A Time-Dependent Quantum Study of
$Li + HF(\nu = 1) \rightarrow LiF(\nu') + H$
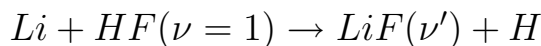
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Abstract

Time-dependent quantum wave packet calculations are performed for a model based (two-dimensional) $Li + HF(\nu = 1) \rightarrow LiF(\nu') + H$ reaction. The reaction probabilities for a broad range of collison energies are calculated by a single solution of the time-dependent Schrödinger equation. The calculated reaction probabilities show many sharp features as a function of energy which are ascribed to scattering resonances.

1. Introduction

The time-dependent quantum wave packet approach has recently become a viable method for studying molecular reaction dynamics. The method relies on the numerical solution of the time-dependent Schrödinger equation, involving only matrix vector multiplications and avoiding the diagonalisation of large matrices which are often required in the time-independent computations [1]. Therefore, the main advantage of the time-dependent techniques is that the computational times scale as N^2, where N is the number of internal states to describe the system. Although time-dependent approaches involve an additional dimension (i.e. time) they have the great compensating advantage of immediately yielding the energy dependence of cross-sections and other physical observables [2-9]. This arises because time and energy are conjugate variables. On the other hand, time-dependent calculations are initial value problems and each wave packet computation yields information relating to only a single initial state of reactants.

Several time-dependent approaches have recently been developed for treating two[2-4] and three-dimensional atom-diatom reactive systems [5-9]. These studies have confirmed the power and the potential of the time-dependent quantum approach. However, the time-dependent technique used in the present work utilises a grid based method rather than operator projection techniques[3-5] or expansions in terms of basis functions [8,9]. It has recently been shown that the grid-based wave packet method discussed here is capable of exactly reproducing all the details of a time-independent computation such as sharp resonance features and threshold behavior of the reaction probability [6,7].

The $Li + HF \rightarrow LiF + H$ reaction has so far been very extensively studied both theoretically [2,7,10-19] and experimentally [20-25]. The reaction has several interesting features that make it an ideal system for investigation. The potential energy surface has a non-linear transition state. There are two potential wells and a barrier along the reaction path. The reaction is classically endoergic but it becomes quantum mechanically exoergic after adding quantum zero point energies. Its mass combination may approximately be regarded as falling into the "light-heavy-light" category. The most complete ab initio calculations of the potential energy surface have been performed by Chen and Schaefer[26] and analytical fits to these theoretical results have been performed by Lagana et al. [27].

In reactive scattering there are different set of coordinates for reactant and product arrangements. A time-dependent calculation of the state-to-state reaction probabilities therefore involves the use of both the reactant and product Jacobi coordinates in the dynamics [28,29]. Thus, some physical quantities (for instance the wave function) are necessarily transformed from one set of coordinates to the others during the propagation and this transformation creates an extra problem in the treatment of the reactive scattering. However, in order to calculate the total cross-sections, it is not necessary to propagate the wave function up to the asymptotic region of the product channel [30,31]. Therefore, the product Jacobi co-ordinates can be eliminated by blocking this channel by a complex damping potential as introduced by Neuhauser and Baer [30].

We have previously performed two [2] and three-dimensional [7] time-dependent quantum wave packet calculations on this system and comparisons with the results of time-independent quantum methods have been made. However, both time-independent and time-dependent calculations have been carried out for reactants in their rotationally excited states. The reason is due to the fact that the system is quantum mechanically exoergic and a time-independent quantum calculation for HF in its vibrationally excited states requires a large number of quantum states in the product channel. Therefore, in this study we performed the calculations for HF in its first vibrationally excited state. The calculations are performed by considering that the $Li - H - F$ angle is held fixed at $74°$ at which the reaction shows the lowest barrier. In order to facilitate the restriction of the system to a fixed $Li - F - H$ angle the mass of the central fluorine atom has been artificially increased 100 fold. This in effect makes it infinitely heavy and simplifies the relationship between the reactant and product Jacobi coordinate systems thus permitting the $Li - F - H$ angle to be fixed without necessitating the imposition of additional constraints on the Jacobi coordinates.

