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Open-Channel Projectors for Rearrangement Processes in Molecular Collisions[*]

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A general form for the projector onto open channels for rearrangement processes in molecular collisions is given. This form is investigated for two special cases of the three-atom process $A+BC\rightarrow AB+C$ on a single potential-energy surface: (a) the rearrangement to and from the ground vibrational and rotational states of BC and AB for arbitrary total angular momentum and (b) the semiclassical limit of this form. The projector for special case (a) can be found exactly under either of two limiting conditions, and for case (b) we find the projector to be a local operator, such that in the semiclassical limit the process $A+BC\rightarrow AB+C$ occurs only when the distance from A to the center of mass of BC equals the distance of C from the center of mass of AB.

I. INTRODUCTION

The unified reaction theory of Feshbach[1] has been applied extensively to problems in nuclear and molecular collisions. The general expressions include an operator P, the projector onto some or all of the open channels and its orthogonal complement $Q=1-P$. Explicit expressions for P can be written formally in a straightforward manner if the collision system involves only elastic or inelastic transitions. For instance, for the inelastic collision of molecules A and B, P can be written as

$$P=\sum_i |\phi_i\rangle\langle\phi_i| , \tag{1.1}$$

where ϕ_i is a product of the internal-state wave functions for each A and B, and the summation runs over all energetically allowed states ϕ_i. P is uniquely defined in this manner to project onto all open channels (corresponding to the states of the system $A+B$ at infinite separation). Q is thus uniquely defined to project onto all closed channels.[2]

The definitions of P and Q for rearrangement collisions in a time-independent theory have presented somewhat of a problem in the past 10 yr. This problem results from the fact that the basis set in one arrangement is not orthogonal to the basis set in another arrangement.[3] A P for rearrangement collisions was first derived by Mittleman[4] and modified by Coz.[5] The complexity of this derivation led Chen and Mittleman[6] to derive simpler expressions for P which, however, did not account in general for possible recoil of the target. Starting with the procedure of Ref. 6, Chen[7] was able to derive explicit expressions for P for general three-body rearrangement collisions, which allowed for recoil of the target.

A general construction of P for rearrangements was given by Hahn[8] in a multidimensional formulation of Feshbach's unified reaction theory that could in principle be applied to any rearrangement collision involving three or more bodies. In this paper we shall present a general construction of P for molecular rearrangements which does not require a multicomponent form. In Sec. II we shall summarize the multicomponent formulation of Hahn and present the general single-component formulation of P. In Sec. III we shall restrict ourselves to rearrangements on a single potential-energy surface and (a) consider a special case for three-body rearrangements, namely, the 0 → 0 rotational and 0 → 0 vibrational state rearrangement process for arbitrary total angular momentum and (b) look at the semiclassical limit of the projector P. In Sec. IV we shall discuss other possible single-component formulations of P along with a summary of the paper.

II. GENERAL SINGLE COMPONENT *P* FOR REARRANGEMENT

The formulation of Hahn[8] begins with the matrix projector P defined as

$$\underline{P}=\begin{bmatrix} P_1 & & & & & \\ & P_2 & & & 0 & \\ & & \ddots & & & \\ & & & P_\alpha & & \\ & 0 & & & \ddots & \\ & & & & & P_N \end{bmatrix}, \qquad (2.1)$$

where P_α is defined by Eq. (1.1) and N is the number of arrangements. $\underline{Q}$ is defined as $\underline{Q}=\underline{1}-\underline{P}$. The total wave function is generalized in a fashion similar to the Faddeev formulation of the three-body problem[9] as

$$\Psi=\begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_N \end{bmatrix}, \qquad (2.2)$$

where Ψ_α is defined such that

$$\Psi\to\begin{bmatrix} 0 \\ \vdots \\ \Psi_\alpha \\ \vdots \\ 0 \end{bmatrix} \qquad (2.3)$$

as the system goes asymptotically to arrangement α. Defining the $N\times N$ matrix $\underline{H}-\underline{E}$ as

$$\underline{H}-\underline{E}=(H-E)\begin{bmatrix} 1 & 1 & 1 & \cdots & 1 \\ 1 & 1 & 1 & \cdots & 1 \\ \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & & \cdot \\ 1 & 1 & 1 & \cdots & 1 \end{bmatrix}, \qquad (2.4)$$

where H is the total Hamiltonian and E is the total energy, we can then write with the help of the Schrödinger equation $(\underline{H}-\underline{E})\Psi=0$ the matrix analog of the Feshbach equations

$$\underline{P}[\underline{H}-\underline{E}]\underline{P}\Psi=-\underline{PHQ}\Psi\ , \quad \underline{Q}[\underline{H}-\underline{E}]\underline{Q}\Psi=-\underline{QHP}\Psi\ . \qquad (2.5)$$

