function, $\omega(\Theta) \to \pi\delta(\Theta)$. In this limit all levels are strongly coupled and the near-adiabatic behavior inherent in the two-level approximation completely breaks down (see Schneiderman and Russek).[11] Thus, any results for $\rho < 0.2$ would be completely spurious. Fortunately, such small impact parameters make a negligible contribution to the total cross section for rotational excitation.

Finally, Fig. 7 shows the total cross section for rotational excitation as a function of incident velocity for the straight-line trajectories used in this paper. Five physical parameters appear in Eqs. (23)–(25): V, b, R_x, v, and ρ. Since the impact parameter is integrated over in obtaining a total cross section σ, this would normally be expected to depend on four variables. Three of these are properties of the projectile plus target molecular system: V, b, and R_x. The fourth is the incident velocity v. However, because of the form of Eqs. (23) and the straight-line approximation for ζ, Eq. (25), the results in Fig. 7 can be expressed in terms of only two variables, with the help of scaling parameters. If the dimensionless quantities

$$x = \rho/R_x\,, \qquad y = \hbar v/bR_x^2 \tag{27}$$

are defined, then $2\pi\rho\, d\rho = 2\pi R_x^2 x\, dx$, and the cross section can be written in the form

$$\sigma_{\rm rot} = \pi R_x^2 \int_0^\infty \wp\,(x,\ y,\ V)\, 2x\, dx\,. \tag{28}$$

The quantity πR_x^2 is the geometric cross section for getting inside the crossing radius. It will be remembered that in the two-independent-crossing picture, $\wp$ is always $\leq \frac{1}{2}$,

$$\sigma \leq \tfrac{1}{2}\pi R_x^2 \tag{29}$$

in the two–independent-crossing picture. A glance at Fig. 7 shows that this is far from the case for rotational excitation.

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Rearrangement-Channel Operator Approach to Models for Three-Body Reactions. I

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The channel operators $\tau_{\gamma\alpha}$ describing scattering from configuration α to configuration γ are utilized in considering a model for three-body rearrangement scattering. The $\tau_{\gamma\alpha}$ are those defined by $V_\alpha + V_\gamma(E - H + i\epsilon)^{-1}\, V_\alpha$. Two well-known forms of integral equations for the $\tau_{\gamma\alpha}$ obtained from this expression are explicitly solved for the model potential surface. Using these explicit solutions, results are examined in the limit that no dissociative continuum is present. It is found that the integral equations in which the $\tau_{\gamma\alpha}$ are not explicitly coupled do not yield the correct results for this limiting case. Integral equations explicitly coupling the $\tau_{\gamma\alpha}$ give limiting results in agreement with those obtained by more-common boundary-matching techniques. These results indicate that the major effects of the dissociative continuum may be accounted for by considering the coupled equations for the $\tau_{\gamma\alpha}$ (at least so long as one is well below threshold for the production of three free particles).

I. INTRODUCTION

The formal theory of rearrangement collisions has been the subject of many investigations which have resulted in a large number of alternative approaches to reactions.[1] These various approaches

are all correct insofar as they can be shown to yield formally identical results if no approximations are made in their solution. The primary differences among them are associated with the fact that a given description of a rearrangement collision may emphasize one or more particular aspects of the collision. One expects that approximate calculations based on different formal approaches will in general yield different results. In addition, the various difficulties associated with reactive scattering may be present to differing degrees depending on the particular formulation under consideration.

Because of recent advances in numerical and analytical techniques[2] and the availability of more powerful computational facilities, it is now feasible to undertake comparisons of these formalisms. Thus, this paper is the first in a series of studies wherein the various formal treatments of rearrangements are applied to some simple models of three-body reactive scattering. These model systems will enable analytical solutions to the various equations to be obtained, thereby allowing interesting comparisons to be made. In addition, various limiting cases of the models are of interest. For example, a model in which the reactant and product species can dissociate is of considerable interest since the role of the continuum in reactive scattering is likely to be very important. For the model system discussed in this first paper, it is then possible to remove the dissociation channel by a simple limiting procedure and compare the results to earlier studies.[3] Also, the sensitivity of the various formulations to the inclusion of the continuum may be studied. It is hoped that these studies will also provide some indication of which formulations of reactive scattering will be practicable for application to more complex and realistic systems.

This first paper contains a consideration of a simple model three-body rearrangement collision using a channel-operator formalism.[3,4] Furthermore, in this study attention is focused on only one of several possible definitions of the various channel operators for a model system.[5] In addition, only two of the possible integral equations for these operators which have appeared in the literature are discussed. The model system to which these equations are applied is one which allows dissociation and for which analytical solutions may be obtained.

We emphasize that no new formal theories of rearrangements are presented. Rather, the purpose of this series of studies is to provide practical comparisons of the existing formalisms. In a forthcoming paper, various other formal developments of the rearrangement scattering for the model system herein considered will be presented and compared with the present results.

In Sec. II the formal equations which form the basis of this paper are reviewed and the notation established. In Sec. III the model system for three-body rearrangement is described. Section IV contains a discussion of the model system based on uncoupled equations for the channel operators defined in Sec. II. A general analytical solution for the integral equations is obtained and the results illustrated by a simple example calculation. In particular, a limiting case of the solution is shown to be incompatible with the requirements that the total flux be conserved. Section V contains a discussion of the same model system based on a second set of formal equations for these same channel operators. It is possible to obtain analytical solutions of these equations also and the limiting case is once again considered. Finally, the role of the dissociative continuum states in the two approaches is briefly considered.

II. GENERAL FORMALISM

It is convenient to present a brief description of the formalism employed in the present study of reactive scattering probabilities. A detailed discussion may be found elsewhere.[1]

The τ operators are defined such that the "matrix" element

$$\tau_{\beta\alpha}(f|i) = \langle \theta(\beta|f) | \tau | \theta(\alpha|i) \rangle \tag{1}$$

is related to the transition probability for going from initial channel configuration α in state i to a final channel configuration β in state f. This precise relation is exhibited in detail in the Appendix. The particular τ operator which we shall consider satisfies an integral equation given by[1,5]

$$\tau = V_\alpha + V_\beta (E - K_\beta + i\epsilon)^{-1} \tau \,, \tag{2}$$

where V_α is the perturbation associated with the initial configuration α, and V_β is the perturbation associated with a final configuration β. K_α and K_β are the unperturbed Hamiltonians for the initial and final configurations. Thus if H is the full Hamiltonian,

$$H = K_\alpha + V_\alpha = K_\beta + V_\beta \,. \tag{3}$$

The operator $(E - K_\beta + i\epsilon)^{-1}$ is a noninteracting final-configuration Green's function which assures that causal boundary conditions on the scattered waves are satisfied. In what follows $\tau_{\alpha\alpha}$ will stand for the τ operator for the nonreactive channel and $\tau_{\beta\alpha}$ will stand for the τ operator for the reactive channel.

