, \gamma_a) = \sum_{n_{l' \ell' m'}} \sqrt{\frac{2l'_{l' m'} + 1}{2j'_{l' m'} + 1}} \langle \ell' m', 0 \mid j'_{l' m'} \mid J_{l' m'} \rangle 2\pi \int_0^\infty Y_{l_a m_a}(r_a, 0) Y^*_{l' m'}(r_a, \gamma_a) \\
\times F_{\ell' \ell m}^{(2)}(r_a, R_a, \gamma_a) \sin\gamma_a d\gamma_a.
\]

We remark here that this transformation is similar to that given by Secrest,46 in connection with an uncoupled SF formulation of the IOS for nonreactive scattering. It is readily seen that this transformation diagonalizes the potential matrix element given in Eq. (35).

We next rewrite Eq. (34) for the transformed wave function, replacing \(\ell'_{l' m'} + 1\) and \(j'_{l' m'} (j'_{l' m'} + 1)\) terms in the centrifugal part by the constants \(l_{l' m'}^2 + j_{l' m'}^2 + l_{l' m'} j_{l' m'}\) and \(l_{l' m'}^2 + j_{l' m'}^2\), respectively. The resulting equations are completely decoupled so far as angular variables are concerned with \(l\), \(j\), and \(\gamma\) entering only parametrically in the equations. Thus, we obtain equations for the \(\gamma\)-dependent IOS functions \(F_{\ell' \ell m}^{(2)}(r_a, R_a, \gamma)\) of the form

\[
\begin{align*}
\left[ \frac{\partial^2}{\partial R_a^2} + \frac{2 \mu}{\hbar^2} \frac{\partial^2}{\partial l_a^2} - \frac{\ell_{l' m'} + 1}{R_a^2} - \frac{j_{l' m'} (j_{l' m'} + 1)}{r_a^2} \right] F_{\ell' \ell m}^{(2)}(r_a, R_a, \gamma) \\
= 2 \mu \left( V(r_a, R_a, \gamma) - E \right) F_{\ell' \ell m}^{(2)}(r_a, R_a, \gamma).
\end{align*}
\]

We remark here that \(J\) and \(\ell\) do not appear explicitly in the differential equation. The IOS wave functions \(F_{\ell' \ell m}^{(2)}\) will depend upon these quantum numbers only through the boundary conditions.

The approximate BF wave functions \(F_{\ell' \ell m}^{(2)}(r_a, R_a)\) are obtained from the \(\gamma\)-dependent IOS wave functions \(F_{\ell' \ell m}^{(2)}(r_a, R_a, \gamma)\) by Eqs. (37) and (33). This gives the result

\[
\begin{align*}
F_{\ell' \ell m}^{(2)}(r_a, R_a) = \sum_{n_{l' \ell' m'}} \sqrt{\frac{2l'_{l' m'} + 1}{2j'_{l' m'} + 1}} \langle \ell' m', 0 \mid j'_{l' m'} \mid J_{l' m'} \rangle Y^*_{l_a m_a}(r_a, 0) F_{\ell' \ell m}^{(2)}(r_a, R_a, \gamma) \\
\times 2\pi \int_0^\infty Y_{l_a m_a}(r_a, 0) Y_{l' m'}(r_a, \gamma) \sin\gamma_a d\gamma_a
\end{align*}
\]

and equivalently

\[
\begin{align*}
F_{\ell' \ell m}^{(2)}(r_a, R_a, \gamma) = \sum_{n_{l' \ell' m'}} \sqrt{\frac{2l'_{l' m'} + 1}{2j'_{l' m'} + 1}} \langle \ell' m', 0 \mid j'_{l' m'} \mid J_{l' m'} \rangle Y^*_{l_a m_a}(r_a, 0) F_{\ell' \ell m}^{(2)}(r_a, R_a, \gamma) \\
\times Y_{l_a m_a}(r_a, 0) F_{\ell' \ell m}^{(2)}(r_a, R_a, \gamma).
\end{align*}
\]

Note that so far we have not specified \(l\) and \(j\). In general, they may be chosen to depend upon \(l_{l' m'}\) and \(j_{l' m'}\), as well as the initial conditions.

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V. INTEGRATION OF THE IOS SCHRÖDINGER EQUATIONS IN ARRANGEMENT CHANNEL \( \lambda \)

The exact treatment of reactive scattering consists in integrating Eq. (27) through a series of regions in the \((\gamma, R_0)\) plane, choosing different sets of pseudovibration and propagation coordinates in various regions and subregions. This procedure is accompanied by smooth matching of the BF wave functions between various regions. The \(R\) matrix is then obtained by taking a linear combination of the BF wave functions that gives smooth matching between various arrangement channels, as well as proper asymptotic behavior.

Our IOS procedure, instead, consists in integrating Eq. (38) for \(F_{j}^{0}(\gamma, R_0, \gamma_j)\) and constructing the approximate BF functions therefrom by employing Eq. (39). The initial conditions and the asymptotic behavior of the \(\gamma\)-dependent IOS functions \(F_{j}^{0}(\gamma, R_0, \gamma_j)\) indeed depend upon those of the BF functions. In this section, we discuss the initial conditions for the IOS functions \(F_{j}^{0}(\gamma, R_0, \gamma_j)\) and the matching conditions on these as we go from one region to another. We note that this procedure can be carried out for a fixed \(\gamma_j\). In the next section, we will discuss the matching equations for the IOS functions as we go from one arrangement channel to another, as well as the asymptotic behavior of the IOS functions. We will see that, with initial \(I\)-labeling, this too can be done for a fixed \(\gamma\), leading to a \(\gamma\)-dependent IOS \(R\) matrix. The physical \(R\) matrix will be shown to be rather simply related to this \(\gamma\)-dependent IOS \(R\) matrix.

The division of the IOS integration into various regions and subregions for a given arrangement channel is similar to that in the exact treatment, because \(\gamma_j\) and \(R_0\) enter quite analogously in the two treatments. Thus, a convenient division into regions may be taken as:

1. Asymptotic region \((\gamma_j, R_0)\);
2. Weak interaction region \((\gamma_j, R_0)\);
3. Strong interaction region \((\rho_j, \phi_j)\).

By contrast, in the exact treatment, each arrangement channel is divided into four regions. We will show later that, within the IOS, the \((\gamma_j, \eta_j)\) region can be deleted and the matching between two arrangement channels done by directly matching solutions from two adjacent strong interaction regions. In the strong interaction region, \(\rho_j\) is the vibrational coordinate and the angle \(\phi_j\) is the propagation variable. These variables are related to the more standard \((\gamma_j, R_0)\) via

\[
R_0 = R_0^2 - \rho_j \cos \phi_j, \tag{41}
\]

and

\[
\gamma_j = \gamma_j^2 - \rho_j \sin \phi_j, \tag{42}
\]

where \((R_0^2, \gamma_j^2)\) is a fixed point which will be discussed later. Within each region, the BF wave function is expanded in terms of pseudovibrational wave functions according to

\[
F_{j}^{0}(\gamma, R_0, \gamma_j) = \sum_{\gamma_j} F_{j}^{0}(\gamma, R_0, \gamma_j) \phi_j^0(\gamma_j), \tag{43}
\]

where we have denoted the propagation variable by \(\rho_j\) and the vibrational coordinate by \(\gamma_j\) corresponding to the region considered. The solutions labeled by a plus are obtained by propagating inward from region I to III and those labeled by a minus are obtained by propagating outward from region III to region I. The functions \(F_{j}^{0}(\gamma, R_0, \gamma_j)\) satisfy a set of coupled differential equations and are obtained subject to the initial conditions

\[
F_{j}^{0}(\gamma, R_0, \gamma_j) = C_j \phi_j^0(\gamma_j), \tag{44}
\]

with similar equations for the derivative of \(g\) with respect to \(\rho_j\).

Alternatively, we can carry out the same procedure in terms of SF functions. Expanding the SF function \(F_{j}^{0}(\gamma, R_0, \gamma_j)\) in Eq. (32) in terms of the same set of pseudovibrational states, we get

\[
F_{j}^{0}(\gamma, R_0, \gamma_j) = \sum_{\gamma_j} g_{j}^{\lambda}(\gamma_j, R_0) \phi_j^0(\gamma_j), \tag{45}
\]

where the space fixed functions \(g_{j}^{\lambda}(\gamma_j, R_0)\) satisfy another set of coupled differential equations subject to the initial conditions

\[
g_{j}^{\lambda}(\gamma_j, R_0) = C_j \phi_j^0(\gamma_j), \tag{46}
\]

and a similar equation for the derivative. From Eqs. (32) and (46), we also find the relation between the SF and the BF \(g\) functions to be

\[
g_{j}^{\lambda}(\gamma_j, R_0) = \sum_{\gamma_j} \frac{\sqrt{2 \lambda_j + 1}(-1)^{\lambda_j}}{(2 \lambda_j + 1) (2 \lambda_j + 1)} \langle i, 0 | j, \lambda_j | J, \Omega \rangle \langle \Omega | i, 0 | \lambda_j \rangle \phi_j^0(\gamma_j), \tag{47}
\]

which is valid in all regions. Inverting this relation, we obtain

\[
g_{j}^{\lambda}(\gamma_j, R_0) = \sum_{\gamma_j} \frac{\sqrt{2 \lambda_j + 1}(-1)^{\lambda_j}}{(2 \lambda_j + 1) (2 \lambda_j + 1)} \langle i, 0 | j, \lambda_j | J, \Omega \rangle \langle \Omega | i, 0 | \lambda_j \rangle \phi_j^0(\gamma_j). \tag{48}
\]

Substitution of Eq. (45) into (36) gives an expansion of the \(\gamma\)-dependent IOS wave functions \(F_{j}^{0}(\gamma, R_0, \gamma_j)\) in terms of the same set of pseudovibrational functions

\[
F_{j}^{0}(\gamma, R_0, \gamma_j) = \sum_{\gamma_j} F_{j}^{0}(\gamma, R_0, \gamma_j) \phi_j^0(\gamma_j). \tag{49}
\]

The relation between the approximate SF \(g\) functions and the \(\gamma\)-dependent IOS \(g\) functions is the same as that between the \(F\) functions [cf. Eqs. (36) and (37)], i.e.,

\[
F_{j}^{0}(\gamma, R_0, \gamma_j) = \sum_{\gamma_j} \sqrt{2 \lambda_j + 1} \langle i, 0 | j, \lambda_j | J, \Omega \rangle 2 \pi \int_0^\pi Y_{j}^{\lambda}(\gamma, 0) \phi_j^0(\gamma_j), \tag{50}
\]

and conversely

\[
F_{j}^{0}(\gamma, R_0, \gamma_j) = \sum_{\gamma_j} \sqrt{2 \lambda_j + 1} \langle i, 0 | j, \lambda_j | J, \Omega \rangle Y_{j}^{\lambda}(\gamma, 0) \phi_j^0(\gamma_j). \tag{51}
\]

Note that, strictly speaking, we should label the approximate SF \(g\) functions also by \(\mathbf{f}\) and \(\mathbf{j}\). However, in
order to avoid too cumbersome notations, we have not done so explicitly.

