Theoretical study of bimolecular collinear reactions using variational $R$ matrix formalism and $p$-version of the finite element method: Application to $H + HD$ reaction

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The study of scattering processes is fundamental to the understanding of several phenomena such as the atmospheric chemistry and the process of combustion. The aim of the paper is to show a computational numerical procedure based on the variational $R$ matrix formalism and the finite element method to study bimolecular reactions. In particular, we analyze the collinear $H + HD$ reactive process and compare the present results with previous ones published in the literature.

Keywords: Scattering theory; atmospheric chemistry; numerical simulation.

El estudio de procesos de colisiones es fundamental para la comprensión de innumerables fenómenos, como la química de la atmósfera y procesos de combustión. El objetivo de este trabajo es enseñar un procedimiento numérico basado en el formalismo variacional de la matriz $R$ y en el método del elemento finito, y su aplicación al estudio de reacciones bimoleculares. En especial, analizamos el proceso de reacción colineal $H + HD$ y comparamos nuestros resultados con otros anteriormente publicados en la literatura.

Descriptores: Dispersión; química de la atmósfera; simulación numérica.

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1. Introduction

The theoretical study of scattering processes in the gas phase is fundamental to the understanding of a huge range of physical phenomena that comprise since the atmospheric chemistry and the process of combustion chemistry, which have important implications for the environment, even phenomena of astrophysical interest that occur in stellar means. Examples of scattering processes are the collision atom-diatom and rovibrational excitation of a molecule through the collision with a particle. Another rather complicated case is of bimolecular reactions. Such reactions have been subject of several theoretical studies over the years, because, in addition to being important in various physical and chemical processes, many quantum effects have been found in cases of collisions at low energies [1].

In this work we have studied the collinear reactive process $H + HD$ which is one of the benchmark of collinear reactions. We use the $R$ matrix variational formalism and the finite element method (FEM) to solve the multidimensional Schrödinger equation. The $R$ matrix is a quantity that relates the wavefunction with its normal derivative on an asymptotic boundary surface. It is real and symmetric so that guarantees the unitarity of the scattering $S$ matrix [2,3]. The FEM is a general nomenclature for a set of procedures which divide the space into elements and expand the wavefunction in basis functions defined on each of these elements [4]. In particular, we utilize the $p$-version of the finite element method (p-FEM) which presents as advantage to make possible the development of an efficient algorithm to invert matrices. This is important for the study of scattering processes because it reduces significantly the computational time in $R$ matrix calculation. Then, we compare our results with those previously published in the literature.

2. Theory

We consider an atom-diatom scattering process where the atoms are maintained in a collinear orientation. Thus, we confine our attention on chemical processes of the type $A + BC(\nu_I) \rightarrow \{ A + BC(\nu_F) \ (Elastic \ / \ Inelastic) \ AB(\nu_F) + C \ (Reactive) \}$ with

$$\hat{H} = -\frac{\hbar^2}{2M_A} \frac{\partial^2}{\partial x_A^2} - \frac{\hbar^2}{2M_B} \frac{\partial^2}{\partial x_B^2} - \frac{\hbar^2}{2M_C} \frac{\partial^2}{\partial x_C^2} + V(x_A, x_B, x_C),$$

where $V(x_A, x_B, x_C)$ is the potential energy surface (PES) in a specific electronic state. Particularly, we study the bimolecular reaction $H + HD \rightarrow H_2 + D$.

![Figure 1. Coordinates of Jacobi for collinear triatomic system.](image)
2.1. System of coordinates

A review about various coordinate sets of triatomic molecular systems can be in Ref. 5. Here we start rewriting the Schrödinger equation, using the different sets of Jacobi coordinates (Fig. 1) which lead to Jacobi coordinates weighted by the mass \( R_{\lambda} \), and is convenient to express asymptotic conditions \( (R_{\lambda} \rightarrow \infty) \), however is disadvantageous in the description of the region of strong interaction. In this region we use the hyperspherical coordinate system which is defined as a hyperradius and a hyperangle:

\[
\begin{align*}
\rho &= (R_a^2 + R_a^2)^{\frac{1}{2}} = (R_\beta^2 + R_\beta^2)^{\frac{1}{2}} \quad 0 \leq \rho < \infty \\
\theta &= \arctg \frac{R_a}{R_\alpha} = \arctg \frac{R_\beta}{R_\beta} - \omega_{\alpha\beta} \quad 0 \leq \theta \leq \theta_{max},
\end{align*}
\]

where

\[
\omega_{\alpha\beta} = \omega_{\alpha\beta} = \arctg \left( \frac{M_A M_C}{M_B M} \right)^{\frac{1}{2}}
\]

and

\[
\theta_{max} = \arctg \left( \frac{M_B M}{M_A M_C} \right)^{\frac{1}{2}}.
\]

