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Donald J. Kouri

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THEORY OF REACTIVE SCATTERING. VI. VOLTERRA EQUATION FORMALISM FOR COUPLED CHANNEL AMPLITUDE DENSITIES AND MODIFIED WAVEFUNCTIONS *

by

Donald J. Kouri

Department of Chemistry

University of Houston

Houston, Texas 77004

ABSTRACT

The homogeneous integral solution procedure of Sams and Kouri is applied to integral equations derived using the coupled channel operator formalism. It is shown how one may obtain Volterra integral equations of the second kind for solving the equations for a "modified channel wavefunction" (or the channel amplitude density). The modified channel wavefunction is found to behave like the scattered portion of the wavefunction.

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I. INTRODUCTION

This paper continues a series of studies the aim of which is the development and application of various techniques for calculating scattering amplitudes for rearrangement collisions.[1] In I the homogeneous integral solution procedure of Sams and Kouri[2] was employed to discuss uncoupled integral equations for the amplitude density function for rearrangement scattering. In a subsequent analysis,[3] it was found that the uncoupled rearrangement channel operator equation required that careful account of the dissociative continuum be taken in order for results to be obtained which conserved flux. As a consequence, numerical applications recently reported have been based on coupled integral equations for the channel operators (or their associated amplitude densities).[1] These procedures have been based not on a solution of the equations by using Volterra equations but rather by algebraic techniques. It is, however, still of interest to see if procedures using the Volterra equation formalism may be derived since they have been demonstrated to be of considerable value in treating nonreactive inelastic scattering problems[4-5] and since they have much better convergence properties with respect to iterative solutions than do the equations previously considered.

In the present paper we begin with a consideration of nonreactive scattering to develop our notation and interpretation of new quantities introduced in the course of the derivation of the Volterra integral equations. Then the procedure is applied to generate coupled integral equations for amplitude densities and "modified channel wavefunctions." It is then shown how these coupled equations may be employed to obtain the Volterra integral equations of the second kind.

II. NONREACTIVE SCATTERING INTEGRAL EQUATIONS

We begin our discussion with the Lippmann-Schwinger integral equation for the scattering wavefunction $|\psi^+\rangle$ given by

$$|\psi^+\rangle = |\varphi\rangle + G_0^+ V |\psi^+\rangle \tag{1}$$

$$= |\varphi\rangle + G_0^+ \tau |\varphi\rangle \tag{2}$$

where G_0^+ is the usual causal Green's operator; τ is the channel operator and $|\varphi\rangle$ is the incident noninteracting state.[1] Following Johnson and Secrest[6] and Sams and Kouri,[2] we define the amplitude density as

$$|\zeta\rangle = V|\psi^+\rangle \tag{3}$$

$$= \tau |\varphi\rangle \tag{4}$$

such that the scattering amplitude is given by

$$f = \langle\varphi|\zeta\rangle. \tag{5}$$

It is readily verified that

$$|\zeta\rangle = V|\varphi\rangle + VG_0^+|\zeta\rangle. \tag{6}$$

We may now define a "modified channel wavefunction" as

$$|\Psi^+\rangle = G_0^+|\zeta\rangle \tag{7}$$

which is seen to satisfy the integral equation

$$|\Psi^+\rangle = G_0^+ V|\varphi\rangle + G_0^+ V|\Psi^+\rangle. \tag{8}$$

The above equation is, of course, reminiscent of the original Lippmann-Schwinger equation except in place of the inhomogeneity $|\varphi\rangle$ one has $G_0^+ V|\varphi\rangle$. Indeed, if we recall the definition of $|\mathcal{C}\rangle$, it is trivially seen that $|\Psi^+\rangle$ is simply the scattered wave portion of $|\psi^+\rangle$. As such, it is seen from either Eqs. (7) or (8) that $|\Psi^+\rangle$ asymptotically contains only outgoing scattered waves (with no plane wave inhomogeneity). Even though Eq. (8) is no more convenient to employ for calculations than Eqs. (1) or (6) from which it was derived, it is still instructive to carry the analysis of Eq. (8) further since it will aid in interpreting the meaning of the modified channel wavefunctions in the general case where reactive collisions are possible.

We now write the Green's function G_0^+ in the form[7]

$$G_0^+ = \tilde{G}_0 + g\mathcal{O} \tag{9}$$

where the operator $\mathcal{O}$ produces a constant when acting on any state $|\ \rangle$:

$$C = \mathcal{O}|\ \rangle. \tag{10}$$

Then in place of Eq. (8), we may write

$$|\tilde{\Psi}\rangle = \tilde{G}_0 V|\varphi\rangle + \tilde{G}_0 V|\Psi^+\rangle \tag{11}$$

where

$$|\tilde{\Psi}\rangle = \tilde{G}_0 |\xi\rangle. \tag{12}$$

It is obvious that

$$|\tilde{\Psi}\rangle = \tilde{G}_0 V|\varphi\rangle + \tilde{G}_0 V|\tilde{\Psi}\rangle + \tilde{G}_0 V g C^+ \tag{13}$$

where

$$C^+ = \vartheta |\xi\rangle. \tag{14}$$

Then following Sams and Kouri,[2] we can write

$$|\tilde{\Psi}\rangle = |\tilde{\Psi}_0\rangle + |\tilde{\Psi}_1\rangle C^+ \tag{15}$$

where

$$|\tilde{\Psi}_0\rangle = \tilde{G}_0 V|\varphi\rangle + \tilde{G}_0 V|\tilde{\Psi}_0\rangle \tag{16}$$

and

$$|\tilde{\Psi}_1\rangle = \tilde{G}_0 V g + \tilde{G}_0 V|\tilde{\Psi}_1\rangle. \tag{17}$$