The above relations between approximate SF functions and γ-dependent IOS functions hold in all the regions and in all arrangement channels. The equations for the γ-dependent g functions are obtained by inserting the expansion (49) into Eq. (38) and properly transforming the propagation variable and the pseudovibrational variable. These equations are similar to those in the exact treatment, but are written for fixed γ. They comprise a set of differential equations coupled with respect to vibrational quantum numbers, and γs enters only parametrically through the potential. Furthermore, the quantum numbers J, Jz, Jz', and Ω do not enter explicitly into the differential equations. The dependence of the γ-dependent IOS functions on these quantum numbers, therefore, enters solely as a multiplicative factor that is independent of pzl, i.e.,

\[ R_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) = R_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) C_{J_{z} J_{z}'}(\gamma_{s}) \],

and a similar expression also holds for the derivative of g with respect to pzl. In Eq. (52), the coefficient C must be chosen in such a way that the approximate SF fixed functions constructed by employing Eq. (50) satisfy the initial conditions given in Eq. (46). It may be readily verified that this leads to initial conditions on \( R_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) \) given by

\[ R_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) = C \delta_{\gamma_{0}}, \]

and a similar differential equation for the derivative with respect to pzl, and [cf. Eq. (51)]

\[ C_{J_{z} J_{z}'}(\gamma_{s}) = \sqrt{\frac{2L_{s} + 1}{2J_{s} + 1}} J_{J_{N}}(J_{N} J_{N}')(\gamma_{s}, 0). \]

Substitution of Eq. (52) into Eqs. (50) and (48) yields the relation between the approximate BF functions and the γ-dependent IOS functions

\[ R_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) = \sum_{J_{z} J_{z}'} \sqrt{\frac{2L_{s} + 1}{2J_{s} + 1}} J_{J_{N}}(J_{N} J_{N}')(\gamma_{s}, 0) \times (C_{J_{z} J_{z}'}(\gamma_{s}) C_{J_{z} J_{z}'}(\gamma_{s})) 2F_{J_{z} J_{z}'}(\gamma_{s}, 0) \]

\[ \times g_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) C_{J_{z} J_{z}'}(\gamma_{s}) \delta_{\theta_{\gamma}, \psi_{\gamma}} \].

The above equation tells us how to construct the approximate BF functions from the γ-dependent IOS functions in each region for a given arrangement channel. In a given channel, as we move from one region to another, the BF functions and their derivatives have to satisfy a continuity condition of the form

\[ R_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) = \sum_{J_{z} J_{z}'} S_{J_{z} J_{z}'} \times g_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) C_{J_{z} J_{z}'}(\gamma_{s}) \delta_{\theta_{\gamma}, \psi_{\gamma}} \],

where \( S_{J_{z} J_{z}'} \) is the overlap matrix. This procedure has also been discussed by KSB in detail and remains the same in the IOS. At this point, we simply notice that, since the overlap matrix depends only upon vibrational quantum numbers, it is sufficient to satisfy the continuity equation for a fixed γ, i.e.,

\[ g_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) = \sum_{J_{z} J_{z}'} S_{J_{z} J_{z}'} g_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) C_{J_{z} J_{z}'}(\gamma_{s}) \delta_{\theta_{\gamma}, \psi_{\gamma}} \].

The approximate BF function formed according to Eq. (55) then automatically satisfies Eq. (56). The same also holds for the derivative of g with respect to the propagation coordinate.

VI. IDENTIFICATION OF THE PARTIAL WAVE PARAMETER

So far, we have kept the partial wave parameter \( \tilde{I} \) quite arbitrary. Thus, in Eq. (58), it can be chosen to be a function of \( \tilde{I} \), \( \tilde{I}' \), and \( J \). It has been shown by Khare and Koury \[57\] that the choice \( \tilde{I} = J \) for nonreactive scattering leads to fundamental difficulties from a physical standpoint. In particular, when carried out consistently, this choice leads to \( \Delta m \) transitions for rotationally inelastic scattering even when the potential is spherically symmetric and to infinite total cross sections. Therefore, results for \( \Delta m \) transitions obtained from a \( J \)-labeled IOS cannot be trusted. These features will also persist in reactive scattering. On the other hand, if \( \tilde{I} \) is chosen to be a function of only \( \tilde{I} \) and \( \tilde{I}' \), there are no formal deficiencies. In fact, unlike the \( J \)-labeled IOS, the \( J \)-labeled IOS becomes exact in the limit of small anisotropies, \[66, 67\] so far as the CS part of the IOS is concerned. In this work, we consider the initial \( \tilde{I} \) choice \( \tilde{I} = \tilde{I}' \), which as we shall see shortly also greatly simplifies the entire IOS formalism.

First, we notice that, with this \( \tilde{I} \) choice, the \( \tilde{I}' \) summation in Eq. (55) can be done analytically giving \( \delta_{\tilde{I}, \tilde{I}'} \), and we obtain the simpler relation

\[ g_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) = \sum_{J_{s}} \sqrt{\frac{2L_{s} + 1}{2J_{s} + 1}} J_{J_{N}}(J_{N} J_{N}')(\gamma_{s}, 0) 2 \pi \int_{0}^{\pi} Y_{J_{s} J_{s}}(\gamma_{s}, 0) \times g_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) \delta_{\tilde{I}_{s}, \tilde{I}_{s}'} \delta_{\theta_{\gamma}, \psi_{\gamma}} \].

We further notice that, if \( \tilde{I} \) is chosen to be independent of \( \tilde{I}' \) and we employ Eqs. (43) and (26), we obtain the expression

\[ g_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) = \frac{1}{\tilde{I}_{s}} \sum_{J_{s}} \sqrt{\frac{2L_{s} + 1}{2J_{s} + 1}} J_{J_{N}}(J_{N} J_{N}')(\gamma_{s}, 0) \times g_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) \delta_{\tilde{I}_{s}, \tilde{I}_{s}'} \delta_{\theta_{\gamma}, \psi_{\gamma}} \]

for the BF wave function \( \psi_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) \).

Now the total wave function is constructed by taking a linear combination of \( \phi_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) \) and employing Eq. (21). We therefore obtain, for a given arrangement channel \( \tilde{I} \), the expression

\[ \psi_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) = \mu_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) \sum_{\gamma_{0} \gamma_{0}'} S_{\gamma_{0} \gamma_{0}'} g_{\gamma_{0}}(\theta_{\gamma}, \psi_{\gamma}) \times g_{\gamma_{0}'}(\theta_{\gamma}, \psi_{\gamma}), \]

where \( \lambda_{\gamma_{0} \gamma_{0}'} \) refer to the initial conditions to be discussed later. A similar expansion holds in terms of the variables in the other channels, i.e.,
\[ \psi_{j\mu}(r, R) = (\gamma_{\nu}, R_{\lambda})^{-1} \sum_{m_{\mu}, m_{\nu}} \sqrt{\frac{2L + 1}{4\pi}} \left( \langle \lambda_j | \Omega_{\nu} \rangle D^j_{\mu}(\phi_{\nu}, \theta_{\nu}, \psi_{\nu}) g^j_{\nu} \right) C^j_{j_{\lambda} \lambda_{\lambda}}(\gamma_{\lambda}) \phi_{\lambda}(q_{\lambda}) C^j_{j_{\lambda} \lambda_{\lambda}}(\gamma_{\lambda} \phi_{\lambda}(q_{\lambda}) + \text{(the minus part)} \right), \]  

(61)

with the same initial quantum numbers \( \lambda_j \), \( \nu_b \), \( \Omega_{\nu} \). The coefficients \( C^j_{j_{\lambda} \lambda_{\lambda}}(\gamma_{\lambda}) \) are to be chosen in such a way that the total wave function satisfies the proper matching conditions and boundary conditions. We discuss these in the next section.

VII. DERIVATION OF THE IOS MATCHING CONDITIONS

In this section, we derive a set of matching equations and asymptotic conditions for the IOS functions closely following the exact treatment.\(^4\)\(^5\) We will see later that the IOS treatment allows for a somewhat more general matching.

We first notice a very important feature of the IOS expansions (60) and (61). The \( g \) functions are independent of the \( \Omega_{\nu} \), \( \Omega_{\lambda} \), and \( \chi_\lambda \) quantum numbers. Furthermore, if \( j_\lambda \) is chosen to be a constant independent of both \( j_\lambda \) and \( j_\lambda \), then all the dependence on \( j_\lambda \) and \( \Omega_{\nu} \) enters through the \( C \) coefficients. With this in mind, we define the following new set of \( \gamma \)-dependent \( C \) coefficients

\[ \frac{1}{R_{\lambda}} \sum_{l_{\mu}, m_{\nu}} g^*_{\lambda l_{\mu} \lambda_{\lambda}}(\Delta_{\lambda}) \sum_{l_{\nu}, m_{\nu}} g^*_{\nu l_{\nu} \nu_{\nu}}(\Delta_{\nu}) C^j_{j_{\lambda} \lambda_{\lambda}}(\gamma_{\lambda}) \phi_{\lambda}(q_{\lambda}) + \text{(the minus part)} \right), \]  

(65)

where, as in the exact treatment,\(^4\)\(^5\) we have made use of the relation

\[ D^j_{\mu}(\phi_{\nu}, \theta_{\nu}, \psi_{\nu}) = \sum_{l_{\nu}} D^j_{\mu l_{\nu}}(\phi_{\nu}, \theta_{\nu}, \psi_{\nu}) D^l_{\mu l_{\nu}}(\Delta_{\nu}). \]  

(66)

Again, as in the exact treatment,\(^4\)\(^5\) Eq. (65) holds for all internal configurations of the triatom.

