Arrangement channel approach to reactive systems: theory and numerical algorithms (as applied to the HFH system)†

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Abstract. In this work a new approach for treating realistic reactive atom–diatom systems is presented. The method is based on an explicit coupling of several Lippmann–Schwinger equations related to the various physical accessible arrangement channels. The uniqueness of this approach is that no matching is employed in transforming from one arrangement channel to the other. The reliability of the method was previously demonstrated; a detailed numerical study of the parameters that enter the algorithm used to solve the integral equations is presented here.

1. Introduction

To treat reactive exchange collisions one may distinguish between two main approaches (Baer 1982): the first approach, which is the more dynamical of the two, is based on propagating the wavefunctions (or other physical magnitudes) from one arrangement channel to the others; the second, more static, approach is based on solving a set of coupled equations (one equation for each arrangement channel) where each channel is treated separately. During the last decade most of the research in this field was based on the first approach and only sporadic attempts (Baer and Kouri 1972a, b, 1973, Micha 1972, Garret and Miller 1978, Top and Shapiro 1982) were made to apply methods within the framework of the second approach. Recently we started a new project aimed at developing a reliable and efficient method to derive reactive S-matrix elements based on the latter approach (Baer and Kouri 1979, Shima and Baer 1982). The method is based on a set of coupled Lippmann–Schwinger equations as originally derived by Baer and Kouri (1972a, b, 1973) then modified by Kouri and Levin (1974, 1975). They were later extended and generalised by Tobocman (1974, 1975). In what follows, we refer to them as the BKLT equations.

The main advance in treating reactive scattering with the aim of deriving exact quantum-mechanical differential and integral cross sections was made within the first (dynamical) approach. However, hardly any further progress has been made since the first three-dimensional cross sections for the H+H2 reaction were obtained (Kuppermann and Schatz 1975, Elkowitz and Wyatt 1975).

The main difficulties encountered in extending this treatment to non-symmetric systems are related to both the bifurcation and the matching. It is not clear yet how the bifurcation can be carried out in a non-symmetrical case. With regard to the

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matching, besides the technical problem of making it work for a non-symmetrical system, it is very delicate from the numerical point of view due to its extreme sensitivity to the detailed topography of the potential energy surface in the interacting region. It turns out that, at most, it can be expected to be reliable if it is performed for a limited region of configuration space. This is the situation in the case of the $H+H_2$ system.

The approach presented in this work is free of all these limitations because the BKLT equations explicitly incorporate the boundary conditions associated with all the arrangement channels. Recently it was shown (Shima and Baer 1982) that the results obtained by this novel procedure, for the (light–heavy–light) exchange $H'+FH\rightarrow H'F+H$ reaction, are identical to those obtained by methods developed within the first approach (Schatz and Kuppermann 1980, Garrett et al 1981). In the present work we describe a detailed numerical study of parameters which enter into the numerical algorithms that lead to the solution of the BKLT equations.

In the next section the theory associated with the BKLT equations and the algorithms needed to solve them are given. In the third section, a numerical study is presented and in the last section the conclusions are given. The theory, as well as the numerical study, are carried out for the collinear arrangement, because, in contrast to the three-dimensional system, it is much simpler and therefore more convenient for introducing a novel treatment. However, it still contains most of the features of the real case (Baer 1982).

2. Theory

We consider a reactive system of two arrangement channels (initial reagents and final products). Given a Hamiltonian $H$ one may partition it in two ways:

$$H = H_\gamma + V_\gamma \quad \gamma = \alpha, \beta$$

where $H_\gamma$ is a non-reactive Hamiltonian and $V_\gamma$ stands for the (reactive) interaction potential such that:

$$\lim_{R_\gamma \rightarrow \infty} V_\gamma (R_\gamma, \ldots) = 0.$$ (2)

The BKLT equations for this case are (Baer and Kouri 1972a, b, 1973, Kouri and Levin 1974, 1975):

$$R_{\alpha\alpha} = V_\alpha G_\beta R_{\beta\alpha}$$ (3)

$$R_{\beta\alpha} = V_\beta + V_\beta G_\alpha R_{\alpha\alpha}$$ (4)

where $R_{\alpha\alpha}$ and $R_{\beta\alpha}$ are the non-reactive and reactive $R$ submatrices and $G_\alpha$ and $G_\beta$ are the corresponding Green's functions given in the form:

$$G_\gamma = (E - H_\gamma)^{-1} \quad \gamma = \alpha, \beta.$$ (5)

