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BKLT equation for reactive scattering. II. Extensions and application to collinear nonsymmetric systems

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The BKLT integral equations were recently introduced with the aim of applying them in numerical studies of exchange collisions. So far only symmetric systems were treated. In this work we extend the treatment to nonsymmetric collinear systems ($D + H_2$ and $F + H_2$) and compare the results with those obtained from a more established method. In addition we also introduced a third set of equations and tested its relevance.

I. INTRODUCTION

Recently we began developing numerical methods and computer codes for solving the three body exchange problem employing the coupled integral equation formulation.[1,2] Interest in the integral equation approach[3,4] has increased recently mainly due to the inability to date of differential equation formulations to provide a practical numerical framework for calculating reactive differential and integral cross sections for three physical dimensional systems other than $H + H_2$. This is in spite of the fact that many efficient numerical methods were developed within the differential equation formulation. Many of them have resulted in computer codes for calculating "exact" reactive transition probabilities for collinear reactions and several have been used as the basis for computer codes for the calculation of three dimensional reactive cross sections for the fully symmetric $H + H_2$ system.[5] However, numerical difficulties related to the matching of wave functions on complicated geometrical surfaces and formal difficulties related to the bifurcation problem have inhibited the extension of these methods to more interesting reactions. The latter problem has to do with how one deals with the wave function in regions where more than one chemical arrangement converge together in coordinate space.

The main advantage of the integral equation formulation is that no matching is encountered and that bifurcation is an inherently built-in feature of the theory[3,4] and therefore does not have to be imposed as must be done within the differential equation approach. This fact promises a much more efficient as well as general treatment of a multiarrangement channel (three or more) problem.

To date, one may distinguish between two main approaches within the integral equation formulation, the arrangement channel approach,[3] and the many-body approach.[4] The arrangement channel approach, originated by Baer and Kouri,[6] was further developed by Kouri and Levin[7,8] and finally generalized to an arbitrary number of particles by Tobocman.[9] This approach can be used to obtain several kinds of independent sets of coupled Lippmann–Schwinger type equations (in each set one encounters an equation for each arrangement) which have been termed in general as the BKLT equations. The second approach is due to Micha[10,11] and is based on the Faddeev–Watson equations.[12,13] By means of introducing spin dependent potentials, this approach was made applicable for studying chemical rearrangement collisions.[4]

In this paper we consider the BKLT approach (one of our objectives is to study a new set of coupled Lippmann–Schwinger equations). This set has already been presented before[8] but has never been employed in any numerical applications. So far, the BKLT equations have been applied only to symmetric collinear reactions[1,2] (HFH and H_3). In this paper we also consider, for the first time within the BKLT approach, the collinear nonsymmetric reactions $D + H_2 \rightarrow HD + H$ and $F + H_2 \rightarrow HF + H$.

In the next section we present briefly the theory that leads to the various BKLT equations primarily with the aim of showing the differences between them. This treatment is carried out, for the sake of simplicity, for a two arrangement channel system. In the third section we present a few results and in the fourth our conclusions are summarized.

II. THEORY

We shall consider three different sets of BKLT equations. The first two have been derived several times in the past and applied in different calculations. Their derivation is done here mainly to show the differences with the approach used in obtaining the third set.

We start by deriving the first two sets. To do that, we consider two alternative definitions of the reactive T operator,[3] i.e.,

$$\tilde{T}_{\beta\alpha} |\chi_\alpha\rangle = V_\beta |\psi_\alpha\rangle, \tag{1}$$

and

$$\langle \chi_\beta | \overline{T}_{\beta\alpha} = \langle \Psi_\beta | V_\alpha. \tag{2}$$

Here $\gamma = \alpha, \beta$ denote the two collinear arrangement channels, $|\chi_\alpha\rangle$ and $|\chi_\beta\rangle$ are the corresponding unperturbed solutions of the Schrödinger equation, $|\psi_\alpha\rangle$ and $|\psi_\beta\rangle$ are the solutions of the full Schrödinger equation with α and β, respectively, being the initial channel and $V_\gamma, \gamma = \alpha, \beta$ are the corresponding pertubation potentials. If H is the full Hamiltonian and H_γ is the γ-arrangement unperturbed Hamiltonian, then

$$H = H_\gamma + V_\gamma; \quad \gamma = \alpha, \beta, \tag{3}$$

where the potential V_γ fulfills the requirement that

$$\lim_{R_\gamma \to \infty} V_\gamma(R_\gamma, ...) = 0. \tag{4}$$

In this equation, R_γ is the distance from the atom to the diatom center of mass in arrangement γ.