(Parenthetically, we note that for nonreactive collisions, $g \equiv |\varphi\rangle$ and from the uniqueness of the solutions of Eqs. (16) - (17), it follows that $|\tilde{\Psi}_0\rangle = |\tilde{\Psi}_1\rangle$) . The constant C^+ is the solution of

$$C^+ = \vartheta |\xi\rangle \tag{18}$$

$$= \vartheta V|\varphi\rangle + \vartheta V|\Psi^+\rangle. \tag{19}$$

Then by Eq. (15), we finally obtain

$$C^{+} = \mathcal{O}V|\varphi\rangle + \mathcal{O}V|\widetilde{\Phi}_0\rangle + \mathcal{O}V|\widetilde{\Phi}_1\rangle C^{+}. \tag{20}$$

Except for the particular inhomogeneity in Eqs. (16) - (17), the above expressions are identical to those in Sams and Kouri's[2] treatment of the nonreactive Lippmann-Schwinger equation. The equations for the $|\widetilde{\Phi}_0\rangle$ and $|\widetilde{\Phi}_1\rangle$ in the coordinate representation are Volterra integral equations of the second kind and therefore the same quadrature procedure can be applied in their solution.

III. AMPLITUDE DENSITY AND MODIFIED WAVEFUNCTION EQUATIONS FOR REACTIVE SCATTERING

In direct analogy with the preceeding discussion, we now consider the amplitude density equations for rearrangement collisions. However, in contrast to the preceeding approach, we shall no longer define the amplitude density by direct recourse to the Lippmann-Schwinger equation[6] for $|\psi_\alpha^{+}(i)\rangle$ but rather we use the approach of Eq. (4) which is based on the channel operator.[1] Again, we do not employ the definition of channel operators as is implied by Eqs. (3) - (4) but instead use the definition[1,8]

$$\tau_{\gamma\alpha} = V_\alpha + V_\gamma (E - H + i\epsilon)^{-1} V_\alpha . \tag{21}$$

If, for simplicity we restrict attention to a problem with two arrangement channels, it has been shown that the channel operators $\tau_{\alpha\alpha}$ and $\tau_{\beta\alpha}$ satisfy coupled integral equations given by[1,3]

$$\tau_{\alpha\alpha} = V_\alpha + V_\alpha \sum_\gamma W_{\alpha\gamma}(E - K_\gamma + i\epsilon)^{-1} \tau_{\gamma\alpha} \tag{22}$$

and

$$\tau_{\beta\alpha} = V_\alpha + V_\beta \sum_\gamma W_{\beta\gamma}(E - K_\gamma + i\epsilon)^{-1} \tau_{\gamma\alpha} . \tag{23}$$

Then the amplitude densities $|\mathcal{L}_{\alpha\alpha}(i)\rangle$ and $|\mathcal{L}_{\beta\alpha}(i)\rangle$ satisfy coupled equations of the form

$$|\mathcal{L}_{\alpha\alpha}(i)\rangle = V_\alpha |\varphi_\alpha(i)\rangle + V_\alpha \sum_\gamma W_{\alpha\gamma} G^+_{o\gamma} |\mathcal{L}_{\gamma\alpha}(i)\rangle , \tag{24}$$

$$|\mathcal{L}_{\beta\alpha}(i)\rangle = V_\alpha |\varphi_\alpha(i)\rangle + V_\beta \sum_\gamma W_{\beta\gamma} G^+_{o\gamma} |\mathcal{L}_{\gamma\alpha}(i)\rangle . \tag{25}$$

We then easily write

$$|\mathcal{L}_{\alpha\alpha}(i)\rangle = V_\alpha |\varphi_\alpha(i)\rangle + V_\alpha \sum_\gamma W_{\alpha\gamma} \tilde{G}_{o\gamma} |\mathcal{L}_{\gamma\alpha}(i)\rangle + V_\alpha \sum_\gamma W_{\alpha\gamma} g_\gamma \vartheta_\gamma |\mathcal{L}_{\gamma\alpha}(i)\rangle \tag{26}$$

and

$$|\mathcal{L}_{\beta\alpha}(i)\rangle = V_\alpha |\varphi_\alpha(i)\rangle + V_\beta \sum_\gamma W_{\beta\gamma} \tilde{G}_{o\gamma} |\mathcal{L}_{\gamma\alpha}(i)\rangle + V_\beta \sum_\gamma W_{\beta\gamma} g_\gamma \vartheta_\gamma |\mathcal{L}_{\gamma\alpha}(i)\rangle . \tag{27}$$

It is natural to define a "modified wavefunction"[8,9] $|\Psi^+_{\gamma\alpha}(i)\rangle$ by

$$|\Psi^+_{\gamma\alpha}(i)\rangle = G^+_{o\gamma} |\mathcal{L}_{\gamma\alpha}(i)\rangle . \tag{28}$$

Furthermore, from the fact that the scattering amplitude for going from $\alpha, i \to \gamma, j$ is

$$f(\gamma j \leftarrow \alpha i) = \langle \varphi_\gamma(j) | \mathcal{C}_{\gamma\alpha}(i) \rangle , \tag{29}$$

it readily follows that in the asymptotic limit of $R_\gamma \to \infty$, $|\Psi^+_{\gamma\alpha}(i)\rangle$ is identical with the scattered wavefunction.[8] Thus, the interpretation of the preceeding section can be carried over even though a different definition of the channel operator has been used to define the modified channel wavefunction.

