

## Arrangement channel approach to exchange processes: Quasisymmetric and symmetric representations

Daniel Neuhauser and Michael Baer  
Soreq Nuclear Research Center, Yavne 70600, Israel  
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In this work are presented two new sets of integral equations for studying three-body exchange processes. The two are obtained from the Baer-Kouri-Levin-Tobocman approach by assuming the  $\mathbf{W}$  matrix, via which the coupling is done, to be dependent on the internal coordinates of the system. In contrast to the channel permuting array structure of the original version of the Baer-Kouri-Levin-Tobocman equations, one set of equations is almost symmetric with respect to the different channels and the other is fully symmetric, thus ensuring a unitary  $S$  matrix. The first set of equations has already been solved for a three-channel, three-dimensional system,  $H + H_2$  ( $J=0$ ), and has been found to yield the correct results. Connectivity, as related to these equations, is discussed.

### I. INTRODUCTION

The use of integral equations in treating three-body exchange processes is attracting more interest, due to difficulties encountered in the application of the Schrödinger equation to three-dimensional reactive systems.<sup>1</sup> Several approaches have been developed and successfully applied to collinear and three-dimensional systems. One of the earlier approaches is due to Baer, Kouri, Levin, and Tobocman.<sup>2-5</sup> According to this approach, the ordinary Lippmann-Schwinger (LS) equation derived for one arrangement channel is extended to a multichannel system, by forming a set of coupled integral equations, one for each arrangement. The coupling is done via a general matrix  $\mathbf{W}$ , of dimensions  $N \times N$ , where  $N$  is the number of arrangement channels.<sup>2</sup> The  $\mathbf{W}$  elements are taken to obey  $N$  equations of the kind:

$$\sum_{\lambda'=1}^N W_{\lambda\lambda'} = 1, \quad \lambda = 1, \dots, N, \quad (1)$$

where  $\lambda$  and  $\lambda'$  are channel indices, and otherwise unrestricted. The main advantage of the Baer-Kouri-Levin-Tobocman (BKLT) equations is in their being general enough so that several other equations (such as, for instance, the well-known Faddeev equations,<sup>6</sup> and the more recent Fock coupling equations<sup>7,8</sup> can be derived from them, by assuming the  $\mathbf{W}$  matrix elements to have a certain form.

$\mathbf{W}$  matrix elements can, in general, be anything from integers to complicated operators: and it was believed, based on early applications, that they could justifiably be assumed to be real numbers. Tobocman went one step further<sup>4</sup> and, by requiring the kernel to be connected, he was able to show that  $\mathbf{W}$  is of a permuting array structure. Thus, in the two-channel case  $\mathbf{W}$  is of the form:

$$\mathbf{W} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (2a)$$

and in the three-channel case it is of the form:

$$\mathbf{W} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \text{ or } \mathbf{W} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}. \quad (2b)$$

All the first applications of the BKLT equations were for two-channel cases, and most of those were carried out with  $\mathbf{W}$  as given in Eq. (2a).<sup>2,9-12</sup> (Note that the connectivity arguments were given several years later.) Confidence in this structure grew following the successful application of this theory to the collinear finite mass<sup>11</sup> and the nonsymmetric systems  $F + H_2$  (Ref. 12) and  $D + H_2$ .<sup>12</sup> However, difficulties were encountered when the structure was employed in a three-channel problem. Shima and Baer<sup>13</sup> tried for some time to get these equations to work for the three-dimensional three-channel  $H + H_2$  and ended up convinced that this structure of the  $\mathbf{W}$  matrix is incapable of yielding a unitary  $S$  matrix for any three-channel system unless three-body continuum states are included.

As a result, Baer and Shima<sup>14</sup> proposed a "more" symmetric form of  $\mathbf{W}$  by assuming its elements to be functions of the internal coordinates. In the particular case that was also treated numerically<sup>15</sup>  $H + H_2$  ( $J=0$ ), the  $\mathbf{W}$  matrix elements were assumed to be dependent on the three orientation angles  $\gamma_\alpha$ ,  $\alpha = \lambda, \nu, k$  defined as  $\gamma_\alpha = \cos^{-1}(\hat{\mathbf{R}}_\alpha \cdot \hat{\mathbf{r}}_\alpha)$ , where  $\mathbf{R}_\alpha$  and  $\mathbf{r}_\alpha$  are the translational and vibrational vectors in the  $\alpha$  arrangement (see Fig. 1). The results obtained employing this form of  $\mathbf{W}$  were identical to those obtained by more established methods.<sup>16</sup>

As mentioned above, the new form of  $\mathbf{W}$  is much more symmetric than the channel permuting array form, but it is still not symmetric enough to yield a fully symmetric generalized potential matrix. Recently, the present authors<sup>8</sup> suggested a new form for  $\mathbf{W}$ , in which the elements depend on all the internal coordinates; its properties are such that the generalized potential matrix  $\mathbf{WV}$  is fully symmetric.

