Arrangement Channel Approach to Reactive Systems: Accurate Three-Dimensional Probabilities for the \( \text{H} + \text{H}_2 \) System

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In this work are reported the first accurate three-dimensional, three-channel reactive probabilities obtained from the arrangement channel approach due to Baer, Kouri, Levin, and Tobocman. The calculations were carried out for \( \text{H} + \text{H}_2 \) (J = 0), and the results were found to compare reasonably well with those due to other approaches.

We report here on the first successful three-dimensional reactive quantum-mechanical calculations employing the Baer-Kouri-Levin-Tobocman equations.\(^1\)\(^\text{-}\)\(^3\) This set of equations consists of three coupled Lippmann-Schwinger equations—one for each arrangement. The coupling of these equations is done via a matrix \( \mathbf{W} \) which fulfills for each arrangement channel number \( \lambda \) the condition

\[
\sum_{\lambda'} W_{\lambda \lambda'} = 1 \quad (1)
\]

but is otherwise not restricted. Various choices were tried, in all of which the \( \mathbf{W} \) elements were assumed to be constant.\(^4\)\(^\text{-}\)\(^5\) One of the most favored schemes was the channel permitting choice,\(^5\) namely

\[
W_{\lambda \lambda'} = \delta_{\lambda, \lambda + 1} \quad (2)
\]

Whereas this choice was found to be most efficient for the two-channel case, it failed entirely when applied to a three-channel case.\(^5\) Recently, the present author, together with Shima,\(^6\) suggested a new choice for the \( \mathbf{W} \) matrix elements. They assumed that the relevant elements depend on the characteristic channel angular coordinate \( \gamma \) (see Figure 1). Thus, the matrix elements which couple the channel \( \lambda \) to the other channels \((\lambda', \nu, \kappa)\), i.e., \( W_{\lambda \lambda'}, W_{\lambda \nu}, W_{\lambda \kappa} \), will depend on \( \gamma \) defined as \( \gamma_{\lambda} = \cos^{-1}(R_{\lambda} F_{\lambda}) \), those responsible for the coupling of the \( \nu \) channel to the other channels will depend on \( \gamma \) defined as \( \gamma_{\nu} = \cos^{-1}(R_{\nu} F_{\nu}) \), and the same will apply for the \( \kappa \) channel. The calculations were done by assuming the various matrix elements to be step functions with respect to the corresponding \( \gamma \) angle. Thus, for instance, \( W_{\lambda \lambda'} \) \((\lambda' = \nu, \kappa, \lambda)\) were assumed to be of the form

\[
W_{\lambda \nu}(\gamma_{\lambda}) = \begin{cases} 1; & 0 \leq \gamma_{\lambda} \leq \pi/2 - \gamma_{\lambda 0} \\ 0; & \text{otherwise} \end{cases} \quad (3a)
\]

\[
W_{\lambda \kappa}(\gamma_{\lambda}) = \begin{cases} 1; & \pi/2 + \gamma_{\lambda 0} \leq \gamma_{\lambda} \leq \pi \\ 0; & \text{otherwise} \end{cases} \quad (3b)
\]

\[
W_{\lambda \lambda'}(\gamma_{\lambda}) = \begin{cases} 1; & \pi/2 - \gamma_{\lambda 0} \leq \gamma_{\lambda} \leq \pi/2 + \gamma_{\lambda 0} \\ 2; & \text{otherwise} \end{cases} \quad (3c)
\]

where \( \gamma_{\lambda 0} \) is some given fixed value. It should be emphasized that this choice of \( W \)'s not only satisfies eq 1 but also leads to a connected kernel integral equation. A discussion of this subject will be given elsewhere.\(^7\) To solve the resulting set of integral equations, we employed a method developed by Shima and Baer.\(^8\)

\[\text{TABLE I: Three-Dimensional Probabilities for the Reaction } \text{H} + \text{H}_2 \left( \nu = 0, j_J = 0 \right) \rightarrow \text{H}_2 \left( \nu = 0, j_J = 0 \right) + \text{H} \]

<table>
<thead>
<tr>
<th>\text{total energy, eV}</th>
<th>0 \rightarrow 0</th>
<th>0 \rightarrow 1</th>
<th>0 \rightarrow 2</th>
<th>0 \rightarrow 3</th>
<th>0 \rightarrow 4</th>
<th>\text{total}</th>
</tr>
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<tbody>
<tr>
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<td>0.037</td>
<td>0.061</td>
<td>0.029</td>
<td>0.14</td>
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<td></td>
</tr>
<tr>
<td>0.67</td>
<td>0.061</td>
<td>0.105</td>
<td>0.055</td>
<td>0.23</td>
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<td></td>
</tr>
<tr>
<td>0.7</td>
<td>0.044</td>
<td>0.074</td>
<td>0.055</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.049</td>
<td>0.093</td>
<td>0.065</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>0.066</td>
<td>0.118</td>
<td>0.049</td>
<td>0.29</td>
<td></td>
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</tr>
<tr>
<td>0.977</td>
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<tr>
<td>1.00</td>
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<td>0.085</td>
<td>0.032</td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td>0.070</td>
<td>0.110</td>
<td>0.047</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[\text{TABLE II: Three-Dimensional Probabilities for the Reaction } \text{H} + \text{H}_2 \left( \nu = 0, j_J = 0 \right) \rightarrow \text{H}_2 \left( \nu = 0, j_J = 0 \right) + \text{H} \text{ Calculated for } E = 0.9 \text{ eV and Different Values of } \gamma_{\lambda} \text{ (See Eq 3)} \]