We now operate on Eq. (26) with $\tilde{G}_{o\alpha}$ and Eq. (27) with $\tilde{G}_{o\beta}$ to obtain

$$\begin{aligned} |\tilde{\Psi}_{\alpha\alpha}(i)\rangle = \tilde{G}_{o\alpha} V_\alpha |\varphi_\alpha(i)\rangle &+ \tilde{G}_{o\alpha} V_\alpha \sum_\gamma W_{\alpha\gamma} |\tilde{\Psi}_{\gamma\alpha}(i)\rangle \\ &+ \tilde{G}_{o\alpha} V_\alpha \sum_\gamma W_{\alpha\gamma} g_\gamma C^+_{\gamma\alpha}(i) \end{aligned} \tag{30}$$

and

$$\begin{aligned} |\tilde{\Psi}_{\beta\alpha}(i)\rangle = \tilde{G}_{o\beta} V_\alpha |\varphi_\alpha(i)\rangle &+ \tilde{G}_{o\beta} V_\beta \sum_\gamma W_{\beta\gamma} |\tilde{\Psi}_{\gamma\alpha}(i)\rangle \\ &+ \tilde{G}_{o\beta} V_\beta \sum_\gamma W_{\beta\gamma} g_\gamma C^+_{\gamma\alpha}(i) . \end{aligned} \tag{31}$$

The major difference between Eqs. (30) - (31) and Eq. (13) is the presence of the coupling between the two channels α and β. It is convenient to express these equations in matrix form by

$$\begin{aligned} \underset{\sim}{\tilde{\Psi}}_\alpha(i) = \underset{\approx}{\tilde{G}}_o \cdot \underset{\sim}{\Phi}_\alpha(i) &+ \underset{\approx}{\tilde{G}}_o \cdot \underset{\approx}{V} \cdot \underset{\sim}{\tilde{\Psi}}_\alpha(i) \\ &+ \underset{\approx}{\tilde{G}}_o \cdot \underset{\approx}{g} \cdot \underset{\sim}{C}^+_\alpha(i) \end{aligned} \tag{32}$$

where $\underset{\approx}{\tilde{G}}_o$ and $\underset{\approx}{g}$ are diagonal matrices given by

$$[\underline{\underline{\tilde{G}}}^{o}]_{\gamma\gamma'} = \delta_{\gamma\gamma'}\,\tilde{G}_{o\gamma} \tag{33}$$

and

$$[\underline{\underline{g}}]_{\gamma\gamma'} = \delta_{\gamma\gamma'}\,g_{\gamma}\,, \tag{34}$$

the matrix $\underline{\underline{V}}$ is of the form

$$[\underline{\underline{V}}]_{\gamma\gamma'} = V_{\gamma}\,W_{\gamma\gamma'} \tag{35}$$

and the vectors $\underline{\tilde{\Psi}}_{\alpha}(i)$, $\underline{\Phi}_{\alpha}(i)$ and $\underline{C}^{+}_{\alpha}(i)$ are given by

$$[\underline{\tilde{\Psi}}_{\alpha}(i)]_{\gamma} = \tilde{\Psi}_{\gamma\alpha}(i)\,, \tag{36}$$

$$[\underline{\Phi}_{\alpha}(i)]_{\gamma} = V_{\alpha}\,|\varphi_{\alpha}(i)\rangle\,, \tag{37}$$

and

$$[\underline{C}^{+}_{\alpha}(i)]_{\gamma} = C^{+}_{\gamma\alpha}(i)\,. \tag{38}$$

Very similar equations hold for the amplitude densities as obtained from Eqs. (26) - (27):

$$\underline{\zeta}_{\alpha}(i) = \underline{\Phi}_{\alpha}(i) + \underline{\underline{V}}\cdot\underline{\underline{\tilde{G}}}_{o}\cdot\underline{\zeta}_{\alpha}(i) + \underline{\underline{V}}\cdot\underline{\underline{g}}\cdot\underline{C}^{+}_{\alpha}(i) \tag{39}$$

where

$$[\underline{\mathcal{L}}_\alpha(i)]_\gamma = \mathcal{L}_{\gamma\alpha}(i). \tag{40}$$

Because of the essential similarity of the Eqs. (32) and (39) for the modified channel wavefunctions and amplitude densities respectively, it is convenient to proceed in our discussion by considering a general matrix integral equation of the form

$$\underline{\mathcal{F}}_\alpha(i) = \underline{\mathcal{J}}_\alpha(i) + \underline{\underline{\mathcal{G}}}_0 \cdot \underline{\mathcal{F}}_\alpha(i) + \mathcal{g} \cdot \underline{C}_\alpha(i) \tag{41}$$

where obviously, for the amplitude density, $\underline{\mathcal{J}}_\alpha(i)$ is $\underline{\Phi}_\alpha(i)$, $\underline{\underline{\mathcal{G}}}_0$ is $\underline{\underline{V}} \cdot \underline{\underline{\tilde{G}}}_0$ and $\mathcal{g}$ is $\underline{\underline{V}} \cdot \mathcal{g}$; whereas for the modified channel wavefunction, $\underline{\mathcal{J}}_\alpha(i)$ is $\underline{\underline{\tilde{G}}}_0 \cdot \underline{\Phi}_\alpha(i)$, $\underline{\underline{\mathcal{G}}}_0$ is $\underline{\underline{\tilde{G}}}_0 \cdot \underline{\underline{V}}$ and $\mathcal{g}$ is $\underline{\underline{\tilde{G}}}_0 \cdot \underline{\underline{V}} \cdot \mathcal{g}$. (The vector $\underline{C}_\alpha(i)$ is of course the same in both equations).

