Time dependent wave packet study of the electronically non-adiabatic Cl + H₂ reaction using a one-dimensional model

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We report a time dependent wave packet calculation of the electronically non-adiabatic Cl + H₂ reaction using a one-dimensional diabatic potential model. The funnel resonances are characterized for a large range of the energy, and the results compared with recent time independent calculations using the same model.

Introduction

Non-adiabatic effects are known to play a fundamental role in the dynamics of many chemical processes, e.g., photodissociation, predissociation, electronic quenching, charge transfer, and spin-changing reactions (see refs. 1–4 and references therein). Moreover, quantum mechanical resonances can appear in both full and half-scattering processes involving more than one electronic state.5,6 Thus, the analysis and characterization of such quasi-bound states (that clearly arise in the pattern of cross sections) becomes crucial to understand the relevant dynamics of the particular system. Due to the unequivocal quantum nature of these phenomena, it is of major importance the development of efficient numerical procedures based on quantum mechanics to treat systems where two or more (diabatic or adiabatic) potential energy surfaces are involved.

A reliable and efficient method which has been used for treating molecular collision processes within the Born–Oppenheimer or adiabatic framework is the time dependent wave packet propagation (see ref. 7 and references therein). This methodology presents several advantages over the time independent quantum calculations using either diabatic and adiabatic representations.8 Moreover, the time dependent wave packet technique allows a straightforward treatment of collision-induced dissociation.9 However, a detailed analysis of resonances due to the non-adiabatic coupling (e.g., calculation of energies and widths of such resonance states) is not very common in time dependent wave packet studies,10 although their effects have been observed in many of such investigations.11–16 An explanation for this is that in the presence of long-lived resonance states such a method needs, in principle, longer propagation times.

On the other hand, the determination of resonance states in adiabatic processes by using time dependent wave packet methods have been studied by several authors (see, e.g., refs. 17–24). In general, several methods have been proposed to avoid a long propagation time. Examples are the Prony method25 as used by Gray18 and the hybrid approach which uses the filter diagonalization method for the calculation of resonances.21,23,26 In these procedures, the initial wave packet is propagated up to some time at which direct scattering is complete, and then the resonance calculation is performed to extrapolate long-time behavior of the wave packet or its correlation function. They are particularly interesting to treat larger systems for which long propagation times become out of reach from a computational point of view. However, it is important to point out that the time dependent calculations by using long time propagation are of interest when it is possible to be done,12 because they can provide the “exact” time dependent results in a numerical sense.

The major goal of this paper stems on showing the capacity of a wave packet procedure to obtain detailed and accurate information about narrow resonances from the scattering information by using a long-time propagation. In particular, this study presents the first detailed comparison between time dependent and time independent quantum calculations of the resonances arising in the non-adiabatic dynamics of the Cl + H₂ reaction, which plays a very important role in atmospheric chemistry. Because of this, the title system has been extensively studied both experimentally and theoretically (see, e.g., ref. 28 and references therein). In order to compare our results with those by Friedman et al.29,30 obtained within the time independent framework, we have used the same one-dimensional diabatic two-state potential model for Cl + H₂. Indeed, the model has been shown to have several isolated narrow resonances associated with states trapped in the upper adiabatic potential curve.29,30 In turn, we characterize 24 of such resonances by calculating the corresponding energies and widths, and also present accurate results for transition probabilities, delay time matrix elements, and lifetime matrix as a function of the energy.

The paper is organized as follows. In the next section we briefly describe the time dependent wave packet methodology employed here to study the resonance states (eigenenergies and widths), and other typical scattering results. In section 3, we give the details of the wave-packet propagations, and present the results as well as a comparison with time-independent calculations. Conclusions are gathered in section 4.

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2. Methodology

The dynamics of the title system has been studied by using the one-dimensional time dependent Schrödinger equation in a diabatic representation, i.e.,

$$\frac{i\hbar}{\partial_t} \Psi = -\frac{\hbar^2}{2\mu} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi$$

(1)

where $V$ is the $2 \times 2$ diabatic potential energy matrix given by

$$V = \begin{pmatrix} V_{11} & V_{12} \\ V_{12} & V_{22} \end{pmatrix}$$

(2)

$\mu$ is the reduced mass of the 35Cl + H$_2$ system, and $\Psi$ is the diabatic wave function vector given by

$$\Psi = \begin{pmatrix} \psi_1(x; t) \\ \psi_2(x; t) \end{pmatrix}$$

(3)