The hamiltonian in hyperspherical coordinates is independent of the arrangement set by the coordinates of Jacobi:

\[
\hat{H} = -\frac{h^2}{2\mu} \left[ \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \theta^2} \right] + V(\rho, \theta),
\]

where \( \mu = (M_A M_B M_C / M)^{\frac{1}{2}} \).

2.2. Variational formulation of the R matrix

The formulation of the problem in the hyperspherical coordinate system permits any calculations in two separate steps [6]. First we diagonalize a matrix in order to find the eigenvalues \( \varepsilon(\rho) \) and eigenfunctions \( g_j(\theta, \rho) \) of hyperangular equation for each value of hyperradius:

\[
\left[ -\frac{h^2}{2\mu} \left( \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \theta^2} \right) + V(\rho, \theta) \right] g(\theta, \rho) = \varepsilon(\rho) g(\theta, \rho).
\]

For that we use a p-FEM with a non-uniform mesh [8]. Second we assume that the wavefunction can be written as

\[
\Psi(\rho, \theta) = \rho^{-\frac{1}{2}} \sum_{j=1}^{n} h_j(\rho) g_j(\theta, \rho)
\]

that reduces the dimension of problem by treating of the hyperradius as an adiabatic variable. Then we get the \( R \) matrix into hyperspherical coordinates which relate the hyperradial functions and its derivatives:

\[
R^h = \frac{h^2}{2\mu} F(\rho_{max}) \frac{1}{H - EO} F^\dagger(\rho_{max}),
\]

where \( F \) depends on hyperradial basis functions and \( H \) and \( O \) are the hamiltonian and overlap matrices respectively (see Ref. 7). To do this, we use a p-FEM with equidistant discretization of the mesh and use the procedure of inversion by block [9].

2.3. Hyperspherical projection

In Jacobi coordinates weighted by the mass, the asymptotic vibrational states are obtained taking the limit \( R_{\lambda} \rightarrow R_{\lambda}^\infty \) but in hyperspherical coordinates, asymptotic vibrational states can only be calculated taking the limit \( \rho \rightarrow \rho_{max} \). Consequently it is necessary to make a projection of the wavefunction defined in a hypersphere in one defined in a suitable surface of Jacobi requiring that [10]

\[
\sum_i U_i(r_{\lambda}) u_i(R_{\lambda}^\infty) = \sum_j \rho^{-\frac{1}{2}} g_j(\theta, \rho) h_j(\rho).
\]

Thus, it is obtained the \( R^J \) matrix that relate the functions \( u_i(R_{\lambda}^\infty) \) and its derivatives from the \( R^h \) matrix. The \( S \) scattering matrix is found employing the formula:

\[
S = [(1 - i\mathbf{R})M^*]^{-1}(1 + i\mathbf{R})M,
\]

where \( M \) is called the momentum matrix and the elements of the \( R \) matrix are

\[
\{R\}_{ij} = \sqrt{k_i k_j} \{R^J\}_{ij}.
\]

2.4. The p-FEM

In the unidimensional p-FEM [8,11,12] we divide the range of integration \([a, b]\) in \( Ne \) elements and the \( i\)-th element is defined in the period \( q\_{i-1} \) up to \( q_i \) with \( q_0 = a \) and \( q_{Ne} = b \). Thus the wavefunction is expanded in the basic set \( \{f_j(q)\} \) as follows:

\[
\Psi(q) = \sum_{i=1}^{Ne} k_i \sum_{j=0}^{i} c_j f_j(q)
\]

where

\[
f_j(q) = 0 \quad \text{if} \quad q \notin [q\_{i-1}, q_i].
\]