In the present paper we shall be concerned mainly with the features of connectivity, associated with the kernels

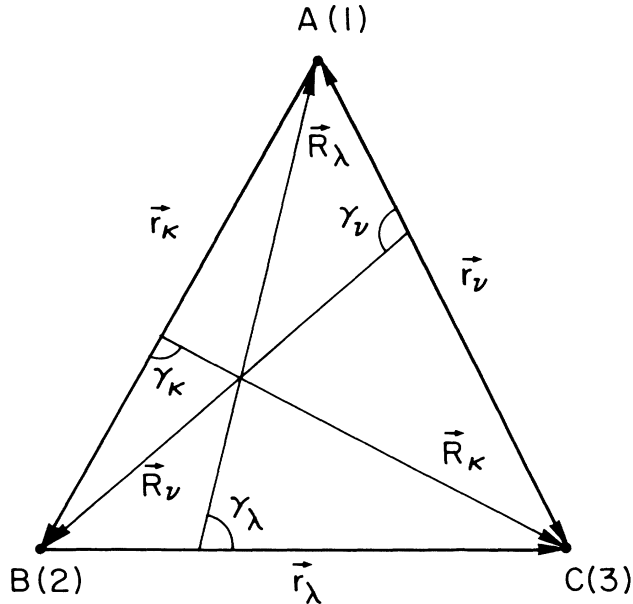


FIG. 1. The three-particle system. Note the three orientation angles  $\gamma_\lambda$ ,  $\gamma_v$ , and  $\gamma_k$ .

of the various resulting integral equations. Thus following the derivation of the BKLT equations, which is done (for the sake of completeness) in Sec. II, we repeat, in Sec. III, Tobocman's analysis<sup>4</sup> as done for the  $\mathbf{W}$  matrix. In Sec. IV we carry out a similar analysis with regards to the  $\gamma$ -dependent  $\mathbf{W}$  matrix, and we show that this coupling scheme also leads to a connected kernel. In Sec. V we propose a new scheme, which leads to a symmetric generalized potential matrix, a feature that guarantees an overall unitary  $S$  matrix.

At this stage one important comment must be made. The BKLT integral equations were invented mainly to avoid having to include three-body continuum states when treating exchange processes. Obviously, there are many cases in physics where three-body continuum states can never be ignored, but on the other hand, there also are cases where three-body continuum states can be ignored provided the integral equations are properly constructed or, what amounts to the same thing, provided the  $\mathbf{W}$  matrix elements are properly chosen. Molecular dynamics is a field in physics where if energy is of the order of the characteristic eigenenergies, three-body continuum states do not have to be included in the numerical treatment. The BKLT equations, as formulated in the past, were found to yield the correct results for any two-channel system that was studied, without it being necessary to include the three-body continuum. However, they failed when the extended version to  $N$  dimensions was used, namely, when the channel permuting array structure was applied to a three-channel case. This failure does not mean that the equations are incorrect, but it means that in order to obtain the correct results one cannot ignore the three-body continuum states. Thus, it was Baer and Shima who found a different  $\mathbf{W}$  matrix which, when applied to the same case, i.e., to the

three-channel, three-dimensional  $H+H_2$  exchange system, yielded the correct results without the need to include the continuum. This means that the new  $\mathbf{W}$  matrix couples the three arrangement channels in a more efficient way than the former one. In the present paper, we show, among other things, that this new choice of  $\mathbf{W}$ , like the former choice, leads to a connected potential and, therefore, guarantees the connectivity (for  $\epsilon \neq 0$ ) of the kernel, whether three-body continuum states are included or not.

In Sec. V we present another coupling scheme, which yields a generalized symmetric potential. This scheme yields, as will be shown, a connected kernel (again, for  $\epsilon \neq 0$ ) only when three-body continuum states are ignored. The resulting new integral equations may not be as general as the former ones, but they are definitely relevant for those cases where the continuum can be ignored.

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

The transition operator  $T_{\alpha\lambda}$  between an initial arrangement channel  $\lambda$  and a final arrangement  $\alpha$  ( $=\lambda, v, k$ ) is defined as

$$T_{\alpha\lambda} |\chi_\lambda\rangle = V_\alpha |\psi_\lambda^+\rangle, \quad (3)$$

where  $V_\alpha$  is the perturbation potential in arrangement  $\alpha$  and  $|\chi_\lambda\rangle$  and  $|\psi_\lambda^+\rangle$  are the unperturbed and the full solutions, respectively, of the corresponding Schrödinger equations. If  $H$  is the complete Hamiltonian and  $H_\alpha$  is the  $\alpha$  arrangement unperturbed Hamiltonian, then

$$H = H_\alpha + V_\alpha, \quad (4)$$

where  $V_\alpha$  fulfills the requirement:

$$\lim_{R_\alpha \rightarrow \infty} V_\alpha(R_\alpha \cdot \cdot \cdot) = 0. \quad (5)$$