The solution of eqn. (1) can be written formally as

$$\Psi(x; t) = \exp \left(-\frac{i}{\hbar} H \right) \Psi(x; 0)$$

(4)

where $H$ is the 1D two-state diabatic Hamiltonian operator as given in eqn. (1) and $\Psi(x; 0)$ is the initial wave packet vector, which has been represented on a equally spaced grid in coordinate space. The fast Fourier transform algorithm 31,32 has been used to evaluate the action of the kinetic energy operator on the wave functions $\psi_1$ and $\psi_2$, while the short-time iterative Lanczos method 33,34 has been applied to propagate the initial wave packet vector $\Psi(x; 0)$ over the two coupled potential energy curves. The two components of the initial wave packet vector are composed by a generalized Gaussian function with the form

$$\psi_{1,2}(x; 0) = \frac{1}{2\sigma^2} \exp \left[-\left(x - x_0\right)^2 \sigma^2 \right] \times \exp \left[\beta \left(x - x_0\right) \right]$$

(5)

and $\psi_{2,1}(x; 0) = 0$, depending whether the wave packet is propagated initially from the right to the left as shown in Fig. 1 or vice-versa. The usual Gaussian parameters $\sigma$, $\beta = 1/(4\sigma^2)$, $p_0$, and $x_0$ are assigned prior to calculation. The parameters $x_0$ and $p_0$ represent the initial wave packet position and initial wave packet momentum, respectively.

Since the diabatic wave function is expected to be trapped in the V$_{11}$ funnel during a long time, we have then multiplied the wave packet vector by a damping function35

$$F(x) = \sin \left[\frac{\pi}{2} \frac{X_{\text{mask}} + \Delta X_{\text{mask}} - x}{\Delta X_{\text{mask}}} \right], \quad x \geq X_{\text{mask}}$$

(6)

at each time step to absorb its scattered parts before it reaches the boundaries of the grid resulting in a sin$^2$ damping. In eqn. (6), $X_{\text{mask}}$ represents the point at which the masking function is initiated and $\Delta X_{\text{mask}} = X_{\text{mask}} - x_0$ is the width over which the function decays. This method of damping is equivalent to add a negative imaginary potential (NIP) to the real potential.17,36

Particularly for systems with many isolated and narrow resonances, its use seems to be more appropriate35 than the NIP method.

In the energy range of interest only two asymptotic channels are open: (i) propagation of $\psi_1$ to $x \rightarrow +\infty$ over V$_{11}$, and (ii) propagation of $\psi_2$ to $x \rightarrow -\infty$ over V$_{22}$. Thus, the scattering matrix (S-matrix) is a $2 \times 2$ symmetric, unitary matrix whose diagonal elements (S$_{11}$ and S$_{22}$) correspond to reflection amplitudes while the off-diagonal S$_{12}$ and S$_{21}$ are the transmission ones. The elements $S_{nm}$ (m, n = 1, 2) may be calculated as

$$S_{nm}(E) = \frac{\sqrt{\langle k_m | r | k_n \rangle}}{2\pi i \mu \rho(k_n)} \int \psi_n(x_n; t) \exp \left(\frac{iEt}{\hbar} \right) \, dt$$

(7)

where $E$ is the total energy of the system, $k_1 = -\sqrt{2\mu [E - V_{11}(x_1)]}$, $k_2 = \sqrt{2\mu [E - V_{22}(x_2)]}$, the function $g$ is the Fourier transform of the non-zero initial wave packet component $\psi_{1,2}(x, 0)$ which is given by

$$g(k) = \frac{\sqrt{2\sigma}}{2\pi \rho(k)} \exp \left[-\sigma^2 (k - p_0)^2 \right] \exp(-ikx_0)$$

(8)

and $x_1$ [$x_2$] is some fixed asymptotically large distance at channel 1 [2].

Finally, the resonances may be characterized by the lifetime matrix $Q$ and the delay-time matrix $\Delta t$, whose elements are given through the expressions:$^{37,38}$

$$Q_{mn} = \frac{\hbar}{2} \sum_{j=1}^{2} S_{nj}^{*} dS_{mj}/dE$$

(9)

$$\Delta t_{mn} = \text{Im}[\hbar (S_{mn})^{\ast} dS_{mn}/dE] \quad (m, n = 1, 2)$$

(10)

where $S_{mn}^{*}$ denotes the complex conjugate of the scattering matrix element $S_{mn}$. In addition, it is important to point out that, close to each resonance $\omega$, the largest eigenvalue of the $Q$ matrix, $q_{1,1}$, which represents the longest lifetime of the incident particle,37,38 has a Lorentzian form given by 39

![Fig. 1](image)

*Fig. 1* One-dimensional diabatic potential model for the Cl+H$_2$ reaction: (a) $V_{11}$ (full line) and $V_{22}$ (dashed line) potential energy curves; (b) $V_{12}$ coupling function. See ref. 29 for details.

