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Arrangement channel approach to atom–diatom reactive systems: Theory and accurate three-dimensional probabilities for the $\text{H} + \text{H}_2$ system^{a)}

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In this work is presented an integral equation approach to exchange collisions between an atom and a diatomic molecule which result from a straightforward extension of the Lippmann–Schwinger equation originally devised to inelastic collisions. The extension to N -arrangement channels is done via a $N \times N$ matrix W which is responsible for the explicit coupling among the various arrangement channels. Different choices of the W matrix elements lead to different sets of integral equations; one of these, in which the W matrix elements are assumed to be dependent on the three orientation angles γ_α ; $\alpha = \lambda, \nu, k$ only, is discussed in detail. In addition to the theoretical derivations, we refer to the corresponding coordinate representation, discuss numerical aspects and present accurate results of the three-dimensional–three-channel $\text{H} + \text{H}_2$ system.

I. INTRODUCTION

In the theory of molecular dynamics, one distinguishes between two “traditions”: the first is based on the differential equation approach, according to which one considers the Schrödinger equation and solves it either by propagation or by finite differences (elements) techniques; and the second is based on the integral equation approach and solving the Lippmann–Schwinger equation.

The main approach employed in the study of atom–diatom exchange processes was based on solving the Schrödinger equation.^{1–4} The theoretical background for this approach is relatively straightforward and therefore has attracted much activity. Progress was rapid mainly from the middle of the 1960s to the middle of the 1970s, during which period many numerical techniques were developed and a wealth of interesting results were produced. The emphasis during this period was on collinear systems where the three particles are restricted to move along a straight line throughout the reaction process. By definition, such a system cannot have more than two arrangement channels. The transition to two and three dimensions, which is usually accompanied by a transition from a two-arrangement-channel to a three-arrangement-channel system, encountered difficulties severe enough^{5–8} for theoreticians to try other approaches—among them those based on the operator formalism which led to the integral equation methods. In general, many integral equation approaches to treat exchange processes are known, but only a few of them were tried within molecular dynamics. Among these we distinguish the Faddeev equation,^{9–11} the Fock coupling scheme,^{12–17} and the most recent Kohn variational method.¹⁸ In this work we will be interested mainly in a fourth approach, namely, the integral equation version of the arrangement channel coupling array, better known as the Baer–Kouri–Tobocman–Levin (BKLT) coupled T equations.^{19–88} According to this approach, the ordinary Lippmann–Schwinger (LS) equation derived for one arrangement is extended to a multichannel system by forming

a set of coupled integral equations—one for each arrangement. The coupling is done via a general matrix W of dimensions $N \times N$, where N is the number of arrangement channels. The W -matrix elements are to a large extent unrestricted and therefore different choices lead to different coupled systems of integral equations. In this work, I will be mainly interested in a choice where the W -matrix elements are step functions (namely equal either to 0 or to 1) which depend on the three orientation angles γ_α ; $\alpha = \lambda, \nu, k$ (see Fig. 1) only. As will be shown, this choice leads to a coupled system of integral equations which from a numerical point of view is more efficient than the other available methods and from a programming point of view is simple and straightforward.

In the next section, the derivation of the coupled Lippmann–Schwinger equation is repeated in detail; the particular choice of the orientation depended W -matrix elements is introduced in the third chapter, the three-dimensional coordinate representation of the BKLT equations is given in the fourth section, numerical results are presented in the fifth section, and concluding results in the sixth section.

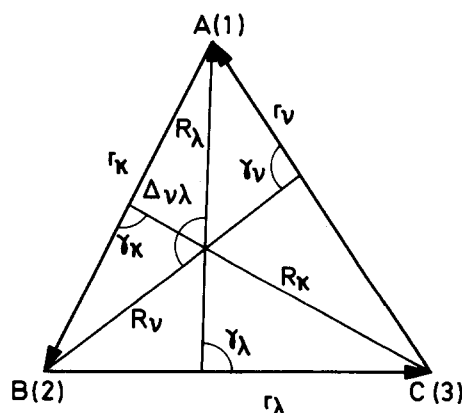


FIG. 1. The three-dimensional system. Note the three orientation angles δ_λ , δ_ν , and δ_k as well as the angle $\Delta\nu_\lambda$.

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II. THE COUPLED LIPPMANN-SCHWINGER INTEGRAL EQUATION FOR EXCHANGE COLLISIONS

The transition operator $T_{\alpha\lambda}$ between an initial arrangement-channel λ and a final arrangement α ($=\lambda, \nu, k$) can be defined either as⁸⁹

$$\tilde{T}_{\alpha\lambda}|\chi_\lambda\rangle = V_\alpha|\Psi_\lambda^+\rangle \quad (2.1)$$

or as

$$\langle\chi_\alpha|\tilde{T}_{\alpha\lambda} = \langle\Psi_\alpha^-|V_\lambda, \quad (2.1')$$

where V_α is the perturbation potential in arrangement α and $|\chi_\alpha\rangle$ and $|\Psi_\alpha^\pm\rangle$ are the α -unperturbed and the α -full solutions, respectively, of the corresponding Schrödinger equations. If H is the complete Hamiltonian and H_α is the α -arrangement unperturbed Hamiltonian, then

$$H = H_\alpha + V_\alpha, \quad (2.2)$$

where V_α fulfills the requirement

$$\lim_{R_{\alpha\lambda} \rightarrow \infty} V_\alpha(R_{\alpha\lambda}, \dots) = 0. \quad (2.3)$$

The two functions $|\chi_\alpha\rangle$ and $|\Psi_\alpha^+\rangle$ are solutions of the equations

$$H_\alpha|\chi_\alpha\rangle = E|\chi_\alpha\rangle, \quad (2.4a)$$

$$H|\Psi_\alpha^+\rangle = E|\Psi_\alpha^+\rangle. \quad (2.4b)$$

We now consider the LS equation for $|\Psi_\alpha^+\rangle$ ⁹⁰:

$$|\Psi_\alpha^+\rangle = |\chi_\alpha\rangle + G^+V_\alpha|\chi_\alpha\rangle \quad (2.5a)$$

and the LS equation for $\langle\Psi_\alpha^-|$:

$$\langle\Psi_\alpha^-| = \langle\chi_\alpha| + \langle\chi_\alpha|V_\alpha G^-, \quad (2.5b)$$

where G^\pm is the Green function of the full Hamiltonian

$$G^\pm = (E - H \pm i\epsilon)^{-1}. \quad (2.6)$$

Multiplying both sides of Eq. (2.5a) from the left by V_α and employing the definition of $\tilde{T}_{\alpha\lambda}$, we get the integral representation of $\tilde{T}_{\alpha\lambda}$:

$$\tilde{T}_{\alpha\lambda}|\chi_\lambda\rangle = V_\alpha|\chi_\lambda\rangle + V_\alpha G^+V_\lambda|\chi_\lambda\rangle \quad (2.7)$$

or

$$\tilde{T}_{\alpha\lambda} = V_\alpha + V_\alpha G^+V_\lambda. \quad (2.8)$$

In the same way, we find for $\tilde{T}_{\alpha\lambda}$ the equation

$$\tilde{T}_{\alpha\lambda} = V_\lambda + V_\alpha G V_\lambda. \quad (2.9)$$

The difference between $\tilde{T}_{\alpha\lambda}$ and $\tilde{T}_{\alpha\lambda}$ can be seen in the inhomogeneity term. Next we consider Eq. (8) and do the following:

(i) We apply for any α' the identity

$$E - H + i\epsilon = E - H_{\alpha'} + i\epsilon - V_{\alpha'} \quad (2.10)$$

which leads to an integral equation for G^+ ,

$$G^+ = G_{\alpha'}^+ + G_{\alpha'}V_{\alpha'}G^+; \quad (2.11)$$

(ii) we introduce a matrix W with the elements $W_{\alpha\alpha'}$ ²² fulfilling for each $\bar{\alpha}$ the condition

$$\sum_{\alpha'} W_{\alpha\alpha'} = 1 \quad \text{for any } \bar{\alpha}; \quad (2.12)$$

(iii) multiply Eq. (2.11) by $W_{\alpha\alpha'}$ and sum over α' to

obtain a more global equation for G^+ , namely²²

$$G^+ = \sum_{\alpha'} W_{\alpha\alpha'} G_{\alpha'}^+ + \sum_{\alpha'} W_{\alpha\alpha'} G_{\alpha'}^+ V_{\alpha'} G^+, \quad (2.13)$$

(iv) substitute Eq. (2.13) into Eq. (2.8) to obtain

$$\begin{aligned} \tilde{T}_{\alpha\lambda} &= V_\alpha + V_\alpha \left[\sum_{\alpha'} W_{\alpha\alpha'} G_{\alpha'}^+ + \sum_{\alpha'} W_{\alpha\alpha'} G_{\alpha'}^+ V_{\alpha'} G^+ \right] V_\lambda \\ &= V_\alpha + V_\alpha \sum_{\alpha'} W_{\alpha\alpha'} G_{\alpha'}^+ (V_\lambda + V_{\alpha'} G^+ V_\lambda) \\ &= V_\alpha + V_\alpha \sum_{\alpha'} W_{\alpha\alpha'} G_{\alpha'}^+ (V_\lambda - V_{\alpha'}) \\ &\quad + V_\alpha \sum_{\alpha'} W_{\alpha\alpha'} G_{\alpha'}^+ (V_{\alpha'} + V_{\alpha'} G^+ V_\lambda) \end{aligned}$$

or

$$\begin{aligned} \tilde{T}_{\alpha\lambda} &= V_\alpha \left[1 + \sum_{\alpha'} W_{\alpha\alpha'} G_{\alpha'}^+ (V_\lambda - V_{\alpha'}) \right] \\ &\quad + \sum_{\alpha'} V_\alpha W_{\alpha\alpha'} G_{\alpha'}^+ T_{\alpha'\lambda}. \end{aligned} \quad (2.14)$$

To continue, we consider the first term on the right-hand side of Eq. (2.14):

$$\begin{aligned} 1 + \sum_{\alpha'} W_{\alpha\alpha'} G_{\alpha'}^+ (V_\lambda - V_{\alpha'}) \\ &= 1 + \sum_{\alpha'} W_{\alpha\alpha'} G_{\alpha'}^+ (G_\lambda^{-1} - G_{\alpha'}^{-1}) \\ &= \sum_{\alpha'} W_{\alpha\alpha'} G_{\alpha'}^+ G_\lambda^{-1} \\ &= W_{\alpha\lambda} + i\epsilon \sum_{\alpha' \neq \lambda} W_{\alpha\alpha'} G_{\alpha'}^+ G_\lambda^{-1}. \end{aligned}$$

The last term on the right-hand side becomes zero when it operates on an initial non-break-up state $|\chi_\alpha\rangle$.^{9,91} Consequently, the final form of the equation for $\tilde{T}_{\alpha\lambda}$ is

$$\tilde{T}_{\alpha\lambda} = V_\alpha W_{\alpha\lambda} + \sum_{\alpha'} V_\alpha W_{\alpha\alpha'} G_{\alpha'}^+ \tilde{T}_{\alpha'\lambda}. \quad (2.15)$$

In a similar, but in a more straightforward way, one may show, employing Eqs. (2.9) and (2.13) that¹⁹⁻²²

$$\tilde{T}_{\alpha\lambda} = V_\lambda + \sum_{\alpha'} V_\alpha W_{\alpha\alpha'} G_{\alpha'}^+ \tilde{T}_{\alpha'\lambda}. \quad (2.16)$$

The two sets of equations are expected to yield similar results; however, from numerical applications, it is known that Eq. (2.15) is more convenient for numerical treatments.