In general the "solution"[5] to the integral equation for $\tau_{\gamma\alpha}$ (where γ might be α or β) can be represented by

$$\tau_{\gamma\alpha} = V_\alpha + V_\gamma (E - H + i\epsilon)^{-1} V_\alpha \,. \tag{4}$$

Insertion of the following identity

$$(E-H+i\epsilon)^{-1}=(E-K_{\gamma'}+i\epsilon)^{-1}+(E-K_{\gamma'}+i\epsilon)^{-1}\times V_{\gamma'}(E-H+i\epsilon)^{-1} \quad (5)$$

into Eq. (4) yields

$$\tau_{\gamma\alpha}=V_\alpha+V_\gamma(E-K_{\gamma'}+i\epsilon)^{-1}[V_\alpha+V_{\gamma'}(E-H+i\epsilon)^{-1}V_\alpha], \quad (6)$$

where γ' can again be either α or β. Recalling (4) we obtain the expression

$$\tau_{\gamma\alpha}=V_\alpha+V_\gamma(E-K_{\gamma'}+i\epsilon)^{-1}\tau_{\gamma'\alpha}\,. \quad (7)$$

Since γ and γ' are independent, there is no unique form of the integral equations for $\tau_{\alpha\alpha}$ and $\tau_{\beta\alpha}$.[1] It is very common to write the uncoupled forms of the equations where one replaces both γ and γ' by β or by α. Thus, one obtains the equations[5]

$$\tau_{\alpha\alpha}=V_\alpha+V_\alpha(E-K_\alpha+i\epsilon)^{-1}\tau_{\alpha\alpha}\,, \quad (8)$$

$$\tau_{\beta\alpha}=V_\alpha+V_\beta(E-K_\beta+i\epsilon)^{-1}\tau_{\beta\alpha}\,. \quad (9)$$

These equations are extremely attractive because they enable one to specify the scattering coordinate in each equation as that most suited to the particular final-configuration channel. Thus, these equations appear to give the advantage one achieves for example by introducing special "reaction" coordinates[2] (but without the occurrence of complicated expressions in the kinetic energy which arise in all reaction coordinate formulations). Unfortunately, as will be seen later, use of these equations in approximate calculations which neglect the dissociative continuum yields unreliable results.[6]

On the other hand, if we replace γ and γ' once by α and β and once by β and α, respectively, we obtain a coupled system of integral equations given by

$$\tau_{\alpha\alpha}=V_\alpha+V_\alpha(E-K_\beta+i\epsilon)^{-1}\tau_{\beta\alpha}\,, \quad (10)$$

$$\tau_{\beta\alpha}=V_\alpha+V_\beta(E-K_\alpha+i\epsilon)^{-1}\tau_{\alpha\alpha}\,. \quad (11)$$

Of course, it is obvious that by substituting Eq. (11) into Eq. (10) and vice versa for Eqs. (10) and (11), one can again obtain an uncoupled system of equations

$$\tau_{\alpha\alpha}=V_\alpha+V_\alpha(E-K_\beta+i\epsilon)^{-1}V_\alpha+V_\alpha(E-K_\beta+i\epsilon)^{-1}\times V_\beta(E-K_\alpha+i\epsilon)^{-1}\tau_{\alpha\alpha}\,, \quad (12)$$

$$\tau_{\beta\alpha}=V_\alpha+V_\beta(E-K_\alpha+i\epsilon)^{-1}V_\alpha+V_\beta(E-K_\alpha+i\epsilon)^{-1}\times V_\alpha(E-K_\beta+i\epsilon)^{-1}\tau_{\beta\alpha}\,. \quad (13)$$

These equations are much more complicated than Eqs. (8) and (9). In what follows we will apply Eqs. (8) and (9) and Eqs. (10) and (11) to a model for three-body scattering.

III. SIMPLE MODEL FOR THREE-BODY REARRANGEMENT SCATTERING

The problem to which the rearrangement-operator formalism is applied concerns the three-body reactive system represented by

$$AB+C\rightarrow\begin{cases}A+BC\\C+AB\,,\end{cases}$$

where A, B, and C are three atoms which are assumed to behave as three structureless particles. The initial state α is taken to be particle C impinging on the bound system of particles A and B vibrating in a given eigenstate i, and the final configuration β consists either of particle C reflected back leaving the bound system vibrating in some energetically accessible final state, or of particle A which is now free and the new bound system BC vibrating in one of its eigenstates. In the following discussion the particles are restricted to motion along a line with the masses of A and C taken to be equal and the mass of B taken to be infinite.

For the particular model being considered, the Schrödinger equation can be written in the form

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{2\mu}{\hbar^2}[E-V(x,y)]\right)\psi=0, \quad (14)$$

where μ is a reduced mass, E is the total energy in the center-of-mass system, $V(x, y)$ is the potential energy with y the distance between A and B and x the distance between B and C (see Fig. 1). Clearly, for the initial configuration α, y is the internal vibrational coordinate and x is the collision coordinate. In order to distinguish the initial and final set of coordinates in the case of rearrangement, the variables u and v are introduced where v is the internal vibrational coordinate and u is the reaction channel coordinate. For the particular case being considered one has

$$x=v\,, \quad (15)$$

$$y=u\,. \quad (16)$$

The potential energy surface $V(x, y)$ is shown in Fig. 2 and is expressed as[7]

$$V(x,y)=\begin{cases}\left.\begin{matrix}\infty, & y<0\\ -V_0, & 0\le y\le l\\ 0\,, & l<y<\infty\end{matrix}\right\} & l<x\\ \left.\begin{matrix}-V_0, & 0\le y<\infty\\ \infty, & y<0\end{matrix}\right\} & 0\le x\le l\\ \infty, \quad \text{elsewhere}.\end{cases} \quad (17)$$

The potential surface in terms of u and v is clearly the same except that v replaces x and u replaces y.

In order to obtain the explicit forms of the various integral equations, it is necessary to know the complete set of eigenfunctions of K_α as well as the complete set of K_β. For the model under consideration the unperturbed initial potential $V_i(x, y)$ is of

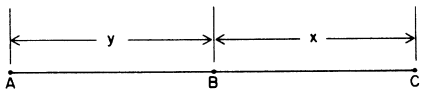

FIG. 1. Coordinates for the collinear collision system.

the form (see Fig. 3)

$$V_i(x,y)=\begin{cases}\infty\ , & y<0\\ -V_0, & 0\le y\le l\\ 0\ , & l<y<\infty\\ \infty\ , & x<0\ ,\ \text{all } y\end{cases}\quad x>0 \tag{18}$$

and the unperturbed final potential $V_f(u,v)$ is

$$V_f(u,v)=\begin{cases}\infty\ , & v<0\\ -V_0, & 0\le v\le l\\ 0\ , & l<v<\infty\\ \infty\ , & u<0,\ \text{all } v\ .\end{cases}\quad u>0 \tag{18'}$$

It is obvious that if the eigenstates of the unperturbed Hamiltonian are written in the form

$$\theta(\alpha)=\xi(x)\varphi(y)\ , \tag{19}$$

then $\xi(x)$ is $\sin kx$ and the form of the $\varphi(y)$ depends on the energy of vibration.

(a) The discrete case is given by

$$\varphi_n(y)=\begin{cases}A_n\sin\lambda_n y\ , & 0\le y\le l\\ B_n e^{-\tau_n y}\ , & l<y<\infty\end{cases} \tag{20}$$

where

$$\begin{aligned}&A_n=[2\tau_n/(\tau_n l+1)]^{1/2}\ , \quad B_n=A_n\sin(\lambda_n l)e^{\tau_n l},\\ &\lambda_n=[(2\mu/\hbar^2)E_n]^{1/2}, \qquad \tau_n=[(2\mu/\hbar^2)V_0-\lambda_n^2]^{1/2}\ .\end{aligned} \tag{21}$$

The eigenvalues are determined by the roots of the transcendental equations

$$\tan\left(\frac{2\mu}{\hbar^2}E_n\right)^{1/2}l=-\left(\frac{E_n}{V_0-E_n}\right)^{1/2} \tag{22}$$

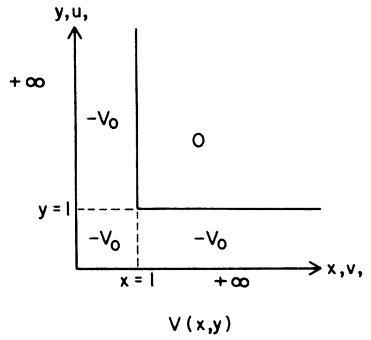

FIG. 2. Interaction potential for full collinear collision system.