### Table 1

<table>
<thead>
<tr>
<th>$\omega$</th>
<th>$E_{\text{max}}/E_{\text{h}}$</th>
<th>$\text{Tr}(Q)/\text{fs}$</th>
<th>$q_{1,1}/\text{fs}$</th>
<th>$q_{2,2}/\text{fs}$</th>
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<td>835.51</td>
<td>835.13</td>
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</table>

\[ q_{zz}(E) = \frac{\Gamma_z}{[(E - E_z)^2 + (\Gamma_z/2)^2]} \]  

(11)

where \( E_z \) and \( \Gamma_z \) are, respectively, the energy and width of resonance \( z \). Once the \( Q \) matrix is calculated by eqn. (9), it is possible to obtain \( E_z \) and \( \Gamma_z \) through a least-squares fit using eqn. (11).

3. Results and comparison

We have carried out a detailed study of the electronically nonadiabatic \( \text{Cl} + \text{H}_2 \) reaction on a one-dimensional model by solving the time dependent Schrödinger equation in a diabatic representation [eqn. (1)]. In turn, we have calculated the \( S \)-matrix, transition probabilities, delay-time matrix elements, and lifetime matrix as a function of the energy, in order to characterize the funnel resonances of the title system. Friedmann et al.\(^{29}\) have proposed one-dimensional potential energy functions (\( V_{11} \) and \( V_{22} \)) and non-adiabatic coupling term (\( V_{12} \)) that models the collinear minimum energy path of the three-dimensional \( \text{ClH}_2 \) surfaces. In order to compare our results with their time-independent ones,\(^{29,30}\) we have used the same potential energy curves that were adopted in ref. 30 (case V of ref. 29). In particular, the diabatic \( V_{11}(x) \) and \( V_{22}(x) \) potential curves and the corresponding coupling \( V_{12}(x) \) term are shown in panel (a) and panel (b) of Fig. 1; \( x \) represents the reaction coordinate. The analytical expressions and the numerical parameters for \( V_{11} \), \( V_{12} \) and \( V_{22} \) are presented in ref. 29 [eqns. (32)–(36) and Tables 1 and 2] and in ref. 30 [eqns. (30)–(34) and Table 1]. These functions may be combined to obtain the corresponding adiabatic potential energy curves whose ground state is similar to \( \text{Cl} + \text{H}_2 \) surface.

![Fig. 2](image)

Snapshots of the time evolution of the \( |c_1(x,t)|^2 \) (full line) and \( |c_2(x,t)|^2 \) (dashed line) wave packet components.

![Fig. 3](image)

Reflection probability \( |S_{11}|^2 \) as a function of scattering energy.

![Fig. 4](image)

Diagonal \( S \)-matrix elements in the vicinity of the \( z = 0 \) resonance position: (a) magnitude and (b) phase of \( S_{11} \). The solid line is the result of this work and the circles represent the results from ref. 29.

<table>
<thead>
<tr>
<th>( z )</th>
<th>( E_{11}^{\text{max}}/E_h )</th>
<th>( \Delta t_{11}/\text{fs} )</th>
<th>( E_{12}^{\text{max}}/E_h )</th>
<th>( \Delta t_{12}/\text{fs} )</th>
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<td>417.97</td>
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<td>417.71</td>
</tr>
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</table>

Table 2. Local maxima in the delay times \( \Delta t_{nm} \) at energies \( E_{nm}^{\text{max}} \). Second entry for each state refers to the results of ref. 29.
of ref. 5 and the excited state has a minimum (exciplex funnel) over the saddle point located at \( x = 0 \) \( a_0 \).\textsuperscript{29,30}

The energy range considered in present work is \( 0.007 E_h < E < 0.302 \), where the first 24 funnel resonances may be found for the title system. To obtain the results shown here, five wave packet propagations have been performed for different values of \( p_0 \). These are obtained from an initial energy \( E \), once \( p_0 = \sqrt{2 \mu (E - V_{11}(x_1))} \) or \( p_0 = -\sqrt{2 \mu (E - V_{22}(x_2))} \), depending on whether the initial wave packet is localized at channel 1 \( (x_0 > 0) \) or channel 2 \( (x_0 < 0) \). In turn, the five values of energy used are: (I) 0.03 \( E_h \); (II) 0.08 \( E_h \); (III) 0.14 \( E_h \); (IV) 0.21 \( E_h \); (V) 0.29 \( E_h \). In each case, a grid with 2048 equally-spaced points extending from \( x = -45 a_0 \) to \( x = 45 a_0 \) has been used to represent the wave functions. Moreover, we have assigned \( \sigma = 0.3 \) and \( x_0 = \pm 9.0 \) (all in au), while the propagation has been taken always during 40 000 time steps of 8 au each; the reduced mass of the \( ^{35}\text{Cl} + \text{H}_2 \) is 3474.057 \( m_e \). An example of the time evolution of the \( \psi_{1,2}(x,t) \) wave packet components is displayed in Fig. 2.

