Quantum mechanical calculations of collision-induced dissociation for atom–diatom reactive systems: on the scattering boundary condition

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Abstract

An approximate method of Sakimoto and Onda for deriving the S-matrix elements for dissociative collisions in collinear atom–diatom reactive systems, which provided accurate total dissociation probabilities, has been tested further. To do this, kinetic energy distributions of atomic products have been calculated and compared with results given by Kaye and Kuppermann. The method of Sakimoto and Onda always gives an artificial dip structure in the kinetic energy distributions. Further studies are required to resolve the double continuum problem in dissociative collisions.

1. Introduction

There remains a fundamental problem in the quantum mechanical study of molecular reaction dynamics at collision energies above the dissociation threshold. In collision-induced dissociation processes of atom–diatom systems,

\[ A + BC \rightarrow A + B + C, \]

we have the double continuum of product states, and it is not yet well known how the S-matrix elements are practically derived for systems in which rearrangement reaction can also occur.

As an exact quantum mechanical approach to dissociative reaction, a time-dependent wavepacket method has frequently been employed [1, 2]. Although the total dissociation probability is calculated accurately in this method, no one has argued on the derivation of the S-matrix elements. Recent progress to resolve the problem of the scattering boundary analysis was made by Manz and Römel [3] and by Kaye and Kuppermann [4, 5] using a time-independent close-coupling method associated with hyperspherical coordinates. The hyperspherical coordinates have the advantage that the reagent, rearrangement and dissociative channels are described on an equal footing. In principle, the S-matrix elements can be obtained rigorously in this coordinate system if the hyperradius \( \rho \) tends to infinity. However, it is impossible to take an infinite value for \( \rho \) in numerical calculations. If the S-matrix elements are evaluated at a finite value of \( \rho \), the resultant reaction probabilities have an oscillatory behavior as a function of \( \rho \) (spurious coupling) [6]. To avoid this problem, the asymptotic wavefunction is usually re-expanded in terms of the eigenfunctions of the isolated molecule in corresponding Jacobi coordinates [7]. Unfortunately, this method is limited only to the case that the dissociative channel is closed. In order to partly suppress the spurious coupling in the dissociative reaction, Kaye and Kuppermann [4, 5] made the re-expansion for the bound-channel component.
of the asymptotic wavefunction but not for the dissociative-channel component, which was left as expressed in hyperspherical coordinates. However, they still had to make the integration up to a large value of \( \rho \) (60–190 bohr).

Sakimoto and Onda have introduced a useful time-independent numerical approach for dissociative reaction, in which the Schrödinger equation is directly solved in hyperspherical coordinates [8]. In deriving the S-matrix elements, they have also approximately re-expanded the dissociative-channel component in terms of the eigenfunctions in Jacobi coordinates. Sakimoto and Onda [8] have carried out the calculation for a model \( \text{H}^+\text{HD} \) system which had been studied by Leforestier [2] using the time-dependent wavepacket method. They have found that in most cases the numerical propagation up to \( \rho = 15 \) bohr is sufficient to obtain the converged total dissociation probabilities, which are in good agreement with those of the time-dependent method. Although their result is encouraging, it is not evident whether their boundary analysis method is satisfactory in any case. To see this, it is desirable to discuss the partitioning of the kinetic energy among the three atoms in dissociative collisions. Until now, only Kaye and Kuppermann [5] have carried out a quantum mechanical calculation of such quantity. Therefore, it is hard to say that a sufficient number of investigations have been made on the derivation of the S-matrix elements. For these reasons, this Letter discusses the kinetic energy partitioning among atomic products in dissociative collisions for collinear atom–diatom systems in which rearrangement reaction can also occur.