In the exact treatment, KSB ensured this continuity requirement by matching the functions and their normal derivatives on a surface that separates the two arrangement channels. It was suggested that an appropriate surface is obtained from the equation

\[ r_{\nu} = r_{\lambda}, \quad 0 < \gamma_{\nu} < \frac{\pi}{2}. \]  

(67)

Similar matchings were employed between the \( \kappa \) and the \( \lambda \) channels

\[ r_{\kappa} = r_{\kappa}, \quad 0 < \gamma_{\kappa} < \frac{\pi}{2}. \]  

(68)

and for the \( \nu \) and \( \kappa \) channels, we have

\[ r_{\nu} = r_{\nu}, \quad 0 < \gamma_{\nu} < \frac{\pi}{2}. \]  

(69)

Within the IOS framework, the choice of the matching surfaces also automatically yields a relation between \( \gamma_{\lambda} \) and \( \gamma_{\nu} \), between \( \gamma_{\kappa} \) and \( \gamma_{\lambda} \) and between \( \gamma_{\nu} \) and \( \gamma_{\nu} \). For the above matching surfaces, it was shown by KSB that

\[ \gamma_{\nu} = \pi - \gamma_{\nu}, \quad \gamma_{\kappa} = \pi - \gamma_{\kappa}, \quad \gamma_{\nu} = \pi - \gamma_{\nu}. \]  

(70)

As already discussed in Sec. II, we choose our matching surfaces between the \( \lambda \) and the \( \nu \) channels to be

\[ r_{\nu} = B_{\lambda} r_{\lambda}, \quad 0 \leq \gamma_{\nu} \leq \gamma_{\nu}(B_{\lambda}), \quad \gamma_{\nu} = \pi - \gamma_{\nu}. \]  

(71)

(and similar surfaces for the other channels). Here, \( B_{\lambda} \) is a yet to be determined constant. In Appendix A, it is shown that once \( B_{\lambda} \) is fixed, the relation between \( \gamma_{\lambda} \) and \( \gamma_{\nu} \) is given by

\[ \cos \gamma_{\nu} = \frac{\cos \gamma_{\nu} + (1 - B_{\lambda}) \cot \phi_{\lambda}}{B_{\lambda} \sqrt{1 + (1 - B_{\lambda}) \cot \phi_{\lambda}}}, \]  

(72)

where \( \cot \phi_{\lambda} \) is given by

\[ \cot \phi_{\lambda} = \frac{\sin \gamma_{\nu} - \cos \gamma_{\nu} \sqrt{B_{\lambda}^2 - \cos^2 \gamma_{\nu} \sin^2 \gamma_{\nu}}}{B_{\lambda} - \cos^2 \gamma_{\nu}}. \]  

(73)

The matching between two arrangement channels is now similar to the matching encountered in collinear sys-
tems with one difference. In the collinear case, the matching is done with respect to a single line which separates the two arrangement channels. Here, since the matching lines are not in the \((\gamma_{a}B_{a})\) plane (except when \(\gamma_{a} = 0\)), the matching is done with respect to solutions on two lines. One is the projection of the off plane line onto the \((\gamma_{a}B_{a})\) plane and the other is the projection onto the \((\gamma_{a}r_{a})\) plane. For a given \(\gamma_{a}\) and \(B_{a}\), the equation of the projected line in the \((\gamma_{a}, r_{a})\) plane is

\[
R_{a} = r_{a} \tan \phi_{a}(\gamma_{a}, B_{a}) ,
\]  
(74a)

and similarly the equation of the projected line in the \((\gamma_{b}, r_{b})\) plane is

\[
R_{b} = r_{b} \tan \phi_{b}(\gamma_{b}, B_{b}) ,
\]  
(74b)

where both \(\phi_{a}\) and \(\phi_{b}\) are defined and calculated in Appendix A. In addition, on the matching surface, \(\Delta_{a}\) is also a function of \(\gamma_{a}\) and the matching surface coefficients \(B_{a}\) given by Eq. (A16).

The fact that the matching is done separately for each \(\gamma_{a}\) (and \(B_{a}\)) has important implications so far as the propagation in each arrangement channel is concerned.

In the KSB method, each channel is divided into four regions: the asymptotic region, the weak interaction region, the strong interaction region, and the matching region. In the first two regions, the propagation is done using the Cartesian coordinates \((r_{a}, R_{a})\). In the third region, it is done with polar coordinates \((\rho_{a}, \phi_{a})\), defined with respect to a point \((\gamma_{a}, B_{a})\) in the plateau region. In the fourth region, it is also done with polar coordinates \((\varepsilon_{a}, \eta_{a})\) but defined with respect to the origin. In the KSB procedure, the point \((\gamma_{a}, B_{a})\) is defined in such a way that, for a given \(r_{a}\), the value of \(R_{a}\) is obtained from the relation

\[
R_{a} = r_{a} \tan \phi_{a}(\gamma_{a} = 0, B_{a} = 1) .
\]  
(75)

In the present IOS treatment, this procedure can be simplified. If, for each given \(\gamma_{a}\) (and \(B_{a}\)) and \(\gamma_{b}\), the value of \(R_{a}(\gamma_{a})\) is calculated from

\[
R_{a}(\gamma_{a}) = r_{a} \tan \phi_{a}(\gamma_{a}, B_{a}) ,
\]  
(76)

then the transformation from \((\rho_{a}, \phi_{a})\) to \((\varepsilon_{a}, \eta_{a})\) is not needed and one is left with three integration regions only. Then, on the matching surface defined by Eq. (71), the matching equation is

\[
\sum_{k_{a}} \sum_{k_{b}} g^{*}_{k_{a}k_{b}}[\phi_{a}(\gamma_{a}), \gamma_{a}]C^{\ast}_{j_{a}k_{a}j_{b}k_{b}}[\gamma_{a}, \gamma_{b}, B_{a}B_{b}] \phi_{b}(\rho_{b}) + \text{(the minus part)}
\]

\[
= Z_{a_{b}}^{1/2} \left[ \sum_{\rho_{a}} \sum_{\gamma_{b}} g^{*}_{\gamma_{a}\rho_{a}}[\phi_{a}(\gamma_{a}), B_{a}] \sum_{\gamma_{b} B_{b}} g^{\ast}_{\gamma_{b}B_{b}}[\phi_{b}(\gamma_{b}, B_{b}), \gamma_{b}B_{b}] C_{j_{a}k_{a}j_{b}k_{b}}[\gamma_{a}, \gamma_{b}, B_{a}B_{b}] \phi_{b}(\rho_{b}) + \text{(the minus part)} \right] ,
\]

\[
0 < \gamma_{a} < \gamma_{a}(B_{a}) , \quad \pi > \gamma_{b} > \gamma_{b}(B_{a}) .
\]  
(77)

and

\[
Z_{a_{b}} = \frac{R_{a_{b}}}{R_{a_{a}}B_{a_{a}}} = B_{a_{a}}[1 + (1 - B_{a_{a}})\cot^{2} \phi_{a_{a}}] ,
\]

where \(\cot \phi_{a_{a}}\) is given in Eq. (73). Multiplying the above equation by \(\phi_{b_{a}}\) on both sides and integrating with respect to \(\rho_{a}\), we obtain

\[
\sum_{k_{a}} \sum_{k_{b}} g^{*}_{k_{a}k_{b}}[\phi_{a}(\gamma_{a}), \gamma_{a}]C^{\ast}_{j_{a}k_{a}j_{b}k_{b}}[\gamma_{a}, \gamma_{b}, B_{a}B_{b}] + \text{(the minus part)} = Z_{a_{b}}^{1/2} \left[ \sum_{\rho_{a}} S_{\phi_{a_{a}}}^{\phi_{b_{a}}} \phi_{b_{a}}(\rho_{a}) \phi_{b_{a}}(\rho_{a}) d\rho_{a} \right] ,
\]

\[
\times \sum_{\rho_{a}} \sum_{\gamma_{b} B_{b}} g^{*}_{\gamma_{a}\rho_{a}}[\phi_{a}(\gamma_{a}, B_{a}), \gamma_{a}B_{a}] C_{j_{a}k_{a}j_{b}k_{b}}[\gamma_{a}, \gamma_{b}, B_{a}B_{b}] + \text{(the minus part)} , \quad 0 < \gamma_{a} < \gamma_{a}(B_{a}) , \quad \pi > \gamma_{b} > \gamma_{b}(B_{a}) ,
\]  
(78)

where the overlap matrix \(S_{\phi_{a_{a}}}^{\phi_{b_{a}}}\) is given by

\[
S_{\phi_{a_{a}}}^{\phi_{b_{a}}} = \int_{0}^{\infty} \phi^{*}_{b_{a}}(\rho_{a}) \phi_{b_{a}}(\rho_{a}) d\rho_{a} .
\]  
(79)

Since \(\{\phi_{a_{a}}\}\) and \(\{\phi_{b_{a}}\}\) are complete orthonormal sets, \(S\) is an orthogonal matrix. In principle, we can choose the \(\{\phi_{a}\}\) and \(\{\phi_{b}\}\) sets to be the same. For this case, \(S_{\phi_{a_{a}}}^{\phi_{b_{a}}}\) equals \(\delta_{\phi_{a_{a}}\phi_{b_{a}}}\) and we obtain the much simpler matching equation

\[
\sum_{k_{a}} g^{*}_{k_{a}k_{b}}[\phi_{a}(\gamma_{a}), \gamma_{a}]C^{\ast}_{j_{a}k_{a}j_{b}k_{b}}[\gamma_{a}, \gamma_{b}, B_{a}B_{b}] + \text{(the minus part)}
\]

\[
= Z_{a_{b}}^{1/2} \left[ \sum_{\rho_{a}} \sum_{\gamma_{b} B_{b}} g^{*}_{\gamma_{a}\rho_{a}}[\phi_{a}(\gamma_{a}, B_{a}), \gamma_{a}B_{a}] C_{j_{a}k_{a}j_{b}k_{b}}[\gamma_{a}, \gamma_{b}, B_{a}B_{b}] + \text{(the minus part)} \right] ,
\]

\[
0 < \gamma_{a} < \gamma_{a}(B_{a}) , \quad \pi > \gamma_{b} > \gamma_{b}(B_{a}) .
\]  
(80)

where \(g\) and \(c\) are matrices in vibrational quantum numbers. We further remark that \(I_{a}\) and \(I_{b}\) both appear as dummy indices. It is therefore sufficient to satisfy the matching equations for each \(l\) separately, i.e.,

\[
g^{*}_{l_{a}l_{b}}[\phi_{a}(\gamma_{a}), \gamma_{a}]C^{\ast}_{j_{a}k_{a}j_{b}k_{b}}[\gamma_{a}, \gamma_{b}, B_{a}B_{b}] + \text{(the minus part)} = Z_{a_{b}}^{1/2} \left[ \sum_{\rho_{a}} \sum_{\gamma_{b} B_{b}} g^{*}_{\gamma_{a}\rho_{a}}[\phi_{a}(\gamma_{a}, B_{a}), \gamma_{a}B_{a}] C_{j_{a}k_{a}j_{b}k_{b}}[\gamma_{a}, \gamma_{b}, B_{a}B_{b}] + \text{(the minus part)} \right] ,
\]

\[
0 < \gamma_{a} < \gamma_{a}(B_{a}) , \quad \pi > \gamma_{b} > \gamma_{b}(B_{a}) .
\]  
(81)

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\[ \times g_{\phi}^{r}(\gamma_{b}, B_{w}, \gamma_{r}, B_{o}), \gamma_{r}(\gamma_{b}, B_{w})c_{r}^{i}c_{o}^{i}c_{o}^{j}c_{o}^{j}[y(\gamma_{b}, B_{w})] + \text{(the minus part)} \}, \quad 0 < \gamma_{r} < \gamma_{o}(B_{w}), \quad \pi > \gamma_{r} > \gamma_{o}(B_{w}). \] (81)

In addition, we also have a corresponding equation for the derivatives normal to the surface. This involves differentiation both with respect to \( \phi \) and \( \gamma \).