The Hamiltonian $H$ is further decomposed in the form:

$$H_\gamma = H_{0\gamma} + U_\gamma (R_\gamma, r_\gamma) + w_\gamma (r_\gamma)$$ (6)

where $H_{0\gamma}$ is the free Hamiltonian which contains the kinetic energy terms, $U_\gamma (R_\gamma, r_\gamma)$ is an inelastic (non-reactive) distortion potential (Baer and Kouri 1979, Shima and Baer 1982), $w_\gamma (r_\gamma)$ is the asymptotic binding potential energy of the diatomic molecules.
and \( R_{\gamma} \) and \( r_{\gamma} \) are the (mass scaled) translational and vibrational coordinates, respectively. By defining \( \theta_{n}^{\gamma}(R_{\gamma}, r_{\gamma}) \) as the \( n \)th state of the system in \( \gamma \) arrangement, the corresponding \( R \) matrix elements are given in the form:

\[
R_{\text{min}} = \langle \theta_{n}^{\gamma}(R_{\gamma}, r_{\gamma}) | R_{\gamma} | \theta_{n}^{\alpha}(R_{\alpha}, r_{\alpha}) \rangle
\]  

(7)

where \( \theta_{n}^{\alpha}(R_{\alpha}, r_{\alpha}) \) is the initial \( n \) state in the \( \alpha \) arrangement. Next we introduce the density functions \( \xi_{n}^{\alpha}(R_{\gamma}, r_{\gamma}) \) defined as:

\[
\xi_{n}^{\alpha}(R_{\gamma}, r_{\gamma}) = R_{\gamma} \theta_{n}^{\alpha}(R_{\alpha}, r_{\alpha}).
\]  

(8)

Substituting equation (8) in equations (3) and (4) yields the two coupled Lippmann–Schwinger-type equations for \( \xi_{n}^{a\alpha}(R_{\alpha}, r_{\alpha}) \) and \( \xi_{n}^{\beta\alpha}(R_{\beta}, r_{\beta}) \) (Baer and Kouri 1972a, b, Kouri and Levin 1974, 1975):

\[
\begin{align*}
\xi_{n}^{a\alpha}(R_{\alpha}, r_{\alpha}) &= V_{a}(R_{\alpha}, r_{\alpha}) \int dR_{\beta} dr_{\beta} G_{a\beta}(R_{\beta}, r_{\beta} | R_{\beta}^{\prime}, r_{\beta}^{\prime}) \xi_{n}^{\beta\alpha}(R_{\beta}, r_{\beta}^{\prime}) \\
\xi_{n}^{\beta\alpha}(R_{\beta}, r_{\beta}) &= V_{\beta}(R_{\beta}, r_{\beta}) \theta_{n}^{\alpha}(R_{\alpha}, r_{\alpha}) \\
&+ V_{\beta}(R_{\beta}, r_{\beta}) \int dR_{\alpha} dr_{\alpha} G_{a\beta}(R_{\alpha}, r_{\alpha} | R_{\alpha}^{\prime}, r_{\alpha}^{\prime}) \xi_{n}^{a\alpha}(R_{\alpha}^{\prime}, r_{\alpha}^{\prime}).
\end{align*}
\]  

(9)

(10)

Our next tasks are to determine the functions \( \theta_{n}^{\gamma}(R_{\gamma}, r_{\gamma}) \) and the coordinate representation of the Green’s function \( G(R_{\gamma}, r_{\gamma} | R_{\gamma}^{\prime}, r_{\gamma}^{\prime}) \). The functions \( \theta_{n}^{\gamma}(R_{\gamma}, r_{\gamma}) \) are the solutions of the Schrödinger equation:

\[
(H_{\gamma} - E) \theta_{n}^{\gamma}(R_{\gamma}, r_{\gamma}) = 0
\]  

(11)

subject to the boundary conditions

\[
\lim_{R_{\gamma} \to \infty} \theta_{n}^{\gamma}(R_{\gamma}, r_{\gamma}) = \frac{1}{k_{\gamma}} \sin(k_{\gamma} R_{\gamma} + \delta_{\gamma}) \phi_{n}(r_{\gamma}).
\]  

(12)

This kind of solution can be obtained only if the potential \( U_{\gamma}(R_{\gamma}, r_{\gamma}) \) in equation (6), is separable, namely

\[
U_{\gamma}(R_{\gamma}, r_{\gamma}) = W_{\gamma}(R_{\gamma}) + u_{\gamma}(r_{\gamma}).
\]  

(13)

However, since \( U_{\gamma}(R_{\gamma}, r_{\gamma}) \) has to be identically zero for \( R_{\gamma} \to \infty \), this necessarily leads to the result that:

\[
u_{\gamma}(r_{\gamma}) = 0.
\]  

(14)

The coordinates \( (R_{\gamma}, r_{\gamma}) \) are the mass scale coordinates related to the physical distances \( (R_{\gamma}^{\prime}, r_{\gamma}^{\prime}) \) as:

\[
R_{\gamma} = \lambda_{\gamma} R_{\gamma}^{\prime} \quad r_{\gamma} = \lambda_{\gamma}^{-1} r_{\gamma}^{\prime} \quad \lambda_{\gamma} = (\mu_{\gamma} / m_{\gamma})^{1/4}
\]  