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2. Time-dependent Quantum Theory

Time-dependent quantum approach evaluates scattering properties by solving the time-dependent Schrödinger equation, which is given for nuclear motion by

$$H\Psi(R_\tau, r_\tau, t) = i\hbar \frac{\partial \Psi(R_\tau, r_\tau, t)}{\partial t}, \tag{1}$$

where τ is the index indicating the arrangement channels, so that $\tau = \beta$ indicates reactants and $\tau = \beta$ the products. H is the nuclear Hamiltonian operator for a fixed angle atom-diatom system given by

$$H = -\frac{\hbar^2}{2\mu} \left\{ \frac{1}{R_\tau} \frac{\partial^2}{\partial_\tau^2} R_\tau + \frac{1}{r_\tau} \frac{\partial^2}{\partial r_\tau^2} r_\tau \right\} + V(R_\tau, r_\tau). \tag{2}$$

Note that mass scaled Jacobi coordinates have been used [28,29]. In order to simplify the kinetic energy operators the wave function may be scaled in the following form

$$\Psi(R_\tau, r_\tau, t) = \frac{1}{R_\tau r_\tau} \Psi(R_\tau, r_\tau, t), \tag{3}$$

which results in the new expression for the Hamiltonian operator as

$$H = -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial R_\tau^2} + \frac{\partial^2}{\partial r_\tau^2} \right] + V(R_\tau, r_\tau). \tag{4}$$

So far several techniques have been developed for solving the time-dependent Schrödinger equation [32]. The most efficiently accurate way to solve the time-dependent Schrödinger equation is to use an expansion in terms of modified Chebychev polynomials as [32]

$$\Psi(R_\tau, r_\tau, t) = \sum_{n=0}^{N} a_n \left(\frac{\Delta E t}{2\hbar} \right) P_n(-iH_{\text{norm}}) \Psi(R_\tau, r_\tau, t = 0), \tag{5}$$

where $\Psi(R_\tau, r_\tau, t = 0)$ is the initial wave function, $a_n(x)$ the Bessel function and ΔE is the magnitude of the range of the eigenvaules of the unnormalised Hamiltonian operator [2,32]. Eq.5 requires the repeated operation of the normalised Hamiltonian operator on the wave function. Hamiltonian operator consists of a kinetic energy and a potential energy operators. The potential and kinetic energy operators do not commute each other. This means that they cannot be diagonalised simultaneously within the same space. In order to perform this operation, Kosloff [1] has developed the fast Fourier technique in which the operation of kinetic energy operator is carried out in momentum space while the potential energy is operated in coordinate space. The transformation between coordinate and momentum spaces is done through fast Fourier transform technique.

3. Definition of the initial wave packet

In this model based treatment, we define the initial wave function as a product of wave functions for vibrational motion of reactants representing vibrationally first excited state of HF and a one dimensional Gaussian wave packet representing translational motion of Li:

$$\Psi(R_\alpha, r_\alpha, t = 0) = e^{-ik(R_\alpha - R_0)} e^{-\sigma(R_\alpha - R_0)^2} \psi_{v=1}(r_\alpha), \tag{6}$$

where R_0 denotes the $Li - HF$ separation at which the incident Gaussian wave packet is centred and σ is the width parameter for the wave packet. The phase factor in the wave function $\exp\{-ik(R_\alpha - R_0)\}$ directs the wave function towards the interaction region. The wave function $(\psi_{v=1}(r_\alpha))$ for the vibrationally first excited state of HF may be calculated by solving Schrdinger equation by Fourier Grid Hamiltonian Method (FGH) [33] for diatomic molecule (HF):

$$\left\{ -\frac{\hbar^2}{2\mu_{HF}} \frac{\partial^2}{\partial r_\alpha^2} + V(R_\alpha \to \infty, r_\alpha) \right\} \psi_{v=1}(r_\alpha) = \varepsilon_v \psi_{v=1}(r_\alpha). \tag{7}$$

The wave packet, $\psi(R_\tau, r_\tau, t = 0)$, is represented on a two dimensional grid which is needed to perform the fast Fourier transforms used in evaluating the action of the Hamiltonian operator on the wave function.