In Appendix B, it is shown that, in case the derivatives with respect to \( \gamma \) are ignored (this is justified at least when \( \gamma_{o} \) is small enough), the relation between \( \frac{d}{d\phi} \) and \( \frac{d}{d\phi_{o}} \) is given by

\[ \frac{d}{d\phi} = f(\gamma) \frac{d}{d\phi_{o}}, \] (82)

where

\[ f(\gamma) = -\cot 2\phi_{o} \frac{\tan \phi_{o} - \rho_{o}}{\rho_{o} - \rho} \frac{\tan \phi_{o}}{\rho_{o} - \rho} \] (83)

In performing the matching for the derivatives, one has to be careful to also include \( R_{o}(\gamma_{o}) \) and \( R_{o}(\gamma_{o}) \) which appear in front of the corresponding summation sign of each term in Eq. (77). In Appendix C, it is shown that

\[ \frac{d}{d\phi} = \left( g(\gamma_{o}) \right) \frac{d}{d\phi_{o}} \] (84)

where \( \rho_{o} = \sqrt{\rho_{0}^{2} - \gamma_{o}^{2}} \), and \( \rho_{o} = \rho_{o} = \rho_{o} \).

Similar matching equations also exist on the \( \pi_{o} \) and \( \pi_{w} \) surfaces for each set of initial conditions \( \lambda_{i}, j_{i}, v_{i}, \) and \( \Omega_{i} \).

A. Asymptotic conditions in the IOS formulation

The coefficients \( c_{r}^{i}c_{o}^{i}c_{o}^{j}c_{o}^{j} \) in Eq. (60) must be chosen so that they satisfy the matching equations as well as the proper asymptotic behavior. In this section, we will see how the asymptotic conditions translate in terms of the \( \gamma \)-dependent \( C \) coefficients defined through Eq. (62). The asymptotic conditions are

\[ \sum_{i_{1}} \sum_{j_{1}} Y_{i_{1}j_{1}}(\gamma_{o})c_{r}^{i_{1}}c_{o}^{i_{1}}c_{o}^{j_{1}}c_{o}^{j_{1}}(R_{o}, \gamma_{o}) + \text{(the minus part)} = (|v_{o}|)^{-1/2} \left[ \delta_{o}^{r} \delta_{o}^{o} Y_{1,1}^{r} \sum_{i_{1}} \frac{(2i_{1} + 1)}{2j_{1} + 1} \langle l_{o} | 0_{o} | \gamma_{o} \rangle \langle l_{o} | 0_{o} | \gamma_{o} \rangle R_{o}^{r}c_{o}^{i_{1}}c_{o}^{i_{1}}(R_{o}) \right] \] (85)

where

\[ v_{o}^{r} = \frac{\pi_{o}^{r}}{e^{\gamma_{o}}} \] (86)

We remark that asymptotically this differs from the corresponding expression in SK by a phase factor, which must be taken into account when constructing the scattering amplitudes. We have included a superscript \( (\ast) \) in the \( g \) functions to denote that they correspond to the asymptotic region where \( R_{o} \) is the propagation coordinate. Now, employing Eqs. (58) and (62) and completeness with respect to the \( Y_{1}^{r}c_{o}^{i}(\gamma_{o}, 0) \), we obtain the asymptotic conditions for IOS functions given by

\[ \sum_{i_{1}} R_{o}^{r}c_{o}^{i_{1}}c_{o}^{i_{1}}(\gamma_{o}) + \text{(the minus part)} = (|v_{o}|)^{-1/2} \left[ \delta_{o}^{r} \delta_{o}^{o} Y_{1,1}^{r} \sum_{i_{1}} \frac{(2i_{1} + 1)}{2j_{1} + 1} \langle l_{o} | 0_{o} | \gamma_{o} \rangle \langle l_{o} | 0_{o} | \gamma_{o} \rangle R_{o}^{r}c_{o}^{i_{1}}c_{o}^{i_{1}}(R_{o}) \right] \] (87)

where we have again replaced \( j \) by \( j \) in Eq. (86).

Again, it is sufficient to satisfy this condition for each \( i_{1} \) separately. Thus, we obtain the asymptotic conditions on the IOS function

\[ g_{i_{1}}^{r}(\gamma_{o})c_{o}^{i_{1}}c_{o}^{i_{1}}(\gamma_{o}) + \text{(the minus part)} = (|v_{o}|)^{-1/2} \left[ \delta_{o}^{r} \delta_{o}^{o} Y_{1,1}^{r} \sum_{i_{1}} \frac{(2i_{1} + 1)}{2j_{1} + 1} \langle l_{o} | 0_{o} | \gamma_{o} \rangle \langle l_{o} | 0_{o} | \gamma_{o} \rangle R_{o}^{r}c_{o}^{i_{1}}c_{o}^{i_{1}}(R_{o}) \right], \] (88)

where \( j_{i}, n_{i}, v_{i}^{r}, g^{r}, c_{o}^{i}c_{o}^{i} \), and \( R_{i_{1}}^{r}c_{o}^{i_{1}}(\gamma_{o}) \) are matrices in the vibrational quantum numbers. The \( \gamma \)-dependent \( R \) matrix is related to the physical \( R \) matrix by [cf. Eq. (87)]

\[ R_{i_{1}}^{r}c_{o}^{i_{1}}c_{o}^{i_{1}}(\gamma_{o}) = \sum_{m_{1}} \frac{(2m_{1} + 1)}{2j_{1} + 1} \langle l_{o} | 0_{o} | \gamma_{o} \rangle \langle l_{o} | 0_{o} | \gamma_{o} \rangle R_{o}^{r}c_{o}^{i_{1}}c_{o}^{i_{1}}(R_{o}), \] (89)

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Equations (88) and (89) together with the corresponding asymptotic condition for the derivative hold in the range \(0 \leq \gamma_s \leq \pi\). In the above equation, we first sum over \(l_s\) and then use the orthogonality of \(Y_{l_s}^m(\gamma_s, 0)\) to obtain the inverted relation

\[
R_{\lambda_1}^{\lambda_2} R_{\lambda_2}^{\lambda_1} \gamma_s = \sum_{l_s} 2\pi \int_0^\pi Y_{l_s}^m(\gamma_s, 0) R_{\lambda_2}^{\lambda_1} Y_{l_s}^m(\gamma_s) \sin \gamma_s \, d\gamma_s .
\]

(90)

Thus, once we know the \(R\) matrix defined by the asymptotic condition (88) and the matching conditions (81) [together with the analog of Eq. (81) on the \(\pi_{ac}\) and \(\pi_{ac}\) surfaces], and the corresponding equation for the derivatives, we can construct the approximate \(BFR\) matrix by using the above equation. However, it is possible to further simplify the equation determining the \(\gamma\)-dependent \(R\) matrix in Eq. (88).

B. Further simplifications of equations determining the \(\gamma\)-dependent IOS \(R\) matrix

An important feature of the IOS matching and asymptotic conditions is that they decouple for a given initial channel index \(\lambda_s\). In this section, we consider the case when \(\lambda_s = \lambda\). The expressions for the other cases can then be written by inspection.

With \(\lambda_s = \lambda\), the matching equation (81) becomes

\[
\Phi_\lambda \left[ \phi_s(\gamma_s), \gamma_s \right] = c_{\lambda_1}^{\lambda_2} \Phi_\lambda \left[ \phi_s(\gamma_s), \gamma_s \right] + (\text{the minus part}) = \sum_{\alpha} c_{\lambda_1}^{\lambda_2} \left[ \Delta_{\alpha}(\gamma_s, B_\alpha) \right] \times c_{\lambda_1}^{\lambda_2} \left[ \phi_s(\gamma_s, B_\alpha), \gamma_s \right] + (\text{the minus part}) , \quad 0 \leq \gamma_s \leq \gamma_{\alpha_0}(B_\alpha)
\]

(91)

and a corresponding equation for the derivative with respect to \(\phi_s\). In addition, Eq. (88) can be rewritten in the form

\[
\tilde{\Phi}_\lambda \left[ \phi_s(\gamma_s), \gamma_s \right] = c_{\lambda_1}^{\lambda_2} \Phi_\lambda \left[ \phi_s(\gamma_s), \gamma_s \right] + (\text{the minus part}) = \left( V \right)^{-1/2} \left[ \Phi_\lambda \left[ \phi_s(\gamma_s), \gamma_s \right] \right] \times \sum_{\alpha} c_{\lambda_1}^{\lambda_2} \left[ \Delta_{\alpha}(\gamma_s, B_\alpha) \right] \times c_{\lambda_1}^{\lambda_2} \left[ \phi_s(\gamma_s, B_\alpha), \gamma_s \right] + (\text{the minus part}) , \quad 0 \leq \gamma_s \leq \pi
\]

(92)

and

\[
\Phi_\lambda \left[ \phi_s(\gamma_s), \gamma_s \right] = c_{\lambda_1}^{\lambda_2} \Phi_\lambda \left[ \phi_s(\gamma_s), \gamma_s \right] + (\text{the minus part}) = \left( V \right)^{-1/2} R_{\lambda_1}^{\lambda_2} \left( \gamma_s, \gamma_{\alpha_0}(B_\alpha) \right) \times \sum_{\alpha} c_{\lambda_1}^{\lambda_2} \left[ \Delta_{\alpha}(\gamma_s, B_\alpha) \right] \times c_{\lambda_1}^{\lambda_2} \left[ \phi_s(\gamma_s, B_\alpha), \gamma_s \right] + (\text{the minus part}) , \quad 0 \leq \gamma_s \leq \pi
\]