(15)

where \( \mu_{\gamma} \) is the reduced mass of the \( \gamma \) channel diatomic molecule and \( m_{\gamma} \) is the reduced mass of the single atom with respect to the corresponding diatomic molecule. Consequently, the mass \( \mu \) defined as:

\[
\mu = (\mu_{\gamma} m_{\gamma})^{1/2}
\]  

(16)

can be shown to be symmetrical with respect to the three masses of the interacting particles and therefore becomes the characteristic mass of the system. Since the potential in equation (6) is separable, its solution can be written as a product of two
functions in the form:
\[ \theta_n^\gamma(R, r) = \psi_{n}^{\gamma}(R, r)\phi_n(r) \] (17)
where \( \phi_n(r) \) fulfills the eigenvalue equations:
\[ \left( -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \omega^\gamma(r) - \epsilon_n^\gamma \right) \phi_n(r) = 0 \] (18)
and \( \psi_{n}^{\gamma}(R, r) \) is the regular solution of the equation
\[ \left( -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + W^\gamma(R) - \frac{\hbar^2 k_n^2}{2\mu} \right) \psi_n^\gamma(R) = 0. \] (19)

Here \( k_n^\gamma \) stands for:
\[ k_n^\gamma = \left( \frac{2\mu}{\hbar^2} (E - \epsilon_n^\gamma) \right)^{1/2}. \] (20)

The Green's functions are given in the form:
\[ G^\gamma(R, r | R', r') = \sum_m g^\gamma_m(R, r | R', r') \phi_m^\gamma(r) \phi_m^\gamma(r') \] (21)
where the \( g^\gamma_m(R, r | R', r') \) functions are
\[ g^\gamma_m(R, r | R', r') = \begin{cases} \psi_{m}^{\gamma}(R, r)\psi_{m}^{\gamma}(R', r') & R < R' \\ \psi_{m}^{\gamma}(R, r)\psi_{m}^{\gamma}(R', r') & R > R' \end{cases} \] (22)
and \( \psi_{m}^{\gamma}(R, r) \) and \( \psi_{m}^{\gamma}(R, r) \) are the regular and the irregular solutions of equation (19). They are normalised in such a way that their Wronskian is equal to 1. Substituting equations (17), (20) and (22) in equations (9) and (10) one obtains:
\[ \xi_{n^0}(\alpha, \alpha) = V_{\alpha}(\alpha, \alpha) \sum_m \phi_{m}^{\alpha}(r) \int \int dR' dr' g_{m}(R, r | R', r') \phi_{m}^{\beta}(r') \xi_{n^0}(\beta, r') \] (23)
\[ \xi_{n^0}(\beta, \beta) = V_{\beta}(\beta, \beta) \psi_{n^0}(\alpha, \alpha) \sum_{\beta} \phi_{\beta}^{\gamma}(r) + V_{\beta}(\beta, \beta) \sum_{\beta} \phi_{\beta}^{\gamma}(r) \] (23)
\[ \times \int \int dR' dr' g_{m}(\alpha, r | R', r') \phi_{\beta}(r') \xi_{n^0}(\alpha, \alpha) \psi_{n^0}(\alpha, r'). \] (23)

From equation (23) it is inferred that both \( \xi_{n^0}(\alpha, \alpha) \) are non-zero only in a finite region of configuration space. To show this we consider \( \xi_{n^0}(\alpha, \alpha) \) and note the following:

(i) The expression on the right-hand side in equation (23) goes to zero when \( r_{\beta} \) becomes infinite because the asymptotic eigenfunctions \( \phi_{m}^{\beta}(r_{\beta}) \) go to zero for any value of \( m \).

(ii) The expression on the right-hand side of equation (23) goes to zero when \( R_{\beta} \) goes to infinity because the interaction potential \( V_{\alpha}(\alpha, r_{\alpha}) \) does (see equation (2)).

(iii) Since \( R_{\alpha} \) and \( r_{\alpha} \) are related to \( R_{\beta} \) and \( r_{\beta} \) in the following way:
\[ R_{\alpha} = R_{\beta} \cos \theta + r_{\beta} \sin \theta \] (24)
\[ r_{\alpha} = R_{\beta} \sin \theta - r_{\beta} \cos \theta. \] (25)
We also obtain
\[ R_\alpha = r_\beta \csc \theta + r_\alpha \cot \theta \]  
\[ r_\alpha = R_\beta \csc \theta - R_\alpha \cot \theta \]  
where \( \theta \) is determined by the equation:
\[ \cos \theta = \left( \frac{m_A m_C}{m_A + m_B} \right)^{1/2} \]  
\[ \sin \theta = (1 - \cos^2 \theta)^{1/2}. \]

Here \( m_A, m_B \) and \( m_C \) are the masses of the three interacting atoms, \( m_B \) being the central atom.