We now consider the Lippmann–Schwinger equation for $|\psi_\alpha\rangle$[3]:

$$|\psi_\alpha\rangle = |\chi_\alpha\rangle + GV_\alpha|\chi_\alpha\rangle, \tag{5}$$

where G is the full green function defined, as

$$G = (E - H + i\epsilon)^{-1}. \tag{6}$$

Multiplying both sides of Eq. (5) by V_β and employing the definition of $\widetilde{T}_{\beta\alpha}$ given in Eq. (1), we find that $\widetilde{T}_{\beta\alpha}$ is given as

$$\widetilde{T}_{\beta\alpha} = V_\beta + V_\beta G V_\alpha. \tag{7}$$

Let us now consider the Lippmann-Schwinger equation for $\langle\psi_\beta|$, i.e.,

$$\langle\psi_\beta| = \langle\chi_\beta| + \langle\chi_\beta|V_\beta G. \tag{8}$$

Again, multiplying Eq. (8) by V_α and employing the definition of $\overline{T}_{\beta\alpha}$ given in Eq. (2), we find that $\overline{T}_{\beta\alpha}$ is given in the form

$$\overline{T}_{\beta\alpha} = V_\alpha + V_\beta G V_\alpha. \tag{9}$$

The difference between $\widetilde{T}_{\beta\alpha}$ and $\overline{T}_{\beta\alpha}$ is simply in the inhomogeneity. The former is called the post T operator and the latter the prior T operator. These operators have matrix elements which are equal for so called on-shell conditions; i.e., if the initial and final unperturbed states both have energy E which must also equal the energy of the green function [Eq. (6)]. However, the full operators are not equal.

In the derivation so far no assumptions were made with respect to α and β and in fact they may or may not be equal. Equations (7) and (9) are formal solutions for the rearrangement T operators because G is unknown. In order to obtain integral equations of which $\widetilde{T}_{\beta\alpha}$ and $\overline{T}_{\beta\alpha}$ will be solutions we have to eliminate G. Applying the identity

$$(E - H + i\epsilon) = (E - H_\gamma + i\epsilon) - V_\gamma, \tag{10}$$

we find that the integral equation for G is

$$G = G_\gamma + G_\gamma V_\gamma G; \quad \gamma = \alpha, \beta. \tag{11}$$

Substituting Eq. (11) into Eq. (9) we find

$$\begin{aligned}\overline{T}_{\beta\alpha} &= V_\alpha + V_\beta[G_\gamma + G_\gamma V_\gamma G]V_\alpha \\ &= V_\alpha + V_\beta G_\gamma[V_\alpha + V_\gamma G V_\alpha]\end{aligned}$$

or

$$\overline{T}_{\beta\alpha} = V_\alpha + V_\beta G_\gamma \overline{T}_{\gamma\alpha}. \tag{12}$$

Equation (12) is true for any γ and therefore also for $\gamma = \alpha$. Thus we obtain[6]

$$\overline{T}_{\beta\alpha} = V_\alpha + V_\beta G_\alpha \overline{T}_{\alpha\alpha}. \tag{13a}$$

The equation for $T_{\alpha\alpha}$ is obtained by assuming in Eq. (9) that $\beta = \alpha$ and consequently taking γ to be $\gamma = \beta$. Thus,

$$\overline{T}_{\alpha\alpha} = V_\alpha + V_\alpha G_\beta \overline{T}_{\beta\alpha}. \tag{13b}$$

Equations (13a) and (13b) were the first set of coupled Lippmann–Schwinger equations that were derived and constitute one realization of the general set of T-operator equations referred to as the BKLT equations (for two channels). The derivation of a second set of BKLT equations is based on Eq. (7). We substitute Eq. (11) into Eq. (7) to obtain

$$\begin{aligned}\widetilde{T}_{\beta\alpha} &= V_\beta + V_\beta[G_\gamma + G_\gamma V_\gamma G]V_\alpha \\ &= V_\beta + V_\beta G_\gamma[V_\alpha + V_\gamma G V_\alpha] \\ &= V_\beta + V_\beta G_\gamma(V_\alpha - V_\beta) + V_\beta G_\gamma [V_\gamma + V_\gamma G V_\alpha]\end{aligned}$$

or

$$\widetilde{T}_{\beta\alpha} = V_\beta[1 + G_\gamma(V_\alpha - V_\gamma)] + V_\beta G_\gamma \widetilde{T}_{\gamma\alpha}. \tag{14}$$