The main results are shown in Figs. 3–7 and Tables 1–3. The calculated reflexion probability \( P_{11} = |S_{11}|^2 \) as a function of energy is displayed in Fig. 3, where we can locate 24 funnel resonances (labeled \( \alpha = 0, \ldots, 23 \)). In Figs. 4 and 5 we have compared our results for diagonal \( (S_{11}) \) and off-diagonal \( (S_{12}) \) elements from eqn. (7) with an accurate time independent scattering calculation\textsuperscript{29} in the vicinity of the first resonance. It can be observed that the agreement is excellent for both the magnitude and the phase of the \( S_{11} \) and \( S_{12} \) elements (the relative errors between our results and the time independent ones shown in Figs. 4 and 5 are lesser than \( 10^{-4} \)). In order to follow the detailed comparison with the quantum time independent

Fig. 5 Off-diagonal \( S \)-matrix elements in the vicinity of the \( \alpha = 0 \) resonance position: (a) magnitude and (b) phase of \( S_{12} \). The solid line is the present result and the circles represent the results from ref. 29.

Fig. 6 Eigenvalues and trace of the lifetime matrix \( \mathbf{Q} \) as a function of scattering energy for \( \alpha = 0 \) and \( \alpha = 1 \) resonances: (a) \( \lambda_{11} \); (b) \( \lambda_{22} \); and (c) trace of \( \mathbf{Q} \). Full lines represent the results of this work, while those from ref. 29 are shown by the dashed lines (they are indistinguishable here because both results are essentially identical).

Fig. 7 Delay time matrix elements \( \Delta t_{nm} \) as a function of scattering energy for \( \alpha = 0 \) and \( \alpha = 1 \) resonances: (a) \( \Delta t_{11} \); (b) \( \Delta t_{22} \); (c) \( \Delta t_{12} \). Full lines represent the results of this work, while those from ref. 29 are shown by the dashed lines (they are indistinguishable here because both results are essentially identical).
The individual values of energies and widths for all 24 resonances have been determined from a least-squares fit of eqn. (11). For the fit we have used the Powell's direction set method,46 where we add a background constant in eqn. (11) to take into account the effects of far away resonances. These energies and widths are presented in Table 3 and compared with those of Friedman and coworkers30 which were calculated using the time independent complex coordinate method. Particularly interesting is that our calculation can mimic their results,29,30 using two different time-independent methodologies. In summary, this work clearly shows which wave packet calculations using a Lanczos method for the long time propagation is extremely accurate to study non-adiabatic dynamics of systems involving isolated, narrow resonances. Although we have not carried out a direct comparison on the performance between the present time-dependent method and the time-independent ones used by Friedman et al.29,30 (which is out of the scope of this work), time-dependent wave packet calculations are, in general, less demanding in terms of computational effort. Moreover, it is also possible to use one of the hybrid methods cited in the Introduction, which avoids long propagation times, when these are not feasible. Thus, we believe that our methodology can be competitive when extended to fully dimensional non-adiabatic treatments. For instance, the work concerning the implementation of a computational code to treat quantum scattering processes with more dimensions involving two or more coupled potential energy surfaces is currently in progress and we expect to publish the first results elsewhere.

4. Conclusion remarks

The importance of metastable funnel resonances in the dynamics of the Cl+H₂ reaction has been investigated using a time dependent wave packet calculation and a one-dimensional non-adiabatic model. The results are in good agreement with those of Friedman et al.29,30 using two different time-independent methodologies. In summary, this work clearly shows that wave packet calculations using a Lanczos method for the long time propagation is extremely accurate to study non-adiabatic dynamics of systems involving isolated, narrow resonances. Although we have not carried out a direct comparison on the performance between the present time-dependent method and the time-independent ones used by Friedman et al.29,30 (which is out of the scope of this work), time-dependent wave packet calculations are, in general, less demanding in terms of computational effort. Moreover, it is also possible to use one of the hybrid methods cited in the Introduction, which avoids long propagation times, when these are not feasible. Thus, we believe that our methodology can be competitive when extended to fully dimensional non-adiabatic treatments. For instance, the work concerning the implementation of a computational code to treat quantum scattering processes with more dimensions involving two or more coupled potential energy surfaces is currently in progress and we expect to publish the first results elsewhere.

Acknowledgements

We are grateful to Ronald S. Friedman for providing us with all of the data from his time independent calculations (refs. 29 and 30).

References


<table>
<thead>
<tr>
<th>Table 3</th>
<th>Eigenenergies and widths for the funnel resonances</th>
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<tr>
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<tr>
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<tr>
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</table>

* Each run represents the time dependent wave packet calculation for a particular initial energy $E$ parameter: I) $E = 0.03E_h$; II) $E = 0.05E_h$; III) $E = 0.14E_h$; IV) $E = 0.21E_h$; and V) $E = 0.29E_h$.