(iv) From equation (26) it may be seen that for a given value of \( r_\alpha \), both \( R_\alpha \) and \( r_\beta \) simultaneously go to infinity, and from equation (27) it can be seen that, for a given value of \( R_\alpha \), both \( r_\alpha \) and \( R_\beta \) simultaneously go to infinity. Our proof follows by combining arguments (i), (ii) and (iv) and recalling that no value of \( R \) or \( r \) can become negative.

The fact that both density functions are not zero in a finite region only implies that they can be expressed by a double set of eigenfunctions. We start by expanding \( \xi_{n_0}^{\gamma_0}(R, r) \) in terms of one basis set \( \tilde{\phi}^\gamma(r_\gamma) \) in the vibrational coordinate:
\[ \xi_{n_0}^{\gamma_0}(R, r_\gamma) = \sum_n \chi_{n_0}(R, r_\gamma) \phi_n(r_\gamma). \]  

Substituting equation (3) in equations (23), multiplying through by the corresponding \( \tilde{\phi}^\gamma_\alpha(r_\gamma) \) and integrating over \( r_\gamma \), one obtains the following set of coupled integral equations:
\[ \chi_\alpha^\beta(R_\alpha) = \int dR_\alpha \tilde{\phi}^\alpha_\alpha(r_\alpha) V_\alpha(R_\alpha, r_\alpha) \sum_m \phi^\beta_m(r_\beta) \sum_i S^\beta_{\gamma i} \int dR_\beta^i g_m(R_\beta | R_\beta^i) \chi^\beta(R_\beta) \]
\[ \chi_\beta^\alpha(R_\beta) = \int dR_\beta \tilde{\phi}^\beta_\beta(r_\beta) V_\beta(R_\beta, r_\beta) \psi_{n_0}^{\gamma_0}(R_\alpha) \phi^\alpha_{n_0}(r_\alpha) \]
\[ + \int dR_\beta \tilde{\phi}_\beta(r_\beta) V_\beta(R_\beta, r_\beta) \sum_k \phi^\gamma_k(r_\gamma) \sum_l S^\gamma_{\gamma l} \int dR_\alpha^l g_k(R_\alpha | R_\alpha^l) \chi^\gamma(R_\alpha) \]
where the obvious indices were dropped from \( \chi_{n_0}^{\gamma_0}(R, r) \) and the overlap matrix elements \( S^\gamma_{\gamma l} \) defined as:
\[ S^\gamma_{\gamma l} = \langle \phi^\gamma_m | \tilde{\phi}^\gamma_l \rangle \]
were introduced. Since part of the numerical study will be devoted to the single-coordinate density functions \( \chi_{n_0}^{\gamma_0}(R, r) \) it is of importance to see how they are related to the relevant \( R \)-matrix elements. Substituting equations (8), (17) and (30) in equation (7), one obtains
\[ R_{mn_0}^{\gamma_0} = \sum_l \langle \psi_{m_0}^{\gamma_0} | \chi_{n_0}^{\gamma_0} \rangle S^\gamma_{\gamma l}. \]

For the case where \( |\phi^\gamma_m \rangle \) and \( |\tilde{\phi}^\gamma_m \rangle \) are the same basis sets, \( S^\gamma_{\gamma l} \) reduces to a Kronecker \( \delta \) function and consequently \( R_{mn_0}^{\gamma_0} \) becomes:
\[ R_{mn_0}^{\gamma_0} = \langle \psi_{m_0}^{\gamma_0} | \chi_{mn_0}^{\gamma_0} \rangle. \]
As mentioned previously, the $\chi Y(R,)$ functions are also non-zero along a finite $R$, interval and therefore can be expressed in terms of a discrete basis set $\zeta_\alpha^Y(R,)$:

$$\chi_\alpha^Y(R,)=\sum_i a_{m\alpha}^Y(R,).$$  \hspace{1cm} (35)$$

Substituting equation (35) in equations (31), multiplying by $\zeta_\alpha^Y(R,)$ and integrating over $R$, we obtain a set of algebraic equations of the form:

$$a_{lq}^\alpha=\sum_{ip}\left[\sum_m\left(\int dR_\beta v_{ipm}^{B\beta}(R_\beta)F_{m\alpha}^\beta(R_\beta)\right)\delta_{ml}\right]a_{ip}^\beta$$

$$a_{ip}^\beta=\int dR_\alpha v_{ipn0}^{B\alpha}(R_\alpha)\psi_{n0}^\alpha(R_\alpha)+\sum_{lq}\left[\sum_m\left(\int dR_\alpha v_{ipm}^{B\alpha}(R_\alpha)F_{m\alpha}^\alpha(R_\alpha)\right)\delta_{nl}\right]a_{lq}^\alpha$$  \hspace{1cm} (36)$$

where

$$v_{5123}^Y(R,)=\int dr_\gamma \phi_{51}^\gamma(r_\gamma)\xi_2^\gamma(R,_{R,\gamma})V_{51}^\gamma(r_\gamma)\phi_{51}^\gamma(r_\gamma)$$  \hspace{1cm} (37)$$

$$F_{512}^Y(R,)=\int dR_\gamma g_{51}^\gamma(r_\gamma)\xi_2^\gamma(R,_{R,\gamma}).$$  \hspace{1cm} (38)$$

In equation (37) the index $\gamma$ always differs from $\gamma'$.