To continue we consider the expression in the parentheses [see also Eq. (3)]

$$\begin{aligned}1 &+ G_\gamma(V_\alpha - V_\gamma) \\ &= 1 + G_\gamma[E - H_\alpha + i\epsilon - (E - H_\gamma + i\epsilon)] \\ &= 1 + G_\gamma(G_\alpha^{-1} - G_\gamma^{-1}).\end{aligned}$$

Thus, we have

$$1 + G_\gamma(V_\alpha - V_\gamma) = G_\gamma G_\alpha^{-1}. \tag{15}$$

This expression is equal to the identity for $\gamma = \alpha$. For $\gamma \neq \alpha$, it is an operator which, when operating on a two body initial state $|\chi_\alpha\rangle$, yields zero in the limit $\epsilon \to 0$ because

$$G_\gamma G_\alpha^{-1}|\chi_\alpha\rangle = G_\gamma(E - H_\alpha + i\epsilon)|\chi_\alpha\rangle = G_\gamma i\epsilon|\chi_\alpha\rangle.$$

Since in using Eq. (15) to calculate physical transition amplitudes we always expect $|\chi_\alpha\rangle$ to stand on the right side, we may define a new operator by the replacement

$$1 + G_\gamma(V_\alpha - V_\gamma) \to \delta_{\alpha\gamma}. \tag{16}$$

Consequently Eq. (14) becomes[7]

$$\widetilde{T}_{\beta\alpha} = V_\beta \delta_{\alpha\gamma} + V_\beta G_\gamma \widetilde{T}_{\gamma\alpha}. \tag{17}$$

Thus, for $\gamma = \alpha$ we obtain

$$\widetilde{T}_{\beta\alpha} = V_\beta + V_\beta G_\alpha \widetilde{T}_{\alpha\alpha} \tag{18a}$$

and for $\beta = \alpha$ and $\gamma = \beta$, we obtain

$$\widetilde{T}_{\alpha\alpha} = V_\alpha G_\beta \widetilde{T}_{\beta\alpha}. \tag{18b}$$

This form of the BKLT family of equations was derived somewhat later and was found to be more convenient for numerical application because it rigorously fulfills the usual Heitler damping equation for any finite basis set.[8] The earlier form [Eqs. (13a) and (13b)] was used successfully in computational studies of a variety of waveguide models for reactions[6(a)] including the first full three-dimensional reaction for a simple but nontrivial model of an atom–heteronuclear diatom reaction. These studies were successful for these model potentials at collision energies well below the dissociation threshold. Subsequently, Tobocman[6(b)] has used them in numerical studies of s-wave scattering and bound state problems in nuclear physics. *In fact, it has been shown*

formally that both sets of equations give identical results if solved exactly[7] but they respond to approximations differently. One important difference in the equations is that Eqs. (13a) and (13b) do not yield the usual Heitler damping equation while Eqs. (18a) and (18b) do. The damping equation satisfied by the $\overline{T}_{\gamma\alpha}$ of Eqs. (13a) and (13b) is more complicated. Thus, if one wishes to use real arithmetic in solving the equations (and this is normally advantageous), it is computationally simpler to use Eqs. (18a) and (18b) since the related (real) $\widetilde{K}_{\gamma\alpha}$ operators satisfy equations which look exactly like Eqs. (18a) and (18b) while those for the $\overline{K}_{\gamma\alpha}$ operators satisfy more complicated coupled integral equations. Because of this, we consider Eqs. (18a) and (18b) to be more useful than Eqs. (13a) and (13b); *the latter equations are not incorrect, but more difficult to solve.*