(93)

We notice next that all the dependence on the \(\Omega\) quantum numbers is in the \(c\) coefficients and the \(R\)-matrix elements. Thus, the \(c\) summation in Eq. (91) can be absorbed into \(\tilde{c}\) coefficients. With this in mind, we make the definitions

\[
\tilde{c}_{\lambda_1}^{\lambda_2} \left( \gamma_s \right) = c_{\lambda_1}^{\lambda_2} \left( \gamma_s \right),
\]

(94)

\[
\tilde{c}_{\lambda_1}^{\lambda_2} \left( \gamma_s \right) = \sum_{\alpha} c_{\lambda_1}^{\lambda_2} \left[ \Delta_{\alpha}(\gamma_s, B_\alpha) \right] c_{\lambda_1}^{\lambda_2} \left( \gamma_s \right),
\]

(95)

and

\[
\tilde{R}_{\lambda_1}^{\lambda_2} \left( \gamma_s \right) = \sum_{\alpha} c_{\lambda_1}^{\lambda_2} \left[ \Delta_{\alpha}(\gamma_s, B_\alpha) \right] R_{\lambda_1}^{\lambda_2} \left( \gamma_s \right).
\]

(96)

We also notice that the transformations (94) and (95) do not affect the inhomogeneous term in Eq. (92). Furthermore, since all the quantities

\[
\tilde{c}_{\lambda_1}^{\lambda_2} \left( \gamma_s \right), \quad \tilde{c}_{\lambda_1}^{\lambda_2} \left( \gamma_s \right), \quad \tilde{R}_{\lambda_1}^{\lambda_2} \left( \gamma_s \right),
\]

and

\[
\tilde{R}_{\lambda_1}^{\lambda_2} \left( \gamma_s \right)
\]

are related by linear equations, they must all have the same common factor as in the inhomogeneous term. We therefore obtain

\[
\begin{bmatrix}
\tilde{c}_{\lambda}^{\lambda_1} \\
\tilde{R}_{\lambda}
\end{bmatrix} = \begin{bmatrix}
\left(2l + 1\right) 2\pi \int_0^\pi Y_{l}^{m}(\gamma_s, 0) R_{\lambda_1}^{\lambda} Y_{l}^{m}(\gamma_s) \sin \gamma_s \, d\gamma_s.
\end{bmatrix}
\]

(97)

We also notice that the transformations (94) and (95) do not affect the inhomogeneous term in Eq. (92). Furthermore, since all the quantities

\[
\tilde{c}_{\lambda_1}^{\lambda_2} \left( \gamma_s \right), \quad \tilde{c}_{\lambda_1}^{\lambda_2} \left( \gamma_s \right), \quad \tilde{R}_{\lambda_1}^{\lambda_2} \left( \gamma_s \right),
\]

and

\[
\tilde{R}_{\lambda_1}^{\lambda_2} \left( \gamma_s \right)
\]

are related by linear equations, they must all have the same common factor as in the inhomogeneous term. We therefore obtain

\[
\begin{bmatrix}
\tilde{c}_{\lambda}^{\lambda_1} \\
\tilde{R}_{\lambda}
\end{bmatrix} = \begin{bmatrix}
\left(2l + 1\right) 2\pi \int_0^\pi Y_{l}^{m}(\gamma_s, 0) R_{\lambda_1}^{\lambda} Y_{l}^{m}(\gamma_s) \sin \gamma_s \, d\gamma_s.
\end{bmatrix}
\]

(98)

In addition, corresponding to Eqs. (98) and (99), we also have three more equations for the derivative. Thus, these six sets of equations are sufficient to determine the six unknown matrices \(\tilde{c}_{\lambda}^{\lambda_1}(\gamma_s), \tilde{c}_{\lambda}^{\lambda_1}(\gamma_s), \tilde{R}_{\lambda}(\gamma_s), \tilde{R}_{\lambda}(\gamma_s), \) and \(\tilde{R}_{\lambda}(\gamma_s)\) in the range \(0 \leq \gamma_s \leq \gamma_{\alpha_0}(B_\alpha)\).
In a similar way, the matching on the \( \pi \) plane determines \( R^{\nu}_{\nu}(\gamma) \) and \( R^{\nu}_{\nu}(\gamma) \) for the range \( \gamma_{\pi} \leq \gamma \leq \pi, \ 0 \leq \gamma \leq \gamma_{\pi} \). Finally, we notice that the matching and the asymptotic equations on the \( \pi \) surface have no inhomogeneous part when \( \lambda = \nu \). We therefore have:

\[
R^{\nu \nu}_{\nu \nu}(\gamma) = 0, \quad \nu > \gamma > \gamma_{\pi}.
\]

(101)

\[
R^{\nu \nu}_{\nu \nu}(\gamma) = 0, \quad 0 > \gamma > \gamma_{\pi}.
\]

(102)

We also notice that, since the asymptotic conditions and the matching conditions are independent of \( j, j_1, \Omega_1 \), and \( \Omega \), the \( R^{\nu \nu}_{\nu \nu}(\gamma) \) are also independent of these quantum numbers. Obviously, this feature also holds for the other possible initial conditions as well (i.e., for \( \lambda = \nu \) or \( \kappa \)).

**VIII. CONNECTION WITH THE COORDINATE REPRESENTATION AND PHYSICAL BODY FIXED R MATRICES**

The IOS approximation for reactive scattering as developed in the previous sections yields a set of R matrices that carry one angular label. They are reminiscent of the coordinate representation R-matrices developed in Sec. II. In this section, we investigate the connection between the IOS approximate \( \gamma \)-dependent R-matrices and \( R(\gamma_{\nu} | \nu) \).

In Sec. II, we have the following relationship between the BF R-matrix elements and \( R(\gamma_{\nu} | \nu) \) [cf. Eq. (8)]:

\[
R^{\nu \nu}_{\nu \nu}(\gamma_{\nu} | \nu) = \sum_{I = j, \Omega} Y_{I \nu}(\gamma_{\nu}, 0)
\]

\[
\times R^{\nu \nu}_{\nu \nu}(\nu, 0) Y^{*}_{I \nu}(\gamma_{\nu}, 0).
\]

(103)

On the other hand, summing over \( I \) in Eq. (89), we obtain for the initial \( I \)-labeled IOS the expression

\[
\sum_{I = j, \Omega} Y_{I \nu}(\gamma_{\nu}, 0) R^{\nu \nu}_{\nu \nu}(\nu, 0) Y^{*}_{I \nu}(\gamma_{\nu}, 0) = \sum_{I = j, \Omega} R^{\nu \nu}_{\nu \nu}(\gamma_{\nu}, 0).
\]

(104)

Now, using Eqs. (96) and (97) in the right hand side of the above equation, we obtain the result

\[
\sum_{I = j, \Omega} Y_{I \nu}(\gamma_{\nu}, 0) R^{\nu \nu}_{\nu \nu}(\nu, 0) Y^{*}_{I \nu}(\gamma_{\nu}, 0) = \sum_{I = j, \Omega} R^{\nu \nu}_{\nu \nu}(\gamma_{\nu}, 0).
\]

(105)

Thus, we now notice a remarkable feature of the I-labeled IOS. The IOS approximate configuration space R-matrix elements are not local in \( \gamma_{\nu} \) and \( \gamma_{\nu} \) (or \( \gamma_{\pi} \)). If, on the other hand, \( I \) is set equal to \( J \), then the \( R \) in Eqs. (106) and (107) are independent of \( I \). The I summation therefore yields \( \delta_{\nu \nu} \nu_{\nu} \) and the \( J \) summation yields \( \delta_{\nu \nu} \gamma_{\nu} \) for the \( I \)-labeled IOS. Thus, with \( J \) labeling, one does obtain localization. This localization, however, is quite undesirable as it leads to several unphysical features as pointed out by Khare and Kouri in connection with rotationally inelastic scattering. This is in contrast to \( R^{\nu \nu}_{\nu \nu}(\gamma_{\nu}) \), which is local in the present reactive IOS. The nonlocality only arises when one constructs the J-labeled quantities. This is similar to the nonreactive situation where the initial-I-labeled IOS conserves the projection of rotor angular momentum along the final momentum axis, but when helicity amplitudes (for a given \( J \)) are computed, they are nondiagonal in helicity.

Thus, the I-labeled IOS results in a nonlocal \( R \) matrix given by Eqs. (106) and (107). Unfortunately, this matrix also depends upon the matching surface as \( \tilde{R} \), depends upon it [cf. Eq. (105)]. It is expected that, for collinear dominated reactive systems, this dependence on \( B \) will not be significant.

Alternatively, we can suggest at least one model to eliminate this \( B \) dependence. For a given \( \gamma_{\nu} \) and \( \gamma_{\nu} \), we choose \( B_{\nu} \) in such a way that

\[
\gamma_{\nu}(\gamma_{\nu}, B_{\nu}) = \gamma_{\nu},
\]

so that now \( B_{\nu}(\gamma_{\nu}, \gamma_{\nu}) \) is a function of \( \gamma_{\nu} \) and \( \gamma_{\nu} \). Therefore, the \( B_{\nu} \) dependence of \( R(\gamma_{\nu} | \nu) \) may be interpreted as an additional dependence on \( \gamma_{\nu} \) and \( \gamma_{\nu} \). This will give a unique result provided that, for each \( \gamma_{\nu} \) and \( \gamma_{\nu} \), there exists a unique \( B_{\nu} \).

Once the \( \nu \)-dependent nonlocal R-matrix elements are known [cf. Eqs. (106) and (107)], the approximate physical R-matrix elements can be obtained by the use of Eq. (9). If \( B_{\nu} \) is chosen as a function of \( \gamma_{\nu} \) and \( \gamma_{\nu} \), this leads to a double integral that must be numerically evaluated. On the other hand, for a fixed \( B \), the \( \gamma_{\nu} \) integral may be trivi-
ally done and we obtain the following:

\[ R_{\lambda_{\alpha\alpha_{\lambda}} \lambda_{\alpha} \lambda_{\alpha}}^{\gamma \gamma_{\gamma} \gamma_{\gamma}} = \sum_{i_{\alpha}} \frac{2l_{\gamma} + 1}{2l_{\gamma} + 1} \langle 0| 0_{\gamma} \lambda_{\gamma} \lambda_{\gamma} | 0_{\gamma} \lambda_{\gamma} \lambda_{\gamma} \rangle \int_{0}^{1} Y_{1,0,0}^* \gamma \gamma_{\gamma} (\gamma, 0) \, d(\cos \gamma) \, , \]

where we remark that the integral formally is written from 0 to π, but it actually extends only from γ, since R(γ) is zero beyond this, as discussed in connection with Eq. (101).