In order to effect the solution of Eq. (41), we begin by analogy with Sams and Kouri[2] to write

$$\underline{\mathcal{F}}_\alpha(i) = \underline{\mathcal{F}}_\alpha^{(0)}(i) + \underline{\underline{\mathcal{F}}}^{(1)} \cdot \underline{C}_\alpha(i) \tag{42}$$

where

$$\underline{\mathcal{F}}_\alpha^{(0)}(i) = \underline{\mathcal{J}}_\alpha(i) + \underline{\underline{\mathcal{G}}}_0 \cdot \underline{\mathcal{F}}_\alpha^{(0)}(i). \tag{43}$$

It immediately follows that

$$\underline{\underline{\mathcal{F}}}^{(1)} = \mathcal{g} + \underline{\underline{\mathcal{G}}}_0 \cdot \underline{\underline{\mathcal{F}}}^{(1)} \tag{44}$$

and the elements of the array $\underline{C}_\alpha(i)$ are found from

$$\underline{C}_\alpha(i) = \underline{\underline{\vartheta}} \cdot \underline{\mathcal{E}}_\alpha(i) \tag{45}$$

with

$$[\underline{\underline{\vartheta}}]_{\gamma\gamma'} = \delta_{\gamma\gamma'} \vartheta_\gamma . \tag{46}$$

Then by Eq. (42) for the choice $\underline{\mathcal{F}}_\alpha(i) = \underline{\mathcal{E}}_\alpha(i)$, we have

$$\underline{C}_\alpha(i) = \underline{\underline{\vartheta}} \cdot \left[\underline{\mathcal{F}}_\alpha^{(0)}(i) + \underline{\underline{\mathcal{F}}}^{(1)} \cdot \underline{C}_\alpha(i) \right] \tag{47}$$

which generates a set of algebraic equations for the constant elements of $\underline{C}_\alpha(i)$. On the other hand, if we are dealing with modified wavefunctions, then noting Eqs. (28) and (39), we have

$$\underline{C}_\alpha(i) = \underline{\underline{\vartheta}} \cdot \left[\underline{\Phi}_\alpha(i) + \underline{\underline{V}} \cdot \underline{\tilde{\Psi}}_\alpha(i) + \underline{\underline{V}} \cdot \underline{\underline{g}} \cdot \underline{C}_\alpha(i) \right] \tag{48}$$

and again using Eq. (42), we arrive at the algebraic equations

$$\underline{C}_\alpha(i) = \underline{\underline{\vartheta}} \cdot \left[\underline{\Phi}_\alpha(i) + \underline{\underline{V}} \cdot \underline{\tilde{\Psi}}_\alpha^{(0)}(i) + \underline{\underline{V}} \cdot \underline{\underline{\tilde{\Psi}}}^{(1)} \cdot \underline{C}_\alpha(i) + \underline{\underline{V}} \cdot \underline{\underline{g}} \cdot \underline{C}_\alpha(i) \right] \tag{49}$$

for determining the $\underline{C}_\alpha(i)$ array.

Up to this point in our discussion, the analogy with the nonreactive case has been relatively strong. However, at this stage it is important to stress that unlike Eqs. (16) - (17), Eqs. (43) - (44) are not Volterra

integral equations of the second kind. Rather they are still of a mixed variety (neither purely Fredholm nor Volterra).

In order to display this more clearly, it is convenient to express the equations in the coordinate representation. However, because both Eqs. (43) - (44) have the same basic structure, we shall deal only with Eq. (43). (In order to treat the equation for $\underline{\underline{\mathcal{F}}}^{(1)}$, it is convenient to split it up into columns labeled $\underline{\mathcal{F}}^{(11)}$ and $\underline{\mathcal{F}}^{(12)}$. Then $\underline{\mathcal{F}}^{(11)}$, $\underline{\mathcal{F}}^{(12)}$ and $\underline{\mathcal{F}}_{\alpha}^{(0)}(i)$ are treated in essentially the same fashion). We take the coordinate representation of $\underline{\mathcal{J}}_{\alpha}(i)$ to be

$$\mathcal{J}_{\alpha\alpha}(i) = \mathcal{J}_{\alpha\alpha}(\underset{\sim}{r}_{\alpha}, \underset{\sim}{R}_{\alpha}), \tag{50}$$

$$\mathcal{J}_{\beta\alpha}(i) = \mathcal{J}_{\beta\alpha}(\underset{\sim}{r}_{\beta}, \underset{\sim}{R}_{\beta}) \tag{51}$$

where $\underset{\sim}{r}_{\alpha}$ denotes the coordinates for internal degrees of freedom in the α configuration and $\underset{\sim}{R}_{\alpha}$ denotes the relative scattering vector in the α configuration. For purposes of concreteness, if we consider an atom-diatom collision, then $\underset{\sim}{r}_{\alpha}$ describes the orientation and vibration of the diatom and $\underset{\sim}{R}_{\alpha}$ is the vector from the incoming atom to the diatom center of mass. (The coordinate representation of $\mathcal{J}_{\beta\alpha}(i)$ is written as a function of α configuration coordinates if one is treating the amplitude density. In the modified channel wavefunction equations, it is a function of $\underset{\sim}{r}_{\beta}$, $\underset{\sim}{R}_{\beta}$. Of course, one may readily transform from one set of coordinates to another without undue difficulty in the case of the inhomogeneity.) The coordinate representation of $\underline{\mathcal{F}}_{\alpha}^{(0)}(i)$ is given by

$$\mathcal{F}^{(0)}_{\alpha\alpha}(i) = \mathcal{F}^{(0)}_{\alpha\alpha}(i|\underset{\sim}{r}_\alpha, \underset{\sim}{R}_\alpha) \tag{52}$$

and

$$\mathcal{F}^{(0)}_{\beta\alpha}(i) = \mathcal{F}^{(0)}_{\beta\alpha}(i|\underset{\sim}{r}_\beta, \underset{\sim}{R}_\beta). \tag{53}$$