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

$$H |\psi_\lambda^+\rangle = E |\psi_\lambda^+\rangle, \quad (6a)$$

$$H_\lambda |\chi_\lambda\rangle = E |\chi_\lambda\rangle. \quad (6b)$$

One may also write  $|\psi_\lambda^+\rangle$  as the solution of the following integral representation:

$$|\psi_\lambda^+\rangle = |\chi_\lambda\rangle + G^+ V_\lambda |\chi_\lambda\rangle, \quad (7)$$

where  $G^+$  is the Green's function:

$$G^+ = (E - H + i\epsilon)^{-1}. \quad (8)$$

Multiplying both sides of Eq. (7), from the left, by  $V_\alpha$  and employing the definition of  $T_{\alpha\lambda}$ , we get the integral representation of  $T_{\alpha\lambda}$ :

$$T_{\alpha\lambda} |\chi_\lambda\rangle = V_\alpha |\chi_\lambda\rangle + V_\alpha G^+ V_\lambda |\chi_\lambda\rangle. \quad (9)$$

Next we do the following. (a) We apply for any  $\alpha'$  the identity

$$E - H + i\epsilon = E - H_{\alpha'} + i\epsilon - V_{\alpha'} \quad (10)$$

which leads to an integral equation for  $G^+$ :

$$G^+ = G_{\alpha'}^+ + G_{\alpha'} V_{\alpha'} G^+ . \quad (11)$$

(b) we introduce a matrix  $\mathbf{W}$  with the elements  $W_{\bar{\alpha}\alpha'}$  fulfilling, for each  $\bar{\alpha}$ , the condition given in Eq. (1), multiply Eq. (11) by  $W_{\bar{\alpha}\alpha'}$  and sum over  $\alpha'$ , which leads to a more global equation for  $G^+$ , namely,

$$G^+ = \sum_{\alpha'} W_{\bar{\alpha}\alpha'} G_{\alpha'}^+ + \sum_{\alpha'} W_{\bar{\alpha}\alpha'} G_{\alpha'}^+ V_{\alpha'} G^+ . \quad (12)$$

This representation of  $G^+$  is now substituted in Eq. (9) and, as has frequently been shown in the past, this leads to a system of coupled integral equations, the BKLT equations, which are of the general form:

$$T_{\alpha\lambda} = V_{\alpha} W_{\bar{\alpha}\lambda} + \sum_{\alpha'} V_{\alpha} W_{\bar{\alpha}\alpha'} G_{\alpha'}^+ T_{\alpha'\lambda} . \quad (13)$$

It can be noted that  $\bar{\alpha}$  is not yet assigned a value, and different choices may lead to different equations. In all our applications  $\bar{\alpha}$  was assumed to be equal to  $\alpha$ . However, in order to obtain the Faddeev equations, for instance,  $\bar{\alpha}$  was chosen differently.<sup>6</sup> The main advantage of this choice is that it enables us to define a generalized potential matrix  $\tilde{\mathbf{V}}$  with the elements:

$$\tilde{V}_{\alpha\alpha'} = V_{\alpha} W_{\alpha\alpha'} . \quad (14)$$

Consequently, Eq. (13) becomes

$$T_{\alpha\lambda} = \tilde{V}_{\alpha\lambda} + \sum_{\alpha'} \tilde{V}_{\alpha\alpha'} G_{\alpha'}^+ T_{\alpha'\lambda} \quad (13')$$

which can also be written as a matrix equation:

$$\mathbf{T} = \tilde{\mathbf{V}} + \tilde{\mathbf{V}}\tilde{\mathbf{G}} + \mathbf{T} , \quad (15)$$

where

$$\tilde{\mathbf{G}}_{\alpha\alpha'}^+ = \delta_{\alpha\alpha'} G_{\alpha}^+ . \quad (16)$$

### III. THE SUPPRESSION OF DISCONNECTED KERNELS

One of the questions one encounters in the theory of integral equations is whether the kernel is connected or not. In the case of the Lippmann-Schwinger (LS) equation, the connectivity of the kernel is guaranteed by the connectivity of the potential. However, since the kernel of the BKLT equations contains a product of the potential and a  $W$  matrix element, the connectivity study will be carried out with regard to this product. We shall consider two cases. In this section we assume the  $\mathbf{W}$  matrix elements to be pure numbers, and in the next section we assume them to be functions of the orientation angles.

The first case was considered by Tobocman<sup>4</sup> and we briefly repeat his derivations, mainly as an introductory study for our second case.

We consider the three-particle potential  $V(r_{12}, r_{13}, r_{23})$  which will be written in the form ( $r_{ij}$  is the distance between particles  $i$  and  $j$ ):

$$V = \frac{1}{2} \sum_{\alpha} V^{\alpha} + V_{\lambda\nu k} , \quad (17)$$

where

$$V^{\lambda} = V_{12} + V_{13}, \quad \lambda = (1, 23) ,$$

$$V^{\nu} = V_{12} + V_{23}, \quad \nu = (2, 13) ,$$

$$V^k = V_{13} + V_{23}, \quad k = (3, 12) ,$$

(18)

The potential  $V_{\lambda\nu k}$  is a three-body potential, which becomes zero whenever one of the interatomic distances becomes large. The potentials  $V_{ij}$  are two-body potentials presented in terms of the interatomic distance  $r_{ij}$ .