It is noted that the index $\bar{\alpha}$ is not yet assigned a value and different choices may lead to different equations. In all our applications, $\bar{\alpha}$ was assumed to be equal to α . However, in order to obtain the Faddeev-Lovelace equations,^{9,92} for instance $\bar{\alpha}$, as can be shown, is chosen differently.⁷⁷ The main advantage of this choice is that it enables us to define a generalized potential matrix \tilde{V} with the elements

$$\tilde{V}_{\alpha\alpha'} = V_\alpha W_{\alpha\alpha'}. \quad (2.17)$$

Consequently, Eq. (2.15) becomes

$$\tilde{T}_{\alpha\lambda} = \tilde{V}_{\alpha\lambda} + \sum_{\alpha'} \tilde{V}_{\alpha\alpha'} G_{\alpha'}^+ \tilde{T}_{\alpha'\lambda} \quad (2.18)$$

which can also be written as a matrix equation

$$\tilde{T} = \tilde{V} + \tilde{V}\tilde{G} + \tilde{T}, \quad (2.19)$$

where

$$\tilde{G}_{\alpha\alpha'}^+ = \delta_{\alpha\alpha'} G_{\alpha}^+. \quad (2.20)$$

In a similar way, Eq. (2.16) will be written as

$$\tilde{T} = UV + \tilde{V}G\tilde{T}, \quad (2.21)$$

where U is the matrix

$$U = \begin{pmatrix} 1, \dots, 1 \\ \vdots \\ 1, \dots, 1 \end{pmatrix}. \quad (2.22)$$

This compact way of writing the BKLT equations is reminiscent of the single-arrangement LS equation.

In what follows we will consider only Eq. (2.19) [or Eq. (2.15)] and consequently the \sim sign over T will be deleted.

An important feature of the BKLT equations as given in Eq. (2.19) is the fact that the global reactance operator K defined as²⁶

$$K = \tilde{V} + \tilde{V}G_0^P K, \quad (2.23)$$

where G_0^P is the principal of value of G_0 and fulfills the Heitler damping equation. The proof will not be given here because it is very similar to the one given for the elastic case. Thus,

$$T = K - i\pi K \delta(EI - H_0) T, \quad (2.24)$$

where

$$\delta(EI - H_0)|_{\lambda\lambda} = \delta_{\lambda\lambda} \delta(E - H_{\lambda}). \quad (2.25)$$

Like the global transition matrix T , we may now introduce the global scattering matrix S which is defined as

$$S = I - 2\pi i \delta(EI - H_0) T. \quad (2.26)$$

Consequently the relation between S and K becomes

$$S = \{I - i\pi \delta(EI - H_0) K\} \{I + i\pi \delta(EI - H_0) K\}^{-1}. \quad (2.27)$$

In all numerical applications, the global K matrix and not the global T matrix elements are calculated because it avoids the need to deal with complex numbers.

III. THE ANGULAR DEPENDENT W MATRIX ELEMENTS

The simplest and most straightforward choice is to assume for the W -matrix elements to be constants (i.e., pure numbers). This choice was made by Baer and Kouri¹⁹⁻²² when they first presented their coupled T equations which later became known as the BKLT equations. Moreover, they found that for a two-arrangement channel system, the best choice for W would be

$$W = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \quad (3.1)$$

One of the main questions one encounters in the theory of integral equations is whether the kernel is connected or not. When the LS equation is considered, the question is asked differently because the kernel consists of a product of a Green function which is assumed to be not necessarily con-

nected and a potential function for which connectivity is required. Connectivity implies that either the potential or one of its powers becomes zero, when any of the interatomic distances goes to infinity. Assuming the W -matrix elements to be constant, Tobocman²⁷ has shown that necessary and sufficient conditions for all kernels to be connected, is that W is of a permuting array structure. Thus,

$$W_{ij} = \begin{cases} 1; & j = i + 1, \quad i = 1, \dots, N - 1 \\ 1; & j = 1, \quad i = N \\ 0; & \text{otherwise} \end{cases}. \quad (3.2)$$

For the three channel case, W becomes

$$W = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \quad \text{or} \quad W = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}. \quad (3.3)$$

In numerical application, it was verified that this choice led to correct results for any two-channel system that it was applied to, but then failed once it was tested for a three-arrangement channel case.⁸² All numerical studies were carried out without including three-body continuum and therefore the failure of the BKLT equations to produce the results for a three-channel case is attributed to the fact that the coupling scheme proposed by a channel permuting array structure is too weak and three-body continuum states have to be included in the calculations in order to obtain the correct results. This weakness seems to be due to the high asymmetry built into the W matrix so that each channel is explicitly coupled only to one other channel.

From the above discussion, it seems that the failure of the BKLT equations to produce relevant results for a three-channel system is related to the assumption that the W -matrix elements are pure numbers. Recently, Baer and Shima⁸³ considered W -matrix elements which are functions of the internal orientation angles γ_{α} of the three-body system defined as (see Fig. 1)

$$\gamma_{\alpha} = \cos^{-1}(\hat{R}_{\alpha} \cdot r_{\alpha}); \quad \alpha = \lambda, \nu, k, \quad (3.4)$$

where R_{α} and r_{α} are the α -arrangement translational and vibrational vectors, respectively.

From Eq. (2.15), it can be seen that $W_{\alpha\alpha'}$ is a matrix element which couples arrangement α' to arrangement α . Thus, for $\alpha = \lambda$, the three matrix elements which couple the arrangement channel λ to itself as well as to the other two, are $W_{\lambda\lambda}$, $W_{\lambda\nu}$, and $W_{\lambda k}$, respectively. Since the channel λ stands for the arrangement (A, BC), the coordinate according to which it will be decided when the channel is coupled to any of the three channels is the angle γ_{λ} (see Fig. 1). Thus, when γ_{λ} is small, the channel is expected to be coupled more intensely to the ν (= B, CA) channel, and when γ_{λ} is close to π , it is expected to be coupled more intensely to the k (= C, AB) channel. For the γ_{λ} interval where the λ channel is only weakly coupled to the other channels (usually for $\gamma_{\lambda} \sim \pi/2$), it will be assumed to be coupled to itself. One could think of many functional forms for the W -matrix elements that would comply with the above description [and fulfill Eq. (2.12)]. However, if again, one requires the kernel to be connected, then these functions have to be chosen with some care.

The simplest choice is the step functions, thus

$$W_{\lambda\nu}(\gamma_\lambda) = \begin{cases} 1; & 0 < \gamma_\lambda < \gamma_\lambda^- \\ 0; & \text{otherwise} \end{cases}, \quad (3.5a)$$

$$W_{\lambda k}(\gamma_\lambda) = \begin{cases} 1; & \gamma_\lambda^+ < \gamma_\lambda < \pi \\ 0; & \text{otherwise} \end{cases}, \quad (3.5b)$$

$$W_{\lambda\lambda}(\gamma_\lambda) = \begin{cases} 1; & \gamma_\lambda^- \leq \gamma_\lambda \leq \gamma_\lambda^+ \\ 0; & \text{otherwise} \end{cases}. \quad (3.5c)$$

The proof for the connectivity was given by Neuhauser and Baer⁸⁷ and will not be repeated here. In what follows, we assume the W -matrix elements to be of that form.

IV. THE THREE-DIMENSIONAL CONFIGURATION

A. The Schrödinger equation

The description of the three-dimensional configuration is given in Fig. 1. The Hamiltonian which describes the motion of these particles may be written as

$$H = -\frac{\hbar^2}{2\mu_\alpha} \nabla_{r_\alpha}^2 - \frac{\hbar^2}{2M_\alpha} \nabla_{R_\alpha}^2 + V(\mathbf{R}_\alpha, \mathbf{r}_\alpha), \quad (4.1)$$

where \mathbf{R}_α and \mathbf{r}_α are the translational and vibrational coordinates respectively, $V(\mathbf{R}_\alpha, \mathbf{r}_\alpha)$ is the potential which governs the motion of the three particles and μ_α and M_α are reduced masses which for $\alpha = \lambda$ are defined as

$$\mu_\lambda = \frac{m_B m_C}{m_B + m_C}; \quad M_\lambda = \frac{m_A (m_B + m_C)}{m_A + m_B + m_C}. \quad (4.2)$$

Here m_A , m_B , and m_C are the masses of the three interacting particles. Similar expressions exist for μ_ν and M_ν and for μ_k and M_k . Scaling the coordinates

$$\mathbf{r}'_\alpha = a_\alpha \mathbf{r}_\alpha; \quad \mathbf{R}'_\alpha = a_\alpha^{-1} \mathbf{R}_\alpha, \quad (4.3)$$

where

$$a_\alpha = (\mu_\alpha / M_\alpha)^{1/4}, \quad (4.4)$$

the Hamiltonian in Eq. (4.1) becomes

$$H = -\frac{\hbar^2}{2\mu} (\nabla_{R_\alpha}^2 + \nabla_{r_\alpha}^2) + V(\mathbf{R}_\alpha, \mathbf{r}_\alpha), \quad (4.5)$$

where we deleted the prime sign from \mathbf{R}_α and \mathbf{r}_α and μ given in the form

$$\mu = \left(\frac{m_A m_B m_C}{m_A + m_B + m_C} \right)^{1/2} \quad (4.6)$$

is defined as the reduced mass of the system.