Employing the p-FEM, the matricial representation of an operator \( \hat{P} \) is sparse and structured in blocks:

\[
B = \begin{bmatrix} B_1 \cdots b_1 \cdots 0 \cdots 0 & & & \\
(b_1^\dagger) & B_2 \cdots b_2 \cdots 0 & & \\
0 & (b_2^\dagger) & B_3 \cdots b_3 \cdots & \\
& \ddots & \ddots & \ddots & \ddots \\
& & b_{Ne} \cdots \cdots B_{Ne} \cdots 0 & & \\
0 & & \cdots & (b_{Ne}^\dagger) & 0 \\
& & \cdots & & (b_{Ne+1}^\dagger)
\end{bmatrix}
\]

\[
B_{jj'} = \int dq f_j^\dagger(q) \hat{P} f_{j'}(q)
\]

The consequences are that we can develop an algorithm for obtain only the last block of the inverse of $B$ reducing the computational time in obtaining the $R$ matrix, and the procedure uses in reversing only the blocks non null of the matrix $B$ reducing the memory required to store the matrix on the computer [9].

<table>
<thead>
<tr>
<th>Transition</th>
<th>Leforestier</th>
<th>Sakimoto and Onda</th>
<th>p-FEM</th>
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<tr>
<td>Inelastic</td>
<td>0 → 0</td>
<td>0.889</td>
<td>0.8924</td>
</tr>
<tr>
<td></td>
<td>0 → 3</td>
<td>0.0004</td>
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<tr>
<td></td>
<td>0 → all</td>
<td>0.993</td>
<td>0.9975</td>
</tr>
<tr>
<td>Reactive</td>
<td>0 → 1</td>
<td>0.0011</td>
<td>0.0012</td>
</tr>
<tr>
<td></td>
<td>0 → 3</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td></td>
<td>0 → all</td>
<td>0.0023</td>
<td>0.0026</td>
</tr>
</tbody>
</table>

3. Results

In order to compare our results with other previously published, we model the system using the known semi-empirical London-Eyring-Polanyi-Sato (LEPS) surface with modified parameters by Leforestier [13]. In Fig. 2 hyperangular is shown the form of potential for two hyperradius values. It can note that the potential gradually varies from a simple minimum in the region of interaction for a double well in the asymptotic region. Examples of angular eigenfunctions are also drawn on the same figures. Note that when $\rho$ grows up the solutions associated with the bounded states of diatomic molecules start to be located in regions around $\theta \approx 0$ or $\theta_{\text{max}}$.

To check the accuracy of our methodology, in Table I is shown some reactive and inelastic probability of transition in the state to state level with entry channel $H + HD$ into a energy of 1.4 eV, and compared with those obtained by Sakimoto and Onda [14], who developed a time independent method using hyperspherical coordinates and the discrete variable representation. It also are shown in the table other results taken from the same article, however, calculated by Leforestier [13] that used a method of time dependent wave package. Note a good agreement of our results with those of two other methods, which indicates the viability of our methodology.

Finally, in Fig. 3 we show the reactive probabilities of transition, with entry channel $H + HD$, in the vibrational state $\nu_I = 0$ for $\nu_F = 0$, as a function of total energy, $E$, which varies in an extension of 0.2 up to 1.77 eV.

4. Conclusion

In this paper we have studied the collinear reactive process $H + HD$. We calculated the reactive and inelastic probability of transition in the state to state level of the reaction at
issue by describing the molecular system in hyperspherical coordinates and expanding the wavefunction in terms of basis functions which are eigenfunctions of hyperangular part more the potential of interaction for a fixed hyperradius thus it was treated as an adiabatic variable. We used the $R$ matrix variational formalism and the p-version of finite element method (p-FEM) to solve the Schrödinger equation. We accentuate that the p-FEM can be applied to a variety of systems without the need of new trial basis functions. Also we verified that our methodology lets to get all probabilities of transition reactive and inelastic, given the total energy. Besides it lets to develop an algorithm to obtain reversal of matrices which reduces significantly the computational time for calculate the $R$ matrix. One advantageous feature of the $R$ matrix formalism is that the matrices just need to be constructed once and saved in memory of the computer and then they can be used to calculate the information of scattering in various energies. As perspective we want to extend the procedure developed for the study of full-dimensional atom-diatom biomolecular reactions.

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6. Here we give a brief description of the formalism. The complete formalism will be described in Ref. 7.
7. M.N. Guimarães and F.V. Prudente, *to be published*