The perturbation  $V_{\lambda}$  is defined as

$$V_{\lambda} = V - V_{23} \quad (19)$$

which becomes, following Eq. (17),

$$V_{\lambda} = V^{\lambda} + V_{\lambda\nu k} . \quad (19')$$

Since  $V^{\lambda}$  is a function of two distances only, i.e.,  $r_{12}$  and  $r_{13}$ , it will not become zero when  $r_{23}$  becomes infinity, and so the kernel of the corresponding integral in Eq. (13) seems to be not connected. However, whether the kernel is connected or not depends on whether, following a finite number of iterations, the resulting kernel does not vanish when any of the three interatomic distances becomes infinite.

In order to carry out the iterative procedure we consider Eq. (15), and it can be seen that following  $n$  iterations Eq. (15) becomes:

$$\mathbf{T} = \sum_{l=0}^{n-1} (\tilde{\mathbf{V}}\mathbf{G})^l \tilde{\mathbf{V}} + (\tilde{\mathbf{V}}\mathbf{G})^n \mathbf{T} . \quad (20)$$

Thus, the kernel is now  $(\tilde{\mathbf{V}}\mathbf{G})^n$ , and to check connectivity we examine  $\tilde{\mathbf{V}}^n$ , i.e.,

$$\tilde{\mathbf{V}}^n = (\mathbf{V}\mathbf{W})^n . \quad (21)$$

For the three-particle system, it is enough to consider the case  $n=3$  (in the more general case, but still with one reaction coordinate per channel,  $n$  is equal to the number of possible clusters). Thus

$$(\tilde{\mathbf{V}}^3)_{\alpha\alpha'} = \sum_{\alpha''\alpha'''} \tilde{V}_{\alpha\alpha''} \tilde{V}_{\alpha''\alpha'''} \tilde{V}_{\alpha'''\alpha'} . \quad (22)$$

In order to evaluate this expression we consider the case  $\alpha=\alpha'$  and  $\alpha \neq \alpha'$  separately. For  $\alpha=\alpha'$ ,

$$\begin{aligned} (\tilde{\mathbf{V}}^3)_{\alpha\alpha} &= \tilde{V}_{\alpha\alpha}^3 + \sum_{\alpha'' \neq \alpha} \tilde{V}_{\alpha\alpha''} \tilde{V}_{\alpha''\alpha'} \tilde{V}_{\alpha'\alpha} \\ &+ 2\tilde{V}_{\alpha\alpha} \sum_{\alpha \neq \alpha''} \tilde{V}_{\alpha\alpha''} \tilde{V}_{\alpha''\alpha} \\ &+ \sum_{\alpha \neq \alpha'' \neq \alpha''' \neq \alpha} \tilde{V}_{\alpha\alpha''} \tilde{V}_{\alpha''\alpha'''} \tilde{V}_{\alpha'''\alpha} . \end{aligned} \quad (23a)$$

For  $\alpha \neq \alpha'$ ,

$$\begin{aligned} (\tilde{\mathbf{V}}^3)_{\alpha\alpha'} &= (\tilde{V}_{\alpha\alpha}^2 + \tilde{V}_{\alpha'\alpha'}^2) \tilde{V}_{\alpha\alpha'} + \tilde{V}_{\alpha\alpha} \tilde{V}_{\alpha'\alpha'} \tilde{V}_{\alpha\alpha'} \\ &+ (\tilde{V}_{\alpha\alpha} + \tilde{V}_{\alpha'\alpha'}) \tilde{V}_{\alpha\alpha''} \tilde{V}_{\alpha''\alpha'} + \tilde{V}_{\alpha\alpha''} \tilde{V}_{\alpha''\alpha'} \tilde{V}_{\alpha'\alpha} \\ &+ V_{\alpha\alpha'} (\tilde{V}_{\alpha'\alpha} \tilde{V}_{\alpha\alpha'} + \tilde{V}_{\alpha\alpha''} \tilde{V}_{\alpha''\alpha} + \tilde{V}_{\alpha'\alpha''} \tilde{V}_{\alpha''\alpha'}) , \end{aligned} \quad (23b)$$

where  $\alpha' \neq \alpha'' \neq \alpha$ .

In Eq. (23a) the first three terms contain diagonal elements, whereas the other kinds are included in the fourth term. In Eq. (23b), the first four terms contain diagonal elements and the fifth contains products of symmetric terms. It can be shown that except for the last term in Eq. (23a) all the others are disconnected. Thus, in order for the whole system of integral equations to be connected, the first three terms in Eq. (23a) and all the terms in Eq. (23b) have to be made identically zero, and this can be achieved by assuming the  $\mathbf{W}$  matrix to have a permuting structure, as given in Eq. (2b). It should be emphasized that assuming  $n$  to be larger than three will not affect this conclusion.

