QUANTUM-MECHANICAL REACTIVE TRANSITION PROBABILITY.
APPLICATION OF THE ARRANGEMENT CHANNEL APPROACH *

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The first reactive transition probabilities obtained by solving coupled arrangement channel integral equations are presented. The uniqueness of this approach is that no matching is employed in transforming from one arrangement channel to the other. The results when compared with those obtained by other (propagative) methods are satisfactory.

1. Introduction

During the last decade much effort has been directed towards developing quantum-mechanical methods to calculate “exact” reactive cross sections [1]. One of the most crucial problems in dealing with exchange collisions is related to the transformation from reagents to products coordinates. Most of the available methods and all of those that were applied to three-dimensional systems are based on propagation of either the wavefunctions [2–4] or the S(R) matrix elements [5,6]. Since most systems are composed of three arrangement channels, the propagation from one arrangement channel to the other two involves a bifurcation which is carried out by simultaneous matching of one wavefunction with each of the others, for all three channels simultaneously [3]. This procedure is one of the main bottlenecks in the extension of the present available treatments to a full (non-symmetric) three-channel system, such as D + H2 or F + H2.

Several attempts to circumvent these difficulties were presented in the past [7–12]. In this work we refer to the approach of Baer and Kouri [7] as modified by Kouri and Levine [8] and extended by Tobocman [9], called in what follows the BKLT theory. The basic idea of this theory is the coupling of the Lippmann–Schwinger integral equations for all (non-dissociative) open arrangements. The outcome is a well-defined set of integral equations obtained by simultaneously imposing the boundary conditions of all the asymptotic regions.

In section 2 we briefly describe the theory, in section 3 the results are presented and discussed. More details of the theory and its applications will be published elsewhere [13].

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
\[ \lim_{R \rightarrow \infty} V(R) = 0. \]  

The BKLT equations for this case are

\[ R_{\alpha\alpha} = V_{\alpha} G_{\beta} R_{\beta\alpha}, \]  

(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 functions given in the form

\[ G_{\nu} = (E - H_{\nu})^{-1}, \quad \nu = \alpha, \beta. \]  

(5)

The hamiltonian \( H_\gamma \) 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 and \( w_\gamma(r_\gamma) \) is the asymptotic binding potential energy of the diatomic molecules. By defining \( \theta^n_\gamma(R_\gamma, r_\gamma) \) as the \( n \)th state of the system in the \( \gamma \) arrangement, the corresponding \( R \)-matrix elements are given in the form

\[ R_{\gamma\gamma}^{n_\gamma} = \langle \theta^n_\gamma(R_\gamma, r_\gamma) | R_{\gamma\gamma}\phi_{n_\gamma}(R_\gamma, r_\gamma) \rangle, \quad \gamma = \alpha, \beta. \]  

(7)

where \( \theta^n_{R_\gamma}(R_\gamma, r_\gamma) \) is the initial \( r_0 \) state in the \( \alpha \) arrangement. Next we introduce the density functions

\[ \xi^n_{R_\gamma}(R_\gamma, r_\gamma) = R_{\gamma\gamma}\phi_{n_\gamma}(R_\gamma, r_\gamma) \]  

(8)

and expand them in terms of a basis set \( \phi_{n_\gamma}(r_\gamma) \), i.e.

\[ \xi^n_{R_\gamma}(R_\gamma, r_\gamma) = \sum_j x^n_{j\gamma}(R_\gamma) \phi_j(r_\gamma). \]  

(9)

Substitution of eqs. (8) and (9) in eq. (7) yields:

\[ R_{\gamma\gamma}^{n_\gamma} = \sum_j \int dR_\gamma dr_\gamma \theta^n_{j\gamma}(R_\gamma, r_\gamma) \chi^n_{j\gamma}(R) \phi_j(r_\gamma). \]  

(10)

Our next task is to determine \( \theta^n_{R_\gamma}(R_\gamma, r_\gamma) \) and the coordinate representation of the Green functions \( G_{\gamma}(R_\gamma, r_\gamma | R'_\gamma, r'_\gamma) \). The functions \( \theta^n_{R_\gamma}(R_\gamma, r_\gamma) \) are the solutions of the Schrodinger equation

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

subject to the boundary conditions

\[ \lim_{R_\gamma \rightarrow \infty} \theta^n_{R_\gamma}(R_\gamma, r_\gamma) = \left( k_{\gamma}^2 \right)^{-1/2} \sin(k_{\gamma}^2 R_\gamma + \delta^n_{R_\gamma}(r_\gamma)). \]  

(12)

This kind of solution can be obtained only if the potential \( U_\gamma(R_\gamma, r_\gamma) \) is separable, for instance

\[ U_\gamma(R_\gamma, r_\gamma) = U_\gamma(R_\gamma, r_\gamma = r_\gamma(0)), \]  

(13)

where \( r_\gamma(0) \) is some given fixed distance.