Equation (2.1) does represent a general form of P for rearrangement collisions, but it requires a matrix formulation of Feshbach's equations. We present in this paper a general formulation of P in a single-component form. To motivate our derivation, we consider the projector onto the nonorthogonal basis $\{u_i\}$. Given some arbitrary function χ, we know that

$$P\chi=\textstyle\sum_i u_i c_i\ , \qquad (2.6)$$

where c_i is some coefficient. Multiplying both sides by $\langle u_j|$ we have the equation

$$\langle u_j|\chi\rangle=\textstyle\sum_i\langle u_j|u_i\rangle c_i\ , \qquad (2.7)$$

where we used the fact that

$$\langle u_j|P\chi\rangle=\langle u_j|\chi\rangle\ . \qquad (2.8)$$

Multiplying both sides of Eq. (2.7) by $(\langle u_k|u_j\rangle)^{-1}$ [we use $(\langle u_k|u_j\rangle)^{-1}$ to designate the kjth matrix element of $\underline{M}^{-1}$, where $\underline{M}$ is the overlap matrix such that $M_{kj}=\langle u_k|u_j\rangle$] and summing over j, we find c_k to be

$$c_k=\textstyle\sum_j(\langle u_k|u_j\rangle)^{-1}\langle u_j|\chi\rangle\ , \qquad (2.9)$$

so that

$$P=\sum_{i,j}u_i(\langle u_i|u_j\rangle)^{-1}\langle u_j|\ . \qquad (2.10)$$

We see that P, depending on the inverse of the overlap matrix, is given in a single-component form by Eq. (2.10).

To proceed in a similar fashion for rearrangement collisions, where we have nonorthogonal channel states, we let R_α designate the radial coordinate between the centers of mass of the two molecules in channel α, and let r_α designate the internal coordinates of the two molecules. The internal coordinates are all those other than that for radial translational motion; i.e., rotation and vibration of the isolated molecules, their electronic states, and the angular part of the translational motion. (The special cases in Sec. III are restricted to a single potential-energy surface, i.e., one over-all electronic state for the scattering system, so that we shall consider only nuclear degrees of freedom for the internal coordinates in Sec. III.) Designating an internal state in channel α as $\phi_{\alpha i}(r_\alpha)$, then for an arbitrary function χ we write in an analogous fashion to Eq. (2.6),

$$P\chi = \sum_{\alpha, i} \phi_{\alpha i}(r_{\alpha i}) C_{\alpha i}(R_\alpha) , \tag{2.11}$$

where the coefficient $C_{\alpha i}(R_\alpha)$ depends on χ and is constructed such that there is no multiple counting of internal degrees of freedom. Multiplying both sides of Eq. (2.11) by $\int dr_\beta \phi^*_{\beta j}(r_\beta)$ we obtain

$$\int dr_\beta \, \phi^*_{\beta j}(r_\beta)\chi = \sum_{\alpha, i} \int dr_\beta \, \phi^*_{\beta j}(r_\beta)\, \phi_{\alpha i}(r_\alpha) C_{\alpha i}(R_\alpha) , \tag{2.12}$$

where we have used the fact that

$$\int dr_\beta \, \phi^*_{\beta j}(r_\beta) P\chi = \int dr_\beta \, \phi^*_{\beta j}(r_\beta)\chi .$$

Defining the overlap kernel[10]

$$\Delta_{\beta j, \alpha i}(R_\alpha, R_\beta) = \int d'(\alpha\beta)\, \phi^*_{\beta j}(r_\beta)\, \phi_{\alpha i}(r_\alpha) , \tag{2.13}$$

where $\int d'(\alpha\beta)$ indicates integration over all variables except R_α and R_β, we rewrite Eq. (2.12) as

$$\int dr_\beta \, \phi^*_{\beta j}(r_\beta)\chi = \sum_{\alpha, i} \int dR_\alpha \; \Delta_{\beta j, \alpha i}(R_\alpha, R_\beta) C_{\alpha i}(R_\alpha) . \tag{2.14}$$

The inverse of the kernel, $\Delta_{\beta j, \alpha i}{}^{-1}(R_\alpha, R_\beta)$, satisfies

$$\sum_{\gamma, k} \int dR_\gamma \, \Delta_{\alpha i, \gamma k}(R_\alpha, R_\gamma) \Delta_{\gamma k, \beta j}{}^{-1}(R_\gamma, R_\beta) = \delta_{\alpha\beta}\delta_{ij}\delta(R_\alpha - R_\beta) , \tag{2.15}$$

so that the coefficients from Eq. (2.14) can be written as

$$C_{\alpha i}(R_\alpha) = \sum_{\beta, j} \int d(r_\beta R_\beta)\, \Delta_{\alpha i, \beta j}{}^{-1}(R_\alpha, R_\beta)\, \phi^*_{\beta j}(r_\beta)\chi , \tag{2.16}$$

and the projector P assumes the form[11]

$$P = \sum_{\alpha, i, \beta, j} \phi_{\alpha i}(r_\alpha) \int d(r_\beta R_\beta)\, \Delta_{\alpha i, \beta j}{}^{-1}(R_\alpha, R_\beta)\, \phi^*_{\beta j}(r_\beta) . \tag{2.17}$$

Equation (2.17) is a single-component expression for the projector onto all open channels for a general rearrangement molecular collision. Such a projector can be defined uniquely, however, only in the asymptotic region $R_\gamma \rightarrow \infty$ where it assumes the form

$$P \rightarrow P_\gamma = \sum_k |\phi_{\gamma k}\rangle\langle\phi_{\gamma k}| \quad \text{as } R_\gamma \rightarrow \infty \tag{2.18}$$

due to the vanishing of the overlap kernel between states of different arrangements. In this region P is identical to Eq. (1.1) defining P for inelastic collisions, and is thus uniquely defined.