The Laplacians $\nabla_{R_\alpha}^2$ and $\nabla_{r_\alpha}^2$ will be written as

$$\begin{aligned} \nabla_R^2 &= \frac{1}{R} \frac{\partial^2}{\partial R^2} R - \frac{l^2}{\hbar^2 R^2}, \\ \nabla_r^2 &= \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{j^2}{\hbar^2 r^2}, \end{aligned} \quad (4.7)$$

where the index α is omitted. Here l and j are the orbital and internal angular momentum operators

$$j^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right), \quad (4.8a)$$

$$l^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right). \quad (4.8b)$$

The angles θ and φ are the spherical angles associated with \mathbf{R} and θ_r and φ_r with \mathbf{r} .

Next are introduced \mathbf{J} , the total angular momentum defined as

$$\mathbf{J} = \mathbf{j} + \mathbf{l} \quad (4.9)$$

and M its z component in a given space-fixed system of coordinates

$$J_z = M. \quad (4.10)$$

If m_l and m_j are the z components of \mathbf{l} and \mathbf{j} , respectively, then

$$M = m_l + m_j. \quad (4.10')$$

Given the Hamiltonian in Eq. (4.5), the solution of the corresponding Schrödinger equation for a given J and M can be written in the form

$$\Psi(\mathbf{R}, \mathbf{r} | JM) = \sum_{ij} \psi(R, r | l_j, J, M) \Gamma(\hat{R}, \hat{r} | l_j, J, M), \quad (4.11)$$

where $\Gamma(\hat{R}, \hat{r} | l_j, J, M)$ is the angular part of the wave function [here $\hat{R} = (\theta, \varphi)$ and $\hat{r} = (\theta_r, \varphi_r)$] which may be represented in terms of the space-fixed coordinates in the following form:

$$\begin{aligned} \gamma(\hat{R}, \hat{r} | l_j, J, M) &= \sum_{m_l + m_j = M} C(l, m_l, j, m_j | JM) y_{lm_l}(\theta, \phi) \\ &\quad \times y_{jm_j}(\theta_r, \phi_r). \end{aligned} \quad (4.12)$$

Here $y_{lm_l}(\theta, \varphi)$ and $y_{jm_j}(\theta_r, \varphi_r)$ are the spherical harmonics and $C(l, m_l, j, m_j | JM)$ are the Clebsch-Gordan coefficients.⁹³ In what follows, the Rose phase convention⁹³ will be employed.

The function $\Gamma(\hat{R}, \hat{r} | l_j, J, M)$ can also be described in terms of the body-fixed angles $(\theta, \varphi, \gamma, \delta)$ where θ and φ are as before and γ and δ are the two angles which replace θ_r and φ_r when rotating the system of coordinates in such a way that the z axis points at the direction of \mathbf{R} . Thus it can be shown that

$$\cos \gamma = \cos \theta \cos \theta_r + \sin \theta \sin \theta_r \cos(\phi - \phi_r) \quad (4.13)$$

and

$$\cot \delta = \sin \theta \cot \theta_r \operatorname{cosec}(\phi - \phi_r) - \cos \theta \cot(\phi - \phi_r). \quad (4.14)$$

The angle γ is recognized as the polar angle between \mathbf{R} and \mathbf{r} :

$$\gamma = \cos^{-1}(\hat{R} \cdot \hat{r}) \quad (4.15)$$

and the angle δ together with θ and φ form the three Euler angles. Consequently, $\Gamma(\hat{R}, \hat{r} | l_j, J, M)$ can also be written in the form

$$\begin{aligned} \Gamma(\hat{R}, \hat{r} | l_j, J, M) &= \sqrt{(2l+1)4\pi} \sum_{\Omega} C(l, 0, j, \Omega | J, \Omega) y_{j\Omega}(\gamma, 0) \\ &\quad \times D_{M\Omega}^J(\theta, \phi, \delta), \end{aligned} \quad (4.16)$$

where the summation over Ω is done for those Ω 's that fulfill $|\Omega| < j, J$ and the $D_{M\Omega}^J(\theta, \varphi, \delta)$ functions are the coefficients of the irreducible representation of the rotation group.⁹³ The Γ functions given in Eq. (4.12) or Eq. (4.16) are eigenfunctions of l^2 and j^2 and consequently the Schrödinger equation

becomes

$$\left\{ -\frac{\hbar^2}{2\mu} \left(\frac{1}{R} \frac{\partial^2}{\partial R^2} R + \frac{1}{r} \frac{\partial^2}{\partial r^2} r \right) + \frac{\hbar^2}{2\mu} \frac{l(l+1)}{R^2} + \frac{\hbar^2}{2\mu} \frac{j(j+1)}{r^2} - E \right\} \times \psi(R, r | l, j, J, M) + \sum_{l'j'} V(R, r | l, j, l', j', J) \psi(R, r | l', j', J, M) = 0 \quad (4.17)$$

where $V(R, r | l, j, l', j')$ is defined as

$$V(R, r | l, j, l', j', J) = \langle \Gamma(\hat{R}, \hat{r} | l, j, J, M) | V(R, r, \gamma) | \Gamma(\hat{R}, \hat{r} | l', j', J, M) \rangle \quad (4.18)$$

and can be shown to be equal to

$$V(R, r | l, j, l', j', J) = 2\pi \frac{\sqrt{(2l+1)(2l'+1)}}{2J+1} \sum_{\Omega} C(l, \Omega, j, -\Omega | J, 0) \times C(l', \Omega, j', -\Omega | J, 0) \langle j\Omega | V(R, r) | j\Omega \rangle, \quad (4.19)$$

where $\langle j, \Omega | V(R, r) | j', \Omega \rangle$ is defined as

$$\langle j\Omega | V(R, r) | j'\Omega \rangle = \int_{-1}^{+1} \gamma_{j\Omega}(\gamma, 0) V(R, r, \gamma) \times y_{j\Omega}(\gamma, 0) d \cos \gamma. \quad (4.20)$$

This will complete the treatment of the angular part of the Schrödinger equation.

B. The coordinate representation of the BKL equations in three dimensions

The equations to be treated in this section are those given in Eq. (2.18). (In what follows, the tilde above T will be deleted.)

We introduce the amplitude density functions

$$|\zeta_{\alpha\lambda}^{\sigma_{\lambda 0}}\rangle = T_{\alpha\lambda} |\theta_{\sigma_{\lambda 0}}\rangle, \quad (4.21)$$

where $\theta_{\sigma_{\lambda 0}}$ is a nonreactive wave function belonging to an initial state characterized by a set of quantum numbers $\sigma_{\lambda 0}$ in the λ arrangement channel. Thus in general σ_{α} stands for

$$\sigma_{\alpha} \equiv (n_{\alpha}, l_{\alpha}, j_{\alpha}), \quad (4.22)$$

where n_{α} is a vibrational quantum number and (l_{α}, j_{α}) were introduced before. The treatment here and in all that follows is assumed to be carried out for a given J and M and therefore they may be occasionally omitted.

Next, the coordinate representation of the various functions and operators are introduced⁹⁴:

$$\langle \mathbf{R}_{\alpha}, \mathbf{r}_{\alpha} | \zeta_{\alpha\lambda}^{\sigma_{\lambda 0}} \rangle = \zeta_{\alpha\lambda}(\mathbf{R}_{\alpha}, \mathbf{r}_{\alpha} | \sigma_{\lambda 0}), \quad (4.23a)$$

$$\langle \mathbf{R}_{\lambda}, \mathbf{r}_{\lambda} | \theta_{\sigma_{\lambda 0}} \rangle = \theta_{\lambda}(\mathbf{R}_{\lambda}, \mathbf{r}_{\lambda} | \sigma_{\lambda 0}), \quad (4.23b)$$

$$\begin{aligned} \langle \mathbf{R}_{\alpha}, \mathbf{r}_{\alpha}, \gamma_{\alpha} | V_{\alpha} | \mathbf{R}'_{\alpha}, \mathbf{r}'_{\alpha}, \gamma'_{\alpha} \rangle \\ = V(R_{\alpha}, r_{\alpha}, \gamma_{\alpha}) \delta(R_{\alpha} - R'_{\alpha}) \\ \times \delta(r_{\alpha} - r'_{\alpha}) \delta(\cos \gamma_{\alpha} - \cos \gamma'_{\alpha}), \end{aligned} \quad (4.23c)$$

$$\langle \mathbf{R}_{\alpha}, \mathbf{r}_{\alpha} | G | \mathbf{R}'_{\alpha}, \mathbf{r}'_{\alpha} \rangle = G(\mathbf{R}_{\alpha}, \mathbf{r}_{\alpha} | \mathbf{R}'_{\alpha}, \mathbf{r}'_{\alpha}), \quad (4.23d)$$

$$I = \int d^3 \mathbf{R}_{\alpha} d^3 \mathbf{r}_{\alpha} | \mathbf{R}_{\alpha}, \mathbf{r}_{\alpha} \rangle \langle \mathbf{R}_{\alpha}, \mathbf{r}_{\alpha} |, \quad (4.23e)$$

and interpret the scalar product $\langle \mathbf{R}_{\beta}, \mathbf{r}_{\beta} | \mathbf{R}_{\alpha}, \mathbf{r}_{\alpha} \rangle$ as an ex-

tended type of a Dirac δ function

$$\langle \mathbf{R}_{\beta}, \mathbf{r}_{\beta} | \mathbf{R}_{\alpha}, \mathbf{r}_{\alpha} \rangle = \delta_{JJ'} \delta_{MM'} \delta[(R_{\beta}, r_{\beta}, \gamma_{\beta}) - (R_{\alpha}, r_{\alpha}, \gamma_{\alpha})] \quad (4.23f)$$

which means

$$R_{\beta} = R_{\beta}(R_{\alpha}, r_{\alpha}, \gamma_{\alpha}), \quad r_{\beta} = r_{\beta}(R_{\alpha}, r_{\alpha}, \gamma_{\alpha}), \quad \gamma_{\beta} = \gamma_{\beta}(R_{\alpha}, r_{\alpha}, \gamma_{\alpha}). \quad (4.24)$$

Multiply Eq. (2.18) from the right by $|\theta_{\sigma_{\lambda 0}}\rangle$ and using Eqs. (4.23), we get

$$\begin{aligned} \zeta_{\alpha\lambda}(\mathbf{R}_{\alpha}, \mathbf{r}_{\alpha} | \sigma_{\lambda 0}) = \tilde{V}_{\alpha\lambda}(\mathbf{R}_{\alpha}, \mathbf{r}_{\alpha}, \gamma_{\alpha}) \theta(\mathbf{R}_{\lambda}, \mathbf{r}_{\lambda} | \sigma_{\lambda 0}) \\ + \sum_{\beta} \tilde{V}_{\alpha\beta}(\mathbf{R}_{\alpha}, \mathbf{r}_{\alpha}, \gamma_{\alpha}) \\ \times \int \int d^3 \mathbf{R}'_{\beta} d^3 \mathbf{r}'_{\beta} G_{\beta}(\mathbf{R}_{\beta}, \mathbf{r}_{\beta} | \mathbf{R}'_{\beta}, \mathbf{r}'_{\beta}) \\ \times \zeta_{\beta\lambda}(\mathbf{R}'_{\beta}, \mathbf{r}'_{\beta} | \sigma_{\lambda 0}). \end{aligned} \quad (4.25)$$

To continue, we will need the explicit forms of the various functions and this will be done in the next section.