Next we introduce the two sets of constants i.e. $C_{51234}^{Y\gamma\gamma'}$ and $b_{5123}(\gamma \neq \gamma')$:

$$C_{51234}^{Y\gamma\gamma'}=\int dR_\gamma v_{5123}^{Y\gamma\gamma'}(R,_{R,\gamma})F_{34}^{\gamma}(R,)$$  \hspace{1cm} (39)$$

$$b_{5123}^{Y\gamma}=\int dR_\gamma v_{5123}^{Y\gamma}(R,_{R,\gamma})\psi_{3}^\gamma(R,).$$  \hspace{1cm} (40)$$

Consequently equations (36) become:

$$a_{lq}^\alpha=\sum_{ip}\left(\sum_m C_{ipmn}^{\alpha\beta}\delta_{ml}\right)a_{ip}^\beta$$

$$a_{ip}^\beta=b_{ipn0}^{B\alpha}+\sum_{lq}\left(\sum_m C_{ipmn}^{\alpha\beta}\delta_{nl}\right)a_{lq}^\alpha$$  \hspace{1cm} (41)$$

For the special case:

$$S_{nl}=\delta_{nl}$$  \hspace{1cm} (42)$$

equations (41) reduce to:

$$a_{lq}^\alpha=\sum_{ip} C_{ipn0}^{\beta\alpha}a_{lp}^\beta$$

$$a_{lp}^\beta=b_{lpn0}^{B\alpha}+\sum_{lq} C_{lpn0}^{\alpha\beta}a_{lq}^\alpha.$$  \hspace{1cm} (43)$$

3. A numerical study

In a previous communication (Shima and Baer 1982) we presented preliminary results for the reaction:

$$\text{HF}+\text{H'}\rightarrow \text{H'F}+\text{H}.$$
The results were compared with those obtained by a different method (Schatz and Kuppermann 1980, Garrett et al 1981) and the fit was found to be satisfactory. In the present study we are mainly interested in the numerical aspects of the problem. The convergence rate of the results will be discussed with respect to the number of basis functions included in the calculations and a sensitivity study with respect to different parameters which were introduced to solve the integral equations will be performed.

In solving the integral equations one distinguishes between three stages:
(i) solving equations (18) for the asymptotic basis sets;
(ii) solving equations (19) for the regular and the irregular (distorted) translational functions;
(iii) forming the functions $v_{\gamma \nu, \nu', \nu''} (R_{\gamma}, \gamma = \alpha, \beta (\gamma \neq \gamma')$ and the functions $F_{\nu, \nu', \nu''} (R_{\gamma})$, which are then used for generating the coefficients $C_{\gamma \nu, \nu', \nu''} (R_{\gamma})$ and the inhomogeneous terms $b_{\gamma \nu, \nu', \nu''}^* (R_{\gamma})$ of the corresponding algebraic equations.

In addition to the above mentioned functions which are all determined by the various potentials (i.e. by $w_{\gamma}(r_{\gamma})$, $W_{\gamma}(R_{\gamma})$ and $V_{\gamma}(R_{\gamma}, r_{\gamma})$), we also encounter the basis functions $\zeta_{\gamma}(R_{\gamma})$ which we introduced for the purpose of expanding the density functions $\chi_{\gamma}(R_{\gamma})$ (see equation (35)). In this study results obtained by applying different kinds of basis sets are presented. We discuss first the various potentials encountered in the numerical treatment, then treat the density functions under different assumptions and finally consider the $R$ matrix and the probability matrix elements.