For the nonreactive part, the inversion of Eq. (64) gives the same result as in the ordinary nonreactive IOS:

\[ R_{\lambda_{\alpha \lambda} \lambda_{\alpha} \lambda_{\alpha}}^{\gamma \gamma_{\gamma} \gamma_{\gamma}} = \sum_{i_{\alpha}} \frac{2l_{\gamma} + 1}{2l_{\gamma} + 1} \langle 0| 0_{\gamma} \lambda_{\gamma} \lambda_{\gamma} | 0_{\gamma} \lambda_{\gamma} \lambda_{\gamma} \rangle \int_{0}^{1} Y_{1,0,0}^* \gamma \gamma_{\gamma} (\gamma, 0) R_{\lambda_{\alpha \lambda} \lambda_{\alpha} \lambda_{\alpha}}^{\gamma \gamma_{\gamma} \gamma_{\gamma}} (\gamma, 0) \, d(\cos \gamma) \, . \]

For the simplest choice B(\gamma) = B(\gamma) = 1, Eq. (109) takes the simple form

\[ R_{\lambda_{\alpha \lambda} \lambda_{\alpha} \lambda_{\alpha}}^{\gamma \gamma_{\gamma} \gamma_{\gamma}} = \sum_{i_{\alpha}} \frac{2l_{\gamma} + 1}{2l_{\gamma} + 1} \langle 0| 0_{\gamma} \lambda_{\gamma} \lambda_{\gamma} | 0_{\gamma} \lambda_{\gamma} \lambda_{\gamma} \rangle \int_{0}^{1} Y_{1,0,0}^* \gamma \gamma_{\gamma} (\gamma, 0) \, d(\cos \gamma) \, . \]

where we have used the result that, for B(\gamma) = 1,

\[ \gamma_{\gamma} (\gamma, B(\gamma)) = \pi - \gamma_{\gamma} . \]

In the same way, we have the result for the R-matrix elements corresponding to the \( \lambda - \kappa \) transition as

\[ R_{\lambda_{\alpha \lambda} \lambda_{\alpha} \lambda_{\alpha}}^{\gamma \gamma_{\gamma} \gamma_{\gamma}} = \sum_{i_{\alpha}} \frac{2l_{\gamma} + 1}{2l_{\gamma} + 1} \langle 0| 0_{\gamma} \lambda_{\gamma} \lambda_{\gamma} | 0_{\gamma} \lambda_{\gamma} \lambda_{\gamma} \rangle \int_{0}^{1} Y_{1,0,0}^* \gamma \gamma_{\gamma} (\gamma, 0) \, d(\cos \gamma) \, . \]

The equations for the other two initial conditions \( \nu \) and \( \kappa \) may be obtained by a cyclic permutation of the indices in the equations given in this paper. All other quantities of physical interest can then be obtained by employing standard formulas.

IX. GENERALIZATION TO OTHER \( \nu \)-LABELED CHOICES

The simple expressions for the R-matrix elements obtained herein hold for the choice \( \nu = 1 \). It is for this choice of \( \nu \) and the choice of \( \nu \) independent of initial and final \( \lambda \) that the physical \( \nu \) on the left hand side of Eq. (59) becomes the same as the \( \nu \) labeling the g functions on the right hand side. Thus, for the matching, the \( \gamma \) (and \( \gamma_{\gamma} \), etc.) labeling the g function spans over the same range as the physical \( \gamma \) defining the matching surface. For a general choice of \( \nu \) and \( \lambda \), the above does not hold any longer and one has to employ Eq. (59) to construct the approximate BF wave function and then carry out matching as in the exact treatment. Although much simpler than a full CC treatment, such a procedure would be significantly more time consuming than the present \( \nu \)-labeling procedure.

On the other hand, the results given in Sec. VIII bear a remarkable resemblance to the results obtained in nonreactive IOS. In fact, the nonreactive part (110) is formally the same as that in the nonreactive case. For this case, for the SF R-matrix elements, one also has the following result for a general \( \nu \)-choice:

\[ R_{\nu \nu}^{\lambda \lambda_{\lambda}} = \sum_{i_{\lambda}} \frac{2l_{\lambda} + 1}{2l_{\lambda} + 1} \langle 0| 0_{\lambda} \lambda_{\lambda} | 0_{\lambda} \lambda_{\lambda} \rangle \int_{0}^{1} Y_{1,0,0}^* \nu \gamma_{\lambda} (\nu, 0) R_{\nu \nu}^{\lambda \lambda_{\lambda}} (\nu, 0) \, d(\cos \nu) \, , \]

where \( \nu \) can be chosen to be any function of \( \lambda \) and \( \lambda' \). With this result in hand, one may now generalize the results obtained in Sec. VIII by writing

\[ R_{\nu \nu}^{\lambda \lambda_{\lambda}} = \sum_{i_{\lambda}} \frac{2l_{\lambda} + 1}{2l_{\lambda} + 1} \langle 0| 0_{\lambda} \lambda_{\lambda} | 0_{\lambda} \lambda_{\lambda} \rangle \int_{0}^{1} Y_{1,0,0}^* \nu \gamma_{\lambda} (\nu, 0) \, d(\cos \nu) \, . \]

\[ \times 2 \int_{0}^{1} Y_{1,0,0}^* \gamma_{\lambda} (\gamma_{\lambda} \nu) \, d(\cos \gamma_{\lambda}) \, , \]

\[ \times 2 \int_{0}^{1} Y_{1,0,0}^* \nu \gamma_{\lambda} (\nu, 0) R_{\nu \nu}^{\lambda \lambda_{\lambda}} (\nu, 0) \, d(\cos \nu) \, , \]

corresponding to Eq. (109) for a general choice \( B(\nu) \). In the above equation, the \( \nu \)-labeled \( \nu \) can again be chosen to correspond to \( \nu \) in the particular case \( B(\nu) = 1 \), this takes the forms [corresponding to Eqs. (110) through (113)]:

\[ R_{\nu \nu}^{\lambda \lambda_{\lambda}} = \sum_{i_{\lambda}} \frac{2l_{\lambda} + 1}{2l_{\lambda} + 1} \langle 0| 0_{\lambda} \lambda_{\lambda} | 0_{\lambda} \lambda_{\lambda} \rangle \int_{0}^{1} Y_{1,0,0}^* \nu \gamma_{\lambda} (\nu, 0) \, d(\cos \nu) \, . \]

\[ R_{\nu \nu}^{\lambda \lambda_{\lambda}} = \sum_{i_{\lambda}} \frac{2l_{\lambda} + 1}{2l_{\lambda} + 1} \langle 0| 0_{\lambda} \lambda_{\lambda} | 0_{\lambda} \lambda_{\lambda} \rangle \int_{0}^{1} Y_{1,0,0}^* \nu \gamma_{\lambda} (\nu, 0) \, d(\cos \nu) \, . \]
for the reactive part corresponding to Eq. (111).

X. CONCLUSIONS

In this paper, we have presented an approach to reactive collisions based on the infinite order sudden approximation. This approximation consists in two separate approximations, the first being the centrifugal sudden approximation and the second being the energy sudden approximation. In our implementation of the IOS, care has been taken to ensure that l labeling is employed, thereby preserving the character of the $l^2$ operator as an orbital angular momentum. This enables one to construct functions corresponding to definite total angular momentum $J$ which have the proper transformation properties (e.g., helicity is in general not conserved even within the separate arrangement channels prior to matching; the coordinate representation of the $R$ matrix at a fixed $J$ is nonlocal in the coordinate representation, etc.). This is expected to be important in obtaining the proper matching conditions for joining solutions in various arrangements and also in satisfying the proper asymptotic boundary conditions.

The major simplifications and features provided by our IOS approximation are as follows: We are able to show by direct derivation of the IOS from the space fixed full CC equations that one may match radial IOS solutions of a single $l$ and still simultaneously fulfill the constraint that the properly rotated BF functions are being matched (cf. Sec. VIIA). Equally important, this matching is shown to be possible separately for each value of $\gamma_\lambda$, provided that one is willing to neglect the effect on the derivative matching arising from $\partial/\partial \gamma_\lambda$. This is expected to be best for collinear dominated reactions. A more complicated procedure which includes the effect of the derivatives is to construct the BF wave functions using Eq. (39) and simply do the matching as in the full CC theory.\cite{4,5} Similar simplifications apply when deriving the IOS asymptotic boundary conditions from the full CC boundary conditions. The integration of the IOS equations [Eq. (27)] proceeds similarly to the exact CC method except that it is done for fixed $\gamma_\lambda$ (or $\gamma_\nu$ or $\gamma_\nu^*$). Also, because one is able to separately match definite l-value solutions for fixed $\gamma$ angles, one is able to work with three integration regions rather than the four regions used in the full CC method.\cite{4,5} The ultimate result of the method is to yield a $\gamma$-dependent $R$ matrix $R_{\gamma \nu}^{\lambda \lambda} (\gamma)$ which describes the reaction from the $\lambda$ arrangement with the $K$ molecule in state $\nu_\lambda$ to the $\nu$ arrangement with the $K\lambda$ molecule in state $\nu_\nu$, where the orientation of the final product molecule relative to the exciting atom vector remains frozen at an angle $\gamma_\nu$. The angle $\gamma_\nu$ is determined by the angle between the initial molecule axis and the incident atom vector $\gamma_\lambda$, and the surface on which the matching between arrangements was done. The construction of the more usual $R$ matrix proceeds via Eq. (109), which, in the case where $\lambda = \nu$, reduces to the standard nonreactive IOS expression.

We are currently carrying out detailed numerical studies for several systems and will report the results later.