III. INVERSE KERNEL

A. Special Case

In general, the inverse kernel, as defined by Eq. (2.15), is difficult to calculate, since it involves the solution of an integral equation whose kernel is not of finite rank.[12] We shall indicate how to find the inverse kernel for a special case of atom-diatom rearrangements on a single potential-energy surface: the case where only two arrangements are open, say $A+BC$ and $AB+C$, and where BC and AB are in their ground vibrational and rotational states. The procedure we follow can, however, be generalized in a straightforward manner to the case where all three arrangements are open, but for simplicity we shall restrict ourselves to two open arrangements.

For our special case we can write Eq. (2.15) as

$$\int dR_3 \begin{pmatrix} \delta(R_1 - R_3) & \Delta_{12}(R_1, R_3) \\ \Delta_{12}(R_1, R_3) & \delta(R_1 - R_3) \end{pmatrix} \begin{pmatrix} K_{11}(R_3, R_2) & K_{12}(R_3, R_2) \\ K_{21}(R_3, R_2) & K_{22}(R_3, R_2) \end{pmatrix} = \begin{pmatrix} \delta(R_1 - R_2) & 0 \\ 0 & \delta(R_1 - R_2) \end{pmatrix} , \tag{3.1}$$

where $K_{ij} \equiv \Delta_{ij}{}^{-1}$ (the subscripts signify arrangements) and R_1 and R_2 are the radial coordinates of arrangements $A+BC$ and $AB+C$, respectively. Writing the four equations resulting from Eq. (3.1) and making the appropriate substitutions of these equations into each other, we arrive at the following four coupled equations:

$$K_{11}(R_1, R_2) = \delta(R_1 - R_2) + \int dR_3 \int dR_4 \; \Delta_{12}(R_1, R_3) \times \Delta_{21}(R_3, R_4) K_{11}(R_4, R_2) , \tag{3.2}$$

$$K_{21}(R_1, R_2) = -\int dR_3 \; \Delta_{21}(R_1, R_3) K_{11}(R_3, R_2) , \tag{3.3}$$

$$K_{22}(R_1, R_2) = \delta(R_1 - R_2) + \int dR_3 \int dR_4 \; \Delta_{21}(R_1, R_3) \times \Delta_{12}(R_3, R_4) K_{22}(R_4, R_2) , \tag{3.4}$$

$$K_{12}(R_1, R_2) = -\int dR_3 \; \Delta_{12}(R_1, R_3) K_{22}(R_3, R_2) . \tag{3.5}$$

Let us concentrate on Eq. (3.2). Both matrices on the left-hand side of Eq. (3.1) are symmetric, so that $\Delta_{12} = \Delta_{21}$. Dispensing with the subscripts on Δ_{12}, we can write $K_{11}(R_1, R_2)$ as

$$K_{11}(R_1, R_2) = \delta(R_1 - R_2) + \Delta^2(R_1, R_2) + \Delta^4(R_1, R_2) + \Delta^6(R_1, R_2) + \cdots , \tag{3.6}$$

where $\Delta^2(R_1, R_2)$, for example, is

$$\Delta^2(R_1, R_2) = \int dR_3 \; \Delta(R_1, R_3)\, \Delta(R_3, R_2) . \tag{3.7}$$

Using harmonic-oscillator vibrational wave functions for AB and BC, we find the kernel for our specific case, with total angular momentum J, to be[13]

$$\Delta(R_1, R_2) = \frac{R_1 R_2}{4\pi} \int_0^{\pi} d\gamma \sin\gamma \, \frac{\alpha^{1/2}\beta^{1/2}}{\pi^{1/2}} \times \exp(-\tfrac{1}{2}\alpha^2 r_1^2 - \tfrac{1}{2}\beta^2 r_2^2) d_{00}^J(\gamma) , \tag{3.8}$$

where γ is the angle between the R_1 and R_2 vectors, and r_1 and r_2 are the vibrational coordinates of BC and AB with force constants α and β. The transformation equations from R_1, R_2 to r_1, r_2 are[10]

$$r_1^2 = \mu_1^2 \left(\frac{R_1^2}{M_2^2} + \frac{R_2^2}{m_2^2} + 2\frac{R_1 R_2}{M_2 m_2} \cos\gamma \right), \tag{3.9}$$

$$r_2^2 = \mu_2^2 \left(\frac{R_2^2}{M_2^2} + \frac{R_1^2}{m_1^2} + 2\frac{R_1 R_2}{M_2 m_1} \cos\gamma \right), \tag{3.10}$$