2. Theory

Let us consider a collinear triatomic system \( \text{A–B–C} \) with masses \( m_A, m_B \) and \( m_C \), respectively. We use the same notation defined in Ref. [8]; i.e. \( r_\kappa \) and \( R_\kappa \) are respectively the mass-scaled internuclear distance of a diatom and the mass-scaled distance of an atom to the center of mass of the diatom, and \( \kappa = \lambda \) (or \( \nu \)) denotes the \( \text{A}+\text{BC} \) (or \( \text{AB}+\text{C} \)) channel described in Jacobi coordinates. Introducing the hyper-radius \( \rho = (R_\lambda^2 + r_\lambda^2)^{1/2} \) and the hyperangle \( \omega = \tan^{-1}(r_\lambda/R_\lambda) \), we have the time-independent Schrödinger equation in the form

\[
\frac{\partial^2 \Psi}{\partial \rho^2} + \rho^{-1} \frac{\partial \Psi}{\partial \rho} + \rho^{-2} \frac{\partial^2 \Psi}{\partial \omega^2} + \left( 2\mu/\hbar^2 \right) \left[ E - V(\rho, \omega) \right] \Psi = 0 ,
\]

where \( \mu = [m_A m_B m_C] / [m_A + m_B + m_C] \) is the characteristic mass of the system, \( V \) is the electronically adiabatic potential energy surface and \( E \) is the total energy measured from the lowest bottom of the diatomic wells. In the collinear system, \( 0 \leq \omega \leq \omega_0 = \tan^{-1}(m_C/\mu) \). We seek the wavefunction \( \Psi \) at sufficiently large distances (\( \rho \approx \rho_0 \)) in the form

\[
\Psi_\nu(\rho, \omega) = \rho^{-\kappa/2} \sum_n \chi_n(\omega, \rho) f_{\nu,n}(\rho) ,
\]

where \( \chi_n(\omega, \rho) \) is the eigenfunction of Eq. (1) in which the first term is dropped (\( \rho \) being fixed as a constant); and the index ‘\( \nu \)’ specifies independent solutions. The details of the numerical method for calculating the radial function \( f_{\nu,n}(\rho) \) are given by Sakimoto and Onda [8].

As in Ref. [8] to obtain the S-matrix elements, we put a boundary wall along the line of \( \omega = \omega_0 \) at \( \rho = \rho_0 \) and assume that a continuum state of the diatom can be approximated by a discrete state belonging to either the \( \lambda \) or \( \nu \) channel. The discrete set is produced by confining the range of diatom motion within a box \( 0 \leq r_\kappa \leq r_{\text{max}} \), where for the \( \lambda \) channel \( r_{\text{max}} = \rho_0 \sin \omega_0 \), and for the \( \nu \) channel \( r_{\text{max}} = \rho_0 \sin (\omega_0 - \omega_0) \). It is evident that the eigenfunctions of these discretized-continuum states and of the diatomic bound states form an orthogonal set. Let us denote these eigenfunctions by \( \phi^{(d)}_{\nu} (r_\kappa) \), normalized to unity. Then, the S-matrix elements \( S_{\nu,\nu'} \) may be defined in Jacobi coordinates by writing the asymptotic wavefunction in the following form:

\[
\Psi_{\nu,\nu'} = \sum_{\nu\nu'} \phi^{(d)}_{\nu}(r_\kappa) \left[ \exp( -ik_{\nu,\nu'} R_\kappa) \delta_{\nu,\nu'} \right. \\
- \exp(ik_{\nu,\nu'} R_\kappa) (k_{\nu,\nu'}/k_{\nu})^{1/2} S_{\nu,\nu'} \left. \sum_{\nu\nu'} \phi^{(d)}_{\nu}(r_\kappa) \right] \left[ \exp( -ik_{\nu,\nu'} R_\kappa) \delta_{\nu,\nu'} \right.

\[ + \sum_{\nu\nu'} \phi^{(d)}_{\nu}(r_\kappa) \left[ \exp( -ik_{\nu,\nu'} R_\kappa) \delta_{\nu,\nu'} \right.

\[ - \exp(ik_{\nu,\nu'} R_\kappa) (k_{\nu,\nu'}/k_{\nu})^{1/2} S_{\nu,\nu'} \right] ,
\]

where \( k_{\nu,\nu'} = [2\mu(E - E_{\nu,\nu'})/\hbar^2]^{1/2} \), \( E_{\nu,\nu'} \) being the eigenenergy of the bound or discretized-continuum state \( \nu_\kappa \). From Eqs. (2) and (3), we have the relation
where \( \langle \psi \rangle \) means integration over \( \omega \) and \( e^\pm_{\nu_\nu} = \exp(\pm i k_\nu R_\nu) \). We can determine the S-matrix elements from Eq. (4).