<table>
<thead>
<tr>
<th>\text{cos } \gamma_{\lambda}</th>
<th>0 \rightarrow 0</th>
<th>0 \rightarrow 1</th>
<th>0 \rightarrow 2</th>
<th>0 \rightarrow 3</th>
<th>0 \rightarrow 4</th>
<th>\text{total}</th>
</tr>
</thead>
<tbody>
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<td>0.009</td>
<td>0.026</td>
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<tr>
<td>0.31</td>
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<td>0.108</td>
<td>0.049</td>
<td>0.011</td>
<td>0.017</td>
<td>0.276</td>
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<tr>
<td>0.454</td>
<td>0.066</td>
<td>0.118</td>
<td>0.049</td>
<td>0.016</td>
<td>0.019</td>
<td>0.290</td>
</tr>
<tr>
<td>0.588</td>
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<td>0.120</td>
<td>0.059</td>
<td>0.023</td>
<td>0.019</td>
<td>0.303</td>
</tr>
<tr>
<td>0.81</td>
<td>0.067</td>
<td>0.125</td>
<td>0.063</td>
<td>0.022</td>
<td>0.017</td>
<td>0.306</td>
</tr>
</tbody>
</table>

which is based on expanding the various amplitude density functions\(^9\) in a given complete basis set. (This method was recently successfully employed also in solving another set of reactive integral equations.\(^8\)) As a result, the coupled system of integral equations is transformed into a system of algebraic equations. The number of equations, \( N \), is (in a three-channel case)

\[
N = \sum_{\lambda} N_{\nu,\lambda} N_{\kappa,\lambda} \quad (4)
\]

where \( N_{\nu,\lambda} \) is the number of basis set functions used for expanding the amplitude density functions in channel \( \lambda' \) and \( N_{\kappa,\lambda} \) is the number of the corresponding asymptotic internal eigenfunctions.

In this Letter are reported reactive probabilities for the \( \text{H} + \text{H}_2 \) system as obtained for the Porter-Karplus potential energy surface\(^10\) assuming \( J = 0 \). The results are shown in Table I, where they are compared with those of Kuppermann and Hipes\(^12\) for the state-to-state transitions and with those of Walker et al.\(^13\) for

(6) Shima, Y.; Baer, M., unpublished results.
(8) Neuhauer, D.; Baer, M., to be published.
Thermal Decomposition of Methanol in the Sonolysis of Methanol-Water Mixtures. 
Spin-Trapping Evidence for Isotope Exchange Reactions

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The spin trap 3,5-dibromo-4-nitrosobenzensulfonate was used to monitor the yield of free radicals produced during sonolysis of water-methanol mixtures. Methyl radicals and CH$_3$OH radicals were observed as well as the isotopically mixed radicals CD$_3$D and CHD$_2$ when CH$_3$OD:CD$_2$O mixtures were studied. The results clearly show that thermal decomposition of methanol to methyl radicals occurs in the gas phase. The methyl radical yield rises sharply at very low concentrations of methanol, reaches a maximum at 5 mol dm$^{-3}$ in water and decreases to a smaller value in methanol. The yield of methyl radicals as a function of methanol concentration is discussed in terms of the different factors influencing the sonochemistry.

The second region of interest is the interface between the hot bubbles and the bulk solvent. In this region, H and OH radicals can be scavenged by radical scavengers with an efficiency which is not predominantly determined by the specific rate constants known from radiation chemistry but by other factors as well.

Introduction

Numerous contributions to the study of the chemical effects of ultrasound in aqueous solutions have been made by Henglein, Hart, and their co-workers. The observed results have been explained in terms of reactions taking place in three different regions. One is the hot bubble created during cavitation (i.e., creation, growth, and collapse of gas bubbles in solution by the acoustic field); in that region typical combustion reactions take place since the bubble implosion generates high local temperatures (several thousand degrees kelvin) and high pressures (hundreds of atmospheres). A typical gas reaction is the isotopic exchange between deuterium and water vapor occurring during the sonolysis of water in the presence of deuterium.

The results change to some extent, and the question is which value should one take? Before answering this question, let us explain the physical meaning of the two extreme choices, i.e. $\gamma_0 = 0$, $\pi/2$. (For reasons of convenience we dropped the index $\lambda$.) Assuming $\gamma_0 = 0$ leads to the decoupling of the various arrangement channel equations. Consequently, in order to obtain the correct answer, one has to include continuum states in the expansions of the Green functions. Since the main advantage of the BKLT approach is to avoid the continuum, this choice should be excluded. The other extreme case, namely $\gamma_0 = \pi/2$, decouples each channel from itself which implies that the Green functions contain “most” of the information concerning the inelastic (nonreactive) process. In the present treatment of the H + H$_2$ system the Green functions contained only the elastic part and therefore the choice of $\gamma_0 = \pi/2$ is probably not good enough. On the basis of what has been said so far, it is my belief that the better one solves the inelastic part of the problem, the weaker will be the dependence on $\gamma_0$. As for our particular case it is not obvious which is the best choice of $\gamma_0$. I chose an intermediate value for $\cos \gamma_0$ which is close to 0.5, and the results in Table I were calculated for this value. I hope that in the future we will be able to say more about this problem.

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