Finally, the form taken for the quantity $\underline{\underline{\mathcal{G}}}_0$ is given by

$$\mathcal{G}_{\gamma\gamma'} = -i\sum_j \frac{W_{\gamma\gamma'}}{k_j} V_\gamma(\underset{\sim}{r}_\gamma, \underset{\sim}{R}_\gamma)\, \chi_{\gamma'}(j|r_{\gamma'})\, \chi^*_{\gamma'}(j|r'_{\gamma'})$$
$$\left[g^1(j|R'_{\gamma'})\, g^2(j|R_{\gamma'}) - g^1(j|R_{\gamma'})\, g^2(j|R'_{\gamma'})\right] \mathcal{Y}(j|\hat{r}_{\gamma'}, \hat{R}_{\gamma'})\, \mathcal{Y}^*(j|\hat{r}'_{\gamma'}, \hat{R}'_{\gamma'}) \tag{54}$$

if, for example, one is dealing with the amplitude density, and is given by

$$\mathcal{G}_{\gamma\gamma'} = -i\sum_j \frac{W_{\gamma\gamma'}}{k_j} V_\gamma(\underset{\sim}{r}'_\gamma, \underset{\sim}{R}'_\gamma)\, \chi_\gamma(j|r_\gamma)\, \chi^*_\gamma(j|r'_\gamma) \left[g^1(j|R'_\gamma)\, g^2(j|R_\gamma)\right.$$
$$\left. - g^1(j|R_\gamma)\, g^2(j|R'_\gamma)\right] \mathcal{Y}(j|\hat{r}_\gamma, \hat{R}_\gamma)\, \mathcal{Y}^*(j|\hat{r}'_\gamma, \hat{R}'_\gamma) \tag{55}$$

if one is treating the modified channel wavefunctions. Here, g^1 is the regular spherical Bessel function, g^2 is the spherical Hankel function of the first kind, $\chi_\gamma(j|r_\gamma)$ is a vibrational internal state function, $\mathcal{Y}(j|\hat{r}_\gamma, \hat{R}_\gamma)$ is a coupled representation

total angular function and $\mathcal{G}_{\gamma\gamma'}$ is always an integral operator on a function of its primed argument. In connection with the integral operator nature of $\mathcal{G}_{\gamma\gamma'}$, it is stressed that the integral over the primed radial scattering coordinate R'_γ is always from zero up to the unprimed radial scattering coordinate R_γ.[7] In what follows, we shall now specifically treat the channel amplitude density choice of $\mathcal{G}_{\gamma\gamma'}$ but the procedure for analyzing the equations using $\mathcal{G}_{\gamma\gamma'}$ given by Eq. (55) is sufficiently similar that no difficulties should arise in visualizing those results.

We therefore substitute Eq. (50) - (54) into Eq. (43) to obtain

$$\mathcal{F}_{\alpha\alpha}(i|\underset{\sim}{r}_\alpha, \underset{\sim}{R}_\alpha) = \mathcal{I}_{\alpha\alpha}(\underset{\sim}{r}_\alpha, \underset{\sim}{R}_\alpha) - i\sum_{\gamma,j} \frac{W_{\alpha\gamma}}{k_j} V_\alpha(\underset{\sim}{r}_\alpha, \underset{\sim}{R}_\alpha)\, \mathcal{X}_\gamma(j|r_\gamma)\, \mathcal{Y}(j|\hat{r}_\gamma, \hat{R}_\gamma)$$
$$\int d\underset{\sim}{r}'_\gamma \int d\hat{R}'_\gamma \int_0^{R_\gamma} dR'_\gamma\, \mathcal{X}^*_\gamma(j|r'_\gamma)\, \mathcal{Y}^*(j|\hat{r}'_\gamma, \hat{R}'_\gamma) \left[g^1(j|R'_\gamma)\, g^2(j|R_\gamma)\right]_D$$
$$\mathcal{F}_{\gamma\alpha}(i|\underset{\sim}{r}'_\gamma, \underset{\sim}{R}'_\gamma) \tag{56}$$

and

$$\mathcal{F}_{\beta\alpha}(i|\underset{\sim}{r}_\beta, \underset{\sim}{R}_\beta) = \mathcal{I}_{\beta\alpha}(\underset{\sim}{r}_\alpha, \underset{\sim}{R}_\alpha) - i\sum_{\gamma,j} \frac{W_{\beta\gamma}}{k_j} V_\beta(\underset{\sim}{r}_\beta, \underset{\sim}{R}_\beta)\, \mathcal{X}_\gamma(j|r_\gamma)$$
$$\mathcal{Y}(j|\hat{r}_\gamma, \hat{R}_\gamma) \int d\underset{\sim}{r}'_\gamma \int d\hat{R}'_\gamma \int_0^{R_\gamma} dR'_\gamma\, \mathcal{X}^*_\gamma(j|r'_\gamma)\, \mathcal{Y}^*(j|\hat{r}'_\gamma, \hat{R}'_\gamma)$$
$$\left[g^1(j|R'_\gamma)\, g^2(j|R_\gamma)\right]_D\, \mathcal{F}_{\gamma\alpha}(i|\underset{\sim}{r}'_\gamma, \underset{\sim}{R}'_\gamma), \tag{57}$$