APPENDIX A: THE $\gamma \to \nu$ TRANSFORMATION ON THE $r_\nu = B_{\nu \lambda} r_\lambda$ SURFACE

The general transformation between $(r_\lambda, R_\lambda)$ and $(r_\nu, R_\nu)$ is given by an orthogonal matrix $M$:

$$
\begin{bmatrix}
R_\nu \\
R_\nu^* 
\end{bmatrix} = M 
\begin{bmatrix}
R_\lambda \\
R_\lambda^* 
\end{bmatrix},
$$

(A1)

where

$$
M = \begin{bmatrix}
\cos \alpha_\nu & -\sin \alpha_\nu \\
\sin \alpha_\nu & \cos \alpha_\nu
\end{bmatrix},
$$

(A2)

and

$$
\cos \alpha_\nu = \frac{m_{\nu} m_{\lambda}}{(m_{\nu} + m_{\lambda})(m_{\nu} + m_{\lambda})}^{1/2},
$$

(A3)

From Eqs. (A1) and (A2), we obtain

$$
\gamma_\nu^2 = R_\nu^2 \sin^2 \alpha_\nu + R_\nu^2 \cos^2 \alpha_\nu + r_\lambda R_\lambda \cos \gamma_\lambda \sin 2\alpha_\nu,
$$

(A4)

and

$$
R_\nu^2 = R_\lambda^2 + r_\lambda^2 - 2 r_\lambda R_\lambda \cos \gamma_\lambda.
$$

(A5)

On the surface $r_\nu = B_{\nu \lambda} r_\lambda$, the three variables $R_\lambda$, $r_\lambda$, and $\gamma_\lambda$ are not independent but fulfill the relation

$$
R_\lambda^2 \sin^2 \alpha_\nu + R_\lambda^2 (\cos^2 \alpha_\nu - B_{\nu \lambda}^2) + r_\lambda R_\lambda \cos \gamma_\lambda \sin 2\alpha_\nu = 0.
$$

(A6)

If $\cot \phi_\lambda$ is defined as

$$
\cot \phi_\lambda = \frac{r_\lambda}{R_\lambda},
$$

then Eq. (A6) yields

$$
\cot \phi_\lambda = \frac{\sin \alpha_\nu}{R_\lambda - \cos \alpha_\nu} \times (\cos \alpha_\nu \cos \gamma_\lambda + B_{\nu \lambda} \sin \gamma_\lambda \cos \alpha_\nu),
$$

(A8)

which reduces to the KSB result for $B_{\nu \lambda} = 1$. The surface $r_\nu = B_{\nu \lambda} r_\lambda$ also determines uniquely the value of $\gamma_\nu$ (the $\gamma$ angle in the $\nu$ channel) corresponding to $\gamma_\lambda$.

It is well known that

$$
\cos \gamma_\nu = \frac{(r_\nu \cdot R_\nu)}{r_\nu R_\nu}.
$$

(A9)

Applying Eq. (A1) leads to

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\[
\cos \gamma_{\nu} = \frac{1}{R_{R_{\nu}}} \left[ \frac{1}{2} (R_{\alpha}^2 - r_{\nu}) \sin 2\alpha_{\nu} + R_{\alpha} r_{\nu} \cos \gamma_{\nu} \cos 2\alpha_{\nu} \right],
\]
which on the surface \( r_{\nu} = B_{a_{\nu}} r_{a} \) reduces to
\[
\cos \gamma_{\nu} = \frac{\cos \gamma_{\nu} + (1 - B_{a_{\nu}}^2) \cot \phi_{a_{\nu}} \cot \alpha_{\nu}}{B_{a_{\nu}}^2 \left( 1 + (1 - B_{a_{\nu}}^2) \cot^2 \phi_{a_{\nu}} \right)},
\]
where \( \cot \phi_{a_{\nu}} \) is given by Eq. (A8). For \( B_{a_{\nu}} = 1 \), \( \cos \gamma_{\nu} \) becomes \(-\cos \gamma_{\nu} \) or \( \gamma_{\nu} = \pi - \gamma_{\nu} \). Another important angle is \( \phi_{a_{\nu}} \), the angle in the \( \nu \) channel which corresponds to \( \phi_{a_{\nu}} \). As in Eq. (A7), we define \( \cot \phi_{a_{\nu}} \) by
\[
\cot \phi_{a_{\nu}} = \frac{r_{\nu}}{R_{R_{\nu}}}.
\]
Again, making use of the relation \( r_{\nu} = B_{a_{\nu}} r_{a} \), we obtain
\[
\cot \phi_{a_{\nu}} = \frac{B_{a_{\nu}}}{\sqrt{1 - B_{a_{\nu}}^2} \cot \phi_{a_{\nu}} + 1},
\]
For \( B_{a_{\nu}} = 1 \), \( \phi_{a_{\nu}} \) becomes equal to \( \phi_{a_{\nu}} \). The last angle of interest is \( \Delta_{a_{\nu}} \). It is defined by
\[
\cos \Delta_{a_{\nu}} = \frac{(R_{\alpha} - R_{a})}{R_{R_{\nu}} R_{\alpha}}.
\]
Applying Eq. (A1), we obtain
\[
\cos \Delta_{a_{\nu}} = \frac{R_{a} \cos \gamma_{\nu} - r_{\nu} \cos \gamma_{\nu}}{\sqrt{1 + (1 - B_{a_{\nu}}^2) \cot^2 \phi_{a_{\nu}}}}.
\]
On the surface \( r_{\nu} = B_{a_{\nu}} r_{a} \), the equation for \( \cos \Delta_{a_{\nu}} \) takes the form
\[
\cos \Delta_{a_{\nu}} = \frac{\cos \gamma_{\nu} - \cos \gamma_{\nu} \sin \gamma_{\nu} \cot \alpha_{\nu}}{\sqrt{1 + (1 - B_{a_{\nu}}^2) \cot^2 \phi_{a_{\nu}}}}.
\]
To conclude this Appendix, we discuss the validity range of \( B_{a_{\nu}} \). By definition, \( B_{a_{\nu}} \) is real and positive and so it has to be in the range \( 0 < B_{a_{\nu}} < \infty \). However, from Eq. (A8), we find that, in order for \( \cot \phi_{a_{\nu}} \) to be real, \( B_{a_{\nu}} \) has to fulfill the constraint
\[
B_{a_{\nu}} > | \sin \gamma_{\nu} \cos \gamma_{\nu} |.
\]
Since Eq. (A17) has to hold for any \( \gamma_{\nu} \), the validity range for \( B_{a_{\nu}} \) becomes
\[
| \cos \gamma_{\nu} | < B_{a_{\nu}} < \infty.
\]
\section*{APPENDIX B: THE RELATION BETWEEN \( \partial / \partial \phi_{a_{\nu}} \) \( \rho_{\nu} \gamma_{\nu} \) and \( \partial / \partial \phi_{a_{\nu}} \) \( \rho_{\nu} \gamma_{\nu} \) ON THE MATCHING SURFACE}

In order to find the relation between \( \partial / \partial \phi_{\alpha} \) and \( \partial / \partial \phi_{\beta} \) on the matching surface, one must first determine the relation between the two for an arbitrary point in configuration space, and then consider it for a point on the surface.

Each point in configuration space can be described in terms of the \( \alpha \) channel coordinates \( \phi_{\alpha}, \rho_{\alpha}, \gamma_{\alpha} \) or the \( \nu \) channel coordinates \( \phi_{\nu}, \rho_{\nu}, \gamma_{\nu} \). For each arrangement channel, we consider three sets of coordinates: \( (R_{\alpha}, r_{\alpha}, \gamma_{\alpha}), (\phi_{\alpha}, \rho_{\alpha}, \gamma_{\alpha}) \), and \( (\phi_{\omega}, \rho_{\omega}, \gamma_{\omega}) \) (see Fig. 2). While \( \gamma_{\alpha} \) is common to all three sets, the other two coordinates in each set are related in the following ways: (1) the \( (R_{\alpha}, r_{\alpha}) \) and \( (\phi_{\alpha}, \rho_{\alpha}) \) relations
\[
\gamma_{\alpha} = \gamma_{\nu} \sin \alpha_{\nu} \cos \gamma_{\nu},
\]
(2) the \( (R_{\alpha}, r_{\alpha}) \) and \( (\zeta_{\alpha}, \eta_{\alpha}) \) relations
\[
\gamma_{\alpha} = \zeta_{\alpha} \sin \eta_{\alpha},
\]
and (3) the \( (\rho_{\alpha}, \phi_{\alpha}) \) and \( (\zeta_{\alpha}, \eta_{\alpha}) \) relations
\[
\zeta_{\alpha} = \sqrt{\rho_{\alpha} \cos \phi_{\alpha}} + (R_{\alpha} - \rho_{\alpha} \sin \phi_{\alpha})^2,
\]
\[
\tan \eta_{\alpha} = \frac{\rho_{\alpha} \cos \phi_{\alpha}}{R_{\alpha} - \rho_{\alpha} \sin \phi_{\alpha}}.
\]
In order to find the relation between \( \partial / \partial \eta_{\nu} \) and \( \partial / \partial \eta_{\nu} \), we have to find the relation between \( \partial / \partial \eta_{\nu} \) and \( \partial / \partial \eta_{\nu} \) because the \( (\zeta_{\alpha}, \eta_{\alpha}) \) coordinates are more convenient for transformation from one arrangement channel to the other. The second and third steps consist of finding the relation between \( \partial / \partial \eta_{\nu} \) and \( \partial / \partial \phi_{\alpha} \), where \( \alpha = \lambda, \nu \). The desired transformation will be, accordingly, a product of the three transformations.