As mentioned in the Introduction, this choice of the  $\mathbf{W}$  matrix elements, although successful for two-channel systems, does not yield the correct results in a numerical study conducted for a three-channel case.<sup>13</sup> The reason seems to be the high asymmetry built into the equations by the assumed permuting structure of the  $\mathbf{W}$  matrix (in the two-channel case, this choice leads to a symmetric  $\mathbf{W}$ ).

#### IV. THE CONSTRUCTION OF A QUASISYMMETRICAL $\mathbf{W}$ MATRIX

From the above discussion, it is quite obvious that one limitation of the BKLT approach is related to the assumption that the  $\mathbf{W}$  matrix elements are pure numbers. Recently, one of the present authors and Shima<sup>14</sup> considered  $\mathbf{W}$  matrix elements which are functions of the internal coordinates of the three-body system. To be more specific, they were assumed to be functions of the three orientation angles  $\gamma_\alpha$  defined as (see Fig. 1):

$$\gamma_\alpha = \cos^{-1}(\hat{\mathbf{R}}_\alpha \cdot \hat{\mathbf{r}}_\alpha), \quad \alpha = \lambda, \nu, k. \quad (24)$$

From Eq. (13') it can be seen that  $W_{\alpha\alpha'}$  is a matrix element which couples arrangement  $\alpha'$  to arrangement  $\alpha$ . Thus for  $\alpha = \lambda$ , the three matrix elements which couple the arrangement channel  $\lambda$  to itself as well as to the other two are  $W_{\lambda\lambda}$ ,  $W_{\lambda\nu}$ , and  $W_{\lambda k}$ . Since the channel  $\lambda$  stands for the arrangement ( $A, BC$ ), the coordinate according to which it will be decided when the channel is coupled to any of the three channels is the angle  $\gamma_\lambda$  (see Fig. 1). Thus when  $\gamma_\lambda$  is small, the  $\lambda$  channel is expected to couple more intensely with the  $\nu$  ( $=B, CA$ ) channel, and when  $\gamma_\lambda$  is close to  $\pi$ , it is expected to couple more intensely with the  $k$  ( $=C, AB$ ) channel. For the  $\gamma_\lambda$  interval where the  $\lambda$  channel is only weakly coupled to the other channels (usually for  $\gamma_\lambda \sim \pi/2$ ), it will be assumed to be coupled to itself. One could think of many functional forms for the  $\mathbf{W}$  matrix elements that would comply with the above description [and fulfill Eq. (1)]. However, if, again, one requires the kernel to be connected, then these functions have to be chosen with some care. The simplest choices are step functions. Thus

$$W_{\lambda\nu}(\gamma_\lambda) = \begin{cases} 1, & 0 \leq \gamma_\lambda \leq \gamma_\lambda^-, \\ 0, & \text{otherwise,} \end{cases} \quad (25a)$$

$$W_{\lambda k}(\gamma_\lambda) = \begin{cases} 1, & \gamma_\lambda^+ \leq \gamma_\lambda \leq \pi, \\ 0, & \text{otherwise,} \end{cases} \quad (25b)$$

$$W_{\lambda\lambda}(\gamma_\lambda) = \begin{cases} 1, & \gamma_\lambda^- \leq \gamma_\lambda \leq \gamma_\lambda^+, \\ 0, & \text{otherwise.} \end{cases} \quad (25c)$$

To show connectivity, we follow Tobocman's lead and consider the three-times-iterated kernel, as given in Eqs. (23). First, we prove that the diagonal element  $\tilde{V}_{\lambda\lambda}$  becomes zero if any of the three interatomic distances becomes infinite.  $V_\lambda$  is presented in Eq. (19) and it is seen that it becomes zero when  $r_{12}$  ( $=r_{AB}$ ) and  $r_{13}$  ( $=r_{AC}$ ) become infinity, but it may stay finite when  $r_{23}$  ( $=r_{BC}$ ) becomes infinite. Let us assume that particle 2 is now moved to infinity such that the distance between particles 1 and 3 remains finite (if not, then  $V_\lambda$  will become zero). However, while we do that, the angle  $\gamma_\lambda$  becomes close to 0 [see Fig. 2(a)], namely:

$$\lim_{r_{23} \rightarrow \infty, r_{13} < \infty} \gamma_\lambda = 0. \quad (26)$$