where we have denoted $\left[g^1(j|R_\gamma')\,g^2(j|R_\gamma) - g^1(j|R_\gamma)\,g^2(j|R_\gamma')\right]$ by $\left[g^1(j|R_\gamma')\,g^2(j|R_\gamma)\right]_D$. We then expand the functions $\mathcal{F}_{\gamma\alpha}(i|\underset{\sim}{r}_\gamma,\underset{\sim}{R}_\gamma)$ in the basis of internal functions $\chi_\gamma(j|r_\gamma)\mathcal{Y}(j|\hat{r}_\gamma,\hat{R}_\gamma)$ to obtain (upon substitution of the expansions into Eqs. (56) - (57)) the equations

$$\mathcal{F}_{\alpha\alpha}(j'|i|R_\alpha) = \int d\underset{\sim}{r}_\alpha \int d\hat{R}_\alpha\, \chi_\alpha^*(j'|r_\alpha)\mathcal{Y}^*(j'|\hat{r}_\alpha,\hat{R}_\alpha)\mathcal{J}_{\alpha\alpha}(\underset{\sim}{r}_\alpha,\underset{\sim}{R}_\alpha)$$
$$-i\sum_{\gamma,j}\frac{W_{\alpha\gamma}}{k_j}\int d\underset{\sim}{r}_\alpha\int d\hat{R}_\alpha\,\chi_\alpha^*(j'|r_\alpha)\mathcal{Y}^*(j'|\hat{r}_\alpha,\hat{R}_\alpha)V_\alpha(\underset{\sim}{r}_\alpha,\underset{\sim}{R}_\alpha)\chi_\gamma(j|r_\gamma)$$
$$\mathcal{Y}(j|\hat{r}_\gamma,\hat{R}_\gamma)\int_0^{R_\gamma} dR_\gamma'\left[g^1(j|R_\gamma')\,g^2(j|R_\gamma)\right]_D \mathcal{F}_{\gamma\alpha}(j|i|R_\gamma') \tag{58}$$

and

$$\mathcal{F}_{\beta\alpha}(j'|i|R_\beta) = \int d\underset{\sim}{r}_\beta \int d\hat{R}_\beta\, \chi_\beta^*(j'|r_\beta)\mathcal{Y}^*(j'|\hat{r}_\beta,\hat{R}_\beta)\mathcal{J}_{\beta\alpha}(\underset{\sim}{r}_\alpha,\underset{\sim}{R}_\alpha)$$
$$-i\sum_{\gamma,j}\frac{W_{\beta\gamma}}{k_j}\int d\underset{\sim}{r}_\beta\int d\hat{R}_\beta\,\chi_\beta^*(j'|r_\beta)\mathcal{Y}^*(j'|\hat{r}_\beta,\hat{R}_\beta)V_\beta(\underset{\sim}{r}_\beta,\underset{\sim}{R}_\beta)\chi_\gamma(j|r_\gamma)$$
$$\mathcal{Y}(j|\hat{r}_\gamma,\hat{R}_\gamma)\int_0^{R_\gamma} dR_\gamma'\left[g^1(j|R_\gamma')\,g^2(j|R_\gamma)\right]_D \mathcal{F}_{\gamma\alpha}(j|i|R_\gamma'). \tag{59}$$

The above equations are interesting in that if one chooses for $W_{\alpha\gamma}$ and $W_{\beta\gamma}$ respectively $\delta_{\alpha\gamma}$ and $\delta_{\beta\gamma}$, then Volterra equations immediately result for $\mathcal{F}_{\gamma\alpha}(j|i|R_\gamma)$. However, the equation for the rearrangement function

has been previously shown to violate conservation of flux if the dissociative continuum eigenstates of K_β are neglected or not properly treated.[3] Since we do not propose in the above equations to include the continuum, we cannot employ this particular choice of $W_{\gamma\gamma'}$. (However, the Volterra equation obtained for $\mathcal{F}_{\alpha\alpha}(j'|i|R_\alpha)$ with this choice of $W_{\gamma\gamma'}$ does give results that conserve flux. Of course, these results are reliable only if the rearrangement channel is unimportant.)

Another choice of $W_{\gamma\gamma'}$ is that used by Baer and Kouri in papers II-V of this series. They take $W_{\alpha\gamma}$ equal to $(1-\delta_{\alpha\gamma})$ and $W_{\beta\gamma}$ equal to $(1-\delta_{\beta\gamma})$. In this case, we note that triple integrals occur on the right hand side of both Eqs. (58) and (59), the first being $\int d\underset{\sim}{r}_\alpha \int d\hat{R}_\alpha \int_0^{R_\beta} dR'_\beta$ and the second is $\int d\underset{\sim}{r}_\beta \int d\hat{R}_\beta \int_0^{R_\alpha} dR'_\alpha$. Following Miller[9] and Baer and Kouri,[1] we can transform integrals of the form $\int d\underset{\sim}{r}_\gamma \int d\hat{R}_\gamma \int_0^{R_{\gamma'}} dR'_{\gamma'}$ to $\int d\Omega \int d(\cos\lambda_{\gamma\gamma'}) \int_0^\infty dR_{\gamma'} \int_0^{R_{\gamma'}} dR_{\gamma'}$ where $\int d\Omega$ is an integral over the three Euler angles defining the orientation of the system and $\int d(\cos\lambda_{\gamma\gamma'})$ is an integral over an internal angle associated with the shape of the system. The significant integrals are $\int_0^\infty dR_{\gamma'} \int_0^{R_{\gamma'}} dR'_{\gamma'}$ which show that the integral equations are of the pure Fredholm kind.