C. Derivation of the Green functions

To calculate the Green functions $G_{\alpha}(\mathbf{R}_{\alpha}, \mathbf{r}_{\alpha} | \mathbf{R}'_{\alpha}, \mathbf{r}'_{\alpha})$ as well as the initial channel wave function $\theta_{\lambda}(\mathbf{R}_{\lambda}, \mathbf{r}_{\lambda} | \sigma_{\lambda 0})$, we consider the Hamiltonian H introduced in Eq. (2.2):

$$H_{\alpha} = -\frac{\hbar^2}{2\mu} (\nabla_{R_{\alpha}}^2 + \nabla_{r_{\alpha}}^2) + V_{0\alpha}(R_{\alpha}, r_{\alpha}, \gamma_{\alpha}). \quad (4.26)$$

The unperturbed potential $V_{0\alpha}(R_{\alpha}, r_{\alpha}, \gamma_{\alpha})$ is written in the form

$$V_{0\alpha}(R_{\alpha}, r_{\alpha}, \gamma_{\alpha}) = U_{\alpha}(R_{\alpha}, \gamma_{\alpha}) + v_{\alpha}(r_{\alpha}), \quad (4.27)$$

where $v_{\alpha}(r_{\alpha})$ is the asymptotic two body potential of the α diatomic and $U_{\alpha}(R_{\alpha}, \gamma_{\alpha})$ is the distortion potential which increases when $R_{\alpha} \rightarrow 0$ and fulfills the asymptotic conditions

$$\lim_{R_{\alpha} \rightarrow \infty} U_{\alpha}(R_{\alpha}, \gamma_{\alpha}) = \begin{cases} 0; & \alpha = \lambda \\ d_{\alpha}; & \alpha \neq \lambda \end{cases}. \quad (4.28)$$

Here d_{β} for instance, is the exothermicity (endothermicity) of the reaction in the β channel. A choice usually done in the calculation is

$$U_{\alpha}(R_{\alpha}, \gamma_{\alpha}) = V(R_{\alpha}, r_{\alpha} = r_{\alpha 0}, \gamma_{\alpha}), \quad (4.29)$$

where $r_{\alpha 0}$ is the equilibrium distance of the α diatomic.

Once $V_{\alpha 0}(R_{\alpha}, r_{\alpha}, \gamma_{\alpha})$ is determined, the perturbation potential is defined as

$$V_{\alpha}(\mathbf{R}_{\alpha}, \mathbf{r}_{\alpha}, \gamma_{\alpha}) = V(\mathbf{R}_{\alpha}, \mathbf{r}_{\alpha}, \gamma_{\alpha}) - U_{\alpha}(R_{\alpha}, \gamma_{\alpha}) - v_{\alpha}(r_{\alpha}). \quad (4.30)$$

The solution of Eq. (4.26) will be written as

$$\begin{aligned} \theta(\mathbf{R}_{\alpha}, \mathbf{r}_{\alpha} | \sigma_{\alpha 0}) = \frac{1}{R_{\alpha} r_{\alpha}} \sum_{\sigma_{\alpha}} \psi_{\alpha}^{\text{re}}(R_{\alpha} | \sigma_{\alpha}, \sigma_{\alpha 0}) \phi_{\alpha}(r_{\alpha} | n_{\alpha}, j_{\alpha}) \\ \times \Gamma(\gamma_{\alpha}, \Lambda_{\alpha} | j_{\alpha}, l_{\alpha}), \end{aligned} \quad (4.31)$$

where $\sigma_{\alpha 0}$ stands for a set of quantum numbers which describe the initial state in the α arrangement channel, the function $\psi_{\alpha}^{\text{re}}(R_{\alpha} | \sigma_{\alpha}, \sigma_{\alpha 0})$ is the regular translational part of the total wave function (in what follows we will also refer to $\psi_{\alpha}^{\text{ir}}(R_{\alpha} | \sigma_{\alpha}, \sigma_{\alpha 0})$ which is the irregular translational part of

the wave function), $\Gamma(\gamma_\alpha, \Lambda_\alpha | j_\alpha, l_\alpha)$ stands for the angular part of the wave function and takes the form given in Eq. (4.16), Λ_α is a symbol which describes the three Euler angles

$$\Lambda_\alpha \equiv (\theta_\alpha, \phi_\alpha, \delta_\alpha) \quad (4.32)$$

and $\phi_\alpha(r_\alpha | n_\alpha j_\alpha)$ are the vibrational wave functions of the α diatomic

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r_\alpha^2} + \frac{\hbar^2 j_\alpha(j_\alpha + 1)}{2\mu r_\alpha^2} + v_\alpha(r_\alpha) - \epsilon_{n_\alpha j_\alpha} \right] \phi_\alpha(r_\alpha | n_\alpha j_\alpha) = 0. \quad (4.33)$$

The translational function $\psi^q(R_\alpha | \sigma_\alpha, \sigma_{\alpha 0})$; $q = \text{re, ir}$ are solutions of the equation

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R_\alpha^2} + \frac{\hbar^2 l_\alpha(l_\alpha + 1)}{2\mu R_\alpha^2} - k_{n_\alpha j_\alpha}^2 \right\} \psi^q(R_\alpha | \sigma_\alpha, \sigma_{\alpha 0}) + \sum_{l'_\alpha j'_\alpha} V_{0\alpha}(R_\alpha | l_\alpha j_\alpha, l'_\alpha j'_\alpha) \psi^q(R_\alpha | \sigma'_\alpha, \sigma_{\alpha 0}) = 0; \quad q = \text{re, ir}, \quad (4.34)$$

where it is assumed that $n_\alpha = n_{\alpha 0}$ and $V_{0\alpha}(R_\alpha | l_\alpha, j_\alpha, l'_\alpha, j'_\alpha)$ is given in Eq. (4.19) for the case $r = r_{\alpha 0}$.

In case the distortion potential $U(R_\alpha, \gamma_\alpha)$ does not depend on γ_α , Eq. (4.34) becomes

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R_\alpha^2} + \frac{\hbar^2 l_\alpha(l_\alpha + 1)}{2\mu R_\alpha^2} + V_{0\alpha}(R_\alpha) - k_{n_\alpha j_\alpha}^2 \right\} \times \psi^q(R_\alpha | \sigma_\alpha, \sigma_{\alpha 0}) = 0; \quad q = \text{re, ir}. \quad (4.34')$$

Equation (4.34) [or Eq. (4.34')] are solved subject to the following asymptotic conditions:

$$\lim_{R_\alpha \rightarrow \infty} \psi_\alpha^{\text{re}}(R_\alpha | \sigma_\alpha, \sigma_{\alpha 0}) = \delta_{\sigma_\alpha \sigma_{\alpha 0}} J_{l_{\alpha 0}}(k_{n_{\alpha 0} j_{\alpha 0}} R_\alpha) + N_{l_\alpha}(k_{n_\alpha j_\alpha} R_\alpha) \langle \sigma_\alpha | K^0 | \sigma_{\alpha 0} \rangle, \quad (4.35)$$

where $\langle \sigma_\alpha | K_\alpha^0 | \sigma_\alpha \rangle$ is an inelastic (elastic) reactance matrix element and $J_{l_\alpha}(k_{n_\alpha j_\alpha} R_\alpha)$ and $N_{l_\alpha}(k_{n_\alpha j_\alpha} R_\alpha)$ are defined as follows:

$$J_{l_\alpha}(k_{n_\alpha j_\alpha} R_\alpha) = \begin{cases} k_{n_\alpha j_\alpha}^{1/2} R_\alpha j_{l_\alpha}(k_{n_\alpha j_\alpha} R_\alpha); & \text{open states} \\ \frac{1}{2} |k_{n_\alpha j_\alpha}|^{-1/2} \exp(|k_{n_\alpha j_\alpha}| R_\alpha); & \text{closed states} \end{cases} \quad (4.36a)$$

$$N_{l_\alpha}(k_{n_\alpha j_\alpha} R_\alpha) = \begin{cases} k_{n_\alpha j_\alpha}^{1/2} R_\alpha n_{l_\alpha}(k_{n_\alpha j_\alpha} R_\alpha); & \text{open states} \\ \frac{1}{2} |k_{n_\alpha j_\alpha}|^{-1/2} \exp(-|k_{n_\alpha j_\alpha}| R_\alpha); & \text{closed states} \end{cases} \quad (4.36b)$$

Here $j_{l_\alpha}(k_{n_\alpha j_\alpha} R_\alpha)$ and $n_{l_\alpha}(k_{n_\alpha j_\alpha} R_\alpha)$ are the spherical Bessel and Neumann functions. As for the irregular translational wave function $\psi_\alpha^{\text{ir}}(R_\alpha | \sigma_\alpha, \sigma_{\alpha 0})$, we require its asymptotic form to be

$$\lim_{R_\alpha \rightarrow \infty} \psi_\alpha^{\text{ir}}(R_\alpha | \sigma_\alpha, \sigma_{\alpha 0}) = \delta_{\sigma_\alpha \sigma_{\alpha 0}} N_{l_\alpha}(k_{n_\alpha j_\alpha} R_\alpha). \quad (4.37)$$

It can be shown that this choice of $\psi_\alpha^{\text{ir}}(R_\alpha | \sigma_\alpha, \sigma_{\alpha 0})$ guarantees that the Wronskian is unity in both the elastic and the inelastic case.