We introduce the fraction of kinetic energy, \( f = \frac{E_A}{(E - D)} \), where \( E_A \) is the final kinetic energy of an atom A in the center-of-mass system, and \( D \) is the energy of three infinitely separated atoms at rest. Kaye and Kuppermann [5] defined the differential dissociation probability for the diatom in the \( \nu_\nu \) state, which describes the kinetic energy partitioning, by

\[
\frac{dP_{\nu\nu}}{df} = \frac{dP_{\nu\nu}}{df} \frac{dP_{\nu\nu}}{d\omega},
\]

where in the limit of \( \rho \to \infty \) and \( \omega \) are related by

\[
f = \left[ \frac{m_A + m_C}{m_A + m_B + m_C} \right] \cos^2 \omega.
\]

Putting \( J^{\text{inc}} \) and \( J^{\text{diss}} \) \( \rho \) \( d\omega \) as respectively the current of the incident motion and of the dissociation into the angular range \( \omega \) to \( \omega + d\omega \), we have \( dP_{\nu\nu}/d\omega = \rho J^{\text{diss}}/J^{\text{inc}} \). The integral of Eq. (5) over all possible values of \( f \) gives the total dissociation probability for the initial state of \( \nu_\nu \). If in Eq. (3) the summation is only taken such that \( E_{\nu\nu}, E_{\nu\nu} > D \), then \( \Psi_{\nu\nu} \) represents the dissociative-channel component. Therefore, using

\[
\frac{\partial}{\partial \rho} = \cos \omega \frac{\partial}{\partial R_\nu} + \sin \omega \frac{\partial}{\partial \rho},
\]

we have as \( \rho \to \infty \)

\[
\frac{dP_{\nu\nu}}{d\omega} = \rho \cos \omega \sum_{E_{\nu\nu} > D} |\phi_{\nu\nu}^\rho S_{\nu\nu,\nu\nu}|^2 \quad \text{for} \quad 0 \leq \omega \leq \omega_b,
\]

\[
\frac{dP_{\nu\nu}}{d\omega} = \rho \cos(\omega_b - \omega) \sum_{E_{\nu\nu} > D} |\phi_{\nu\nu}^\rho S_{\nu\nu,\nu\nu}|^2 \quad \text{for} \quad \omega_b \leq \omega \leq \omega_\nu.
\]

At \( \omega = \omega_b \), the present result (8) becomes \( dP_{\nu\nu}/d\omega = 0 \) because \( \phi_{\nu\nu}^{\rho} = 0 \). This is an artifact due to the introduction of the boundary wall. It should be noted that expression (8) is not valid at \( \omega \sim \omega_b \). In the calculation, the S-matrix elements have been estimated for some values of \( \rho_0 \), and the differential probabilities have been evaluated from Eqs. (5), (6) and (8).

### 3. Results and discussion

The calculation has been made for the model \( H + H_2 \) potential energy surface of Kaye and Kuppermann [4,5], in which \( D = 0.22 \) eV, and only two bound states are supported for \( H_2 \). Since the system is symmetric, we have taken \( \omega_b = \frac{\omega_0}{2} \). Table 1 shows the calculated total dissociation probabilities as a function of \( \rho_0 \) at which the S-matrix elements are evaluated as mentioned in Section 2. Also made is comparison with the results of Kaye and Kuppermann [5]. As in Ref. [8], by the choice of \( \rho_0 \sim 20 \text{ bohr} \), the probabilities are converged within 0.01 or much better, and also agree well with those of Kaye and Kuppermann. In the calculation of Kaye and Kuppermann, they needed \( \rho_0 > 60 \text{ bohr} \) to obtain the convergence [4,5]. The above result shows that the boundary analysis method of Sakimoto and Onda