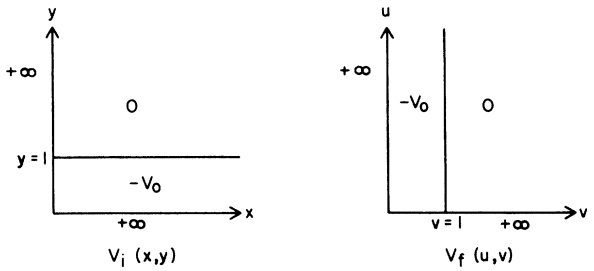

FIG. 3. Initial and final configuration potentials $V_i(x, y)$ and $V_f(u, v)$.

which can be written in the form

$$\tan\lambda_n l=-\lambda_n/\tau_n\ . \tag{22'}$$

(b) The continuous case is given by

$$\varphi_\lambda(y)=\begin{cases}A_\lambda\sin\lambda y\ , & 0\le y\le l\\ B_\lambda e^{i\tau_\lambda y}+B_\lambda^* e^{-i\tau_\lambda y}\ , & l<y<\infty\end{cases} \tag{23}$$

where

$$\lambda=[(2\mu/\hbar^2)E_\lambda]^{1/2},\quad \tau_\lambda=[\lambda^2-(2\mu/\hbar^2)V_0]^{1/2}\ ,$$

$$A_\lambda=\left(\frac{2\tau_\lambda^2}{\pi(\lambda^2\cos^2\lambda l+\tau_\lambda^2\sin^2\lambda l}\right)^{1/2}\ , \tag{24}$$

$$B_\lambda=A_\lambda e^{-i\tau_\lambda l}[\lambda(\cos\lambda l)/\tau_\lambda+i\sin\lambda l]/2i\ .$$

The normalization for φ_λ is such that

$$\int_0^\infty \varphi_\lambda^*(y)\varphi_{\lambda'}(y)dy=\delta(\lambda-\lambda')\ .$$

The relations between k_n and λ_n and between k_λ and λ are given by

$$\lambda_n^2+k_n^2=2\mu E/\hbar^2\ ,\qquad \lambda^2+k_\lambda^2=2\mu E/\hbar^2\ ,$$

where E is the given total energy of the system in the center-of-mass reference frame.

IV. USE OF THE UNCOUPLED OPERATOR EQUATIONS

We begin with a discussion of the model using the system of uncoupled equations and will show that the results derived are incorrect We introduce "amplitude density functions" $\tau_{\gamma\alpha}\theta(\alpha|\lambda)$ which are essentially functions containing the same information as the product of V_γ and the scattering wave function $\psi_\alpha^+(i)$ (see the Appendix).

Expanding the total amplitude density functions $\tau_{\alpha\alpha}\theta(\alpha|i)$ and $\tau_{\beta\alpha}\theta(\alpha|i)$ in terms of the respective orthonormal sets $\varphi_n(y)$ and $\varphi_n(v)$, one has

$$\tau_{\alpha\alpha}\theta(\alpha|i)=\textstyle\sum_n\chi_n(x)\varphi_n(y)\ , \tag{25}$$

$$\tau_{\beta\alpha}\theta(\alpha|i)=\textstyle\sum_n\zeta_n(u)\varphi_n(v)\ , \tag{26}$$

where the summation includes an integration over the continuous states. Substituting Eq. (25) into Eq. (8), multiplying both sides by $\varphi_n(y)$ and inte-

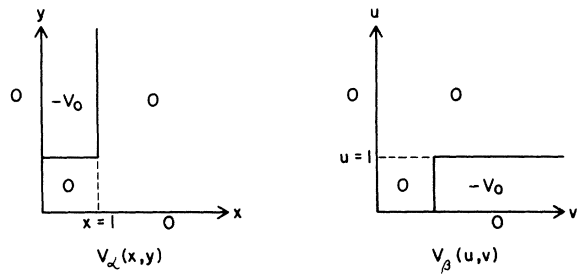

FIG. 4. Initial and final configuration perturbations $V_\alpha(x, y)$ and $V_\beta(u, v)$.

grating over y, and substituting Eq. (26) into Eq. (9), multiplying both sides by $\varphi_n(v)$ and integrating over v leads to

$$\chi_m(x) = \int_0^\infty \varphi_m(y) V_\alpha(x, y)\theta(\alpha|i)dy + \int_0^\infty dy\,\varphi_m(y)V_\alpha(x, y)\int_0^\infty\int_0^\infty dx'dy'G(x, y|x', y') \times \sum_n \chi_n(x')\varphi_n(y') , \quad (27)$$

$$\zeta_m(u) = \int_0^\infty dv\,\varphi_m(v)V_\alpha(x, y)\theta(\alpha|i) + \int_0^\infty dv\,\varphi_m(v)V_\beta(u, v)\int_0^\infty\int_0^\infty du'dv'G(u, v|u', v') \times \sum_n \zeta_n(u')\varphi_n(v') . \quad (28)$$

Here $\theta(\alpha|i)$ is the initial state given by

$$\theta(\alpha|i) = \sin(k_{n_0}x)\,\varphi_{n_0}(y); \quad (29)$$

$V_\alpha(x, y)$ and $V_\beta(u, v)$ are the two perturbations associated with the initial configuration α and with the final configuration β, respectively. Thus (see Fig. 4)

$$V_\alpha(x, y) = \begin{cases} -V_0, & 0 \le x \le l\ , \quad l < y \le \infty \\ 0\ , & \text{elsewhere} \end{cases} \quad (30)$$

$$V_\beta(u, v) = \begin{cases} -V_0, & 0 \le u \le l\ , \quad l < v < \infty \\ 0\ , & \text{elsewhere}\ . \end{cases} \quad (31)$$

The function $G(x, y|x', y')$ [as well as $G(u, v|u', v')$] is the coordinate representation of the Green's function which is given by

$$G(x, y|x', y') = \frac{1}{\pi}\int_{-\infty}^{\infty} dk\left[\sum_n \frac{\varphi_n(y)\sin kx\,\varphi_n(y')\sin kx'}{E - k^2 - \lambda_n^2 + i\epsilon} + \int_0^\infty d\lambda \frac{\varphi_\lambda(y)\sin kx\,\varphi_\lambda^*(y')\sin kx'}{E - k^2 - \lambda^2 + i\epsilon}\right] . \quad (32)$$

It is convenient to define $V_{rs}^{(\alpha)}(x)$ by

$$V_{rs}^{(\alpha)}(x) = \int_0^\infty dy\,\varphi_r(y)V_\alpha(x, y)\varphi_s(y) , \quad (33)$$

where r and s can be either discrete or continuous indices. The same definition will be applied to $V_{rs}^{(\beta)}(u)$. From Eq. (30) we obtain

$$V_{rs}^{(\alpha)}(x) = \begin{cases} -V_0\int_l^\infty \varphi_r(y)\varphi_s(y)dy\ , & 0 \le x \le l \\ 0\ , & l < x < \infty\ . \end{cases} \quad (34)$$

In a similar fashion one defines $W_{rn_0}^{(\alpha)}(x)$ and $W_{rn_0}^{(\beta)}(u)$ (where again r might be either discrete or continuous) by

$$W_{rn_0}^{(\alpha)}(x) = \int_0^\infty \varphi_r(y)V_\alpha(x, y)\theta(\alpha|i)dy\ . \quad (35)$$

Applying Eqs. (15)–(16) and (30)–(31) one finds

$$W_{rn_0}^{(\alpha)}(x) = V_{rn_0}^{(\alpha)}(x)\sin k_{n_0}x\ , \quad (36)$$

$$W_{rn_0}^{(\beta)}(u) = \begin{cases} -V_0\varphi_{n_0}(u)\int_l^\infty \varphi_r(v)\sin k_{n_0}v\,dv\ , & l \le u < \infty \\ 0\ , & 0 \le u \le l\ . \end{cases} \quad (37)$$

Since $V_{rs}^{(\alpha)}(x) = V_{rs}^{(\beta)}(u)$, the superscripts α and β will be omitted in what follows.