where m_1 is the reduced mass of BC, m_2 is the reduced mass of AB, M_2 is the mass of B, and μ_1 and μ_2 are the reduced channel masses of arrangements $A+BC$ and $AB+C$, respectively. With Eqs. (3.9) and (3.10) we can write the kernel as

$$\Delta(R_1, R_2) = R_1 R_2 (-1)^{-J} \tfrac{1}{2} C_1 \exp(-C_2 R_1^2 - C_3 R_2^2) \times \int_{-1}^{1} d(\cos\gamma) \exp(C_4 R_1 R_2 \cos\gamma) P_J(\cos\gamma) , \tag{3.11}$$

where $P_J(\cos\gamma) = d_{00}^J(\cos\gamma)$, and the constants C_i are defined as

$$\begin{aligned} C_1 &= (\alpha^{1/2}\beta^{1/2}/2\pi^{3/2})(-1)^J , \\ C_2 &= \alpha^2\mu_1^2/2M_2^2 + \beta^2\mu_2^2/2m_1^2 , \\ C_3 &= \beta^2\mu_2^2/2M_2^2 + \alpha^2\mu_1^2/2m_2^2 , \\ C_4 &= \alpha^2\mu_1^2/M_2 m_2 + \beta^2\mu_2^2/M_2 m_1 . \end{aligned} \tag{3.12}$$

The exponential function can be expanded as[14]

$$e^{-C_4 R_1 R_2 \cos\gamma} = \sum_{J'=0} (-1)^{J'} (2J'+1) \times \left[\left(\frac{\pi}{2C_4 R_1 R_2} \right)^{1/2} I_{J'+1/2}(C_4 R_1 R_2) \right] P_{J'}(\cos\gamma) , \tag{3.13}$$

where $i_J(z)$, defined as

$$i_J(z) \equiv (\pi/2z)^{1/2} I_{J+1/2}(z) , \tag{3.14}$$

is a modified spherical Bessel function of the first kind and is defined in terms of $J_{J+1/2}(z)$ for our case as

$$i_J(z) = (\pi/2z)^{1/2} e^{-J\pi i/2} J_{J+1/2}(z e^{\pi i/2}) . \tag{3.15}$$

Using the orthogonality relation

$$\int_{-1}^{1} d(\cos\gamma) P_{J'}(\cos\gamma) P_J(\cos\gamma) = 2\delta_{JJ'}/(2J+1) , \tag{3.16}$$

the kernel in Eq. (3.11) is thus found to be

$$\Delta(R_1, R_2) = R_1 R_2 C_1 \exp(-C_2 R_1^2 - C_3 R_2^2) i_J(C_4 R_1 R_2) . \tag{3.17}$$

To calculate K_{11} as given by Eq. (3.6), we begin by calculating Δ^2 in Eq. (3.7),

$$\Delta^2(R_1, R_2) = \int_0^{\infty} dR_3 \, R_2 R_1 R_3^2 C_1^2 \times \exp[-C_2 R_1^2 - (C_2 + C_3) R_3^2 - C_3 R_2^2] \times i_J(C_4 R_1 R_3) i_J(C_4 R_2 R_3) . \tag{3.18}$$

Rewriting $\Delta^2(R_1, R_2)$ with the help of Eq. (3.15) as

$$\Delta^2(R_1, R_2) = \frac{C_1^2 (R_1 R_2)^{1/2}}{C_4} \exp(-C_2 R_1^2 - C_3 R_2^2) \frac{\pi}{2} \times \int_0^{\infty} dR_3 \, R_3 e^{-(C_2+C_3)R_3^2} e^{-J\pi i} \times J_{J+1/2}(iC_4 R_1 R_3) J_{J+1/2}(iC_4 R_2 R_3) , \tag{3.19}$$

we can write the result directly from integral tables as[15]

$$\Delta^2(R_1, R_2) = R_1 R_2 \frac{C_1^2 \sqrt{\pi}}{4(C_2 + C_3)^{3/2}} e^{-2J\pi i} \times \exp\left[-\left(C_2 - \frac{C_4^2}{4(C_2+C_3)} \right) R_1^2 - \left(C_3 - \frac{C_4^2}{4(C_2+C_3)} \right) R_2^2 \right] \times i_J\left(\frac{C_4^2 R_1 R_2}{2(C_2+C_3)} \right) . \tag{3.20}$$