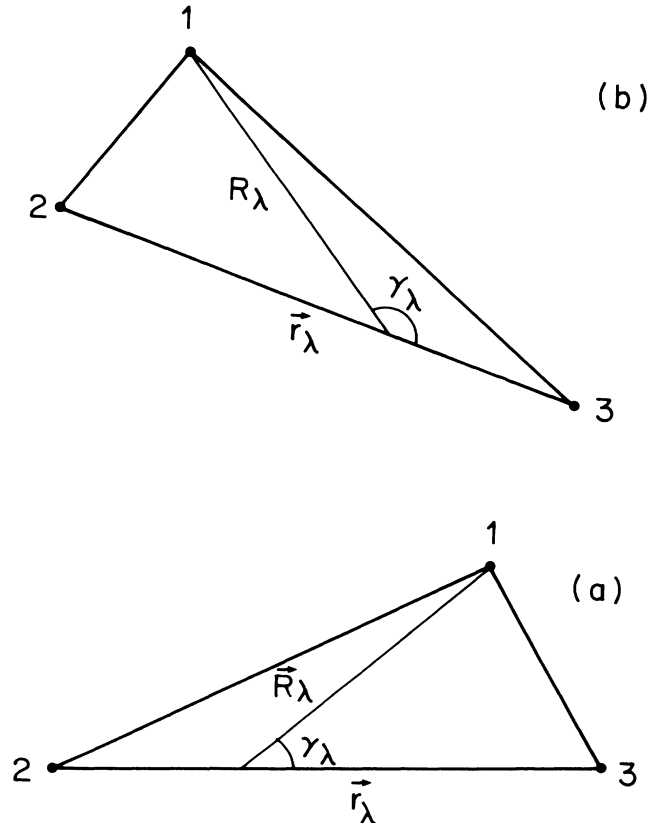


FIG. 2. The three-particle system in extreme cases. (a) The case when particle 2 is moved to infinity such that the  $r_{13}$  distance stays finite. The angle  $\gamma_\lambda$  becomes zero. (b) The case when particle 3 is moved to infinity such that the  $r_{12}$  distance stays finite. The angle  $\gamma_\lambda$  becomes  $\pi$ .

Recalling Eq. (25c), it is noticed that, as a result of that process (and assuming  $\gamma_{\lambda}^{-} \neq 0$ ),  $W_{\lambda\lambda}$  becomes zero, thus making zero the corresponding diagonal element of the generalized potential matrix  $\tilde{V}$ . Next, we must show that any product of two symmetrical elements of the generalized potential matrix, i.e.,  $\tilde{V}_{\lambda\nu}\tilde{V}_{\nu\lambda}$  also becomes zero when any of the three distances becomes infinite. The product  $V_{\lambda}V_{\nu}$  becomes zero when either particle 1 or particle 2 is moved to infinity but differs from zero when particle 3 is moved to infinity (assuming  $r_{12}$  is finite). However, moving particle 3 to infinity causes  $\gamma_{\lambda}$  to become  $\pi$  [see Fig. 2(b)] and consequently  $W_{\lambda\nu}$ , which is only nonzero for angles much smaller than  $\pi$ , will become zero, thus making the product  $\tilde{V}_{\lambda\nu}\tilde{V}_{\nu\lambda}$  zero.

So far, we have proved that three out of the four terms in Eq. (23a) and all terms in Eq. (23b) will become zero when any of the three particles is moved to infinity. The fourth term in Eq. (23a) will go to zero because at least one of the three  $V_{\alpha}$ 's will be zero when any of the three distances is infinity, like in the channel permuting array case. Thus the kernel with the new choice of  $W$  is connected.

## V. THE SYMMETRIC GENERALIZED POTENTIAL

In the two previous sections we treated cases where the connectivity of the LS equation kernel was guaranteed by the connectivity of the generalized potential. In this section we consider a choice of  $W$  which yields a generalized potential matrix that is symmetric but, as a result, the connectivity of the kernel, is not only guaranteed by the potential.

At this stage, a clarifying comment must be made. Connectivity of the potential is a sufficient and a necessary condition for the kernel to be connected in case of a two-particle system. In a three-particle system, connectivity of the (generalized) potential is a necessary and sufficient condition for the kernel to be connected in the general case. However, in a case where the three-body continuum can be ignored (in molecular dynamics, this is by far the most common case), it is not always necessary for the potential to be entirely connected. Consequently, in order for the kernel to be fully connected, the missing connected portion must be satisfied by the projected Green's functions.

Considering Eq. (15), we choose  $W$  in such a way that<sup>8</sup>

$$\tilde{V}_{\alpha\alpha'} = \tilde{V}_{\alpha'\alpha} \implies V_{\alpha}W_{\alpha\alpha'} = V_{\alpha'}W_{\alpha'\alpha} . \quad (27)$$

Equations (27), together with Eq. (1), are not enough to determine the elements of  $W$ . Thus in case of two channels, the number of unknown  $W$  matrix elements is four, with only three equations to determine them, and in the case of three channels, the number is nine, with only six equations to determine them.

It turns out that the two-channel case is more complicated than the three-channel case, and therefore we start the derivations of the generalized potentials for the three-channel case.