4. Analysis of final wave packet

In grid-based time-dependent wave packet method described here, the initial wave function is located in the asymptotic reactant region. The wave packet is then propagated on the potential energy surface through interaction region and the propagation is continued until the wave packet has completely left the interaction region. The information we seek is the probability of reaction at a fixed energy. As the time-dependent solutions provides us with functions of time it is clear that the energy dependent quantities can be obtained by means of a fast Fourier transformation over the time of time-dependent functions. As the wave function evolve, some portion of it passes from reactant to the product valley. The remaining portion is reflected back along the entrance channel and can be disposed of in the asymptotic region of entrance channel since it does not contribute to reactive scattering. However, it is clear that the form of the wave packet passing through asymptotic region of the exit valley must contain the basic scattering information.

In practice, an analysis line, corresponding to a fixed value of LiF separation $(R_{\beta,\infty})$ is defined to lie perpendicularly across the exit valley. The time evolution of the wave packet is therefore monitored by taking cuts through it at a fixed product scattering coordinate at each time step. The wave function along such a cut is then analysed into its contribution from different product vibrational states to yield a time-dependent coefficient for each state

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$$C_{v'}(t) = \int_{r}^{\infty} \psi_{v'}(r_\beta)\Psi(R_\beta = \infty, r_\beta, t)dr_\beta, \qquad (8)$$

where $\psi_{v'}(r_\beta)$ is the vibrational wave function of the product molecule evaluated by FGH method. The Fourier transform of these time-dependent coefficients gives the energy dependent amplitudes as:

$$A_{v'}(E) = \frac{1}{2\pi} \int_{t=0}^{\infty} e^{iEt/\hbar} C_{v'}(t)dt. \qquad (9)$$

The partial reaction probabilities to yield specific product vibrational states, from a specified initial reactant level, are then calculated as:

$$P_{v,v'}(E) = \frac{\hbar^2}{\mu^2} k_v k_{v'} \left| \frac{A_{v'}(E)}{f(k_v)} \right|^2, \qquad (10)$$

where $f(k_v)$ is the Fourier transform of the initial translational wave function. The grid on which the time-dependent propagation is performed is necessarily finite. However, the propagation time must be allowed to become very long. The high energy components of the wave function may reach the end of the grid whilst the low kinetic energy component are still in the strong interaction region. In this case, the propagation is still necessary to be continued in order to allow all the wave function to leave the interaction region. However, the high kinetic energy components of the wave function will be reflected back into the interaction region and destroy the original wave function. Therefore, the wave function in both arrangement channels must be disposed of before reaching the edges of the grid. There are few techniques suggesting the use of complex absorbing potentials near the edges of the grid to tackle this problem [34-40]. McCurdy and Strud [34] have developed a technique in which the co-ordinates themselves become complex near the edge of grid. Neauhauser and Baer[37] have examined a linear form of complex absorbing potential and have discussed the conditions which a satisfactory absorbing potential must obey. Based on the ideas of Neuhauser and Baer [37], Vibok and Balint-Kurti [39,40] have recently discussed different form of absorbing potentials and the most probable way to optimise them. In this study, a complex damping potential of a quadratic form [39,40] has been used to avoid reflections from the edges of the grid.

5. Results and Discussion

Figure 1 shows a contour map of the potential energy surface for $Li + HF \rightarrow LiF + H$ reaction with $Li - F - H$ angle fixed at $74°$. The zero of energy is taken to lie at the bottom of the reactant channel in the $Li - HF$ asymptote. The figure clearly shows the existence of two potential wells and a barrier in the strong interaction region. The initial wave function is located at a $Li - F$ separation of 13.30 a.u. and given an initial kinetic energy of 0.251 eV along the entrance channel. The analysis line