The corresponding Green function is

$$G(\mathbf{R}_\alpha^< \mathbf{r}_\alpha | \mathbf{R}_\alpha^> \mathbf{r}'_\alpha) = -\frac{2\mu}{\hbar^2} \frac{1}{R_\alpha r_\alpha R'_\alpha r'_\alpha} \sum_{\sigma_\alpha} \sum_{\sigma'_\alpha} g(R_\alpha^< | R_\alpha^> | \sigma_\alpha, \sigma'_\alpha) \times \phi_\alpha(r_\alpha | n_\alpha j_\alpha) \phi_\alpha(r'_\alpha | n'_\alpha j'_\alpha) \times \Gamma(\gamma_\alpha, \Lambda_\alpha | j_\alpha, l_\alpha) \Gamma(\gamma'_\alpha, \Lambda'_\alpha | j'_\alpha, l'_\alpha), \quad (4.38)$$

where $R_\alpha^<$ and $R_\alpha^>$ are the lesser and the greater between R_α and R'_α and the function $g(R_\alpha^< | R_\alpha^> | \sigma_\alpha, \sigma'_\alpha)$ is defined as $g(R_\alpha^< | R_\alpha^> | \sigma_\alpha, \sigma'_\alpha) = \psi_\alpha^{\text{re}}(R_\alpha^< | \sigma_\alpha, \sigma'_\alpha) \psi_\alpha^{\text{ir}}(R_\alpha^> | \sigma_\alpha, \sigma'_\alpha)$. (4.39)

In what follows, we will be interested only in case the distortion potential $U_\alpha(R_\alpha, r_\alpha)$ is dependent on γ_α and consequently $\theta(\mathbf{R}_\alpha, \mathbf{r}_\alpha | \sigma_{\alpha 0})$ as well as $G_\alpha(\mathbf{R}_\alpha^< \mathbf{r}_\alpha | \mathbf{R}_\alpha^> \mathbf{r}'_\alpha)$ become

much simpler. Thus

$$\theta(\mathbf{R}_\alpha, \mathbf{r}_\alpha | \sigma_{\alpha 0}) = \frac{1}{R_\alpha r_\alpha} \psi_\alpha^{\text{re}}(R_\alpha | \sigma_{\alpha 0}) \times \phi_\alpha(r_\alpha | n_{\alpha 0} j_{\alpha 0}) \Gamma(\gamma_\alpha, \Lambda_\alpha | j_{\alpha 0}, l_{\alpha 0}) \quad (4.31')$$

and

$$G(\mathbf{R}_\alpha^> \mathbf{r}_\alpha | \mathbf{R}_\alpha^< \mathbf{r}'_\alpha) = -\frac{2\mu}{\hbar^2} \frac{1}{R_\alpha r_\alpha R'_\alpha r'_\alpha} \sum_{\sigma_\alpha} g(R_\alpha^< | R_\alpha^> | \sigma_\alpha) \times \phi_\alpha(r_\alpha | n_\alpha j_\alpha) \phi_\alpha(r'_\alpha | n'_\alpha j'_\alpha) \Gamma(\gamma_\alpha, \Lambda_\alpha | j_\alpha, l_\alpha) \times \Gamma(\gamma'_\alpha, \Lambda'_\alpha | j'_\alpha, l'_\alpha). \quad (4.38')$$

This completes the derivation of the Green functions.

D. The derivation of the T -matrix elements

The derivations to be carried out for calculating the T -matrix elements are very similar to the ones done for the collinear case.⁸⁸ Consequently only a few of them will be presented. Following Eq. (4.21), an ordinary T -matrix element is obtained by multiplying Eq. (4.21) from the left by a final α -state $2\mu/\hbar^2 < \theta_{\sigma_\alpha}$:

$$\langle \sigma_\alpha | T_{\alpha\lambda} | \sigma_\lambda \rangle = \frac{2\mu}{\hbar^2} \langle \theta_{\sigma_\alpha} | \xi_{\alpha\lambda}^{\sigma_{\alpha 0}} \rangle. \quad (4.40)$$

From the definitions of the coordinate representation of

$\langle \theta_\alpha |$ and $|\xi_{\alpha\lambda}^{\sigma_{\lambda_0}}\rangle$ [see Eqs. (4.23)], we get

$$\langle \sigma_\alpha | T_{\alpha\lambda} | \sigma_{\lambda_0} \rangle = \frac{2\mu}{\hbar^2} \iint d^3\mathbf{R}_\alpha d^3\mathbf{r}_\alpha \theta_\alpha(\mathbf{R}_\alpha, \mathbf{r}_\alpha | \sigma_\alpha) \times \xi_{\alpha\lambda}(\mathbf{R}_\alpha, \mathbf{r}_\alpha | \sigma_{\lambda_0}). \quad (4.40')$$

Next we expand $\xi_{\alpha\lambda}(\mathbf{R}_\alpha, \mathbf{r}_\alpha | \sigma_{\lambda_0})$ in terms of the α -channel basis sets

$$\xi_{\alpha\lambda}(\mathbf{R}_\alpha, \mathbf{r}_\alpha | \sigma_{\lambda_0}) = \frac{1}{R_\alpha r_\alpha} \sum_{\sigma_\alpha t_\alpha} a_{\alpha\lambda}(\sigma_\alpha | t_\alpha | \sigma_{\lambda_0}) \chi_\alpha(R_\alpha | t_\alpha) \times \phi_\alpha(r_\alpha | n_\alpha, j_\alpha) \Gamma(\gamma_\alpha, \Lambda_\alpha | l_\alpha, j_\alpha), \quad (4.41)$$

where $\chi_\alpha(R_\alpha | t_\alpha)$ is a translational basis set function. Recalling the explicit form of $\theta_\alpha(\mathbf{R}_\alpha, \mathbf{r}_\alpha)$ given in Eq. (4.31') we get the final expression for the T -matrix element

$$\langle \sigma_\alpha | T_{\alpha\lambda} | \sigma_{\lambda_0} \rangle = \frac{2\mu}{\hbar^2} \sum_{t_\alpha} a_{\alpha\lambda}(\sigma_\alpha | t_\alpha | \sigma_{\lambda_0}) w_\alpha(\sigma_\alpha, t_\alpha), \quad (4.42)$$

where

$$w_\alpha(\sigma_\alpha, t_\alpha) = \int dR_\alpha \psi^e(R_\alpha | \sigma_\alpha) \chi_\alpha(R_\alpha | t_\alpha). \quad (4.43)$$

Our next task is to construct the set of algebraic equations to determine $a_{\alpha\lambda}(\sigma_\alpha | t_\alpha | \sigma_{\lambda_0})$. This is done by substituting Eqs. (4.31'), (4.38'), and (4.41) in Eq. (4.25), multiplying from the left by $(R_\alpha r_\alpha)^{-1} \chi_\alpha(R_\alpha | t_\alpha) \theta_\alpha(r_\alpha | n_\alpha, j_\alpha) \Gamma(\gamma_\alpha, \Lambda_\alpha | l_\alpha, j_\alpha)$ and integrating over all variables. Thus:

$$a_{\alpha\lambda}(\sigma_\alpha | t_\alpha | \sigma_{\lambda_0}) = b_{\alpha\lambda}(\sigma_\alpha | t_\alpha | \sigma_{\lambda_0}) + \sum_B \sum_{\sigma_\beta t_\beta} C_{\alpha\beta}(\sigma_\alpha, t_\alpha | \sigma_\beta, t_\beta) \times a_{\beta\lambda}(\sigma_\beta | t_\beta | \sigma_{\lambda_0}). \quad (4.44)$$

Here the inhomogeneity $b_{\alpha\lambda}(\sigma_\alpha | t_\alpha | \sigma_{\lambda_0})$ is

$$b_{\alpha\lambda}(\sigma_\alpha | t_\alpha | \sigma_{\lambda_0}) = \iiint \frac{R_\alpha r_\alpha}{R_\lambda r_\lambda} dR_\alpha dr_\alpha d\cos\gamma_\alpha \chi_\alpha(R_\alpha | t_\alpha) \phi_\alpha(r_\alpha | n_\alpha, j_\alpha) (j_\alpha, l_\alpha | \tilde{V}_{\alpha\lambda}^J(R_\alpha, r_\alpha, \gamma_\alpha) | j_{\lambda_0}, l_{\lambda_0}) \phi_\lambda(r_\lambda | n_{\lambda_0}, j_{\lambda_0}) \psi^e(R_\lambda | \sigma_{\lambda_0}) \quad (4.45)$$

and the C -matrix element $C_{\alpha\beta}(\sigma_\alpha, t_\alpha | \sigma_\beta, t_\beta)$ is

$$C_{\alpha\beta}(\sigma_\alpha, t_\alpha | \sigma_\beta, t_\beta) = \iiint \frac{R_\alpha r_\alpha}{R_\beta r_\beta} dR_\alpha dr_\alpha d\cos\gamma_\alpha \chi_\alpha(R_\alpha | t_\alpha) \phi_\alpha(r_\alpha | n_\alpha, j_\alpha) (j_\alpha, l_\alpha | \tilde{V}_{\alpha\beta}^J(R_\alpha, r_\alpha, \gamma_\alpha) | j_\beta, l_\beta) \phi_\beta(r_\beta | n_\beta, j_\beta) F_\beta(R_\beta | \sigma_\beta, t_\beta), \quad (4.46)$$

where

$$F_\beta(R_\beta | \sigma_\beta, t_\beta) = -\frac{2\mu}{\hbar^2} \int dR'_\beta g_\beta(R_\beta | R'_\beta | \sigma_\beta) \chi_\beta(R'_\beta | t_\beta) \quad (4.47)$$

and

$$(j_\alpha, l_\alpha | \tilde{V}_{\alpha\beta}^J(R_\alpha, r_\alpha, \gamma_\alpha) | j_\beta, l_\beta) = 2\pi \frac{\sqrt{(2l_\alpha + 1)(2l_\beta + 1)}}{2J + 1} \sum_{\Omega_\alpha \Omega_\beta} C(l_\alpha, \Omega_\alpha, j_\alpha, -\Omega_\alpha | J, 0) C(l_\beta, \Omega_\beta, j_\beta, -\Omega_\beta | J, 0) \times y_{j_\alpha \Omega_\alpha}(\gamma_\alpha, 0) \tilde{V}_{\alpha\beta}(R_\alpha, r_\alpha, \gamma_\alpha) y_{j_\beta \Omega_\beta}(\gamma_\beta, 0) d_{\Omega_\alpha \Omega_\beta}^J(\Delta_{\alpha\beta}). \quad (4.48)$$