The third set of BKLT equations is derived from a *coupled* system of Schrödinger equations[8]

$$(E - H_\alpha)|\zeta_\alpha\rangle = V_\beta|\zeta_\beta\rangle, \tag{19a}$$

$$(E - H_\beta)|\zeta_\beta\rangle = V_\alpha|\zeta_\alpha\rangle. \tag{19b}$$

Here $|\zeta_\alpha\rangle$ and $|\zeta_\beta\rangle$ are components of the wave function such that their sum yields the usual wave function

$$|\psi\rangle = |\zeta_\alpha\rangle + |\zeta_\beta\rangle, \tag{20}$$

which is the solution of the usual Schrödinger equation. To prove this, we simply add Eq. (19b) to Eq. (19a) and recall Eq. (3). Thus, the sum is either a solution of the Schrödinger equation or zero. The latter solutions are easily recognized and eliminated. Next, we consider the relevant Lippmann–Schwinger equations which follow from Eqs. (19). They are

$$|\zeta_\alpha\rangle = |\chi_\alpha\rangle + G_\alpha V_\beta|\zeta_\beta\rangle, \tag{21a}$$

$$|\zeta_\beta\rangle = G_\beta V_\alpha|\zeta_\alpha\rangle, \tag{21b}$$

where α is taken as the initial channel. Multiplying Eq. (21a) by V_α and Eq. (21b) by V_β and introducing two new operators by

$$\widehat{T}_{\gamma\alpha}|\chi_\alpha\rangle = V_{\gamma'}|\zeta_{\gamma'}\rangle, \gamma\neq\gamma'; \quad \gamma, \gamma' = \alpha, \beta, \tag{22}$$

Eqs. (21) lead to the following coupled equations for $\widehat{T}_{\gamma\alpha}$; $\gamma = \alpha, \beta$:

$$\widehat{T}_{\alpha\alpha} = V_\beta G_\beta \widehat{T}_{\beta\alpha}, \tag{23a}$$

$$\widehat{T}_{\beta\alpha} = V_\alpha + V_\alpha G_\alpha \widehat{T}_{\alpha\alpha}. \tag{23b}$$

Equations (23) differ from any of the previous equations and consequently $\widehat{T}_{\gamma\alpha}$ is expected to differ, *as an operator*, from both $\overline{T}_{\gamma\alpha}$ and $\widetilde{T}_{\gamma\alpha}$; $\gamma = \alpha, \beta$. The above set of equations has a rather surprising structure compared to what is normally encountered as well as compared to Eqs. (13) or (18). In the equation for $\widehat{T}_{\alpha\alpha}$, the last interaction is V_β while for $\widehat{T}_{\beta\alpha}$, the last interaction is V_α! Ordinarily, one expects to see the last interaction in $\widehat{T}_{\gamma\alpha}$ be V_γ. [It is precisely because of this unusual structure that we have carried out a numerical study of Eqs. (23) for comparison with Eqs. (18).] Indeed, a moments consideration will lead one to an even more surprising realization and that is the fact that the form of the right hand side of Eq. (23b) appears to be *exactly* equal to $T_{\alpha\alpha}$! Thus, by Eq. (12),

$$\overline{T}_{\alpha\alpha} = V_\alpha + V_\alpha G_\alpha \overline{T}_{\alpha\alpha}, \tag{12'}$$

which provides one with the paradox that $\widehat{T}_{\beta\alpha}$ seems to equal