required for the projection of the time-dependent coefficients is taken in the asymptotic region of exit channel at a $H - F$ separation of 12.13 a.u. The coordinate grid covers $Li - F$ separations of 1.2-16.3 a.u. and H-F separations of 0.7-20.8 a.u. In both reactant and product channels 256 evenly spaced grid points were used. The time-dependent coefficients should decrease to zero with increasing time. In order the time-dependent coefficients to go zero the wave function has been propagated for a propagation time of 62 000 a.u. (1500 fs).
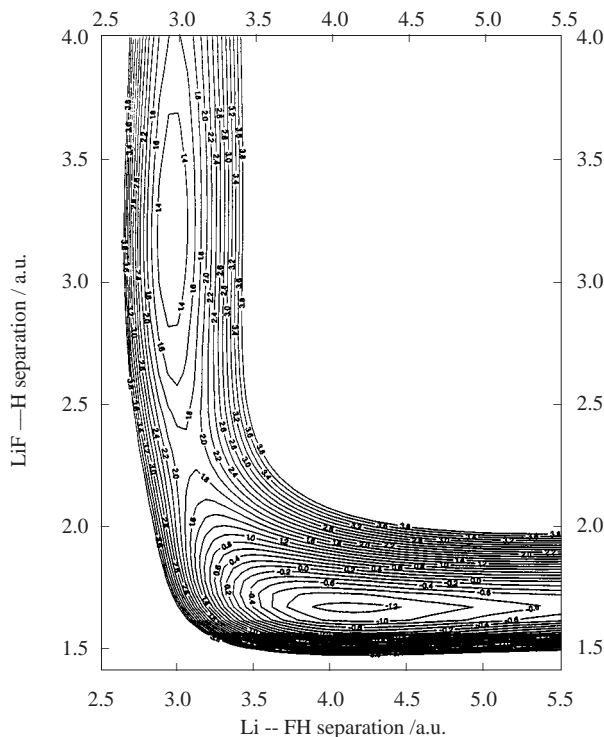
Figure 1. Contour map of the potential energy surface for the $Li + HF \rightarrow LiF + H$ reaction in the strong interaction region with the Li-F-H angle fixed at $74°$. The zero of energy is at the bottom of the entrance valley (lower right hand corner). The contours are 0.02 eV apart. The energy is given in units of 0.1 eV

Several snapshots of the wave packet as it proceeds along the potential energy surface are given in Figure 2. The propagation time for depicted wave functions are given on each panel in femtoseconds. Panels 2(A), (B) and (C) show interestingly the excitation of the vibrational mode in HF separation. The wave function shown in the figure spans a total energy range of 0.77-1.35 eV. This energy range corresponds to the significant part of the wave function. The most attractive feature of the time-dependent

wave packet method used here is that a single propagation of the wave packet (that is, a single solution of the time-dependent Schrödinger equation) automatically yields reaction probabilities over a large range of collision energy.
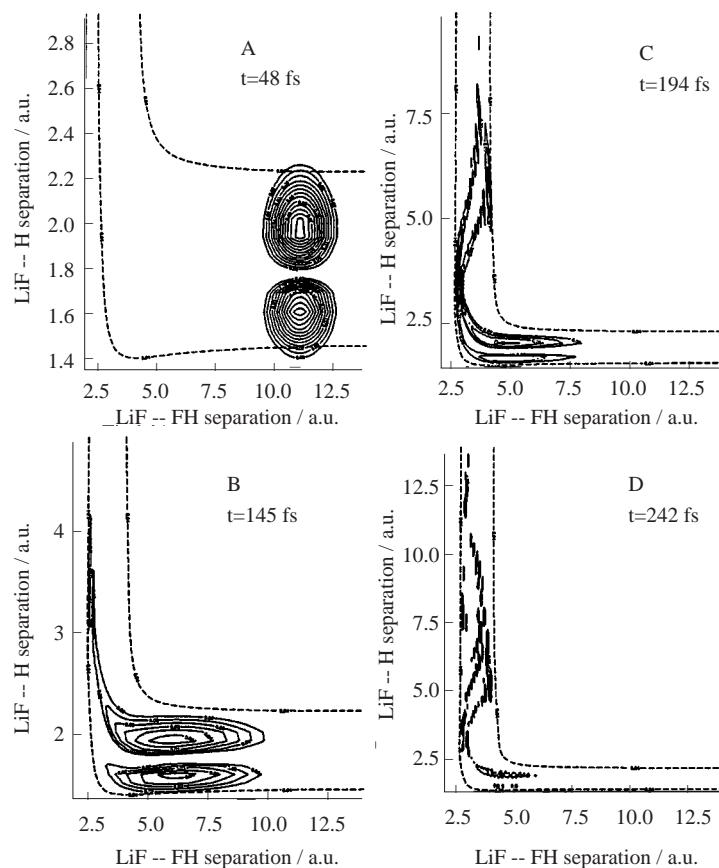