This result is most interesting, for Δ^2 has the same form as Δ. We can therefore write the general expression for Δ^m ,

$$\Delta^m(R_1, R_2) = R_1 R_2 C_1^{(m)} \exp(-C_2^{(m)} R_1^2 - C_3^{(m)} R_2^2) \times i_J(C_4^{(m)} R_1 R_2) , \tag{3.21}$$

where we have the recursion relations for the constants $C_i^{(m)}$ [$C_i^{(1)}$ being equal to C_i of Eq. (3.12)]:

$$\begin{aligned} C_1^{(m)} &= \frac{(C_1^{(m-1)})^2 \sqrt{\pi}}{4(C_2^{(m-1)} + C_3^{(m-1)})^{3/2}} , \\ C_2^{(m)} &= C_2^{(m-1)} - \frac{(C_4^{(m-1)})^2}{4(C_2^{(m-1)} + C_3^{(m-1)})} , \\ C_3^{(m)} &= C_3^{(m-1)} - \frac{(C_4^{(m-1)})^2}{4(C_2^{(m-1)} + C_3^{(m-1)})} , \\ C_4^{(m)} &= \frac{(C_4^{(m-1)})^2}{2(C_2^{(m-1)} + C_3^{(m-1)})} . \end{aligned} \tag{3.22}$$

If $\Delta^2(R_1, R_2)$ is small, say less than unity for all R_1 and R_2, then Eq. (3.21) is quite useful, for we can write $K_{11}(R_1, R_2)$ through Eq. (3.6), retaining only a small number of terms which we can write down immediately from Eq. (3.21). We know K_{22} since $K_{22} = K_{11}$, and the off-diagonal terms of the inverse kernel matrix are

$$K_{12}(R_1, R_2) = K_{21}(R_1, R_2) = \Delta(R_1, R_2) + \Delta^3(R_1, R_2) + \Delta^5(R_1, R_2) + \cdots . \tag{3.23}$$

We can therefore write P if the kernel is less than

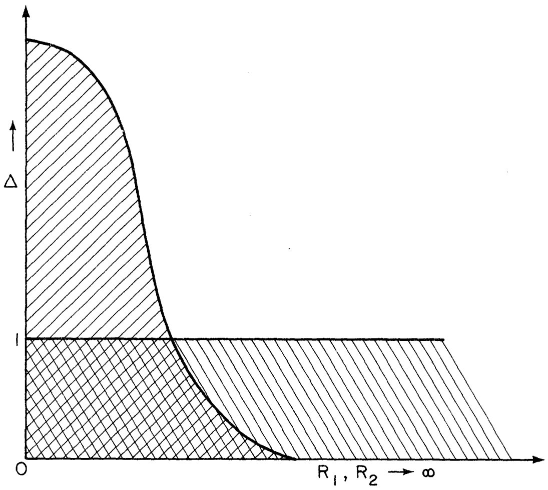

FIG. 1. Range is the overlap kernel $\Delta=\Delta(R_1,R_2)$ for a three-atom rearrangement process and the abscissa is either R_1 or R_2. For the special case considered, i.e., the ground-to-ground vibrational and rotational state transition, the inverse kernel can be found exactly if Δ falls in the shaded area. See the text for an explanation of the two overlapping parts of the shaded area.

unity for all R_1 and R_2, which is indicated by the shady area in Fig. 1 below the horizontal line at unity.

On the other hand, if the kernel goes to zero quickly as R_1 or $R_2\rightarrow\infty$, as shown, for example, by the shaded area under the "Gaussian" in the figure, then we can use the fact that the kernel can be made separable in this case to solve for K_{ij} exactly. We can expand $i_J(z)$ in a series as[14]

$$i_J(z)=\frac{z^J}{1\cdot 3\cdot 5\cdots(2J+1)}\left(1+\frac{\frac{1}{2}z^2}{1!\,(2J+3)}+\frac{(\frac{1}{2}z^2)^2}{2!\,(2J+3)(2J+5)}+\cdots\right). \tag{3.24}$$

$K_{11}(R_1,R_2)$ is written from Eq. (3.6) as

$$K_{11}(R_1,R_2)=\delta(R_1-R_2)+\int dR_3\;\Delta^2(R_1,R_3)K_{11}(R_1,R_3). \tag{3.25}$$

$\Delta^2(R_1,R_3)$ can be expanded in a complete set $h_n(R_3)$,[16]

$$\Delta^2(R_1,R_3)=\sum_{n=1}^{\infty} g_n(R_1)h_n(R_3). \tag{3.26}$$

If Δ behaves as the Gaussian in Fig. 1 (i.e., it approaches zero quickly as R_1 or $R_2\rightarrow\infty$), then we need only a few terms in the summation in Eq. (3.26), which we can identify immediately from Eq. (3.24). Defining $A_n(R_2)$ as

$$A_n(R_2)=\int dR_3\,h_n(R_3)K_{11}(R_3,R_2), \tag{3.27}$$

K_{11} then is written as

$$K_{11}(R_1,R_2)=\delta(R_1-R_2)+\textstyle\sum_n g_n(R_1)A_n(R_2). \tag{3.28}$$

Substituting Eq. (3.27) into Eq. (3.28), we arrive at the following set of equations for $A_m(R_2)$:

$$\sum_{m=1}(\delta_{nm}-\alpha_{nm})A_m(R_2)=h_n(R_2), \tag{3.29}$$

where

$$\alpha_{nm}=\int dR_3\,h_n(R_3)g_m(R_3). \tag{3.30}$$

For example, if we need only one term of the series for $i_J(z)$, then $K_{11}(R_1,R_2)$ is (for $J=0$)

$$K_{11}(R_1,R_2)=\delta(R_1-R_2)+\frac{C_1^{(2)}R_1R_2\exp(-C_2^{(2)}R_2^2-C_3^{(2)}R_3^2)}{1-C_1^{(2)}\sqrt{\pi}/4(C_2^{(2)}+C_3^{(2)})^{3/2}}. \tag{3.31}$$