In Eq. (4.48), we encounter the function $d_{\Omega_\alpha \Omega_\beta}^J(\Delta_{\alpha\beta})$ which is defined as

$$d_{\Omega_\alpha \Omega_\beta}^J(\Delta_{\alpha\beta}) = D_{\Omega_\alpha \Omega_\beta}^J(0, \Delta_{\alpha\beta}, 0) \quad (4.49)$$

and the angle $\Delta_{\alpha\beta}$ which can be shown to be (see also Fig. 1)

$$\Delta_{\alpha\beta} = \theta_\beta - \theta_\alpha. \quad (4.50)$$

In case that $\alpha = \beta$ the function $d_{\Omega_\alpha \Omega_\beta}^J(0)$ becomes

$$d_{\Omega_\alpha \Omega_\beta}^J(\Delta_{\alpha\beta} = 0) = \delta_{\Omega_\alpha \Omega_\beta}. \quad (4.51)$$

Equation (4.44) can be written as a matrix equation. To do that the following matrices are introduced:

(i) the square homogeneous matrix C ,

$$C = \begin{pmatrix} C_{\lambda\lambda} & C_{\lambda\nu} & C_{\lambda k} \\ C_{\nu\lambda} & C_{\nu\nu} & C_{\nu k} \\ C_{k\lambda} & C_{k\nu} & C_{kk} \end{pmatrix} \quad (4.52)$$

where the elements of each submatrix is designated by the row indices (σ_β, t_β) and the column indices $(\sigma_\alpha, t_\alpha)$

(ii) The inhomogeneous matrix b ,

$$b = \begin{pmatrix} b_{\lambda\lambda} & b_{\lambda\nu} & b_{\lambda k} \\ b_{\nu\lambda} & b_{\nu\nu} & b_{\nu k} \\ b_{k\lambda} & b_{k\nu} & b_{kk} \end{pmatrix}, \quad (4.53)$$

where the elements of each submatrix is designated by the row indices (σ_β, t_β) and the column index σ_{α_0} .

(iii) The solution matrix **a** which has an identical structure to **b**.

In both matrices, **b** and **a**, each column stands for an initial state in a given arrangement and therefore the columns are designated by one index only (which in fact stands for the three quantum numbers ($n_\alpha, j_\alpha, l_\alpha$)).

Having introduced **C**, **b**, and **a** Eqs. (4.44) can be written as

$$\mathbf{a} = \mathbf{b} + \mathbf{C}\mathbf{a}. \quad (4.54)$$

One way of solving it is by inverting matrix (**I** - **C**). Thus

$$\mathbf{a} = (\mathbf{I} - \mathbf{C})^{-1}\mathbf{b}. \quad (4.55)$$

E. The L^2 translational basis set

In order to carry out the calculations of the **b**- and the **C**-matrix elements, one has to specify the L^2 translational basis functions $\chi_\alpha(R_\alpha|t_\alpha)$: $\alpha = \lambda, \nu, k$. In their first collinear treatment of the HFH system, Shima and Baer^{58,62} employed the harmonic oscillator potential wave functions which are characterized by two parameters, the position parameter $R_{0\alpha}$ and the width of the potential d_α defined as

$$d_\alpha = \sqrt{\hbar/\mu_\alpha \nu_\alpha}, \quad (4.56)$$

where ν_α is the frequency.

In all later applications, the sine functions were employed. Thus,

$$\chi_\alpha(R_\alpha|t_\alpha) = \frac{2}{R_{2\alpha} - R_{1\alpha}} \sin\left(t_\alpha \pi \frac{R_\alpha - R_{1\alpha}}{R_{2\alpha} - R_{1\alpha}}\right), \quad (4.57)$$

where ($R_{2\alpha}, R_{1\alpha}$) is the R_α interval along which the amplitude density functions $\zeta_{\alpha\lambda}(R_\alpha, r_\alpha|n_{\lambda 0})$ are assumed to be different from zero.

V. NUMERICAL RESULTS

During the last 18 years, since the derivation of the Baer-Kouri (BK) equations [see Eqs. (2.16) or Eq. (2.21)], the BKLT equations were exposed to several numerical treatments. The first applications were all carried out for a two-arrangement-channel systems of the kind



where **B**, the atom common to the two diatomics, was assumed to be infinitely heavy (thus yielding a skewing angle of $\pi/2$). Baer and Kouri calculated transition probabilities for the collinear wave guide model²⁰ and integral and differential cross sections for the three-dimensional version of it.²¹ The collinear results fitted reasonably well with those obtained by other methods.⁹⁵ The BK equations were also applied to the low energy e - H scattering process²² and the calculated phase shifts were in good agreement with those of Schwartz.⁹⁶ The Kouri-Levin version [see Eqs. (2.15) and (2.19)] which, as mentioned previously, is more convenient for numerical application has been applied since then. Their first applications were again carried out for the above mentioned collinear wave guide models³² and the e - H scattering process.^{24,25,54} More recently, the BKLT equations were ap-

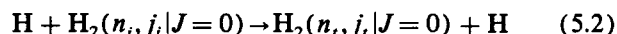
TABLE I. Three-dimensional probabilities for $\text{H} + \text{H}_2(n_i = 0, j_i|J = 0) \rightarrow \text{H}_2(n_f = 0, j_f|J = 0) + \text{H}$ for $E_{\text{tot}} = 0.6$. The calculations are carried out with (12, 12, 6) vibrotational states and eight translations L^2 states.

| $\cos \gamma_0$ | 0→0 | 0→1 | 0→2 | Total | 1→0 | 1→1 | 1→2 | Total |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|
| 0.156 | 0.015 | 0.028 | 0.016 | 0.068 | 0.029 | 0.048 | 0.033 | 0.125 |
| 0.309 | 0.021 | 0.037 | 0.017 | 0.083 | 0.037 | 0.054 | 0.029 | 0.133 |
| 0.454 | 0.026 | 0.044 | 0.016 | 0.094 | 0.045 | 0.063 | 0.028 | 0.145 |
| 0.588 | 0.027 | 0.049 | 0.017 | 0.097 | 0.049 | 0.071 | 0.030 | 0.155 |
| 0.891 | 0.025 | 0.047 | 0.021 | 0.095 | 0.049 | 0.078 | 0.041 | 0.173 |
| Ref. 98 | 0.025 | 0.044 | 0.023 | 0.097 | 0.044 | 0.077 | 0.040 | 0.168 |

plied to a number of collinear atom-diatom systems with smooth potentials and all three atoms having finite masses. The following systems were studied: the $\text{H} + \text{FH}$ system,^{58,62} the $\text{H} + \text{H}_2$ system,^{63,64,79} the $\text{D} + \text{H}_2$ system,⁷² and the $\text{F} + \text{H}_2$ system.⁷² In all cases, the results were compared with those obtained by more established methods and were found to be in good agreement with them.

All the above mentioned applications, whether collinear or three-dimensional, were two-channel systems and the corresponding 2×2 **W** matrix given in Eq. (3.1) was found to yield the relevant coupling between the two arrangements.

Difficulties were encountered once the BKLT equations were applied to three-dimensional three-channel systems. In the first application, the channel permuting array structure of **W**, given in Eqs. (3.3), was employed for the study of the exchange process



and no relevant results could be obtained. More recently, the present author^{84,88} applied the orientation-dependent **W**-matrix elements given in Eq. (3.5); the results of this numerical study, which was carried out applying the Porter-Karplus potential,⁹⁷ are presented in Tables I-IV.

The results in Tables I-III are given mainly to show their dependence on γ_{λ_0} . The interval $[0, \gamma_{\lambda_0}]$ is the range of the orientation angle γ_λ for which the strongest coupling between the initial λ arrangement and the final ν arrangement is expected (see Fig. 1). In the same way the interval $[\gamma_{\lambda_0}^+, \pi]$ is the range of γ_λ for which the strongest coupling between the λ arrangement and the final k arrangement channel is expected. Due to the high symmetry of this reaction, not only $\gamma_{\lambda_0}^- = \pi - \gamma_{\lambda_0}^+$, but also all three $\gamma_{\alpha_0}^-$; $\alpha = \lambda, \nu, k$ are equal. Thus the final results will depend on one single undetermined parameter γ_0 .