Figure 2. Snapshots of the wave packet motion on the potential energy surface. The figure shows contours of the absolute value of the wavepacket

The method discussed here is a grid based method and aims to compute state-to-state partial cross-sections rather than total cross-sections. Therefore, the wave function is propagated up to the asymptotic product region increasing the computing time.

The state-to state reaction probabilities for the $Li+HF(\nu=1) \rightarrow LiF(\nu')+H$ are shown in Figures 3 to 6. All the reaction probabilities displayed in the figures are obtained from a single propagation of the time-dependent wave packet motion followed by a single Fourier transformation of the time-dependent coefficients arising form it. The reaction probabilities from the first vibrationally excited state of HF to the several vibrational

quantum states of LiF shown in the figures are seen to be highly structured and to display many sharp resonance features. In a previous paper [2] we developed a new technique to project out the time-independent continuum wave functions at the energies corresponding to several resonance peaks appeared at reaction probability plots. As the nodal structures of these continuum wave functions were plotted for different resonances, it was clearly seen that there is a relation between the resonances and vibrational modes of product molecule. That is, the number of nodes in the wave function plots at various resonances systematically increases with increasing resonance energy. Hence we proved that these resonances are Feshbach type resonances in which the translational energy is temporarily trapped in a transverse Li-F vibrational motion and is not available for relative kinetic energy of the putative products [29]. In other words, the system is temporarily excited to a higher internal state, thereby delaying the translational motion along the reaction co-ordinate. On the other hand, there are several example of resonances with appearance of Fano profile [41]. The Fano type resonances have a maximum followed by a decrease to the average value of the broad background and a subsequent further decrease to a minimum [41].
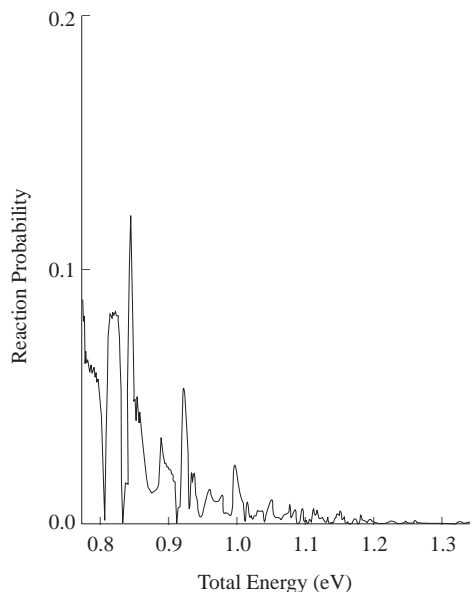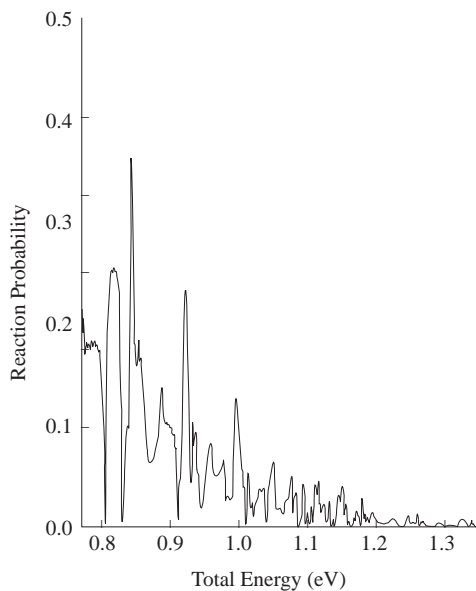