Substitution of Eqs. (15)–(16), (32), (34), (36), and (37) into Eqs. (27) and (28), respectively, yields

$$\chi_m(x) = W_{mn_0}^{(\alpha)}(x) - \sum_n [V_{mn}(x)/k_n]\int_0^\infty dx' e^{ik_n x_>} \times \sin(k_n x_<)\chi_n(x') \quad (38)$$

and

$$\zeta_m(u) = W_{mn_0}^{(\beta)}(u) - \sum_n [V_{mn}(u)/k_n]\int_0^\infty du' e^{ik_n u_>} \times \sin(k_n u_<)\zeta_n(u'), \quad (39)$$

where $x_>$ and $x_<$ are the greater and the lesser of x and x', respectively, and similarly for $u_>$ and $u_<$.

These two systems of equations are very similar and differ only in the inhomogeneity term. Consequently we shall explicitly solve only the second system and apply its solution to the first.

Following Sams and Kouri[2] we use the matrix notation

$$\{\vec{\zeta}(u)\}_m = \zeta_m(u)\ , \quad \{\vec{W}_{n_0}^{(\gamma)}\}_n = W_{rn_0}^{(\gamma)}, \quad \{\vec{\vec{V}}\}_{mn} = V_{mn}\ , \quad \{\vec{\vec{\mathcal{E}}}\}_{mn} = \delta_{mn}e^{ik_n u}\ , \quad \{\vec{\vec{S}}\}_{mn} = \delta_{mn}(\sin k_n u)/k_n\ . \quad (40)$$

Consequently, Eq. (39) can be rewritten as

$$\vec{\zeta}(u) = \vec{W}_{n_0}^{(\beta)}(u) - \vec{\vec{V}}(u)\cdot\vec{\vec{\mathcal{E}}}(u)\cdot\int_0^u \vec{\vec{S}}(u')\cdot\vec{\zeta}(u')du' + \vec{\vec{V}}(u)\cdot\vec{\vec{S}}(u)\cdot\int_0^u \vec{\vec{\mathcal{E}}}(u')\cdot\vec{\zeta}(u')du' - \vec{\vec{V}}(u)\cdot\vec{\vec{S}}(u)\cdot\int_0^\infty \vec{\vec{\mathcal{E}}}(u')\cdot\vec{\zeta}(u')du' , \quad (41)$$

where we have for the continuous indices an integra-

tion instead of a summation. We define a column vector $\vec{C}^{(\beta)}$ by

$$\vec{C}^{(\beta)} = -\int_0^\infty \vec{\mathcal{E}}(u)\cdot\vec{\xi}(u)du \tag{42}$$

and write $\vec{\xi}(u)$ in the form

$$\vec{\xi}(u)=\vec{\xi}^{(0)}(u)+\overleftrightarrow{\xi}^{(s)}(u)\cdot\vec{C}^{(\beta)}\ , \tag{43}$$

where $\vec{\xi}^{(0)}$ is a column matrix and $\overleftrightarrow{\xi}^{(s)}$ is a square matrix. Following Sams and Kouri[2] we obtain the equation

$$\vec{\xi}^{(0)}(u)=\vec{W}^{(\beta)}_{n_0}(u)-\overleftrightarrow{V}(u)\cdot\int_0^u\overleftrightarrow{S}(u'-u)\cdot\vec{\xi}^{0}(u')du' \tag{44}$$

for $\vec{\xi}^{(0)}$ and for $\overleftrightarrow{\xi}^{(s)}$ the equation

$$\overleftrightarrow{\xi}^{(s)}(u)=\overleftrightarrow{V}(u)\cdot\overleftrightarrow{S}(u)-\overleftrightarrow{V}(u)\cdot\int_0^u\overleftrightarrow{S}(u'-u)\cdot\overleftrightarrow{\xi}^{(s)}(u')du'\ . \tag{45}$$

We now consider the solution of Eq. (45). It can be seen that each column of the square matrix $\overleftrightarrow{\xi}^{(s)}(u)$ is determined independently of all the others. Thus, if the mth column of $\overleftrightarrow{\xi}^{(s)}(u)$ is denoted as $\vec{\xi}^{(m)}(u)$, one finds

$$\vec{\xi}^{(m)}(u)=\overleftrightarrow{V}(u)\cdot\vec{S}^{(m)}(u)-\overleftrightarrow{V}(u)\cdot\int_0^u\overleftrightarrow{S}(u'-u)\cdot\vec{\xi}^{(m)}(u')du\ , \tag{46}$$

where $\vec{S}^{(m)}(u)$ is the mth column of a diagonal matrix $\overleftrightarrow{S}(u)$ given by

$$\{\vec{S}^{(m)}(u)\}_n=\frac{\sin k_n u}{k_n}\delta_{nm}\ . \tag{47}$$

For the following it is noted that $\overleftrightarrow{V}(u)$ is independent of u for $0\le u\le l$ [cf. Eq. (40)] and therefore it may be replaced by $\overleftrightarrow{V}$.

The solution of this system of equations is then written in the form

$$\vec{\xi}^{(m)}(u)=\overleftrightarrow{A}^{(m)}\cdot\vec{S}(u)\ , \tag{48}$$

where $\overleftrightarrow{A}^{(m)}$ is a square matrix whose elements are to be determined and $\vec{S}(u)$ is a column matrix whose elements are

$$\{\vec{S}(u)\}_l=\sin\alpha_l u\ . \tag{47'}$$

In order to determine the matrix elements of $\overleftrightarrow{A}^{(m)}$ and the α_l values, it is sufficient to write $\vec{\xi}^{(m)}(u)$ in the form

$$\vec{\xi}^{(m)}(u)=\vec{A}^{(m)}\sin\alpha u\ , \tag{48'}$$

where $\vec{A}^{(m)}$ is now a column matrix. Substituting Eq. (48′) into Eq. (46) and performing the integration over u', one obtains the equation

$$\vec{A}^{(m)}\sin\alpha u=\overleftrightarrow{V}\cdot\vec{S}^{(m)}(u)+\alpha\overleftrightarrow{V}\cdot\overleftrightarrow{K}\cdot\overleftrightarrow{S}(u)\cdot\vec{A}^{(m)}-\overleftrightarrow{V}\cdot\overleftrightarrow{K}\cdot\vec{A}^{(m)}\sin\alpha u\ , \tag{49}$$

where $\overleftrightarrow{K}$ is a diagonal matrix whose elements are given by

$$\{\overleftrightarrow{K}\}_{nm}=(\alpha^2-k_n^2)^{-1}\delta_{nm}\ . \tag{50}$$

It is convenient to define the column matrix $\vec{B}^{(m)}$ as

$$\vec{B}^{(m)}=\overleftrightarrow{K}\cdot\vec{A}^{(m)}\ . \tag{51}$$

Then Eq. (49) can be rewritten as

$$\overleftrightarrow{K}^{-1}\cdot\vec{B}^{(m)}\sin\alpha u=\overleftrightarrow{V}\cdot\vec{S}^{(m)}(u)+\overleftrightarrow{V}\cdot\overleftrightarrow{S}(u)\cdot\alpha\vec{B}^{(m)}-\overleftrightarrow{V}\cdot\vec{B}^{(m)}\sin\alpha u \tag{52}$$

and by equating the coefficients of $\sin\alpha u$ one finds

$$(\overleftrightarrow{V}+\overleftrightarrow{K}^{-1})\cdot\vec{B}^{(m)}=0\ . \tag{53}$$