1. The relation between \( \partial / \partial \eta_{\nu} \) \( \gamma_{\nu} \) and \( \partial / \partial \eta_{\nu} \) \( \gamma_{\nu} \) on the matching surface

In general, \( \partial / \partial \eta_{\nu} \) \( \gamma_{\nu} \) takes the form
\[
\frac{\partial}{\partial \eta_{\nu}} = \frac{\partial \eta_{\nu}}{\partial \eta_{\nu}} \frac{\partial}{\partial \gamma_{\nu}} + \frac{\partial \gamma_{\nu}}{\partial \rho_{\nu}} \frac{\partial}{\partial \rho_{\nu}} + \frac{\partial \gamma_{\nu}}{\partial \phi_{\nu}} \frac{\partial}{\partial \phi_{\nu}}.
\]
This equation can be simplified because \( \zeta_{\nu} \) (like \( \xi_{\nu} \)) is an independent variable and therefore is not dependent on \( \eta_{\nu} \). Furthermore, it is found that \( \partial / \partial \gamma_{\nu} \) derivatives always appear with a multiplicative factor proportional to \( \sin \gamma_{\nu} \). In our IOS treatment, we consistently neglect these terms. Consequently,
\[
\frac{\partial}{\partial \eta_{\nu}} \frac{\partial}{\partial \gamma_{\nu}} = \frac{\partial \eta_{\nu}}{\partial \eta_{\nu}} \frac{\partial}{\partial \gamma_{\nu}}.
\]
To derive \( \partial / \partial \eta_{\nu} \), we have to express \( \eta_{\nu} \) in terms of \( \eta_{\nu} \). To do this, we make use of the transformation given in Eqs. (A1) and (A2), so that
\[
R_{\alpha}^2 = R_{\alpha}^2 \cos \alpha_{\alpha} + R_{\alpha}^2 \sin \alpha_{\alpha} - R_{\alpha} \gamma_{\nu} \sin 2\alpha_{\nu} \cos \gamma_{\nu},
\]
\[
R_{\nu}^2 = R_{\nu}^2 \sin \gamma_{\nu} + R_{\nu}^2 \sin \gamma_{\nu} \cos \gamma_{\nu} + R_{\nu} \sin 2\alpha_{\nu} \cos \gamma_{\nu}.
\]
Dividing Eq. (B7) by (B6) and applying Eq. (B2), we obtain
\[
\tan \gamma_{\nu} = \sin \gamma_{\nu} + \tan \gamma_{\nu} \sin \gamma_{\nu} + \tan \gamma_{\nu} \sin 2\alpha_{\nu} \cos \gamma_{\nu}.
\]
\[
\cos \gamma_{\nu} + \tan \gamma_{\nu} \sin \gamma_{\nu} - \tan \gamma_{\nu} \sin 2\alpha_{\nu} \cos \gamma_{\nu}.
\]
Since
\[ \frac{\delta \eta_a}{\delta \eta_k} = \frac{1}{2} \cos^2 \eta_k \cot \phi_r \frac{d}{d (\tan \eta_k)}, \]  
(B9)
we obtain
\[ \frac{\delta \eta_a}{\delta \eta_k} = \frac{\delta \eta_a}{\delta \phi_r} \frac{\delta \phi_r}{\delta \eta_k} \frac{\delta \phi_r}{\delta \phi_r} \times (\cot 2 \eta_a \sin 2 \alpha_r \cos \gamma_k + \cos 2 \alpha_r), \]  
(B10)
On the matching surface, the following relations hold:
\[ r = B_a r, \ \phi = \frac{\pi}{2} - \eta_a, \ \phi = \frac{\pi}{2} - \eta_k, \]  
(B11)
\[ \cot \phi_a = \frac{B_a}{B_a - \cos \alpha_r}, \]  
\[ \times (\cos \alpha_r \cos \gamma_k + \frac{1}{\sqrt{1 + (1 - B_a^2) \cot^2 \phi_a}}), \]  
(B12)
\[ \cot \phi_a = \frac{B_a}{(1 - B_a^2) \cot \phi_a + 1}, \]  
(B13)
[Equations (B12) and (B13) were derived in Appendix A].
Substitution of Eq. (B11) in (B10) leads to
\[ \frac{\delta \eta_a}{\delta \eta_k} = B_a^2 \cot \phi_r (\cot 2 \phi_a, \sin 2 \alpha_r \cos \gamma_k + \cos 2 \alpha_r), \]  
(B14)
which together with Eqs. (B11) and (B12) form the desired transformation.

2. The relation between \(\partial/\partial \eta_k\) and \(\partial/\partial \phi_a\) on the matching surface.
From Eq. (B2), it can be seen that, in general, \(\phi_a\) depends on \(\eta_k\) and \(\eta_k\). Consequently,
\[ \frac{\partial}{\partial \phi_a} = \frac{\partial \eta_a}{\partial \phi_a} \frac{\partial}{\partial \eta_k} + \frac{\partial \eta_a}{\partial \phi_a} \frac{\partial}{\partial \eta_k}. \]  
(B15)
However, as we are interested in this relation on the matching surface, it can be shown that there is one has
\[ \frac{\partial \eta_a}{\partial \phi_a} = 0, \]  
(B16)
and therefore we have to consider
\[ \frac{\partial}{\partial \phi_a} = \frac{\partial \eta_a}{\partial \phi_a} \frac{\partial}{\partial \eta_k}. \]  
(B17)
Applying Eq. (B3), we obtain
\[ \frac{\partial \eta_a}{\partial \phi_a} = \frac{\partial \eta_a}{\partial \phi_a} \cos \eta_a \sin \eta_a \cos \phi_a. \]  
(B18)
On the surface, \(\eta_a = \frac{\pi}{2} - \phi_a\) and so Eq. (B18) becomes
\[ \frac{\partial \eta_a}{\partial \phi_a} = - \frac{\partial}{\partial \phi_a} \sin \phi_a. \]  
(B19)
Thus, we obtain
\[ \frac{\partial}{\partial \phi_a} = - \frac{\partial}{\partial \phi_r} \sin \phi_a \frac{\partial \eta_a}{\partial \phi_a}. \]  
(B20)

3. The final transformation.
Our aim is to find the relation between \(\partial/\partial \phi_a\) and \(\partial/\partial \phi_r\) on the matching surface. According to the preceding analysis, this relation can be written as
\[ \frac{\partial}{\partial \phi_a} = \frac{\partial}{\partial \phi_r} \frac{\partial \eta_a}{\partial \phi_r} \frac{\partial}{\partial \phi_r}, \]  
(B21)
Substitution of Eqs. (B14) and (B20) into Eq. (B21) leads to the final result
\[ \frac{\partial}{\partial \phi_a} = \frac{B_a^2 \cot \phi_a}{\cot \phi_a} (- \cot 2 \phi_a \sin 2 \alpha_r \cos \gamma_k + \cos 2 \alpha_r), \]  
(B22)
If Eq. (A13) is now applied for the ratio \(\cot \phi_a/\cot \phi_k\), then Eq. (B22) becomes
\[ \frac{\partial}{\partial \phi_a} = - \frac{\cot 2 \phi_a \sin 2 \alpha_r \cos \gamma_k + \cos 2 \alpha_r}{\sqrt{1 + (1 - B_a^2) \cot^2 \phi_a}} \frac{\partial}{\partial \phi_a}. \]  
(B23)
For the case \(B_a = 1\), this relation takes the form
\[ \frac{\partial}{\partial \phi_a} = - \frac{1}{\sin \gamma_k} \frac{\partial}{\partial \phi_a}, \]  
(B24)
or, since \(\gamma_k\) is always assumed to be small,
\[ \frac{\partial}{\partial \phi_a} = - \frac{\partial}{\partial \phi_a}. \]  
(B24')

**APPENDIX C: DERIVATION OF \(\partial/\partial \phi_a\) ON THE MATCHING SURFACE**

In general, we have that
\[ \frac{\partial}{\partial \phi_a} \frac{r_x R_x}{r_x R_x} = \frac{1}{(r_x R_x)^2} \frac{d}{d \phi_a} \frac{r_x R_x}{d \phi_a} \frac{g_r}{r_x R_x}. \]  
(C1)
To perform \(\partial/\partial \phi_a\) \((r_x R_x)\), we need to know the relation between \(\partial/\partial \phi_a\) and \(\partial/\partial \phi_r\), which was derived in Appendix B. Thus, if
\[ f(\gamma_k) = \frac{\cot \phi_a \sin 2 \alpha_r \cos \gamma_k + \cos 2 \alpha_r}{B_a \sqrt{1 + (1 - B_a^2) \cot^2 \phi_a}}, \]  
(C2)
then
\[ \frac{\partial}{\partial \phi_a} f(\gamma_k) = \frac{\partial}{\partial \phi_a}. \]  
(C3)
From Eq. (B1), it can be seen that
\[ r_x R_x = (r_x - \rho \cos \phi_a)(R_x - \rho \sin \phi_a), \ \alpha = \lambda, \nu, \]  
(C4)
and consequently
\[ \frac{\partial}{\partial \phi_a} (r_x R_x) = - \rho (r_x \cos \phi_a - R_x \sin \phi_a), \ \alpha = \lambda, \nu, \]  
(C5)
which on the surface becomes
\[ \frac{\partial}{\partial \phi_a} (r_x R_x) = - \rho r_x \frac{\cos 2 \phi_a}{\cos \phi_a}, \ \alpha = \lambda, \nu. \]  
(C6)
Substituting Eqs. (C2), (C3), and (C6) into Eq. (C1) leads to
\[ \frac{\partial}{\partial \phi_a} \left[ \frac{r_x R_x}{r_x R_x} \right] = - \frac{B_a \rho}{B_a \cos \phi_a} \frac{\cos 2 \phi_a \sin \phi_a \cos \gamma_k}{\sin \phi_a \cos \phi_a}. \]  
(C7)
This can also be written as

\[ \frac{\partial}{\partial \phi_a} \left[ \frac{r_x R_x}{r_x R_x} \right]. \]  

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\[ -2B_\alpha \rho \left( \frac{\tan \phi_{\alpha \beta}}{\rho_{\alpha \beta}} - \rho \tan \phi_{\alpha \beta} \right) [f(\gamma) \cot 2\phi_{\alpha \beta} - \cot 2\phi_{\alpha \beta}] \]  \hspace{1cm} (C8)

where

\[ \rho_{\alpha \beta} = \sqrt{R_{\alpha \beta}^2 + \rho_{\alpha \beta}^2}, \quad \rho_{\alpha \beta} = \rho_{\alpha \beta}. \]  \hspace{1cm} (C9)

For \( B_\alpha = 1 \), this equation becomes

\[ \frac{\delta}{\delta \phi_{\alpha \beta}} \left( \frac{r_{\beta \gamma}}{r_{\alpha \beta}} \right) = -4 \frac{\rho}{\rho_{\alpha \beta} - \rho} \cot 2\phi_{\alpha \beta} (-1 + \cos^2 \alpha_{\gamma} \sin^2 \gamma), \]  \hspace{1cm} (C10)

or, neglecting \( \sin^2 \gamma \), we obtain

\[ \frac{\delta}{\delta \phi_{\alpha \beta}} \left( \frac{r_{\beta \gamma}}{r_{\alpha \beta}} \right) = 4 \frac{\rho}{\rho_{\alpha \beta} - \rho} \cot 2\phi_{\alpha \beta}. \]  \hspace{1cm} (C11)

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1. M. Baer and D. J. Kouri, Chem. Phys. Lett. 11, 238 (1971);
18, 167 (1977).
19A. Kumar, D. J. Kouri, and Z. H. Top, unpublished.
25See also the basic work by C. F. Curtiss, J. O. Hirschfelder, and F. T. Adler, J. Chem. Phys. 18, 1638 (1950).