<table>
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<tr>
<th>( \rho_0 ) (bohr)</th>
<th>( E = 0.26 ) eV</th>
<th>( E = 0.30 ) eV</th>
<th>( E = 0.38 ) eV</th>
<th>( E = 0.47 ) eV</th>
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<td>( \nu_\nu = 0 )</td>
<td>( \nu_\nu = 1 )</td>
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<td>0.203</td>
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<td>0.143</td>
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* Kaye and Kuppermann [5].
Fig. 1. Differential dissociation probabilities $dP_{ij}/df$ for the model $H+H_2(v_j=0$ and 1) system as a function of the kinetic energy fraction $f$ at total energy $E=0.26$ eV. The curves are the present calculations for various choices of $\rho_0$ at which the $S$-matrix elements are evaluated. (-----) $\rho_0=10$; (-----) $\rho_0=20$; (-----) $\rho_0=30$, (-----) $\rho_0=40$; bold line: $\rho_0=50$. (O) The results of Kaye and Kuppermann [5]. The dip structure at $f\sim 0.5$ in the present results is an artifact due to the approximation in the boundary analysis.

reliable in obtaining the total probabilities.

In Figs. 1 and 2, the differential dissociation probabilities (5) are shown for the same model $H+H_2$ system at the total energies of $E=0.26$ and 0.47 eV. All the present results for the various choices of $\rho_0$ (10–50 bohr) show the qualitatively similar behavior that the differential probabilities oscillate around the two end points of $f$ ($=\frac{1}{2}$ and $\frac{3}{2}$). This oscillation reflects the behavior of the wavefunction in the regions of the diatomic wells where an effective kinetic energy is larger than that of the free motion. In the limit of $\rho_0\rightarrow\infty$, these diatomic regions are negligibly small compared with that of the dissociation plateau. The oscillation always appears in any kind of boundary analysis unless $\rho_0\rightarrow\infty$. It should be noted that ‘error bars’ in the results of Kaye and Kuppermann [5], though not shown in the present figures, are also large in the diatomic regions. (They gave the mean of the results calculated for some different integration distances $\rho=110–190$ bohr. Their ‘error bars’ indicate one standard deviation of the mean.) Also at $f\sim 0.5$, the present probabilities have an oscillation and a dip. However, they do not have a physical meaning because $f\sim 0.5$ corresponds to $\omega=\omega_0$. If we restrict the range of $f$ to $0.25<f<0.65$ and exclude the neighborhood of the unphysical dip at $f=0.5$, we see that $\rho_0\geq 30$ bohr is required to obtain the converged probabilities. This indicates that the convergence of the differential probabilities is slower than that of the total probabilities. The converged values, which are not oscillating, are close to those of Kaye and Kuppermann [5] except for the case of $E=0.47$ eV and $v_j=1$. Probably, the difference for $E=0.47$ eV and $v_j=1$ originates because the differential probabilities for this case are relatively large at $f\sim 0.5$ in the calculation of Kaye and Kuppermann while the pres-
The total dissociation probabilities for the model H+HD($v_l$) system at total energies of $E=1.78$ and 1.85 eV as a function of $\rho_0$ or $\omega_b$