Recalling the definition of $\overleftrightarrow{K}$ and defining a square matrix $\overleftrightarrow{V}'$ by

$$\{\overleftrightarrow{V}'\}_{nm}=\begin{cases}V_{nm}\ , & n\neq m\\ V_{nn}-k_n^2\ , & \end{cases} \tag{54}$$

Eq. (52) becomes

$$(\overleftrightarrow{V}'+\alpha^2\overleftrightarrow{I})\cdot\vec{B}^{(m)}=0 \tag{55}$$

which is an ordinary eigenvalue problem for α and $\vec{B}^{(m)}$. Clearly, $\overleftrightarrow{V}'$ is a real symmetric matrix so that the eigenvalues of $\overleftrightarrow{V}'$ are real. Consequently, α will be either real (open channels) or purely imaginary (closed channels). Returning to Eq. (51) we notice that the square matrix $\overleftrightarrow{A}^{(m)}$ is related to the orthogonal matrix $\overleftrightarrow{B}^{(m)}$ by the relation $(\overleftrightarrow{B}^{(m)})_{in}=(\overleftrightarrow{A}^{(m)})_{in}/(\alpha_i^2-k_n^2)$ so we have obtained an explicit solution for the column matrix $\vec{\xi}^{(m)}(u)$. This is true for the α values and for the $\vec{A}^{(m)}$ matrix elements as well. However, one has to keep in mind that the $\overleftrightarrow{B}^{(m)}$ matrix elements are only determined up to a normalization factor and consequently this is true also for the $\overleftrightarrow{A}^{(m)}$ matrix elements. Thus in order to determine the $\overleftrightarrow{A}^{(m)}$ elements uniquely, one has to apply some "normalization" rule. This normalization rule can be derived very easily by returning to Eq. (52) and equating the coefficients of $\sin k_n u$.

Thus we have

$$\overleftrightarrow{V}\cdot[\vec{S}^{(m)}(u)+\overleftrightarrow{S}(u)\cdot\overleftrightarrow{B}^{(m)}\cdot\vec{\alpha}]=\vec{0}\ , \tag{56}$$

where $\vec{\alpha}$ is now a column vector the elements of which are the square roots of the eigenvalues. One can easily show that the independence of the $\sin k_n u$ function leads to

$$\overleftrightarrow{B}^{(m)}\cdot\vec{\alpha}=\vec{I}^{(m)}\ , \tag{57}$$

where $\vec{I}^{(m)}$ is a column matrix

$$\{\vec{I}^{(m)}\}_l=-\delta_{lm}\ . \tag{58}$$

Up to this point we have obtained the solution for the square matrix $\overleftrightarrow{\xi}^{(s)}(u)$. Equation (38) is treated exactly in the same manner. Thus if one represents

the solution of this system by the expression

$$\vec{\chi}(u) = \vec{\chi}^{(0)}(u) + \overleftrightarrow{\chi}^{(s)}(u) \cdot \vec{C}^{\alpha} , \tag{59}$$

where $\vec{C}^{\alpha}$ is defined as

$$\vec{C}^{(\alpha)} = \int_0^{\infty} \overleftrightarrow{\mathcal{G}}(u) \cdot \vec{\chi}(u) du , \tag{60}$$

then it is easily seen that

$$\overleftrightarrow{\chi}^{(s)}(u) = \overleftrightarrow{\xi}^{(s)}(u) . \tag{61}$$

We have now to derive the solution of $\vec{\xi}^{(0)}(u)$ and $\vec{\chi}^{(0)}(u)$.

As to $\vec{\xi}^{(0)}(u)$ it turns out that Eq. (44) has a very simple solution. Recalling the definitions of $\vec{W}_{n_0}^{(\beta)}(u)$ and $\overleftrightarrow{V}(u)$ one finds that

$$\vec{W}_{n_0}^{(\beta)}(u) \begin{cases} \neq 0, & u > l \\ = 0, & 0 \le u \le l \end{cases} \tag{62}$$

$$\overleftrightarrow{V}(u) \begin{cases} = 0, & u > l \\ \neq 0, & 0 \le u \le l \end{cases}$$

and consequently

$$\vec{\xi}^{(0)}(u) = \vec{W}_{n_0}^{(\beta)}(u) . \tag{63}$$

As to $\vec{\chi}^{(0)}(u)$ we recall the definition of $\vec{W}^{(\alpha)}(u)$. From Eq. (36) we get that

$$\vec{W}_{n_0}^{(\alpha)} = \vec{V}_{n_0} \sin k_{n_0} x . \tag{64}$$

Equation (64) can also be written as

$$\vec{W}_{n_0}^{(\alpha)} = k_{n_0} \overleftrightarrow{V} \cdot \vec{S}^{(n_0)}(x) \tag{65}$$

and consequently $\vec{\chi}^{(0)}(u)$ is given as

$$\vec{\chi}^{(0)}(u) = k_{n_0} \vec{\chi}^{(n_0)}(u) = k_{n_0} \vec{\xi}^{(n_0)}(u) . \tag{66}$$

To sum up the results derived we see that the solutions of the two systems of integral equations are given by

$$\vec{\chi}(u) = k_{n_0} \vec{\xi}^{(n_0)}(u) + \overleftrightarrow{\xi}^{(s)}(u) \cdot \vec{C}^{(\alpha)} , \tag{67}$$

$$\vec{\xi}(u) = \vec{W}_{n_0}^{(\beta)}(u) + \overleftrightarrow{\xi}^{(s)}(u) \cdot \vec{C}^{(\beta)} \tag{68}$$

where the mth column of $\overleftrightarrow{\xi}^{(s)}$ is given by a linear combination of $\sin\alpha u$ functions. However one has to keep in mind that all the matrix elements of $\overleftrightarrow{\xi}^{(s)}(u)$ are different from zero for $0 \le u \le l$ whereas elsewhere they are zero. Similarly we have that $\vec{W}_{n_0}^{(\beta)}(u)$ is identically zero for $0 \le u \le l$ and different from zero for u larger than l.

Once $\vec{\xi}^{(0)}(u)$ and $\overleftrightarrow{\xi}^{(s)}(u)$ are given there is no essential difficulty in determining the two column matrices $\vec{C}^{(\alpha)}$ and $\vec{C}^{(\beta)}$ and therefore the problem of determining $\vec{\chi}(u)$ and $\vec{\xi}(u)$ can be considered as solved.

In order to get additional insight we consider now the one-channel case in detail. Here the various matrices reduce the single numbers or functions and consequently all the subscripts can be omitted.

The single element of the matrix of $\overleftrightarrow{V}' + \alpha^2 \overleftrightarrow{I}$ is $V - k^2 + \alpha^2$ and since the determinant of this matrix has to vanish we find

$$\alpha = (k^2 - V)^{1/2} . \tag{69}$$

Combining Eqs. (51) and (57) we find

$$\alpha A / (\alpha^2 - k^2) = 1 \tag{70}$$

so that

$$A = V / (k^2 - V)^{1/2} . \tag{71}$$

Thus, we find

$$\xi(u) = [V / (k^2 - V)^{1/2}] \sin (k^2 - V)^{1/2} u . \tag{72}$$

From Eqs. (67) and (68) we find the complete solution is

$$\chi(u) = \begin{cases} (k + C^{(\alpha)}) \dfrac{V}{(k^2 - V)^{1/2}} \sin (k^2 - V)^{1/2} u, & 0 \le u \le l \\ 0, & l < u < \infty \end{cases} \tag{73}$$

and

$$\xi(u) = \begin{cases} C^{(\beta)} [V / (k^2 - V)^{1/2}] \sin (k^2 - V)^{1/2} u , & 0 \le u \le l \\ - V_0 w \varphi(u), & l < u < \infty \end{cases} \tag{74}$$

where

$$w = \int_0^l \varphi(v) \sin (kv) dv \tag{75}$$

and

$$V = - V_0 \int_l^{\infty} |\varphi(y)|^2 dy . \tag{76}$$

(Here V_0 is given in units of $2\mu/\hbar^2$.)