3.1. The potential energy surface

The potential energy surface $V_{T}(R_{\gamma}, r_{\gamma})$ employed in this treatment was presented before (Schatz and Kuppermann 1980) and is shown in figure 1 as a function of the mass scaled coordinates $(R, r)$ introduced earlier. Following the discussion in § 2, $V_{T}(R_{\gamma}, r_{\gamma})$ is written as:

$$ V_{T}(R_{\gamma}, r_{\gamma}) = V_{\gamma}(R_{\gamma}, r_{\gamma}) + W_{\gamma}(R_{\gamma}) + w_{\gamma}(r_{\gamma}) $$  \hspace{1cm} (44) 

where $w_{\gamma}(r_{\gamma})$ is the potential of the diatomic molecule. $V_{\gamma}(R_{\gamma}, r_{\gamma})$ is the interaction

![Figure 1](image-url)
potential and $W_\gamma(R, \gamma)$ is the distortion potential. In our treatment $W_\gamma(R, \gamma)$ was chosen to be:

$$W_\gamma(R, \gamma) = V_T(R, \gamma, r_\gamma = r_{\gamma_0})$$

(45)

where $r_{\gamma_0}$ is the equilibrium distance of the diatomic molecule. Due to the fact that the HFH potential energy surface is relatively simple, $W_\gamma(R, \gamma)$ is very close to the potential along the minimum energy path of the system in the $\gamma$ arrangement. The function $W_\gamma(R, \gamma)$ is shown in figure 3.

Once $W_\gamma(R, \gamma)$ and $w_\gamma(r_\gamma)$ are well defined, $V_\gamma(R, \gamma, r_\gamma)$ becomes uniquely determined. Thus

$$V_\gamma(R, \gamma, r_\gamma) = V_T(R, \gamma, r_\gamma) - W_\gamma(R, \gamma) - w_\gamma(r_\gamma).$$

(46)
Recalling equation (45), one can easily see that

\[ V_\gamma (R_\gamma, r_\gamma = r_{0\gamma}) = 0 \]  

(47)

The interaction potential \( V_\gamma (R_\gamma, r_\gamma) \) is shown in figure 2 where both properties described by equations (2) and (47) are manifested. It is useful to notice that for physical \( r_\gamma \) values the potential \( V_\gamma (R_\gamma, r_\gamma) \) becomes zero already for \( R_\gamma = 1.6 \text{ Å} \).

3.2. The density functions

The various density functions \( \chi_\gamma (R_\gamma) \) will be more explicitly designated as \( \chi^{\alpha\alpha}_{\gamma n_{\alpha}} (R_\alpha) \) or \( \chi^{\beta\alpha}_{\gamma p_{\mu}} (R_\beta) \). The first function stands for an inelastic transition in the (reagent) channel from an initial state \( n_{\alpha} \) to a final state \( q \). The second function stands for an exchange (reactive) transition where \( p \) is a final state in the product channel \( \beta \). In figures 4–7 \( \chi^{\alpha\alpha}_{\gamma 00} (R_\alpha), \chi^{\beta\alpha}_{\gamma 00} (R_\beta), \chi^{\beta\alpha}_{\gamma 10} (R_\beta) \) and \( \chi^{\beta\alpha}_{\gamma 11} (R_\beta) \) are presented as a function of the corresponding translational coordinate. These functions (as well as all other parameters) were calculated for the total energy \( E_1 = 1.0 \text{ eV} \)—an energy for which there are two open

![Figure 4](image-url)

**Figure 4.** The density functions \( \chi (R) \) for different transitions: (a) \( \chi (R) \) for the reactive \( r \rightarrow 1 \) transition; (b) \( \chi (R) \) for the reactive \( 0 \rightarrow 1 \) transition; (c) \( \chi (R) \) for the reactive \( 0 \rightarrow 0 \) transition; (d) \( \chi (R) \) for the non-reactive (elastic) \( 0 \rightarrow 0 \) transition. The calculations were performed for \( \hbar \omega = 0.3 \text{ eV}, N = 9, M = 10 \) but for different \( R_0 \) values; three curves are shown in each box: \( \cdots \cdots \cdots R_0 = 0.9 \text{ Å}; \cdots \cdots \cdots R_0 = 1.0 \text{ Å}; \cdots \cdots \cdots R_0 = 1.1 \text{ Å}. \)
The density functions $\chi(R)$ for different transitions as calculated for $R_o = 1 \text{ Å}$, $N = 9$, $M = 10$ but for different values of $h\omega$: $- - - - h\omega = 0.1 \text{ eV}$; $- - - h\omega = 0.3 \text{ eV}$; $- - - h\omega = 0.5 \text{ eV}$. Other details are as in figure 4.

states in each channel. The calculation of the density functions is performed employing equation (35) where the coefficients $a_{ni}^2$ were solved from equations (43). It should be emphasised again that the various $\chi(R)$ functions (like the $\xi(R, r)$ functions) are non-zero only along a finite $R$ interval which in this case is $0.6 \text{ Å} \leq R \leq 1.6 \text{ Å}$ (see discussion following equation (23)). In figures 4 and 5 results calculated with different basis sets are shown. In fact, all the basis sets are harmonic, but each case differs from the other by the location $R_o$ of the harmonic potential along the reaction coordinate or by its width $d$. (The harmonic potential for $R_o = 1.1 \text{ Å}$ and $h\omega = 0.3 \text{ eV}$ is shown in the lower part of figure 3.) Since $d$ is closely related to the frequency $\omega$