$\overline{T}_{\alpha\alpha}$. The resolution of this difficulty is simply that $\widehat{T}_{\alpha\alpha}$ is *not* equal to $\overline{T}_{\alpha\alpha}$ but rather [by Eq. (23a)] to $V_\beta G_\beta^+ \widehat{T}_{\beta\alpha}$. Substitution of Eq. (23a) into Eq. (23b) immediately shows that $\widehat{T}_{\beta\alpha}$ does not satisfy the same equation as $\overline{T}_{\alpha\alpha}$. In order to get some feeling for the fact that the final interaction in the $\widehat{T}_{\gamma\alpha}$ equation is $V_{\gamma'}, \gamma'\neq\gamma$, it is necessary to consider again the equations for the wave function components $|\zeta_\gamma\rangle$. By Eqs. (21), $|\zeta_\gamma\rangle$ *does* provide the scattered flux in arrangement γ since the Green function occurring is G_γ. The only question as to whether these are valid equations centers on whether $G_\alpha V_\beta|\zeta_\beta\rangle$ produces convergent amplitudes only in arrangement α and similarly whether $G_\beta V_\alpha|\zeta_\alpha\rangle$ does this in arrangement β. That is, normally, one has terms of the form $G_\alpha V_\alpha|\psi\rangle$ and in the limit that $R_\alpha\to\infty$, $V_\alpha\to0$ so that well-defined scattering amplitudes result. [Recall that $G_\alpha V_\alpha|\psi\rangle$ contains an integral over R'_α of an unperturbed translational state $\phi_{k_n}(R'_\alpha)$ times $V_\alpha(R'_\alpha)\psi(R'_\alpha r'_\alpha)$, with r'_α being an internal variable for the system. Because $\psi(R'_\alpha r'_\alpha)$ and $\phi_{k_n}(R'_\alpha)$ do *not* go to zero with $R'_\alpha\to\infty$, $G_\alpha V_\alpha|\psi\rangle$ will diverge unless $V_\alpha(R'_\alpha)\to0$ as $R'_\alpha\to\infty$.] In the present case, one has $G_\gamma V_{\gamma'}|\zeta_{\gamma'}\rangle$ and in this the integral over R_γ does *not* converge due to the potential! *In fact, it can be shown that* $V_\gamma\zeta_\gamma(R_\gamma r_\gamma), \gamma = \alpha, \beta$, *tends to zero in the limit that either* $R_\gamma \to\infty$ *or* $r_\gamma\to\infty$ *so long as one is below the dissociation threshold.*[3] Thus, the $V_\gamma\zeta_\gamma$ products are "confined" and ensure that the integrals over R_γ and r_γ converge. Then by Eqs. (20) and (21) one sees that $|\zeta_\alpha\rangle$ contributes the scattering in arrangement α only and $|\zeta_\beta\rangle$ contributes the scattering in arrangement β. Now by Eq. (22), Eqs. (21) can be rewritten as

$$|\zeta_\alpha\rangle = |\chi_\alpha\rangle + G_\alpha\widehat{T}_{\alpha\alpha}|\chi_\alpha\rangle, \tag{21a'}$$

$$|\zeta_\beta\rangle = G_\beta\widehat{T}_{\beta\alpha}|\chi_\alpha\rangle, \tag{21b'}$$

and Eqs. (23) for the $\widehat{T}_{\gamma\alpha}$ are the direct result of this. As a final remark, the above discussion is not mathematically rigorous but such a formal discussion of these equations has been given in the work of Evans, Hoffman, and Kouri.[8] However, as stated above, the present numerical study was undertaken in part to examine how this third set of equations responded to the approximations which were used in solving Eqs. (18a) and (18b).

So far we discussed in each case a set of equations where the α channel is the initial channel. Another set of equations is obtained by taking β as the initial channel and so we have altogether four operators; i.e., $T_{\alpha\alpha}$, $T_{\beta\alpha}$, $T_{\alpha\beta}$, and $T_{\beta\beta}$ which can be arranged in a 2×2 matrix. In the same way we may arrange V_α and V_β, as well as G_α and G_β, in 2×2 matrices; i.e., **V** and **G**, where both are diagonal. Consequently, Eqs. (13) can be written as

$$\overline{\mathbf{T}} = \mathbf{UV} + \mathbf{VWG}\overline{\mathbf{T}}, \tag{13c}$$

Eqs. (18) can be written as

$$\widetilde{\mathbf{T}} = \mathbf{VW} + \mathbf{VWG}\widetilde{\mathbf{T}} \tag{18c}$$

and Eqs. (23) as

$$\widehat{\mathbf{T}} = \mathbf{WV} + \mathbf{WVG}\widehat{\mathbf{T}}. \tag{23c}$$

Here **U** and **W** are defined by

$$\mathbf{U} = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}; \quad \mathbf{W} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{24}$$

TABLE I. Reactive transition probabilities for the DH_2 reaction as calculated for different numerical parameters at two energies, using both forms of the BKLT equations.

