TIME-DEPENDENT QUANTUM MECHANICAL APPROACH TO REACTIVE SCATTERING

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ABSTRACT

There has been a renewed interest in the time-dependent quantum mechanical approach to reactive scattering in the last few years. The different computational methods and applications that have created such an interest are reviewed here.

1. INTRODUCTION

ALTHOUGH it was realised more than fifty years ago that, in principle, any chemical problem could be solved by an appropriate formulation of it in quantum-mechanical terms[1], in practice, developments in that direction had to await the arrival of modern electronic computers. In the early seventies one could calculate reaction probabilities (P^R) readily for exchange reactions of the type

$$A + BC \rightarrow AB + C \qquad (R1)$$

in collinear geometries by solving the time-independent Schrödinger equation for the nuclear motion, given the electronic energy (for example, see ref. 2). That exact (converged) solutions to the problem in three dimensions (3D) also could be obtained was demonstrated in 1975 when Kuppermann and Schtaz[3a, 3b] and Elkowitz and Wyatt[3c] published their results for the reaction

$$H + H_2 \rightarrow H_2 + H \qquad (R2)$$
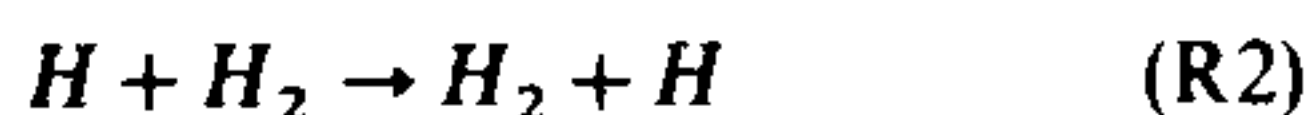
at low energies, making full use of the symmetry of the system. There has not been any report on results of similar accuracy for any other reactive system in the past ten years. Even for the reaction (R2), some converged results have become available[4] only recently on the chemically accurate Siegbahn-Liu-Truhlar-Horowitz[5] (SLTH) potential-energy surface (PES) for the ground and

the first excited vibrational states (v = 0.1) of the reactant. While some progress can be expected in the next few years, thanks to the supercomputers/parallel processors becoming available, yet the enormity of the problem remains. In a parallel development, Mazur and Rubin[6a] showed that the time-dependent Schrödinger equation (TDSE) could be solved for a reaction of the type (R1) using a model potential based on Harmuth integration scheme[6b]. McCullough and Wyatt[7] (MW) did an elaborate study in which they solved the TDSE for the reaction (R2) in collinear geometries using a realistic PES[8]. Unfortunately their approach could not be used readily for many systems as (i) the computer memory and time requirements were large (ii) the resolution of the state-to-state P^R information was poor and (iii) there was very little hope of the method being extended to three dimensions. In the last few years, however, the situation has changed dramatically. Newer methods[9,10] of solving the TDSE have become available and they are an order of magnitude faster than that one used by MW. Thus there is a renewed hope of studying 3D atom-diatom exchange reactions quantum mechanically. Also Kulander[11] and Leforestier[12] have shown that it is possible to deconvolute the average reaction probabilities ($\langle P^R \rangle$) that result from a time-dependent quantum mechanical (TDQM) study. They have also shown that the TDQM approach can be used successfully in studying collision-induced dissociation (CID) processes – an area where the time-independent approach has been carried out successfully only for a model system[32] because of the continuum

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problem. There are also other attractions offered by the time-dependent approach. It is analogous to classical trajectories in that a pictorial representation of the chemical reaction is possible—giving us a "feel" for the molecular collision. It has been shown[7] that flux patterns could be obtained for a chemical reaction on a PES and the whirlpools in the resulting picture can provide insight into reactive scattering resonances. Very recently we have also shown[13] that by solving the TDSE, we can construct the probability density function and predict the absorption spectrum for the transition state of the collinear reaction (R2). Gas-surface scattering problems have also been shown[14] to be amenable to solution via the TDSE. Because of the renewed interest in the area, we present here a review of the existing methodology and applications of the TDQM approach to a study of reactive scattering processes.

2. METHODOLOGY

Mazur and Rubin[6] solved the TDSE

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

by separating the real and imaginary parts in Ψ. Letting $\Psi = u + iv$, the equation becomes

$$Hu = -\hbar\frac{\partial\Psi}{\partial t}$$

$$Hv = \hbar\frac{\partial u}{\partial t}.$$

They approximated the spatial derivative in the hamiltonian and the temporal derivative by second order and first order finite differences respectively. Subsequent workers could deal with the complex wavefunction directly. Kulander[11] used a five-point finite difference formula for the spatial derivative and a fifth order predictor-corrector method for propagating the wavefunction in time. Kosloff and Kosloff[10] have shown recently that the second order spatial derivative can be evaluated by a fast fourier transform (FFT) of the wavefunction accurately. They used a

second order finite difference formula for evaluating $\partial\Psi/\partial t$.