Defining

$$Z = [V / (k^2 - V)^{1/2}] \int_0^l \sin [(k^2 - V)^{1/2} u] e^{iku} du , \tag{77}$$

$$\xi = - V_0 w \int_l^{\infty} \varphi(u) e^{iku} du , \tag{78}$$

we have

$$C^{(\alpha)} = - kZ / (1 + Z) , \tag{79}$$

$$C^{(\beta)} = - \xi / (1 + Z) . \tag{80}$$

From the definitions of the τ matrix elements we have

$$R = \tau_{\alpha\alpha}(1 \to 1) = \int_0^{\infty} \chi(x) \sin (kx) dx , \tag{81}$$

$$T = \tau_{\beta\alpha}(1 \to 1) = \int_0^{\infty} \xi(u) \sin (ku) du , \tag{82}$$

and consequently

$$R = \mathrm{Im}(Z) / (1 + Z) , \tag{83}$$

$$T = \mathrm{Im}(\xi) - \xi\,\mathrm{Im}(Z)/(1+Z)\ . \tag{84}$$

It is very interesting to see what happens in the limit that V_0 tends to infinity. In such a case it can be seen that $V \to 0$ and consequently $Z \to 0$. On the other hand ξ is finite and satisfies

$$\lim_{V_0 \to \infty} \xi = -\lambda(2/l)^{1/2} w\, e^{ikl}\ . \tag{85}$$

Clearly

$$\lim_{V_0 \to \infty} \mathrm{Im}(\xi) = -\lambda(2/l)^{1/2} w \sin kl\ , \tag{86}$$

so consequently

$$R \to 0, \tag{87}$$

$$T \to -\lambda(2/l)^{1/2} w \sin kl\ . \tag{88}$$

These results can be compared with those derived by the more direct method of Hulburt and Hirschfelder.[3] It can be shown that in the one-channel case this method leads to the coupled equations

$$\begin{aligned} R - T w\lambda e^{ikl}(2/l)^{1/2}/k &= 0\ , \\ -Rw\lambda e^{ikl}(2/l)^{1/2}/k + T &= (2/l)^{1/2} w\lambda \sin kl\ . \end{aligned} \tag{89}$$

Thus we notice that the terms that are responsible for the interaction between the reactive and the nonreactive channels are missing from Eqs. (87) and (88). It can be shown that in the limit $V_0 \to \infty$ for the many-channel problem, all the R values are identically zero. This means that in the nonreactive channel the system behaves as if no reactive channel is open at all, and the scattering is purely elastic.

V. USE OF COUPLED OPERATOR EQUATIONS

Again the total amplitude density functions are expanded as in Eqs. (25) and (26). Substituting these expansions into Eqs. (10) and (11) and going through the same procedure as described in the Sec. IV we obtain the following coupled equations:

$$\chi_n(x) = V_{nn_0}(x) \sin k_{n0} x + V_0 \sum_{n'} \alpha_{nn'}(x)\, \varphi_{n'}(x)\ , \tag{90}$$

$$\zeta_n(u) = -w_{nn_0}(u)\, V_0\, \varphi_{n_0}(u) + V_0 \sum_{n'} \beta_{nn'}(u)\, \varphi_{n'}(u)\ . \tag{91}$$

Here

$$V_{nn_0}(x) = \begin{cases} -V_0 \int_l^\infty \varphi_n(y)\, \varphi_{n_0}(y)\, dy\ , & 0 \le x \le l \\ 0\ , & l < x < \infty \end{cases} \tag{92}$$

$$w_{nn'}(u) = \begin{cases} \int_0^l \varphi_n(v) \sin k_n v\, dv\ , & l \le u < \infty \\ 0\ , & 0 \le u < l \end{cases} \tag{93}$$

$$\alpha_{nn'}(x) = \begin{cases} (1/k_{n'}) \int_l^\infty \varphi_n(y)\, dy \int_0^\infty e^{ik_{n'}y_>} \sin k_{n'} y_< \\ \qquad \times \zeta_{n'}(y')\, dy'\ , & 0 \le x \le l \\ 0\ , & l < x < \infty \end{cases} \tag{94}$$

and

$$\beta_{nn'}(u) = \begin{cases} (1/k_{n'}) \int_l^\infty \varphi n(v)\, dv \int_0^\infty e^{ik_{n'}v_>} \sin k_{n'} v_< \\ \qquad \times \chi_{n'}(v')\, dv'\ , & 0 \le u \le l \\ 0\ , & l < u < \infty\ . \end{cases} \tag{95}$$

From the definitions of $V_{nn_0}(x)$ and $\alpha_{nn'}(x)$ it is easily seen that $\chi_n(x)$ is different from zero for $0 \le x \le l$ and is identically zero for $x > l$. As to $\zeta_n(x)$, one can see from the definitions of $w_{nn_0}(u)$ and $\beta_{nn_0}(u)$ that it is different from zero along the whole interval, but for $u > l$ it is equal to the inhomogeneity term, i.e.,

$$\zeta_n(u) = -V_0 w_{nn_0} \varphi_{n_0}(u)\ , \quad u > l\ . \tag{96}$$

We now define

$$R_n = \tau_{\alpha\alpha}(n_0 \to n) = \int_0^\infty \chi_n(x) \sin k_n x\, dx\ , \tag{97}$$

$$T_n = \tau_{\beta\alpha}(n_0 \to n) = \int_0^\infty \zeta_n(u) \sin k_n u\, du\ , \tag{98}$$

such that

$$R_n = V_{nn_0} S_{nn_0} + V_0 \sum_{n'} \alpha_{nn'} w_{n'n}\ , \tag{99}$$

$$T_n = q_{n_0 n} w_{nn_0} + V_0 \sum_{n'} \beta_{nn'} w_{n'n}\ . \tag{100}$$

The quantities q_{nn_0} and S_{nn_0} are given by

$$q_{nn'} = -V_0 \int_l^\infty \varphi_n(v) \sin k_{n'} v\, dv \tag{101}$$

and

$$S_{nn'} = \int_0^l \sin k_n x \sin k_{n'} x\, dx\ . \tag{102}$$

We still must calculate $\alpha_{nn'}$ and $\beta_{nn'}$ and we first consider $\beta_{nn'}$. Since $\chi_n(y)$ is different from zero only in the interval $0 \le y \le l$, $\beta_{nn'}$ can be written as

$$\beta_{nn'} = (1/k_{n'}) \int_l^\infty \varphi_n(v)\, e^{ik_{n'}v}\, dv \int_0^l \sin k_{n'} v'\, \chi_{n'}(v')\, dv'\ . \tag{103}$$

However, the limits of the inner integral are independent of v so one can write

$$-V_0 \beta_{nn'} = (1/k_{n'})\, Q_{nn'} R_{n'}\ , \tag{104}$$

where $R_{n'}$ is defined by Eq. (97) and for $Q_{nn'}$ we have that

$$Q_{nn'} = -V_0 \int_l^\infty \varphi_n(v)\, e^{ik_{n'}v}\, dv\ . \tag{101'}$$

For $\alpha_{nn'}$ we have a somewhat more complicated expression because $\zeta_n(y)$ [in contrast to $\chi_n(x)$] is defined also for y values larger than l. The expression for $\alpha_{nn'}$ is given by

$$\alpha_{nn'} = (1/k_{n'}) \int_l^\infty \varphi_n(y)\, dy \left[e^{ik_{n'}y} \int_0^y \zeta_{n'}(y') \sin k_{n'} y'\, dy' + \sin k_{n'} y \int_y^\infty \zeta_{n'}(y') e^{ik_{n'}y'}\, dy'\right] \quad (105)$$

which can be written as

$$\alpha_{nn'} = (1/k_{n'}) \left\{\left[\int_l^\infty \varphi_n(y) e^{ik_{n'}y}\, dy\right] \times \left[\int_0^\infty \zeta_{n'}(y') \sin k_{n'} y'\, dy'\right] - V_0 w_{n'n_0} \int_l^\infty \varphi_n(y)\, dy \times \int_y^\infty \left[-e^{ik_{n'}y} \sin k_{n'} y' + e^{ik_{n'}y'} \sin k_{n'} y\right] \varphi_{n_0}(y')\, dy'\right\} . \quad (106)$$

The second term is obtained by using Eq. (96) and recalling that the lower limit of the inner integral in the second term is always larger than l.