E_{trans}(eV)	N_α[a]	M_α[b]	N_β[a]	M_β[b]	$P_{0\leftarrow0}$		$P_{1\leftarrow0}$		Maximum error in unitarity (%)		Maximum relative error in symmetry (%)	
	3	10	4	10	0.948[c]	0.950[d]			0.2[c]	0.1[d]	0.2[c]	0.07[d]
	4	10	5	10	0.950	0.953			2.2	1.6	2.4	0.8
	5	10	6	10	0.876	0.889			0.9	2.0	1.0	1.1
	6	8	7	8	0.872	0.876			3.8	0.6	4.2	0.3
	6	10	7	10	0.862	0.876			2.2	2.6	2.6	1.5
	7	7	8	7	0.882	0.895			1.1	1.6	1.3	0.9
	7	8	8	8	0.888	0.899			2.5	0.2	2.7	0.1
0.28	7	9	8	9	0.893	0.899			2.5	2.0	2.7	1.1
	7	10	8	10	0.893	0.900			2.2	2.1	2.6	1.2
	8	10	9	10	0.909	0.916			1.3	1.2	1.6	0.7
	9	10	10	10	0.902	0.916			0.7	0.9	0.6	0.5
	10	10	10	10	0.902	0.916			0.7	1.0	0.6	0.5
	10	10	11	10	0.902	0.916			0.7	0.5	0.6	0.3
	11	10	11	10	0.902	0.916			0.7	0.6	0.6	0.4
	7	10	8	10	0.881	0.871	0.0032[c]	0.0037[d]	2.1	1.7	1.1	0.9
	8	10	9	10	0.875	0.865	0.0031	0.0032	1.6	1.7	0.9	1.0
	9	10	10	10	0.883	0.874	0.0028	0.0029	0.3	0.7	0.2	0.4
0.48	10	8	10	9	0.888	0.889	0.0025	0.0032	1.7	0.7	1.0	0.4
	10	10	10	10	0.884	0.875	0.0027	0.0028	0.8	1.1	0.5	0.6
	10	10	11	10	0.884	0.876	0.0027	0.0028	0.2	0.3	0.1	0.2
	11	10	12	10	0.884	0.876	0.0027	0.0028	0.6	0.4	0.3	0.2

[a] The number of (asymptotic) original vibrational eigenfunctions included in the expansion.
[b] The number of translational basis functions included in the expansion.
[c] Calculated with the BKLT equations given in Eqs. (18).
[d] Calculated with the BKLT equations given in Eqs. (23).

Equations (13c), (18c), and (23c) were derived for a two channel case; however, it can be shown that similar equations apply for any number of channels.

In previous publications[1,2] we described in detail how one obtains from the operator equations the corresponding integral equations which enable one to calculate the corresponding T matrix elements. We assume here that the reader is familiar with this procedure and therefore we do not repeat it.

III. RESULTS

We present results for the two nonsymmetric reactions

$$D + H_2(v_i)\longrightarrow HD(v_f) + H \tag{I}$$

and

$$F + H_2(v_i = 0)\longrightarrow HF(v_f) + H. \tag{II}$$
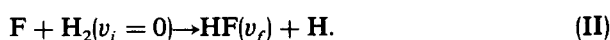
For reaction (I) we employed the SLTH surface[14] and for reaction (II) the Muckerman V surface.[15] The first part of the

TABLE II. Comparison of the reactive transition probabilities for the DH_2 reaction calculated with both forms of the BKLT equations.

E_{trans}(eV)	$P_{0\leftarrow0}$		$P_{1\leftarrow0}$		$P_{0\leftarrow1}$		$P_{1\leftarrow1}$	
0.28	0.902[a]	0.915[b]						
0.32	0.973	0.972						
0.36	0.957	0.953						
0.40	0.948	0.944						
0.44	0.935	0.935	0.0002[a]	0.0002[b]				
0.48	0.884	0.877	0.003	0.003				
0.52	0.710	0.685	0.082	0.088	0.0000[a]	0.0001[b]	0.0001[a]	0.0001[b]
0.56	0.302	0.290	0.520	0.535	0.002	0.002	0.006	0.007
0.60	0.445	0.451	0.495	0.492	0.016	0.015	0.037	0.039
0.64	0.534	0.540	0.303	0.293	0.118	0.119	0.244	0.252
0.68	0.401	0.400	0.307	0.298	0.216	0.226	0.386	0.385
0.72	0.318	0.302	0.288	0.280	0.266	0.280	0.389	0.390
0.76	0.169	0.160	0.319	0.321	0.325	0.327	0.404	0.397
0.80	0.113	0.114	0.360	0.356	0.289	0.286	0.349	0.356
0.84	0.110	0.110	0.322	0.315	0.257	0.261	0.313	0.318

[a] Calculated with the BKLT equations given by Eqs. (18).
[b] Calculated with the BKLT equations given by Eqs. (23).