$$d = \hbar/(h\omega \mu)^{1/2}$$

we distinguish between the various cases by values of $(h\omega)$ as well as by values of $R_o$. The different density functions for a given value of $h\omega = 0.3 \text{ eV}$, but for various values of $R_o = 0.9$, 1.0, 1.2 Å, are shown in figures 4. All the calculations were carried out employing nine asymptotic (Morse-type) eigenfunctions and ten harmonic wavefunctions. Due to the symmetric character of the system similar expansions were carried out in both channels. In each part of the four in each figure, results for one of the
Figure 6. The density functions $\chi(R)$ for different transitions as calculated for $R_0 = 1.0 \, \text{Å}$, $\hbar \omega = 0.3 \, \text{eV}$, $M = 10$ but for different numbers $N$ of asymptotic states; $- - - N = 3$, $- - N = 7$, $- - - - N = 11$. Other details are as in figure 4.

four above mentioned functions are given. It is easily seen that as the harmonic potential is shifted to the right, more portions of the density functions are uncovered. Thus, for instance, in the case of $R_0 = 0.9 \, \text{Å}$ the density functions are close to zero beyond the value $R = 1.4 \, \text{Å}$, the reason being that all ten harmonic oscillator wavefunctions employed in this calculation are also very close to zero beyond this point. Shifting the harmonic potential to $R_0 = 1.2 \, \text{Å}$ uncovers the missing parts of the density functions. The density functions calculated for one fixed value of $R_0$, $R_0 = 1.1 \, \text{Å}$, but for different values of $\hbar \omega$, $\hbar \omega = 0.1, 0.3, 0.5 \, \text{eV}$ are shown in figure 5. The results obtained for $\hbar \omega = 0.3 \, \text{eV}$ and $\hbar \omega = 0.5 \, \text{eV}$ are almost identical but differ appreciably from the results for $\hbar \omega = 0.1 \, \text{eV}$. The reason is related to the width of the oscillator. As seen from equation (48) the smaller the value of $\hbar \omega$ the larger the width. If the width becomes too big, a larger basis set is needed in order to represent the density function accurately in the region where it is not zero and at the same time to ensure that the same combination of basis functions will yield zero values outside that region. In the case of $\hbar \omega = 0.1 \, \text{eV}$, ten harmonic wavefunctions are not enough. Reducing the width of the oscillator (or increasing $\hbar \omega$) automatically makes the density functions zero at the relevant regions and therefore a smaller number of basis functions is
needed to present the non-zero region of the density function correctly. Thus in the
case of $\hbar\omega = 0.3$ eV ten wavefunctions are enough. Increasing $\hbar\omega$ far beyond 0.3 eV
might again require a larger basis set because a smaller one will yield zero values for
the density functions at regions where they are not zero.

The density functions for $R_0 = 1.0$ Å, $\hbar\omega = 0.3$ eV calculated for ten harmonic
wavefunctions but for different numbers of asymptotic wavefunctions, namely $N = 3$, $7$ and $11$, are presented in figure 6. The rate of convergence is clearly represented.
Whereas large changes are observed for the transition from $N = 3$ to $N = 7$, minor ones are seen for the transition from $N = 7$ to $N = 11$.

The density functions for $R = 0 = 1.0$ Å, $\hbar\omega = 0.3$ eV calculated for nine asymptotic
functions but for different numbers of harmonic wavefunctions, i.e. $M = 4, 6, 8$ and
10 are given in figure 7. Again the convergence is clearly seen. We thus see how a
simple function obtained with three harmonic wavefunctions develops into a much
more structured function by adding more wavefunctions. The main changes are
observed in the regions which in the case of $M = 3$ were identically zero and became
non-zero once more functions were added. However, in the transition from $M = 8$
to $M = 10$ only slight changes are observed.
3.3. The $R$ matrix and the probability matrix elements

Numerical results for $E_{\text{tot}} = 1.0$ eV are shown in table 1 for various $R$-matrix elements and in table 2 for transition probabilities. The $R$-matrix elements are calculated using equation (34) which is essentially an overlap integral between the density function and the corresponding regular solution of equation (19). These functions, for the two open states, are shown in figure 3. It is seen that $\psi_{n=0}(R)$ is practically zero in the region $0 < R < 0.7$ Å whereas the zero region for $\psi_{n=1}(R)$ extends to $R = 0.85$ Å.

The various non-reactive and reactive transition probabilities are calculated from the corresponding $S$-matrix elements, where the latter are derived from the $R$-matrix elements by employing Heitler's radiation damping equation, i.e.

$$ S = (1 - iR)/(1 + iR). $$

The tables are divided into four main parts.