In Table I are shown transition probabilities for the re-

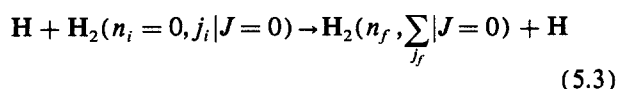
TABLE II. The same as Table I, but for $E_{\text{tot}} = 0.7$ eV and with (12, 12, 9) vibrotational states and nine translations L^2 states.

| $\cos \gamma_0$ | 0→0 | 0→1 | 0→2 | 0→3 | 0→4 | Total |
|-----------------|-------|-------|-------|-------|-------|-------|
| 0.454 | 0.046 | 0.074 | 0.055 | 0.029 | 0.006 | 0.209 |
| 0.588 | 0.054 | 0.090 | 0.055 | 0.021 | 0.006 | 0.225 |
| 0.891 | 0.053 | 0.094 | 0.058 | 0.012 | 0.001 | 0.218 |
| Ref. 99 | 0.048 | 0.092 | 0.060 | ... | ... | 0.21 |

TABLE III. Three-dimensional probabilities for $\text{H} + \text{H}_2(n_i = 0, j_i | J = 0) \rightarrow \text{H}_2(n_f = 0, j_f | J = 0) + \text{H}$ for $E_{\text{tot}} = 0.9$ eV.

| $\cos \gamma_0$ | Vibrotational states | L^2 states | 0→0 | 0→1 | 0→2 | 0→3 | 0→4 | Total |
|-----------------|----------------------|--------------|-------|-------|-------|-------|-------|-------|
| 0.588 | (12,12,10) | 9 | 0.037 | 0.072 | 0.041 | 0.020 | 0.016 | 0.20 |
| | (12,12,9,7) | 9 | 0.044 | 0.088 | 0.055 | 0.031 | 0.016 | 0.25 |
| | (12,12,10,7) | 10 | 0.048 | 0.091 | 0.055 | 0.028 | 0.016 | 0.25 |
| 0.707 | (12,12,10,7) | 10 | 0.052 | 0.098 | 0.059 | 0.028 | 0.015 | 0.26 |
| | (12,12,9,6) | 11 | 0.051 | 0.098 | 0.061 | 0.034 | 0.016 | 0.27 |
| 0.808 | (12,12,10,7) | 10 | 0.064 | 0.116 | 0.061 | 0.034 | 0.019 | 0.29 |
| | (12,12,9,6) | 11 | 0.063 | 0.113 | 0.061 | 0.026 | 0.014 | 0.28 |
| Ref. 8 | | | 0.062 | 0.108 | 0.060 | 0.024 | 0.017 | 0.28 |

action (5.2) as well as for the reaction



as calculated for the total energy $E_{\text{tot}} = 0.6$ eV. The calculations were done for the vibrational basis set (12,12,6). The set of numbers (12,12,6) means that in the calculations were employed three vibrational states with 12 rotational states in the first and second vibrations and six in the third. It is important to note that for $E_{\text{tot}} = 0.6$ eV, one encounters only seven open states, all of which belong to the ground vibrational states. Thus, in the present case, 30 vibrational states are employed although only seven were open. In addition we also had to employ the L^2 translational basis set. The results in Table I were obtained using eight of these functions for each vibrational state in each arrangement. Thus, altogether $3 \times 8 \times 30 = 720$ algebraic equations had to be solved in order to obtain all possible transition probabilities.

TABLE IV. Three-dimensional probabilities for the reaction $\text{H} + \text{H}_2(n_i = 0, j_i | J = 0) \rightarrow \text{H}_2(n_f = 0, j_f | J = 0) + \text{H}$.

| E_{tot} | 0→0 | 0→1 | 0→2 | 0→3 | 0→4 | Total |
|------------------|-------|-------|-------|-------|-------|-------|
| 0.6 | 0.025 | 0.047 | 0.021 | 0.003 | 0.0 | 0.10 |
| | 0.025 | 0.044 | 0.022 | ... | 0.0 | 0.10 |
| 0.7 | 0.053 | 0.094 | 0.058 | 0.012 | 0.001 | 0.022 |
| | 0.048 | 0.092 | 0.060 | ... | ... | 0.021 |
| 0.8 | 0.034 | 0.077 | 0.063 | 0.039 | 0.019 | 0.22 |
| | 0.037 | 0.079 | 0.068 | ... | ... | 0.23 |
| 0.9 | 0.061 | 0.113 | 0.061 | 0.026 | 0.014 | 0.28 |
| | 0.062 | 0.108 | 0.060 | 0.024 | 0.017 | 0.27 |

^a Upper row: present results. Lower row: state-to-state probabilities (Ref. 99) for energies $E = 0.6, 0.7$, and 0.8 eV and Ref. 8 for energy $E = 0.9$ eV; total probabilities (Ref. 100).

The results in Table I are compared with those of Schwenke *et al.*⁹⁸ which were obtained by the Fock scheme.^{12,13} However, it should be noted that there are several other results available^{8,99,100} and they are very similar to each other (differences are mainly in the second significant digit). The main reasons for the slight differences could be inaccuracies related to calculations for eigenvalues, eigenfunctions, translational wave functions, etc., as well as slight errors in the application of physical constants.

From the results shown in Table I the following is noticed:

(i) the smaller the γ_0 (the larger $\cos \gamma_0$), the better are the results, i.e., the closer they come to those obtained by other methods.

(ii) For practical purposes, most of the results for $j_i = 0$ obtained for $\cos \gamma_0$ in the range $0.891 < \cos \gamma_0 < 0.454$ are relevant. However, this range becomes smaller when the $j_i = 1$ results are considered.

The conclusion of this study is that if γ_0 is not chosen properly, one is forced to increase the size of his basis set in order to achieve convergence. Thus, for instance, the results for $\cos \gamma_0 = 0.309$, as shown in Table I, are not the final ones. In order to obtain for this value of $\cos \gamma_0$ the correct results, one has to add vibrotational states or L^2 translational states or both until convergence is attained.

Results for the same system, but for $E_{\text{tot}} = 0.7$ eV are presented in Table II. This time, however, the results are compared with those of Hipes and Kuppermann,⁹⁹ which were obtained following a close-coupling study employing hyperspherical coordinates. Again, the fit improves as γ_0 becomes smaller.

Results for $E_{\text{tot}} = 0.9$ eV, as calculated for different $\cos \gamma_0$ and different sizes of basis sets are presented in Table III. The results in this case are compared with those of Pack and Parker,¹² who also carried out a close-coupling calculation employing hyperspherical coordinates. As usual, the better fit is obtained for the larger $\cos \gamma_0$, namely, $\cos \gamma_0 = 0.707, 0.808$. However, it should be mentioned that significantly different results were obtained for $\cos \gamma_0 = 0.891$ (not shown here), probably mainly because for the relative high energy $E_{\text{tot}} = 0.9$ eV the range $[1, 0.891]$ for $\cos \gamma_0$ is too small to furnish the size of coupling (between the various arrangement channels) needed to obtain relevant results. From Table III one can also notice how, for $\cos \gamma_0 = 0.588$, augmenting the size of the basis set makes the results increasingly relevant.

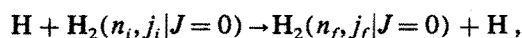
All our results, as calculated for the energies $E_{\text{tot}} = 0.6, 0.7, 0.8, 0.9$ eV are summarized in Table IV and compared with those obtained by other methods^{8,99,100}. The fit is reasonably good.

VI. CONCLUDING REMARKS

In this work, we described a theoretical approach to studying atom-diatom exchange collisions which is based on a straightforward extension of the Lippmann-Schwinger integral equation. The extension is done in an *ad hoc* fashion via a $N \times N$ W matrix (N being the number of arrangement channels) which is responsible for the coupling of the various arrangements. We have shown on different occasions

that this approach is quite general in the sense that one can obtain not only different kinds of known equations (e.g., the Faddeev-Lovelace equations and the Fock coupling scheme), but also new sets of equations, which may be numerically tractable and/or theoretically attractable. One of them follows from the assumption that the generalized potential matrix VW is symmetric and was discussed elsewhere⁸⁷ and the other considered here, is obtained by assuming the W -matrix elements to be dependent on the orientation angles $\gamma_\alpha, \alpha = \lambda, \nu, k$.

In this work we presented three-dimensional transitional probabilities obtained for the reactive three-channel system



where n_i and j_i are the initial vibrational and rotational states and n_f and j_f are the final ones. The results were obtained employing the *orientation-angle-dependent* W -matrix, elements. Although their introduction may look somewhat clumsy ("too many words"), they have two important features: (i) they yield connected potentials which guarantee the connectivity of the kernels; and (ii) they are numerically not only very tractable, but yield, to date, one of the more efficient numerical methods for treating exchange collisions. It is true that in the final structure of the equations there appear a few undetermined parameters, namely, the angles γ_α^\pm ; $\alpha = \lambda, \nu, k$ but correct results can be obtained for any combination of those, although the rate of convergence, may depend on the different choices. However, since the various γ_α^\pm have a clear physical interpretation, they can be chosen *a priori* in such a way that a fast rate of convergence is guaranteed. Moreover, the integral equations are usually solved by converting them into algebraic equations. To do that one integrates over all variables (coordinates) along their whole range of definition. Some of the integrations, like those with respect to the Euler angles, can be done analytically. The others have to be carried out numerically and most of the computer time is consumed by this process. In all available methods, the integrations over the angles $\gamma_\lambda, \gamma_\nu$, and γ_k are carried out each time from zero to π . In our case, the integration over the angles γ is done in parts. Thus, for instance, for γ_λ , the integration in the case of the $\lambda\nu$ exchange term is done from zero to γ_λ^- ; in the case of the λk exchange, it is done from γ_λ^+ to π ; and in the case of the elastic terms (nonexchange), it is done from γ_λ^- to γ_λ^+ . This fact alone can reduce the consumption of computer time by one order of magnitude as compared with the other available methods.

The integral equation approach is now used in different laboratories and might be considered as one of the more efficient and reliable methods to study three-dimensional, three-channel systems. It is my belief that the approach described here within enhances the efficiency of the similar existing approaches.

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APPENDIX: THE APPLICATION OF DISTORTED WAVE GREEN FUNCTIONS

The Green functions can be presented in terms of wave functions which are solutions either of a free Hamiltonian or of a perturbed one. While studying collinear systems we tried both and found out that although the free wave Green functions are much simpler and easily handled, the resulting coupled LS equations are numerically unstable.⁷⁹ Thus, one has to add to the free Hamiltonian a distortion potential such that the regular solutions of the extended Hamiltonians are forced to go to zero when penetrating the classical forbidden region in the vicinity of $R = 0$.^{58,62}

The employment of the distorted wave Green functions does not affect the final solution of the coupled LS equation. However, more care has to be taken regarding the calculation of the transition matrix elements. In the next chapter, we will derive the relation between a free wave and a "distorted" wave T -matrix elements for the inelastic and the rearranged collisions.

The Hamiltonian H can be written in the form

$$H = H_{0\alpha} + w_\alpha; \quad \alpha = \lambda, \nu, \quad (A1)$$

where

$$H_{0\alpha} = T_{\text{kin}}^\alpha; \quad \alpha = \lambda, \nu \quad (A2)$$

is the α th kinetic operator and w_α is the potential which will be presented as

$$w_\alpha = v_\alpha + u_\alpha; \quad \alpha = \lambda, \nu. \quad (A3)$$

Here u_α is the *distortion* potential and v_α is the perturbation. In what follows, u_α is assumed to be a potential which does not permit rearrangement. Consequently, the inelastic (unperturbed) Hamiltonian is introduced:

$$H_{u\alpha} = H_{0\alpha} + u_\alpha; \quad \alpha = \lambda, \nu. \quad (A4)$$

Next we define three wave functions:

(i) The free wave function which describes either an initial state or a final state $|\phi(\alpha, q_\alpha)\rangle$, where $q_\alpha; \alpha = \lambda, \nu$ stands for a set of quantum numbers needed to describe the specific state;

(ii) the distorted (nonreactive) wave function $|\chi(\alpha, q_\alpha)\rangle$;

(iii) the full solution of the Schrödinger equation for the initial state $q_{\lambda 0}$, i.e., $|\psi(\lambda, q_{\lambda 0})\rangle$.