numerical study deals with a comparison of results as obtained with the two different sets of BKLT equations; i.e., Eqs. (18) and (24). The comparison is carried out for reaction (I) and the results are shown in Table I. The table contains various vibrational state-to-state function probabilities as calculated for different parameters and a few energies. The parameters N_α and N_β stand for the number of *vibrational* states included in the expansion in arrangements $\gamma = \alpha, \beta$ and M_α and M_β are, respectively, the number of basis functions included in the expansion of the scattering distance dependence of the amplitude density functions. It will be noticed that the two sets of equations yield very similar results when the same N_γ and M_γ; $\gamma = \alpha, \beta$, are used. This suggests that the rate convergence in both cases is similar.

The comparison is extended to a larger number of energies in Table II. Again the results are very similar and the relative deviation is never larger than 3%. Thus, we see computationally that the unusual form of the BKLT equations [Eqs. (23)] nevertheless yields the proper results just as one would expect from the formal analysis.[3]

In Figs. 1–3 we compare BKLT vibrational state-to-state transition probabilities with probabilities obtained from a differential equation method.[16] In Fig. 1 are shown results for the reaction
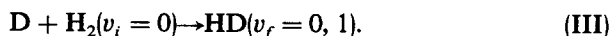
$$D + H_2(v_i = 0) \rightarrow HD(v_f = 0, 1). \qquad (III)$$

The curves are results obtained using a propagative method to solve the relevant differential equations and the points are

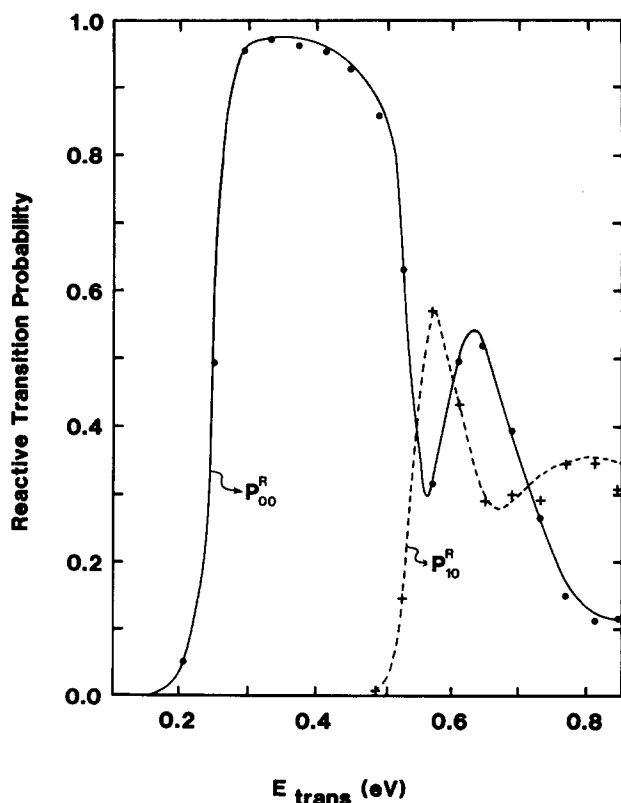FIG. 2. The same as Fig. 1 but for the reaction $D + H_2(v_i = 1) \rightarrow HD(v_f = 0,1) + H$.

calculated from the BKLT equations. In Fig. 2 are shown the results for the reaction

$$D + H_2(v_i = 1) \rightarrow HD(v_f = 0, 1) + H. \qquad (IV)$$
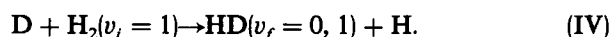
In solving the equations, we must expand the r_γ and R_γ dependencies of the scattering functions $V_\gamma | \zeta_\gamma \rangle$. Because $V_\gamma | \zeta_\gamma \rangle$ is confined, we use bound state type basis functions for *both* the r_γ and R_γ variable dependences. In the H_2 arrangement, we require ten vibrational states of the unperturbed H_2 molecule for the r_{H_2} and ten states for the R_{H_2} dependences while for HD, we require eleven vibrational states of the unperturbed HD molecule for the r_{HD} and ten states for the R_{HD} dependences. (The scattering coordinate R_γ dependence is expanded using a sinusoidal basis defined on a *finite* range. These are just particle in a box states. The length of the box is chosen to ensure that the full interaction region is covered.[2])