In order to derive Volterra equations for describing reactive plus nonreactive scattering we can now choose $W_{\gamma\gamma'}$ to be 1/N where N is the number of channel configurations (in the present case, two). Equations (58) and (59) then are written as

$$\mathcal{F}_{\alpha\alpha}(j'|i|R_\alpha) = \mathcal{J}_{\alpha\alpha}(j'|R_\alpha)$$
$$-\frac{i}{2}\sum_j \frac{1}{k_j} V_\alpha(j'|j|R_\alpha)\int_0^{R_\alpha} dR_\alpha' \left[g^1(j|R_\alpha')\, g^2(j|R_\alpha)\right]_D \mathcal{F}_{\alpha\alpha}(j|i|R_\alpha')$$
$$-\frac{i}{2}\sum_\ell \frac{1}{k_\ell}\int_0^\infty dR_\beta \int_0^{R_\beta} dR_\beta' \left[g^1(\ell|R_\beta')\, g^2(\ell|R_\beta)\right]_D \mathcal{F}_{\beta\alpha}(\ell|i|R_\beta') V_\alpha(j'|\ell|R_\alpha, R_\beta)$$

(60)

and

$$\mathcal{F}_{\beta\alpha}(\ell'|i|R_\beta) = \mathcal{J}_{\beta\alpha}(\ell'|R_\beta)$$
$$-\frac{i}{2}\sum_\ell \frac{1}{k_\ell} V_\beta(\ell'|\ell|R_\beta)\int_0^{R_\beta} dR_\beta' \left[g^1(\ell|R_\beta')\, g^2(\ell|R_\beta)\right]_D \mathcal{F}_{\beta\alpha}(\ell|i|R_\beta')$$
$$-\frac{i}{2}\sum_j \frac{1}{k_j}\int_0^\infty dR_\alpha \int_0^{R_\alpha} dR_\alpha' \left[g^1(j|R_\alpha')\, g^2(j|R_\alpha)\right]_D \mathcal{F}_{\alpha\alpha}(j|i|R_\alpha') V_\beta(\ell'|j|R_\beta, R_\alpha).$$

(61)

It is now apparent that in order to generate Volterra integral equations, an analysis similar to that which lead to the original $\underline{\mathcal{F}}_\alpha(i)$ equations may be employed. However, an important distinction now arises due to the presence in the terms $\int_0^\infty dR_\gamma \int_0^{R_\gamma} dR_\gamma' \left[g^1(j|R_\gamma')\, g^2(j|R_\gamma)\right]_D$ $\mathcal{F}_{\gamma\alpha}(j|i|R_\gamma') V_{\gamma'}(\ell|j|R_{\gamma'}, R_\gamma)$.

The important point is that the quantity $V_{\gamma'}(\ell|j|R_{\gamma'}, R_\gamma)$ in general is not a separable function of $R_{\gamma'}, R_\gamma$. If, however, it is expanded in a complete set of functions φ_λ, then Eqs. (60) - (61) can be represented by

$$\mathcal{F}_{\gamma\alpha}(j'|i|R_\gamma) = \mathcal{J}_{\gamma\alpha}(j'|R_\gamma)$$
$$-\frac{i}{2}\sum_{\ell}\frac{1}{k_\ell}\int_0^\infty dR_{\gamma'}\int_0^{R_{\gamma'}} dR'_{\gamma'}\left[g^1(\ell|R'_{\gamma'})\,g^2(\ell|R_{\gamma'})\right]_D \mathcal{F}_{\gamma'\alpha}(\ell|i|R'_{\gamma'})$$
$$\sum_\lambda V_{\gamma\lambda}(j'|\ell|R_{\gamma'})\,\varphi_\lambda(R_\gamma)$$
$$-\frac{i}{2}\sum_j\frac{1}{k_j}V_\gamma(j'|j|R_\gamma)\int_0^{R_\gamma} dR'_\gamma\left[g^1(j|R'_\gamma)\,g^2(j|R_\gamma)\right]_D \mathcal{F}_{\gamma\alpha}(j|i|R'_\gamma).$$

(62)

It immediately follows that constants $B^{\alpha}_{\gamma\gamma'}(\lambda|j)$ may be defined by

$$B^{\alpha}_{\gamma\gamma'}(\lambda|j) = \frac{-i}{2}\sum_{j'}\frac{1}{k_{j'}}\int_0^\infty dR_{\gamma'}\int_0^{R_{\gamma'}} dR'_{\gamma'}\,V_{\gamma\lambda}(j|j'|R_{\gamma'})$$
$$\left[g^1(j'|R'_{\gamma'})\,g^2(j'|R_{\gamma'})\right]_D \mathcal{F}_{\gamma'\alpha}(j'|i|R'_{\gamma'}),$$

(63)

and therefore Eq. (62) becomes

$$\mathcal{F}_{\gamma\alpha}(j'|i|R_\gamma) = \mathcal{J}_{\gamma\alpha}(j'|R_\gamma)$$
$$-\frac{i}{2}\sum_j\frac{1}{k_j}V_\gamma(j'|j|R_\gamma)\int_0^{R_\gamma} dR'_\gamma\left[g^1(j|R'_\gamma)\,g^2(j|R_\gamma)\right]_D \mathcal{F}_{\gamma\alpha}(j|i|R'_\gamma)$$
$$+\sum_\lambda B^{\alpha}_{\gamma\gamma'}(\lambda|j')\,\varphi_\lambda(R_\gamma).$$