Figure 3. Reaction probabilities for the $Li + HF(\nu = 1) \rightarrow LiF(\nu' = 0) + H$ reaction. The wavepacket used for the time-dependent calculations encompassed an energy range of 0.77 to 1.35 eV. The LiFH angle fixed is at $74°$

The probabilities to the ground state $(v' = 0)$ and first vibrational quantum state $(v' = 1)$ of LiF, in Figures 3 and 4, show almost the same shape and most of the

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resonance features are common. The reaction probabilities to these two final quantum states decreases sharply over the energy range shown. The probabilities to second $(v' = 2)$ and third $(v' = 3)$ vibrational quantum states of LiF show again a structured shape and an energy dependence which peaks and then decreases. The transition from $v=1$ of reactants to $(v' = 3)$ of products, as seen from figure 6, is an endoergic transition. As may be seen from the reaction probability plots, the peaks in the reaction probability graph are pushed to higher energies with increasing product vibrational quantum number.
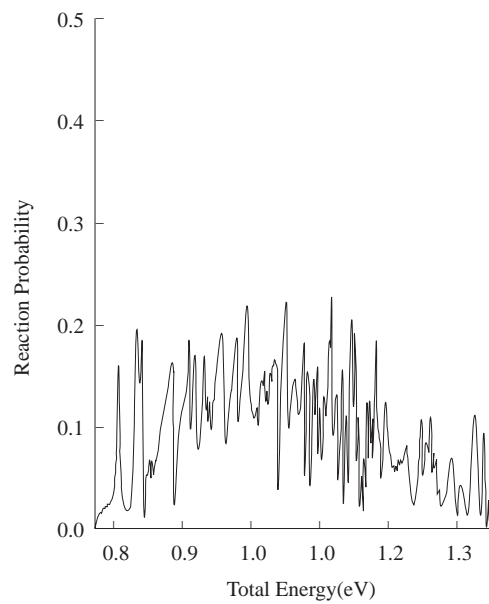

Figure 4. Reaction probabilities for the $Li + HF(\nu = 1) \rightarrow LiF(\nu' = 1) + H$ reaction. The wavepacket used for the time-dependent calculations encompassed an energy range of 0.77 to 1.35 eV. The LiFH angle fixed is at $74°$

Although we have only shown the transitions to first four product quantum states, it must be stressed that the analysis of the time evolution of a single wave packet by the technique discussed above gives the probabilities to all final quantum states. On the other hand, a full three-dimensional quantum wave packet study of state-to-state reaction probabilities from several vibrational states of HF is still under progress and they will be ready for publications soon.
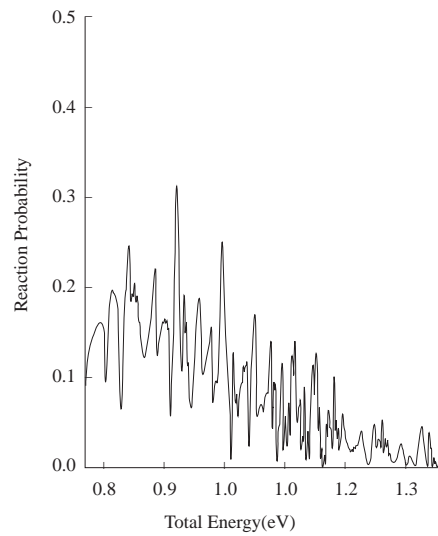
Figure 5. Reaction probabilities for the $Li + HF(\nu = 1) \rightarrow LiF(\nu' = 2) + H$ reaction. The wavepacket used for the time-dependent calculations encompassed an energy range of 0.77 to 1.35 eV. The LiFH angle fixed is at 74°

Figure 6. Reaction probabilities for the $Li + HF(\nu = 1) \rightarrow LiF(\nu' = 3) + H$ reaction. The wavepacket used for the time-dependent calculations encompassed an energy range of 0.77 to 1.35 eV. The LiFH angle fixed is at 74°

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Acknowledgement

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