Given $|\phi(\alpha, q_\alpha)\rangle$, the function $|\chi(\alpha, q_\alpha)\rangle$ can be presented as an integral of the form

$$|\chi(\alpha, q_\alpha)\rangle = |\phi(\alpha, q_\alpha)\rangle + G_{u\alpha} u_\alpha |\phi(\alpha, q_\alpha)\rangle; \quad \alpha = \lambda, \nu, \quad (A5)$$

where $G_{u\alpha}$ is the distorted wave Green function

$$G_{u\alpha} = (E + i\varepsilon - H_{u\alpha})^{-1}, \quad \alpha = \lambda, \nu. \quad (A6)$$

The full solution of the Schrödinger equation can be written, via the LS equation, in various forms:

(i) The most straightforward representation is in terms of the free state employing λ arrangement potentials and Green functions

$$|\psi(\lambda, q_{\lambda 0})\rangle = |\phi(\lambda, q_{\lambda 0})\rangle + G_{0\lambda} w_{\lambda} |\psi(\lambda, q_{\lambda 0})\rangle, \quad (\text{A7a})$$

where $G_{0\lambda}$ is the free Green function

$$G_{0\lambda} = (E + i\varepsilon - H_{0\lambda})^{-1}. \quad (\text{A6}')$$

(ii) The solution can also be represented in terms of an initial distorted wave function

$$|\psi(\lambda, q_{\lambda 0})\rangle = |\chi(\lambda, q_{\lambda 0})\rangle + G_{u\lambda} v_{\lambda} |\psi(\lambda, q_{\lambda 0})\rangle. \quad (\text{A7b})$$

(iii) A less common representation is the one employing the rearranged potentials and Green functions. Thus it can be shown that $|\psi(\lambda, q_{\lambda 0})\rangle$ can also be written as

$$|\psi(\lambda, q_{\lambda 0})\rangle = |\phi(\lambda, q_{\lambda 0})\rangle + G_{0v}(w_{\lambda} - w_v) |\phi(\lambda, q_{\lambda 0})\rangle + G_{0v} w_v |\psi(\lambda, q_{\lambda 0})\rangle, \quad (\text{A8a})$$

or in terms of the distorted wave function

$$|\psi(\lambda, q_{\lambda 0})\rangle = |\chi(\lambda, q_{\lambda 0})\rangle + G_{uv}(v_{\lambda} - v_v) |\chi(\lambda, q_{\lambda 0})\rangle + G_{uv} v_v |\psi(\lambda, q_{\lambda 0})\rangle. \quad (\text{A8b})$$

Next are introduced three kinds of T -matrix elements:

(i) The ordinary (free wave) T -matrix element $\tau(\alpha, q_{\alpha} | \lambda, q_{\lambda 0})$ defined as

$$\tau(\alpha, q_{\alpha} | \lambda, q_{\lambda 0}) = \langle \phi(\alpha, q_{\alpha}) | T_{\alpha\lambda} | \phi(\lambda, q_{\lambda 0}) \rangle = \langle \phi(\alpha, q_{\alpha}) | w_{\alpha} | \psi(\lambda, q_{\lambda 0}) \rangle. \quad (\text{A9})$$

(ii) The distorted T -matrix element $\tau_{\text{dis}}(\alpha, q_{\alpha} | \lambda, q_{\lambda 0})$ defined as

$$\tau_{\text{dis}}(\alpha, q_{\alpha} | \lambda, q_{\lambda 0}) = \langle \chi(\alpha, q_{\alpha}) | T_{\alpha\lambda}^{\text{dis}} | \chi(\lambda, q_{\lambda 0}) \rangle = \langle \chi(\alpha, q_{\alpha}) | v_{\alpha} | \psi(\lambda, q_{\lambda 0}) \rangle. \quad (\text{A10})$$

(iii) In addition to these two, we also introduce the (inelastic) unperturbed T -matrix element $\tau^{\text{ie}}(\lambda, q_{\lambda} | \lambda, q_{\lambda 0})$ defined as

$$\tau^{\text{ie}}(\lambda, q_{\lambda} | \lambda, q_{\lambda 0}) = \langle \phi(\lambda, q_{\lambda}) | T_{\lambda\lambda}^{\text{ie}} | \phi(\lambda, q_{\lambda 0}) \rangle = \langle \phi(\lambda, q_{\lambda}) | u_{\lambda} | \chi(\lambda, q_{\lambda 0}) \rangle. \quad (\text{A11})$$

To continue, we distinguish between the nonreactive channel and the reactive one.

1. The nonreactive channel

We start with Eq. (A10) and replace $\langle \chi(\lambda, q_{\lambda}) |$ by the integral given in Eq. (A5),

$$\tau_{\text{dis}}(\lambda, q_{\lambda} | \lambda, q_{\lambda 0}) = \langle \phi(\lambda, q_{\lambda}) | v_{\lambda} | \psi(\lambda, q_{\lambda 0}) \rangle + \langle \phi(\lambda, q_{\lambda}) | u_{\lambda} G_{u\lambda} v_{\lambda} | \psi(\lambda, q_{\lambda 0}) \rangle. \quad (\text{A12})$$

Next, we replace $G_{u\lambda} v_{\lambda} |\psi(\lambda, q_{\lambda 0})\rangle$ appearing in the second term of Eq. (A12) by Eq. (A7b). Thus,

$$\tau_{\text{dis}}(\lambda, q_{\lambda} | \lambda, q_{\lambda 0}) = \langle \phi(\lambda, q_{\lambda}) | v_{\lambda} | \psi(\lambda, q_{\lambda 0}) \rangle + \langle \phi(\lambda, q_{\lambda}) | u_{\lambda} | \psi(\lambda, q_{\lambda 0}) \rangle - \langle \phi(\lambda, q_{\lambda}) | u_{\lambda} | \chi(\lambda, q_{\lambda 0}) \rangle. \quad (\text{A13})$$

Recalling Eqs. (A9) and (A11), it can be seen that Eq.

(A13) leads to the relation

$$\tau(\lambda, q_{\lambda} | \lambda, q_{\lambda 0}) = \tau^{\text{dis}}(\lambda, q_{\lambda} | \lambda, q_{\lambda 0}) + \tau^{\text{ie}}(\lambda, q_{\lambda} | \lambda, q_{\lambda 0}). \quad (\text{A14})$$

This expression is the generalization for the case of (elastic) scattering by two potentials.

2. The rearranged channel

Again we start with Eq. (A10) and again replace $|\chi(\alpha, q_{\alpha})\rangle$ by the integral given in Eq. (A5),

$$\tau^{\text{dis}}(\nu, q_{\nu} | \lambda, q_{\lambda 0}) = \langle \phi(\nu, q_{\nu}) | v_{\nu} | \psi(\lambda, q_{\lambda 0}) \rangle + \langle \phi(\nu, q_{\nu}) | u_{\nu} G_{uv} v_{\nu} | \psi(\lambda, q_{\lambda 0}) \rangle. \quad (\text{A15})$$

Again, as before, $G_{uv} v_{\nu} |\psi(\lambda, q_{\lambda 0})\rangle$ is replaced, but this time by the expressions given in Eq. (A8b). Consequently Eq. (A15) becomes

$$\tau^{\text{dis}}(\nu, q_{\nu} | \lambda, q_{\lambda 0}) = \langle \phi(\nu, q_{\nu}) | v_{\nu} | \psi(\lambda, q_{\lambda 0}) \rangle + \langle \phi(\nu, q_{\nu}) | u_{\nu} | \psi(\lambda, q_{\lambda 0}) \rangle + \langle \phi(\nu, q_{\nu}) | u_{\nu} Z_{\nu} | \chi(\lambda, q_{\lambda 0}) \rangle, \quad (\text{A16})$$

where Z_{ν} is the operator

$$Z_{\nu} = I + G_{uv}(v_{\lambda} - v_v) \quad (\text{A17})$$

and I is the unit operator. Recalling the definition of G_{uv} [see Eq. (A6) as well as Eqs. (A1), (A3), and (A4)], Z_{ν} can be evaluated as follows:

$$Z_{\nu} = G_{uv}(E + i\varepsilon - H_{0v} - u_{\nu} + v_{\lambda} - v_v) = G_{uv}(E + i\varepsilon - H_{u\lambda})$$

and, consequently,

$$Z_{\nu} |\chi(\lambda, q_{\lambda 0})\rangle = G_{uv}(E + i\varepsilon - H_{u\lambda}) |\chi(\lambda, q_{\lambda 0})\rangle.$$

However $|\chi(\lambda, q_{\lambda 0})\rangle$ is the solution of the equation

$$(E - H_{u\lambda}) |\chi(\lambda, q_{\lambda 0})\rangle = 0 \quad (\text{A18})$$

so that

$$Z_{\nu} |\chi(\lambda, q_{\lambda 0})\rangle = G_{uv} i\varepsilon |\chi(\lambda, q_{\lambda 0})\rangle \quad (\text{A19})$$

which becomes zero when ε is let to go to zero (the Lippmann identity).⁹¹ Thus the contribution of the third term in Eq. (A16) can be ignored and consequently

$$\tau^{\text{dis}}(\nu, q_{\nu} | \lambda, q_{\lambda 0}) = \langle \phi(\nu, q_{\nu}) | w_{\nu} | \psi(\lambda, q_{\lambda 0}) \rangle,$$

or recalling Eq. (A9), we have

$$\tau(\nu, q_{\nu} | \lambda, q_{\lambda 0}) = \tau^{\text{dis}}(\nu, q_{\nu} | \lambda, q_{\lambda 0}). \quad (\text{A20})$$

It is noted that in contrast to the nonreactive T -matrix elements the reactive ones do not have to be modified when presented in terms of distorted solutions of the Schrödinger equations.¹⁴

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