If the kernel falls anywhere in the shaded area in Fig. 1, we are able to calculate K_{ij}, and thus P, exactly. Let us consider an example, such as the rearrangement $H+H_2\rightarrow H_2+H$ on the lowest adiabatic electronic surface and with $J=0$. The constant γ in the Morse potential for H_2 in the singlet state, $V(r)=D_e(1-e^{-\gamma(r-r_e)})^2$, where D_e is the well depth and r_e is the equilibrium distance, is given as 1.04 a.u.[17] We have used the ground harmonic-oscillator wave functions for the vibrational state of H_2 in our expression for Δ, so we expand $V(r)$ to second order, equate it to the harmonic-oscillator potential, and find that γ and α are related in this approximation by the equation $\frac{1}{2}\alpha=\gamma^2D_e$. We thus estimate α to be near 0.38 a.u. and list in Table I the values of $C_i^{(n)}$ for $\alpha=\beta=0.48$, 0.38, and 0.28 a.u. [see Eq. (3.22)]. The odd values of n appear in the series expression for K_{12}, K_{21} [Eq. (3.23)] and the even values appear in the series expression for K_{11}, K_{22} [Eq. (3.6)]. As we see from Table I, we need retain only a few terms in the series expressions for K_{ij} due to their rapid convergence. The kernel falls into the shaded area beneath the horizontal line at unity in Fig. 1.

As α and β are decreased, the Gaussian wave functions for the internal vibrational states of the two arrangements broaden, so that the amount of overlap between them increases. In Table II we see for the system of masses $H+H_2\rightarrow H_2+H$ that when the value of α goes from 0.130 to 0.129, $C_1^{(n)}$ no longer decreases as n increases. $C_2^{(n)}$ and $C_3^{(n)}$ decrease as α and β decrease, which we expect from the form of Δ^2 in Eq. (3.20), i.e., smaller $C_2^{(n)}$ and $C_3^{(n)}$ mean larger Δ^2. The value of $\alpha=\beta=0.130$ for the mass combination $H+H_2$ seems to be critical as far as the rapid convergence of the series in Eq. (3.6), so that the results of Eqs. (3.7) and (3.20) are useful only for α and β above that critical value. $\Delta^{(n)}(R_1,R_2)$, of course, goes to zero as $R_1,R_2\rightarrow\infty$ for α,β below, as well as above, 0.130 since $C_2^{(n)}$ and $C_3^{(n)}$ are positive.

TABLE I. $C_i^{(n)}$ [Eq. (3.22)] are listed for the rearrangement process $H+H_2 \rightarrow H_2+H$ to and from the ground vibrational and rotational states of H_2 for $J=0$. Different sets of $C_i^{(n)}$ are shown for the values of the force constant α of H_2 set equal to 0.48, 0.38, and 0.28 a.u. (in comparison with the results of Ref. 17 for the potential-energy curve of H_2, 0.38 a.u. appears to be the most reasonable choice). It is seen that the convergence of the series for K_{ij} [Eqs. (3.6) and (3.22)] is quite rapid for all R_1 and R_2 for the above values of α.

	n	$C_1^{(n)}$	$C_2^{(n)}$	$C_3^{(n)}$	$C_4^{(n)}$
$\alpha=\beta=0.48$	1	4.31×10^{-2}	2.56×10^{-1}	2.56×10^{-1}	4.10×10^{-1}
	2	2.25×10^{-3}	1.74×10^{-1}	1.74×10^{-1}	1.64×10^{-1}
	3	1.09×10^{-5}	1.55×10^{-1}	1.55×10^{-1}	3.86×10^{-2}
	4	3.05×10^{-10}	1.54×10^{-1}	1.54×10^{-1}	2.40×10^{-3}
	5	2.42×10^{-19}	1.54×10^{-1}	1.54×10^{-1}	9.38×10^{-6}
	6	1.53×10^{-37}	1.54×10^{-1}	1.54×10^{-1}	1.43×10^{-10}
$\alpha=\beta=0.38$	1	3.41×10^{-2}	1.60×10^{-1}	1.60×10^{-1}	2.57×10^{-1}
	2	2.84×10^{-3}	1.09×10^{-1}	1.09×10^{-1}	1.03×10^{-1}
	3	3.50×10^{-5}	9.70×10^{-2}	9.70×10^{-2}	2.42×10^{-2}
	4	6.36×10^{-9}	9.63×10^{-2}	9.63×10^{-2}	1.50×10^{-3}
	5	2.12×10^{-16}	9.63×10^{-2}	9.63×10^{-2}	5.88×10^{-6}
	6	2.36×10^{-31}	9.63×10^{-2}	9.63×10^{-2}	8.97×10^{-11}
$\alpha=\beta=0.28$	1	2.51×10^{-2}	8.71×10^{-2}	8.71×10^{-2}	1.39×10^{-1}
	2	3.85×10^{-3}	5.92×10^{-2}	5.92×10^{-2}	5.58×10^{-2}
	3	1.61×10^{-4}	5.27×10^{-2}	5.27×10^{-2}	1.31×10^{-2}
	4	3.37×10^{-7}	5.23×10^{-2}	5.23×10^{-2}	8.17×10^{-4}
	5	1.49×10^{-12}	5.23×10^{-2}	5.23×10^{-2}	3.19×10^{-6}
	6	2.90×10^{-23}	5.23×10^{-2}	5.23×10^{-2}	4.87×10^{-11}