Applying the definitions of $Q_{nn'}$ and T_n, we find that

$$V_0 \alpha_{nn'} = (T_{n'}/k_{n'})\, Q_{nn'} + V_0^2 (w_{n'n_0}/k_{n'}) \int_l^\infty \varphi_n(y)\, dy \times \int_y^\infty \varphi_{n_0}(y') \sin[k_{n'}(y-y')]\, dy' . \quad (107)$$

If $Z_{nn'n_0}$ is defined by

$$Z_{nn'n_0} = (V_0^2/k_{n'}) \int_l^\infty \varphi_n(y)\, dy \times \int_y^\infty \sin[k_{n'}(y-y')]\, \varphi_{n_0}(y')\, dy' , \quad (108)$$

then we obtain the equation

$$-V_0 \alpha_{nn'} = (T_{n'}/k_{n'})\, Q_{nn'} + Z_{nn'n_0} w_{n'n_0} . \quad (109)$$

Substituting Eqs. (109) and (104) in Eqs. (99) and (100), respectively, we obtain a system of algebraic equations given by

$$R_n = V_{nn_0} S_{n_0 n} - \sum_{n'} w_{n'n} Z_{nn'n_0} w_{n'n_0} - \sum_{n'} (T_{n'}/k_{n'})\, Q_{nn'} w_{n'n} \quad (110)$$

and

$$T_n = q_{n_0 n} w_{nn_0} - \sum_{n'} (R_{n'}/k_{n'})\, Q_{nn'} w_{n'n} . \quad (111)$$

We now again consider the limit when $V_0 \to \infty$. In this case it can be verified by using Eqs. (20), (21), and (22′) that

$$\lim_{V_0 \to \infty} V_{nn_0} = 0 , \quad (112)$$

$$\lim_{V_0 \to \infty} \omega_{nn'} = \frac{(2/l)^{1/2}(-1)^n \lambda_n \sin k_{n'}}{(k_{n'}^2 - \lambda_n^2)} \qquad (\lambda_n l = n\pi) ; \quad (113)$$

$$\lim_{V_0 \to \infty} q_{nn'} = (-1)^n (2/l)^{1/2} \lambda_n \sin k_{n'} l , \quad (114)$$

$$\lim_{V_0 \to \infty} Q_{nn'} = (-1)^n (2/l)^{1/2} \lambda_n e^{ik_{n'}l} , \quad (114')$$

$$\lim_{V_0 \to \infty} S_{nn'} = \text{finite} , \quad (115)$$

$$\lim_{V_0 \to \infty} Z_{nn_0 n'} = 0 . \quad (116)$$

Substituting Eqs. (112), (113), and (114) into (110) and (111) we obtain the coupled albegraic equations

$$R_n = -\sum_{n'} (T_{n'}/k_{n'}) Q_{nn'} \omega_{n'n} , \quad (110')$$

$$T_n = q_{n_0 n} \omega_{nn_0} - \sum_{n'} (R_{n'}/k_{n'}) Q_{nn'} \omega_{n'n} \quad (111')$$

and substitution for $Q_{nn'}$ and $\omega_{n'n}$ leads at last to

$$R_n = \frac{2}{l} (-1)^n \lambda_n \sin k_n l \sum_{n'} \frac{T_{n'} \lambda_{n'} e^{ik_{n'}l} (-1)^{n'}}{k_{n'}(k_n^2 - \lambda_{n'}^2)} , \quad (117)$$

$$T_n = -\frac{2}{l} \frac{\lambda_{n_0} \lambda_n (-1)^{n+n_0} \sin k_{n_0} l \sin k_n l}{(k_n^2 - \lambda_{n_0}^2)} + \frac{2}{l} (-1)^n \lambda_n \sin k_n l \sum_{n'} \frac{R_{n'} \lambda_{n'} e^{ik_{n'}l} (-1)^{n'}}{k_{n'}(k_n^2 - \lambda_{n'}^2)} . \quad (118)$$

It can be shown that these equations are exactly those that are obtained by the method of Hulburt and Hirschfelder. In case of one channel, Eqs. (110) and (111′) reduce to Eqs. (89) where Q_{11} is replaced by $Q_{11} = (2/l)^{1/2} \lambda\, e^{ikl}$, and ω_{11} stands for ω. Again, the relationship of the T_n and R_n to transmission and reflection probabilities is presented in the Appendix.

VI. SUMMARY

In this paper two methods for treating the three-body rearrangement collision are discussed. Both methods are based on a τ operator formalism.[1]

In the first we used the uncoupled integral equation system in which the nonreactive channel and the reactive one are treated independently. In the second use is made of the coupled system where both the reactive and nonreactive channels are explicitly treated simultaneously. The equations were applied to a solvable model for three-body rearrangement collisions.

It is, of course, to be kept in mind that all the results derived were based on the particular model considered and it may be that they are not general enough to apply to other more complex systems.

Our analysis appears to indicate that the solution of the uncoupled integral equation system is fundamentally incorrect (at least so long as the contributions from the continuum are either ignored or approximated by a quadrature sum).[6,8] Support for this conclusion comes from the fact that in the limit $V_0 \to \infty$, the uncoupled equations do not yield the known

correct results.[3] Of course, a major feature of such a limiting case is the absence of a dissociative continuum.

On the other hand, the solution obtained for the coupled operator equations appears correct in that the proper limiting equations are obtained when $V_0 \to \infty$. This is true even though no special attention is paid to the role of the continuum states. Consequently, although the uncoupled equations appear very attractive, it appears that one must be much more careful in dealing with the continuum so that any apparent advantages are illusory. Indeed, it appears that in the uncoupled equations it is only through the continuum states that information about reacted flux enters the nonreactive equations so that probability can be conserved. In the coupled operator equations method, the information stored in the continuum is less important so that solutions of these equations are less sensitive to the way in which such states are treated. (All the above dissussion is restricted to energies below threshold for breakup.)

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APPENDIX: DERIVATION OF TRANSITION PROBABILITIES RELATED TO τ OPERATOR MATRIX ELEMENTS

In order to derive the transition probabilities we refer to the wave equation and study its behavior in two limits, namely when x goes to infinity and y is finite (nonreactive collision) and when y goes to infinity and x is finite (reactive collision).