(64)

These equations are easily put in matrix form so that

$$\underline{\mathcal{F}}_\alpha = \underline{\mathcal{J}}_\alpha - \frac{i}{2}\,\underline{\underline{\tilde{V}}}\cdot\underline{\underline{\tilde{G}}}_0\cdot\underline{\mathcal{F}}_\alpha + \sum_\lambda \underline{\varphi}_\lambda\cdot\underline{\underline{B}}^\alpha_\lambda \tag{65}$$

where $\underline{\underline{\tilde{V}}}$ and $\underline{\underline{\tilde{G}}}_0$ are diagonal matrices the definition of which is easily inferred by comparison of Eqs. (64) and (65) and the matrices $\underline{\underline{B}}_\lambda$ have a structure given by

$$\left[\underline{\underline{B}}^\alpha_\lambda\right]_{\gamma\gamma'} = (1-\delta_{\gamma\gamma'})\,B^\alpha_{\gamma\gamma'}\,. \tag{66}$$

Then the solution of Eqs. (64) can be written as

$$\underline{\mathcal{F}}_\alpha = \underline{\mathcal{F}}^{(0)}_\alpha + \sum_\lambda \underline{\mathcal{F}}_\lambda\cdot\underline{\underline{B}}^\alpha_\lambda \tag{67}$$

where

$$\underline{\mathcal{F}}^{(0)}_\alpha = \underline{\mathcal{J}}_\alpha - \frac{i}{2}\,\underline{\underline{\tilde{V}}}\cdot\underline{\underline{\tilde{G}}}_0\cdot\underline{\mathcal{F}}^{(0)}_\alpha \tag{68}$$

and

$$\underline{\mathcal{F}}_\lambda = \underline{\varphi}_\lambda - \frac{i}{2}\,\underline{\underline{\tilde{V}}}\cdot\underline{\underline{\tilde{G}}}_0\cdot\underline{\mathcal{F}}_\lambda\,. \tag{69}$$

Both $\underline{\mathcal{F}}^{(0)}_\alpha$ and $\underline{\mathcal{F}}_\lambda$ therefore satisfy Volterra integral equations. This result completes the derivation of Volterra equations describing reactive and nonreactive scattering. In conclusion, these equations will again have the property that, in solving Eqs. (68) and (69) for the $\underline{\mathcal{F}}^{(0)}_\alpha$ and $\underline{\mathcal{F}}_\lambda$, no matrix inversions are

required[2] as a consequence of the particular form of $\underline{\underline{\tilde{G}}}_{\alpha}$. Of course, it is necessary to perform matrix inversions to obtain $\underline{\mathcal{F}}_{\alpha}$ from $\underline{\mathcal{F}}_{\alpha}^{(0)}$ and the $\underline{\mathcal{F}}_{\lambda}$ but these are performed once and the order of the matrix inverted does not depend on the number of quadrature points used to solve the integral equations. Also, because these integral equations have a triangular kernal, it follows that iterative solutions of the Eqs. (68) - (69) converge under quite loose conditions.[10] Finally, it is realized that the present procedure for obtaining Volterra equations from coupled channels operators is not the only way this can be done and other approaches are presently under study.

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7. In order to clarify the Green's function $\tilde{G}_0$ and the operator $\mathcal{O}$, we note that for a given partial wave (and spherically

symmetric potential) the coordinate representation of the Lippmann-Schwinger equation is $\psi_\ell^+(r) = kr j_\ell(kr) - ir\int_0^\infty dr' j_\ell(kr_<) h_\ell^1(kr_>) r' \psi_\ell^+(r')$. Now we eliminate the $r_<, r_>$ variables to write

$$\psi_\ell^+(r) = kr j_\ell(kr) - ikr\int_0^r dr' r' \left[j_\ell(kr') h_\ell^1(kr) - j_\ell(kr) h_\ell^1(kr') \right] V(r') \psi_\ell^+(r') - ikr j_\ell(kr) \int_0^\infty dr' r' h_\ell^1(kr') V(r') \psi_\ell(r').$$

Then $kr j_\ell(kr)$ is the coordinate representation of g in Eq. (9), $\mathcal{J}|\xi\rangle$ is given by $-i\int_0^\infty dr\, r h_\ell^1(kr) V(r) \psi_\ell^+(r)$ and the coordinate representation of $\tilde{G}_0|\xi\rangle$ is

$$-ikr\int_0^r dr' \left[j_\ell(kr') h_\ell^1(kr) - j_\ell(kr) h_\ell^1(kr') \right] \xi(r') .$$

8. The functions $|\Psi_{\gamma\alpha}^+(i)\rangle$ are essentially the scattered parts of the wavefunction and that the integral equations they satisfy have a nonzero inhomogeneity. They are closely related to what one would get if the Lippmann-Schwinger equation were resolved in the γ noninteracting states. When this is done for the Lippmann-Schwinger equation, care must be exercised with respect to the limit as $\epsilon \to 0+$ since careless passage to this limit leads to a homogeneous integral equation whose solution is not unique. This question has been discussed by numerous investigators (see, e.g., S. T. Epstein, Phys. Rev. 106, 598 (1957); L. L. Foldy and W. Tobocman, Phys. Rev. 105, 1099 (1957) and the references and discussion in R. D. Levine, Quantum Mechanics of Molecular Rate Processes (Oxford U. P., London, 1969), p. 114.

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