B. Semiclassical Form

Continuing to restrict the rearrangement to a single potential-energy surface,[18] we go to the momentum representation, where P_1 and P_2 are the generalized momenta which designate the initial and final scattering states, respectively (for further discussion of P_1 and P_2, see Miller[13]). The matrix element $\langle P_2 | P_1 \rangle$ is given in the classical limit as[13]

$$\langle P_2 | P_1 \rangle = J e^{i f_4 (P_2, P_1)} , \qquad (3.32)$$

where f_4 is the generator of the rearrangement, and

$$J = \left(\frac{1}{2\pi i \hbar} \frac{\partial^2 f_4(P_2, P_1)}{\partial P_2 \, \partial P_1} \right)^{1/2} . \qquad (3.33)$$

Since $\langle P_2 | P_1 \rangle$ is the Fourier transform of the kernel,[13] we can Fourier transform $\langle P_2 | P_1 \rangle$ to obtain

$$\Delta(R_1, R_2) = (2\pi\hbar)^{-1} \int dP_1 \int dP_2 \, J \exp \frac{i(R_2 P_2 - R_1 P_1)}{\hbar} \times \exp \frac{i f_4(P_2, P_1)}{\hbar} . \qquad (3.34)$$

$K_{11}(R_1, R_2)$, for example, is written as

$$K_{11}(R_1, R_2) = \delta(R_1 - R_2) + \int dR_3 \int dR_4 \, \Delta(R_1, R_3) \times \Delta(R_3, R_4) K_{11}(R_4, R_2) , \qquad (3.35)$$

and when we perform the integrations over coordinates and momenta by stationary phase, we find $K_{ij}(R_1, R_2)$ to be a local operator. This means that in the classical limit the contribution to exchange occurs only when $R_1 = R_2$.

IV. DISCUSSION

We have shown how one can construct the inverse kernel, and thus P, for the special case of the rearrangement collision of an atom with a diatomic molecule $A + BC \rightarrow AB + C$, restricting ourselves to the ground vibrational and rotational states of BC and AB but allowing the total angular momentum to be arbitrary. We were able to do this by considering the general form of P in Eq. (2.17). The construction of the inverse kernel is very difficult except for special cases, such as the one we considered. Our construction was made particularly easy by the use of Gaussian wave functions for the vibrational states of BC and AB.

Although the form of P in Eq. (2.17) is the most general that we know of for molecular rearrangements, it is by no means unique. P is unique only

TABLE II. $C_i^{(n)}$ are listed for $H + H_2 \rightarrow H_2 + H$ under the same conditions as Table I, where it is seen that as α is changed from 0.130 to 0.129 a.u., the series for K_{ij} no longer converges.