Consequently, if for finite y values and for x values going to infinity the wave function takes the form

$$\lim_{x\to\infty}\psi(x,y)=C\left(e^{-ik_{n_0}x}\varphi_{n_0}(y)+\sum_{n=1}^{N}\rho_n e^{ik_n x}\varphi_n(y)\right), \quad \text{(A1)}$$

where N is the number of open channels and C is an arbitrary constant, then the various transition probabilities $P_{n_0\to n}(R)$ for nonreactive scattering are given by

$$P_{n_0\to n}(R)=(k_n/k_{n_0})|\rho_n|^2 . \quad \text{(A2)}$$

Similarly, if for finite values of x and for y values going to infinity, the wave function takes the form

$$\lim_{y\to\infty}\psi(x,y)=C\sum_{n=1}^{N}t_n e^{ik_n y} , \quad \text{(A3)}$$

then the various probabilities $P_{n_0\to n}(T)$ for having rearrangement are given by

$$P_{n_0\to n}(T)=(k_n/k_{n_0})|t_n|^2 . \quad \text{(A4)}$$

The wave function in general can be written as

$$\psi_\alpha=\theta_\alpha(n_0)+(E-H+i\epsilon)^{-1}V_\alpha\theta_\alpha(n_0) . \quad \text{(A5)}$$

Again, applying the identity

$$(E-H+i\epsilon)^{-1}=(E-K_\gamma+i\epsilon)^{-1}+(E-K_\gamma+i\epsilon)^{-1}V_\gamma \times(E-H+i\epsilon)^{-1} \quad \text{(A6)}$$

to Eq. (A5) one notices that

$$\psi_\alpha=\theta_\alpha(n_0)+(E-K_\gamma+i\epsilon)^{-1} \times[V_\alpha+V_\gamma(E-H+i\epsilon)^{-1}V_\alpha]\theta_\alpha(n_0) . \quad \text{(A7)}$$

But since $\tau_{\gamma\alpha}$ is defined as

$$\tau_{\gamma\alpha}=V_\alpha+V_\gamma(E-H+i\epsilon)^{-1}V_\alpha , \quad \text{(A8)}$$

we find that

$$\psi_\alpha=\theta_\alpha(n_0)+(E-K_\gamma+i\epsilon)^{-1}\tau_{\gamma\alpha}\theta_\alpha(n_0) , \quad \text{(A9)}$$

where $\tau_{\gamma\alpha}\theta_\alpha(n_0)$ is the total amplitude density for going from channel α to γ and where γ is independent of α and can therefore be either α (nonreactive collision) or β (reactive collision). It is clear from Eq. (A9) that $\tau_{\gamma\alpha}\theta_\alpha$ contains the same information that $V_\gamma\psi_\alpha$ contains. We shall treat first the nonreactive channel and consequently we insert $\gamma=\alpha$ to obtain

$$\psi_\alpha=\theta_\alpha(n_0)+(E-K_\alpha+i\epsilon)^{-1}\tau_{\alpha\alpha}\theta_\alpha(n_0) . \quad \text{(A10)}$$

In the following, we suppress the initial state index. Assuming $\psi(x,y)$ to be of the form

$$\psi(x,y)=\sum_n\psi_n(x)\varphi_n(y) \quad \text{(A11)}$$

and recalling Eq. (23),

$$\tau_{\alpha\alpha}\theta_\alpha=\sum_n\chi_n(x)\varphi_n(y) , \quad \text{(A12)}$$

one derives an equation for $\psi_l(x)$ by substituting Eqs. (A11) and (A12) into Eq. (A10), multiplying both sides by $\varphi_l(y)$ and integrating over y. Thus, we find that

$$\psi_l(x)=\sin k_{n_0}x\int_0^\infty dy\,\varphi_l(y)\varphi_{n_0}(y) +(1/\pi)\sum_n\int_{-\infty}^{\infty}dk\sin kx \times\left[\int_0^\infty dy\,\varphi_l(y)\varphi_m(y)\right](k_n^2-k^2+i\epsilon)^{-1} \times\int_0^\infty dy'\int_0^\infty dx'\sin kx'\,\varphi_m(y')\sum_j\chi_j(x')\varphi_j(y') , \quad \text{(A13)}$$

where the coordinate representation of the Green's functions have been used. Performing the various integrations over y and y', we obtain

$$\psi_l(x)=\delta_{l,n_0}\sin k_{n_0}x+\frac{1}{\pi}\int_0^\infty dx'\chi_l(x')$$

$$\times \int_{-\infty}^{\infty} dk \frac{\sin kx \sin kx'}{k_l^2 - k^2 + i\epsilon} \quad . \qquad \text{(A14)}$$

In order to evaluate the inner integral use is made of the residue theorem by which the following result is obtained:

$$\frac{1}{\pi} \int_{-\infty}^{\infty} dk \frac{\sin kx \sin kx'}{k_l^2 - k^2 + i\epsilon} = -\frac{1}{k_l} \times \begin{cases} e^{ik_l x} \sin k_l x' , & x > x' \\ e^{ik_l x'} \sin k_l x , & x < x' \end{cases} . \qquad \text{(A15)}$$

Consequently, when x tends to infinity we have

$$\lim_{x \to \infty} \psi_l(x) = \delta_{l,n_0} \sin k_{n_0} x - [e^{ik_l x}/k_l] \int_0^{\infty} dx' \sin k_l x' \chi_l(x') . \qquad \text{(A16)}$$

We now recall the definition of R_l given by Eq. (97) to obtain

$$\lim_{x \to \infty} \psi_l(x) = \delta_{l,n_0} \sin k_{n_0} x - (R_l/k_l) e^{ik_l x} . \qquad \text{(A17)}$$

Substituting Eq. (A17) in Eq. (A11), we obtain

$$\lim_{x \to \infty} \psi(x, y) = -\frac{1}{2i} e^{-ik_{n_0} x} \varphi_{n_0}(y) + \left(\frac{1}{2i} - \frac{R_{n_0}}{k_{n_0}}\right) e^{ik_{n_0} x} \varphi_{n_0}(y) - \sum_{m \neq n_0} \frac{R_n}{k_n} e^{ik_n x} \varphi_n(y) \qquad \text{(A18)}$$

or

$$\lim_{x \to \infty} \psi(x, y) = -\frac{1}{2i} \left[e^{-ik_{n_0} x} \varphi_{n_0}(y) - \left(1 - \frac{2iR_{n_0}}{k_{n_0}}\right) \times e^{ik_{n_0} x} \varphi_{n_0}(y) + \sum_{m \neq n_0} \frac{2iR_n}{k_n} e^{ik_n x} \varphi_n(y) \right] . \qquad \text{(A19)}$$

Comparing this expansion and the one given in Eq. (A1) we see that, up to an arbitrary constant factor, the two comparisons coincide if

$$\rho_{n_0} = -(1 - 2iR_{n_0}/k_{n_0}) \qquad \text{(A20)}$$

and

$$\rho_n = 2iR_n/k_n , \quad n \neq n_0 . \qquad \text{(A21)}$$

Consequently,

$$P_{n_0 \to n_0}(R) = |1 - 2iR_{n_0}/k_{n_0}|^2 \qquad \text{(A22)}$$

and

$$P_{n_0 \to n}(R) = 4 |R_n|^2 / k_{n_0} k_n , \quad n \neq n_0 . \qquad \text{(A23)}$$

By proceeding through a similar analysis for the reactive channel, it can be shown that

$$P_{n_0 \to n}(T) = 4 |T_n|^2 / k_{n_0} k_n . \qquad \text{(A24)}$$

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[4]The model we consider reduces to that discussed in Ref. 3 above in the limit that no dissociative continuum is allowed.

[5]The definition employed is that discussed in Chaps. 3–5 of the excellent reference text by M. L. Goldberger and K. Watson (see Ref. 1).

[6]This has been pointed out in various formal discussions. A particularly lucid discussion may be found in the reference work by R. G. Newton (see Ref. 1) on pp. 201–202 and 555–557.

[7]The model in Ref. 3 has $V(x, y)$ equal to ∞ for $l < y < \infty$, $l < x < \infty$ instead of the finite value 0.

[8]We have carried out calculations using "box"-type normalization and continuum normalization boundary conditions. The results obtained are essentially identical for the two normalization conditions but nevertheless they are all incorrect in that flux is never conserved.