### A. The three-channel case

In this case we have, as mentioned earlier, nine unknowns and six equations. Consequently, we shall express the six off-diagonal elements in terms of the three diagonal ones. Thus if

$$W_{\alpha\alpha} = 1 - \Gamma_{\alpha}, \quad \alpha = \lambda, \nu, k , \quad (28)$$

it can be shown that

$$\tilde{V}_{\alpha\alpha'} = \frac{1}{2}(\Gamma_{\alpha}V_{\alpha} + \Gamma_{\alpha'}V_{\alpha'} - \Gamma_{\alpha\alpha'}V_{\alpha\alpha'}) , \quad (29)$$

where  $\alpha \neq \alpha' \neq \alpha'' \neq \alpha$  and the  $\Gamma_{\alpha}$ 's may or may not be constants. Next, we prove that  $\Gamma_{\alpha} = \Gamma_{\alpha'} = \Gamma_{\alpha''}$ ,  $\alpha \neq \alpha' \neq \alpha'' \neq \alpha$ . To do that we consider the kernels of the equation

$$T_{\lambda\lambda} = \tilde{V}_{\lambda\lambda} + \tilde{V}_{\lambda\lambda}G_{\lambda}T_{\lambda\lambda} + \tilde{V}_{\lambda\nu}G_{\nu}T_{\nu\lambda} + \tilde{V}_{\lambda k}G_{k}T_{k\lambda} \quad (13'')$$

and analyze their behavior in the three asymptotic regions, i.e.,  $R_{\alpha} \rightarrow \infty$ ,  $\alpha = \gamma, \nu, k$ . Before continuing, we shall introduce the assumption that none of the three unperturbed Green's functions  $G_{\alpha}$ ;  $\alpha = \lambda, \gamma, k$  contains a contribution of the continuum other than the one along its own translational coordinate  $R_{\alpha}$ . Thus

$$\lim_{R_{\alpha'} \rightarrow \infty} G_{\alpha}(\epsilon \neq 0) = 0 \quad \text{for } \alpha \neq \alpha' . \quad (30)$$

In other words, contributions from the bound two-particle continuum are ignored. In this context, it should be reiterated that our aim is to find  $W$  matrix elements (or generalized potential matrix elements) such that the neglect of these portions of the Green's functions will not affect any of the results of the computations. This assumption is known to be relevant for *molecular* systems where for low enough energies (chemical energies) many of the closed two-particle *discrete* states, not to mention the corresponding continuum states, can be ignored. Let us now consider each kernel separately.

(i) *The kernel  $\tilde{V}_{\lambda\lambda}G_{\lambda}$ .* The kernel  $\tilde{V}_{\lambda\lambda}G_{\lambda}$  decays to zero along all three asymptotes, either by definition [see Eq. (5)]

$$\lim_{R_{\lambda} \rightarrow \infty} V_{\lambda} = 0 \quad (5')$$

or by Eq. (30)

$$\lim_{R_{\alpha} \rightarrow \infty} G_{\lambda}(\epsilon \neq 0) = 0 \quad \text{for } \alpha = \gamma, k . \quad (30')$$

(ii) *The kernel  $\tilde{V}_{\lambda\nu}G_{\nu}$ .* This kernel decays to zero when  $R_{\lambda} \rightarrow \infty$  or  $R_k \rightarrow \infty$  because  $G_{\nu}(\epsilon \neq 0)$  does so according to Eq. (30). As for  $R_{\nu} \rightarrow \infty$ , we have to consider  $\tilde{V}_{\lambda\nu}$  given in the form:

$$\tilde{V}_{\lambda\nu} = \frac{1}{2}(\Gamma_{\lambda}V_{\lambda} + \Gamma_{\nu}V_{\nu} - \Gamma_k V_k) \quad (31)$$

in greater detail. Recalling the definitions of  $V_{\alpha}$ ;  $\alpha = \lambda, \nu, k$  and considering the *finite*  $r_{\nu}$  case, we get [see Fig. 1, and Eq. (19)]

$$\lim_{R_{\nu} \rightarrow \infty} V \rightarrow V_{13} \quad (32)$$

and

$$\lim_{R_v \rightarrow \infty} V_{12} = \lim_{R_v \rightarrow \infty} V_{23} = 0. \quad (33)$$

It can be shown that

$$\lim_{R_v \rightarrow \infty} \tilde{V}_{\lambda\nu} = \frac{1}{2} V_{13} (\Gamma_\lambda - \Gamma_k). \quad (34)$$

Thus, to guarantee the complete compactness of the kernel  $\tilde{V}_{\lambda\nu} G_\nu$  (employing only the discrete portions of the Green's functions), one must choose  $\Gamma_\lambda$  and  $\Gamma_k$  such that  $\Gamma_\lambda = \Gamma_k$ . In the same way, we can prove that  $\Gamma_\lambda = \Gamma_\nu$  and therefore also  $\Gamma_\nu = \Gamma_k$ . Thus we have

$$\Gamma_\lambda = \Gamma_\nu = \Gamma_k = \Gamma. \quad (35)$$

Consequently, the generalized potentials have the form:

$$V_{\alpha\alpha'} = \frac{\Gamma}{2} (V_\alpha + V_{\alpha'} - V_{\alpha''}), \quad \alpha \neq \alpha' \neq \alpha'' \neq \alpha \quad (36a)$$

and

$$V_{\alpha\alpha} = (1 - \Gamma) V_\alpha, \quad (36b)$$

where  $\Gamma$  is a constant not yet determined.