	n	$C_1^{(n)}$	$C_2^{(n)}$	$C_3^{(n)}$	$C_4^{(n)}$
$\alpha=\beta=0.130$	1	1.17×10^{-2}	1.88×10^{-2}	1.88×10^{-2}	3.00×10^{-2}
	2	8.30×10^{-3}	1.28×10^{-2}	1.28×10^{-2}	1.20×10^{-2}
	3	7.47×10^{-3}	1.14×10^{-2}	1.14×10^{-2}	2.83×10^{-3}
	4	7.23×10^{-3}	1.13×10^{-2}	1.13×10^{-2}	1.76×10^{-4}
	5	6.85×10^{-3}	1.13×10^{-2}	1.13×10^{-2}	6.88×10^{-7}
	6	6.15×10^{-3}	1.13×10^{-2}	1.13×10^{-2}	1.05×10^{-11}
	7	4.95×10^{-3}	1.13×10^{-2}	1.13×10^{-2}	2.44×10^{-21}
	8	3.21×10^{-3}	1.13×10^{-2}	1.13×10^{-2}	1.32×10^{-40}
	9	1.35×10^{-3}	1.13×10^{-2}	1.13×10^{-2}	3.89×10^{-79}
	10	2.38×10^{-4}	1.13×10^{-2}	1.13×10^{-2}	3.36×10^{-156}
	11	7.40×10^{-6}	1.13×10^{-2}	1.13×10^{-2}	0
	12	7.18×10^{-9}	1.13×10^{-2}	1.13×10^{-2}	0
	13	6.75×10^{-15}	1.13×10^{-2}	1.13×10^{-2}	0
	14	5.96×10^{-27}	1.13×10^{-2}	1.13×10^{-2}	0
$\alpha=\beta=0.129$	1	1.16×10^{-2}	1.85×10^{-2}	1.85×10^{-2}	2.96×10^{-2}
	2	8.36×10^{-3}	1.26×10^{-2}	1.26×10^{-2}	1.18×10^{-2}
	3	7.77×10^{-3}	1.12×10^{-2}	1.12×10^{-2}	2.78×10^{-3}
	4	7.99×10^{-3}	1.11×10^{-2}	1.11×10^{-2}	1.73×10^{-4}
	5	8.57×10^{-3}	1.11×10^{-2}	1.11×10^{-2}	6.77×10^{-7}
	6	9.84×10^{-3}	1.11×10^{-2}	1.11×10^{-2}	1.03×10^{-11}
	7	1.30×10^{-2}	1.11×10^{-2}	1.11×10^{-2}	2.41×10^{-21}
	8	2.26×10^{-2}	1.11×10^{-2}	1.11×10^{-2}	1.30×10^{-40}
	9	6.86×10^{-2}	1.11×10^{-2}	1.11×10^{-2}	3.83×10^{-79}
	10	6.31×10^{-1}	1.11×10^{-2}	1.11×10^{-2}	3.31×10^{-156}
	11	$5.34\times10^{+1}$	1.11×10^{-2}	1.11×10^{-2}	0
	12	$3.82\times10^{+5}$	1.11×10^{-2}	1.11×10^{-2}	0
	13	$1.96\times10^{+13}$	1.11×10^{-2}	1.11×10^{-2}	0
	14	$5.15\times10^{+28}$	1.11×10^{-2}	1.11×10^{-2}	0
$\alpha=\beta=0.01$	1	8.98×10^{-4}	1.11×10^{-4}	1.11×10^{-4}	1.78×10^{-4}
	2	1.08×10^{-1}	7.56×10^{-5}	7.56×10^{-5}	7.11×10^{-5}
	3	$2.77\times10^{+3}$	6.72×10^{-5}	6.72×10^{-5}	1.67×10^{-5}
	4	$2.19\times10^{+12}$	6.67×10^{-5}	6.67×10^{-5}	1.04×10^{-6}
	5	$1.38\times10^{+30}$	6.67×10^{-5}	6.67×10^{-5}	4.07×10^{-9}
	6	$5.48\times10^{+65}$	6.67×10^{-5}	6.67×10^{-5}	6.21×10^{-14}

in the asymptotic channels, and as long as P is correct asymptotically, we are free to construct it in the way most suitable for the system of interest. One possible construction is to avoid the nonorthogonality problem by choosing wave functions of the same zeroth-order Hamiltonian to describe reactant and product states.[19,20] We consider, for example, the three-body rearrangement $A+BC \rightarrow AB+C$ with the channel $AC+B$ closed. The Hamiltonian for the system can be written as

$$H=K+V_{AB}+V_{BC}+V_{AC}+V_{ABC} ,$$

where K is the kinetic energy, V_{AB} is the potential interaction between A and B, and V_{ABC} is the three-body potential interaction. We designate $\psi_{\alpha i}$ as the eigenfunction of $H_0=K+V_{AB}+V_{BC}$, which goes asymptotically to internal state i of arrangement $\alpha(A+BC)$, and $\psi_{\beta j}$ as the eigenfunction of H_0 going asymptotically to internal state j of arrangement $\beta(AB+C)$. Then the rearrangement, which is a transition from $\psi_{\alpha i}$ to $\psi_{\beta j}$, can occur only through the residual interaction $V_{AC}+V_{ABC}$. The projector onto open channels can then be written as

$$P=\sum_i |\psi_{\alpha i}\rangle\langle\psi_{\alpha i}| + \sum_j |\psi_{\beta j}\rangle\langle\psi_{\beta j}| , \qquad (4.1)$$

where the summation runs over all energetically accessible states. One must use caution, however, in choosing P in this manner. For example, in a coupled-channel calculation on the equation

$$(PHP-E)P\Psi=0 , \qquad (4.2)$$

where Ψ is the total wave function, the above choice of P is most likely poor if there are significant long-range forces present.[20]

The procedure of choosing some zeroth-order Hamiltonian H_0 is a familiar one in collision theory. In nuclear physics H_0 could be the shell-model Hamiltonian.[21] In molecular rearrangements H_0 could be chosen to be the Hartree-Fock Hamiltonian, in which case the P, constructed as in Eq. (4.1), can be a projector onto the electronic space only. If P is defined more generally as in Eq. (2.17), then it does not necessarily commute with a chosen H_0. However, the construction of P as in Eq. (4.1) can prove convenient since it commutes with H_0.[19]

As a final comment, P is not always needed explicitly. For example, the coupled equations for open channels for rearrangements can be constructed without P,[22] but the solution of the coupled equations can be facilitated with an explicit form for P.

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