<table>
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<td>0.0229</td>
<td>0.0007</td>
<td>0.0243</td>
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<tr>
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<td>0.0248</td>
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<td>0.0255</td>
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<table>
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<th>$\rho_0 = 20$ bohr</th>
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<tbody>
<tr>
<td>$E=1.78$</td>
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<td>0.2852</td>
<td>0.0291</td>
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<td>$E=1.85$</td>
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Fig. 3. Differential dissociation probabilities $dP_{\nu l}/df$ for the model H+HD($v_l=6$) system as a function of the kinetic energy fraction $f$ at total energies $E=1.78$ and $E=1.85$ eV. The curves are the calculations for various choices of $\rho_0$ at which the $S$-matrix elements are evaluated. $\omega_b$ is taken to be 0.5120 rad. The dip structure at $f-f_b$ is an artifact due to the approximation in the boundary analysis. ($\cdots$) $\rho_0 = 20$; ($\cdot\cdot\cdot$) $\rho_0 = 30$; ($\cdot\cdot\cdot\cdot$) $\rho_0 = 40$; bold line: $\rho_0 = 50$. 

Further calculation has been made on the model H+HD system of Leforestier [2]; $D=1.77$ eV, and $H_2$ and HD have respectively six and seven bound states. The choice for $\omega_b$ is not unique in this asymmetric system. In Ref. [8], $\omega_b=0.5120$ rad was taken. It was found in Ref. [8] that the total dissociation probability for HD in the highest vibrational state ($v_l=6$) might not be converged so well with respect to $\rho_0$ at energies near the dissociation threshold. Since only the range of $\rho_0<20$ bohr was considered in Ref. [8], here the calculation has been extended beyond $\rho_0 \geq 20$. Table 2 shows the $\rho_0$ dependence of the dissociation probabilities for $v_l=4-6$ at $E=1.78$ and 1.85 eV. The convergence is slow for the dissociation from $v_l=6$ at $E=1.78$ eV (just above the dissociation threshold). However, when the energy becomes slightly higher ($E=1.85$ eV), $\rho_0=20$ bohr gives a satisfactory result. Therefore, the convergence is poor only in a narrow range of energies just above the dissociation threshold. If the calculated probability is sensitively dependent on the choice of $\omega_b$, the present boundary analysis is meaningless. Table 2 also shows the dissociation probabilities for other choices of $\omega_b=0.4$ and 0.6 rad ($\rho_0=40$ bohr). We see that the $\omega_b$ dependence is reasonably small in the range of $\omega_b=0.4-0.6$ rad.

Fig. 3 shows the differential probabilities for $v_l=6$. At $E=1.78$ eV, the convergence is poor. At $E=1.85$ eV, however, $\rho_0 \geq 30$ is sufficient to obtain the convergence in some part as seen in Figs. 1 and 2. 

The agreement of the total probability between the two methods is also good for $E=0.47$ eV and $v_l=1$ (Table 1).
results for different choices of $\omega_b$ are shown in Fig. 4, where $p_0$ is taken to be 40 bohr. The unphysical dip region is large at $E=1.78$ eV. As suggested in Ref. [8], it is probable that the dissociative-channel component of the wavefunction has a large amplitude along a potential ridge line for $E=1.78$ eV and $v_n=6$. In such a case, the present boundary analysis may be no more reliable. At higher energies ($E=1.85$ eV), the values converged with respect to $p_0$ almost coincide with each other for the different choices of $\omega_b$.

In conclusion, the scattering boundary analysis of Sakimoto and Onda [8] is promising for the calculation of the total dissociation probability because of the good convergence with respect to $p_0$. The present differential dissociation probabilities are almost in agreement with those of Kaye and Kuppermann [5] if we exclude the region of the unphysical dip. However, it is a defect of the method of Sakimoto and Onda that we cannot discuss the differential probabilities around $f=f_0$ corresponding to $\omega=\omega_b$. The boundary analysis method of Kaye and Kuppermann [4,5] gives one possibility of deriving totally accurate differential probabilities. However, their results actually have a $p_0$-dependent structure of oscillation over all the range of $f$ [5], and hence we must probably continue the integration beyond $p_0>200$ bohr in their method. In any case, the problem of the scattering boundary analysis is still unresolved. Since a deep understanding of the dissociation mechanism comes from investigation of the kinetic energy partitioning, it is highly desirable to develop an accurate and practical way to derive the $S$-matrix elements.

Acknowledgement

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References