### B. The two-channel case

In this context, we present two versions. (i) One version is identical to the three-channel case, where the third term namely the  $k$  term in Eq. (13'), are simply ignored. Thus we have

$$\begin{aligned} \tilde{V}_{\alpha\alpha} &= (1 - \Gamma) V_\alpha, \quad \alpha = \lambda, \nu, \\ \tilde{V}_{\lambda\nu} &= \frac{\Gamma}{2} (V_\lambda + V_\nu - V_k). \end{aligned} \quad (36')$$

The neglect of these terms is justified by the fact that the third channel either is energetically closed (as is frequently encountered in molecular dynamics) and therefore  $G_k$  ( $\epsilon \neq 0$ ) is identically zero, in all asymptotes or it cannot be reached as, for instance, in the collinear case.

(ii) The representation of the off-diagonal term, as given in Eqs. (36'), is somewhat odd, because of the appearance of  $V_k$ , a perturbation related to an ignored channel. It can be shown that any representation of this kind, ignoring  $V_k$  and assuming  $\Gamma$  to be a constant, will lead to a disconnected kernel. We shall, therefore, write

$$W_{\alpha\alpha} = 1 - \Gamma_\alpha, \quad (28')$$

where  $\Gamma_\alpha$  is assumed to be a function of the coordinates. Recalling Eqs. (1) and (27), we get

$$\begin{aligned} \tilde{V}_{\alpha\alpha} &= (1 - \Gamma_\alpha) V_\alpha, \\ \tilde{V}_{\alpha\beta} &= \tilde{V}_{\beta\alpha} = \Gamma_\alpha V_\alpha, \quad \alpha \neq \beta \equiv \lambda, \nu, \\ V_{\beta\beta} &= V_\beta - \Gamma_\alpha V_\alpha. \end{aligned} \quad (37)$$

We analyze the term  $\tilde{V}_{\alpha\beta} G_\beta$  ( $\epsilon \neq 0$ ). From previous discussions we know that both  $\tilde{V}_{\alpha\beta}$  ( $= \Gamma_\alpha V_\alpha$ ) and  $G_\beta$  ( $\epsilon \neq 0$ ) decay to zero when  $R_\alpha \rightarrow \infty$ , but they will not become zero when  $R_\beta \rightarrow \infty$  unless  $\Gamma_\alpha$  is defined in such a way that

$$\lim_{R_\beta \rightarrow 0} \Gamma_\alpha = 0. \quad (38)$$

A similar representation of Eq. (37) for the generalized potential elements can be obtained by taking  $W_{\beta\beta} = 1 - \Gamma_\beta$  and assuming  $\Gamma_\beta$  to be dependent on the coordinates. However, in order to ensure connectivity we need to assume that

$$\lim_{R_\alpha \rightarrow \infty} \Gamma_\beta = 0. \quad (38')$$

In order for the two choices to lead to the same set of integral equations, we must assume

$$\Gamma_\beta V_\beta = \Gamma_\alpha V_\alpha. \quad (39)$$

The requirements (38) and (38') can now be fulfilled if

$$\Gamma_\alpha = \Gamma V_\beta, \quad \alpha \neq \beta, \quad (40)$$

where  $\Gamma$  may or may not be a constant. Combining Eqs. (37), (39), and (40), we get

$$\begin{aligned} \tilde{V}_{\lambda\lambda} &= V_\lambda - \Gamma V_\lambda V_\nu, \\ \tilde{V}_{\lambda\nu} &= \Gamma V_\lambda V_\nu, \\ V_{\nu\nu} &= V_\nu - \Gamma V_\lambda V_\nu, \end{aligned} \quad (41)$$

where, like in the three-channel case,  $\Gamma$  is yet undetermined.

## VI. CONCLUSIONS

In this work we presented two new sets of integral equations for studying exchange processes. Both sets follow from the BKLT equations. The first set was obtained by assuming the  $\mathbf{W}$  matrix elements to be dependent on the corresponding orientation  $\gamma$  angles. As a result, the previous permuting array channel structure is replaced by a more symmetric shape, without the connectivity feature being lost. In contrast to the channel permuting array equations, this set yields the correct results for the three-channel three-dimensional  $H + H_2$  ( $J = 0$ ) system.<sup>15</sup> The second set of equations is derived by requiring the generalized potential matrix to be symmetric.

The symmetric structure of the  $\tilde{\mathbf{V}}$  matrix is very attractive, because it guarantees a unitary  $S$  matrix and possibly avoids various kinds of spurious solutions which are irrelevant and may cause numerical instabilities. However, this choice does not yield a connected potential. This does not necessarily mean that the kernel is not connected. For instance, in cases where the Green's functions are constructed from channel Hamiltonians with single reaction coordinates, and the energy is low enough so that no three-body continuum states must be included, the connectivity of the kernel is partially guaranteed by the Green's functions themselves.

Recently, Haug *et al.*<sup>7</sup> obtained results from the Fock coupling scheme applied to three-dimensional systems (with  $J = 0$ ). There, like in our symmetric case, the potential is not connected; nevertheless, no difficulties are encountered during the numerical treatment and the re-

sults fit very nicely with those obtained by other, more established methods.

It should be mentioned that this new set of equations is at present being exposed to numerical treatments and the results look promising.

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