FIG. 1. Reactive transition probability for the reaction $D + H_2(v_i = 0) \rightarrow HD(v_f = 0,1) + H$. Smooth curves are due to an established method, points are due to the BKLT equations.
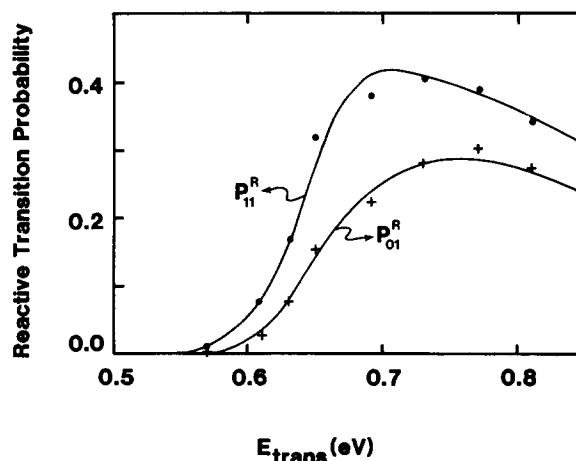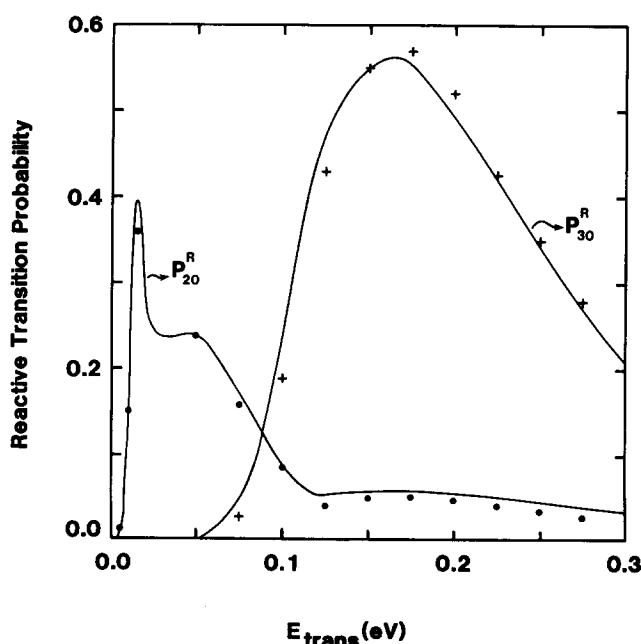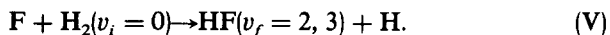

FIG. 3. The same as Fig. 1 but for the reaction $F + H_2(v_i = 0) \rightarrow HF(v_f = 2,3) + H$.

In Fig. 3 are shown the results for the reaction

$$F + H_2(v_i = 0) \rightarrow HF(v_f = 2, 3) + H. \qquad (V)$$

In these calculations, a basis consisting of 15 vibrational states for the r_γ dependence was used in both the H_2 and HF arrangements and similarly 15 states for the R_γ dependence in each arrangement, except close to the resonance. In that region, 18 vibrational and 12 translational basis states in each arrangement were used. In all three cases, the BKLT results are practically the same as those obtained by the well-established propagative method. It is particularly gratifying to see that the BKLT equations are able to reproduce results for such a nonsymmetric and exothermic reaction system as $F + H_2$.

IV. SUMMARY

In this paper we have further explored the computational aspects of the BKLT equations. This was done in two ways:

(i) We subjected the new set of coupled Lippmann–Schwinger equations [Eqs. (23)] to a numerical treatment. It is established that calculations done under similar conditions yield, for Eqs. (18) and (23), essentially identical results. The convergence properties of two sets of equations appear to be essentially the same for the systems considered. Furthermore, although the potentials in the two sets of equations are switched (i.e., V_α and V_β are exchanged in the two sets of equations), the on-shell T-matrix elements are essentially equal. Thus, the unusual set Eqs. (23) are shown computationally to yield correct results.

(ii) For the first time the BKLT equations have been applied to nonsymmetric reactions. We have compared state-to-state transition probabilities for the $H_2 + D$ and the $H_2 + F$ systems with those obtained by a well-established propagative method. For all practical purposes the results were the same.

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