In the first part of the two tables, results are presented as a function of $R_0$. Whereas changes are observed in both the $R$ matrix elements and the probabilities when $R_0$ is varied from $R_0 = 0.9$ Å to $R_0 = 1.1$ Å, only minor changes are noticed when $R_0$ is further shifted from $R_0 = 1.1$ Å to $R_0 = 1.2$ Å. In the second part of the tables, results are presented as a function of various values of $\hbar \omega$. Here the results are seen to improve when $\hbar \omega$ is changed from $\hbar \omega = 0.1$ eV to $\hbar \omega = 0.2$, $0.3$ eV, but then become worse again as $\hbar \omega$ is further increased to $\hbar \omega = 0.4$, $0.5$ eV. The explanation is given in the previous subsection where we discussed the dependence of the density functions on $\hbar \omega$.

In the third and the fourth parts of the tables results are shown as a function of the number $N$ of (asymptotic) Morse functions and the number $M$ of the harmonic wavefunctions for $\hbar \omega = 0.3$ eV and $R_0 = 1.1$ Å. It is noticed that in both cases the results converge to the same limits. An interesting feature of this method is that the unitarity is almost always fulfilled. This is certainly not the case with the propagative methods.

4. Conclusions

In this work we presented to some extent the details of coupled integral equations which when solved will permit the calculation of the $R$ matrix elements. It was proven analytically that the solutions of these equations are of finite range in both the vibrational coordinate $r$ and the translational coordinate $R$. This fact was used to expand these (density) functions in term of two (bound) basis sets, one with respect to $r$ and the other with respect to $R$. Whereas the structure of the integral equation almost dictates the type of the vibrational basis set to be employed, no hints are given for the best choice of the translational coordinate basis set. Therefore most of this numerical study was devoted to this problem. We chose a harmonic basis set and assumed its position $R_0$ and its width $d$ to be parameters. In addition, we assumed the number $N$ of the Morse functions and the number $M$ of the harmonic eigenfunctions to be parameters as well. We found that the three parameters $R_0$, $d$ and $M$, related to the chosen harmonic potential, are very closely interrelated. If we define $\tilde{M}$ as the number of harmonic states necessary to obtain converged results for given values of $R_0$ and $d$, we find that the function

$$ \tilde{M} = \tilde{M}(R_0, d) $$

(50)
Table 1. Inelastic and reactive $R$-matrix elements for $E_t = 0.1$ eV as calculated for different numerical parameters (the results in the last line are the converged ones).

<table>
<thead>
<tr>
<th>$h\omega$ (eV)</th>
<th>$R_0$ (Å)</th>
<th>$N$</th>
<th>$M$</th>
<th>Inelastic</th>
<th>Reactive</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0-0</td>
<td>0-1</td>
</tr>
<tr>
<td>0.3</td>
<td>0.9</td>
<td>9</td>
<td>10</td>
<td>-1.303</td>
<td>0.114</td>
</tr>
<tr>
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<td>1.0</td>
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<td>-0.564</td>
<td>0.262</td>
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<tr>
<td></td>
<td>1.1</td>
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<td>-0.626</td>
<td>0.255</td>
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<td>1.2</td>
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<td></td>
<td>-0.644</td>
<td>0.265</td>
</tr>
<tr>
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<td>1.1</td>
<td>9</td>
<td>10</td>
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<td>-0.632</td>
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<tr>
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<td></td>
<td>-0.626</td>
<td>0.255</td>
</tr>
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<td></td>
<td></td>
<td>-0.684</td>
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<td>1.1</td>
<td>9</td>
<td>4</td>
<td>-1.833</td>
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<td></td>
<td>10</td>
<td>-0.621</td>
<td>0.269</td>
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Table 2. Inelastic and reactive transition probabilities for $E_i = 1.0$ eV as calculated for different numerical parameters (the results in the last line are the converged ones).

<table>
<thead>
<tr>
<th>$h\omega$ (eV)</th>
<th>$R_0$ (Å)</th>
<th>$N$</th>
<th>$M$</th>
<th>Inelastic</th>
<th>Reactive</th>
<th>Unitarity</th>
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<td>0.135</td>
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<td></td>
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<td>0.127</td>
<td>0.129</td>
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<tr>
<td>0.3</td>
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<td></td>
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<td>0.014</td>
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<td>0.135</td>
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<td>0.102</td>
<td>0.099</td>
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<td>0.085</td>
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<td>0.008</td>
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<tr>
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<td>0.011</td>
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<td>0.3</td>
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<td>0.011</td>
<td>0.142</td>
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</table>
is strongly dependent on $R_0$ and $d$. Since the efficiency of the method is, among other things, dependent on the size of $M$, $R_0$ and $d$ should be optimally chosen to make the calculation less time consuming. Although, in general, this choice might be energy dependent, this dependence is not expected to be too sensitive. As for the rate of convergence with respect to $N$, this seemed to be independent of $M$, $R_0$ and/or $d$. However, the value of the limiting value will depend on them and therefore will change accordingly.

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