Combining eqs. (6) and (13), we obtain the equation

\[ \left[ -(\hbar^2/2\mu) (\partial^2/\partial R_\gamma^2 + \partial^2/\partial r_\gamma^2) + U_\gamma(r_\gamma, r_\gamma = r_\gamma(0)) \right] \psi^n_{R_\gamma}(r_\gamma) = 0, \]  

(14)

where \( \mu \) is a characteristic mass of the system and \( \psi^n_{R_\gamma}(r_\gamma) \) can be written as a product:

\[ \theta^n_{R_\gamma}(r_\gamma) = \psi^n_{m}(r_\gamma) \phi^n_{n}(r_\gamma), \]  

(15)

where \( \phi^n_{n}(r_\gamma) \) and \( \psi^n_{m}(r_\gamma) \) fulfill the equations

\[ \left[ -(\hbar^2/2\mu) \partial^2/\partial r_\gamma^2 + w_\gamma(r_\gamma) - \delta^n_{R_\gamma}(r_\gamma) \right] \phi^n_{n}(r_\gamma) = 0, \]  

(16)

\[ \left[ -(\hbar^2/2\mu) \partial^2/\partial R_\gamma^2 + U_\gamma(r_\gamma) - (k_{\gamma}^2)^2 \right] \psi^n_{m}(r_\gamma) = 0. \]  

(17)

Here \( k_{\gamma}^2 \) stands for:

\[ k_{\gamma}^2 = [(2\mu/\hbar^2) (E - \delta^n_{R_\gamma}(r_\gamma))]^{1/2}. \]  

Consequently the Green function is given in the form

\[ G_{\gamma}(R_\gamma, r_\gamma | R'_\gamma, r'_\gamma) = \sum_m g_{m}(R_\gamma | R'_\gamma) \phi_m(r_\gamma) \phi_m(r'_\gamma), \]  

(19)

where \( g_{m}(R_\gamma | R'_\gamma) \) are written:

\[ g_{m}^{\gamma}(R_\gamma | R'_\gamma) = \psi_{m}^{\gamma}(R_\gamma) \psi_{m}^{\gamma}(R'_\gamma), \quad R_\gamma < R'_\gamma, \]  

(20)

\[ = \psi_{m}^{\gamma}(R_\gamma) \psi_{m}^{\gamma}(R'_\gamma), \quad R_\gamma > R'_\gamma. \]  

Here \( \psi_{m}^{\gamma}(R_\gamma) \) and \( \psi_{m}^{\gamma}(R_\gamma) \) are the regular and the irregular solutions of eq. (17). They are normalized in such a way that their wronskian is equal to 1.

Substitution of eq. (15) with \( \phi = \psi^{\gamma} \), in eq. (10) yields

\[ R_{\gamma\gamma}^{n_\gamma} = \sum_l \langle \psi_{m}^{\gamma}(R_\gamma) | \phi_{n_\gamma}(r_\gamma) \rangle \phi_{m}(r_\gamma) \psi_{m}^{\gamma}(r_\gamma), \]  

(21)

which for the case \( \phi = \phi \) becomes:
Fig. 1. The reactive transition probability of the reaction HF(0) + H* → H F(0) + H as a function of the total energy (in eV). * present work; A, ref. [14].

$$R^{\alpha}_{m n_0} = \langle \psi^T | \chi^{\alpha}_{m n_0} \rangle.$$  

(22)

Thus the aim is to calculate $\chi^{\alpha}_{m n_0}(R_a)$. This is done by applying eq. (3). Substituting eqs. (8), (9), (15), (19) and (21) in eq. (3), multiplying through by the corresponding $\phi_j(r_a)$ and integrating over $r_a$, one obtains the corresponding equations for $\chi^{\alpha}_{m n_0}(R_a)$, namely

$$\chi^{\alpha}_{m n_0}(R_a) = \int dr_a \phi^{\alpha}_{n_0}(r_a) V_{\alpha}(R_a, r_a)$$

$$\times \sum_j \phi_j(R_p) \int dr'_p \psi^{\alpha}_{j n_0}(R'_p) \chi^{\alpha}_{m n_0}(R'_p).$$

(23)

And

$$\chi^{\alpha}_{m n_0}(R_b) = \int dr_b \phi^{\alpha}_{m n_0}(r_b) V_{\alpha}(R_b, r_b) \psi^{\alpha}_{n_0}(R_a) \chi^{\alpha}_{m n_0}(r_a)$$

$$+ \int dr_b \phi^{\alpha}_{m n_0}(r_b) V_{\alpha}(R_b, r_b)$$

$$\times \sum_k \phi_k(r_a) \int dr'_a \phi^{\alpha}_{k n_0}(R'_a) \chi^{\alpha}_{m n_0}(R'_a).$$

Fig. 2. The reactive transition probability of the reaction HF(0) + H* → H F(0) + H as a function of the total energy (in eV). * present work; A, ref. [14].

More details of this procedure and the description of the way eqs. (23) were finally solved will be given elsewhere [13]. Once $\chi^{\alpha}_{m n_0}(R_a)$ are known, eq. (10) is applied to calculate the corresponding $R$-matrix elements. Assuming all the elements are given, the matrix $T$ is calculated from the relation

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

(24)

The entire procedure was programmed and a few preliminary results are given in section 3.

3. Results and discussion

The transition probabilities for the reactions

HF(0) + H* → H F(0) + H,
HF(0) → H F(0) + H*,
HF(0) + H* → H F(0) + H,

are presented in figs. 1, 2 and 3, respectively. The first two are exchange processes and the third is an inelastic process. The results of Schatz and Kuppermann [14] (see also ref. [15]) obtained by propagative methods are shown together with our results (full line) obtained by solving the coupled system of integral equations (23). The fit is seen to be satisfactory.

It should be emphasized that this work demonstrates for the first time that the BKL equations are capable of producing reliable results for a realistic potential. This fact is most encouraging because, in
contrast to the other available methods, no difficulties are anticipated in extending this treatment to a multi-channel system in three dimensions.

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References