The time-evolution of the wavefunction can be expressed elegantly in terms of a time evolution operator U as

$$\Psi(t) = U\Psi(t_0)$$

with $U = \exp[-iH(t-t_0)/\hbar]$. For practical reasons, this exponential operator has to be truncated. It was represented by MW as

$$U = [1 - iH(t-t_0)/\hbar]/[1 + iH(t-t_0)/\hbar]$$

which is unitary as is the untruncated U. But using it for determining the time evolution of a chemical system, involves inverting a very large matrix. Therefore the method is computationally expensive and it requires a large computer memory. As a result it has been applied to a few systems only[15,16].

Askar and Cakmak[9] have proposed an explicit method in which U was truncated after the linear term. By combining the forward and the backward evolution operators, they could devise an algorithm which was an order of magnitude faster than the implicit method of MW.

The first order explicit-method proposed by Askar and Cakmak[9] is equivalent to the second order finite difference in time used by Kosloff and Kosloff[10]. It also turns out that the first order explicit is identical to a second order explicit method. (As a matter of fact, truncation upto an odd order in time is equivalent to truncation upto the next higher order.) Therefore, the errors are of third order. The stability criteria to be met by the choice of steps in time and space for the method have been worked out elsewhere[17a].

The above methods have been applied to different *collinear* triatomic systems. The only exception is the study of Jackson and Wyatt[14] who studied the time evolution of a *planar* H_3 system. The speed of the explicit method gives us the hope of extending it to atom-diatom exchange reactions in *three dimensions* in the very near future.

In solving the TDSE for an atom-diatom exchange reaction, the initial wavefunction is represented by a product of the eigen-function for the vth vibrational state of the diatom (say, a

Morse oscillator) and a translational wavepacket which is gaussian in the momentum (k) space, centered at k_0 corresponding to the classical relative translational energy of the reactants. The width (δ) of the gaussian is chosen to be 'optimal' $(= 0.25$ a.u. in our studies). Such a wavefunction, when time evolved, would yield an average probability $\langle P^R \rangle$ for reaction into all the available product vibrational (v') states. If we are interested in a state (v) – selected rate coefficient at a translational temperature T, the wavepacket can be chosen accordingly[17b]. If an overall rate constant is desired, an appropriate summation over the v states can also be incorporated in the initial wavefunction. Recently, it has been shown that the $\langle P^R \rangle$ can be deconvoluted to obtain the dependence of P^R on the translational energy E_{trans} and also the product state specified reaction probability $\langle P^R \rangle_{v'}$[11, 12].

3. APPLICATIONS

3.1 *Atom-diatom exchange reactions*

By far the predominant application of the TDQM approach has been to calculate $\langle P^R \rangle$ for a variety of atom-diatom exchange reactions. MW[7] computed the $\langle P^R \rangle$ at different energies for the reaction (R2) on the Porter-Karplus[8] PES. Agrawal and Raff[7b] used the explicit method to compute rate coefficients for the reaction

$$T + HD \rightarrow TH + D \qquad (R3)$$
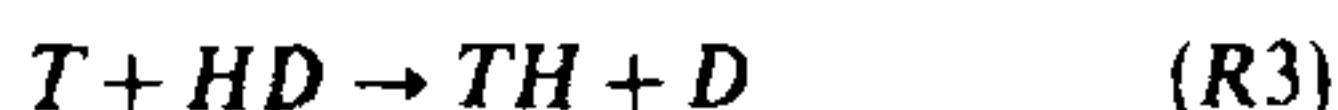
on a London-Eyring-Polanyi-Sato (LEPS) surface. The results were shown to be in good agreement with the time-independent results of Garrett *et al*[19]. Values of $\langle P^R \rangle$ computed[13] on the SLTH surface also have been shown to be in accord with the time-independent results[20].

Kellerhals *et al*[15] computed $\langle P^R \rangle$ for the reaction (R1) on a model LEPS surface and studied its dependence on the location of the saddle point. It became clear that $\langle P^R \rangle$ was sensitive to changes in the PES. Stroud *et al*[16] investigated the influence of v on $\langle P^R \rangle$ and its sensitivity to features of the PES for the reaction

$$He + H_2^+ \rightarrow HeH^+ + H \qquad (R4)$$
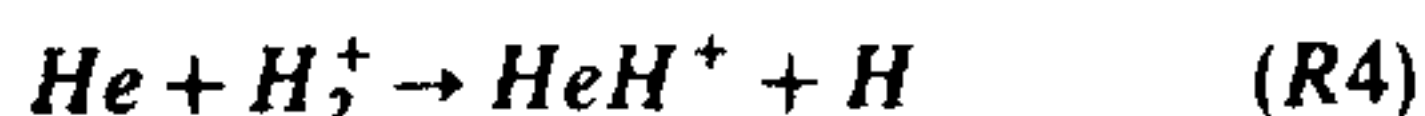
using a diatomics-in-molecules and a slightly different spline-fitted ab initio surface. Studies by Zuhrt *et al*[21] using three different PESs for the reaction

$$F + H_2 \rightarrow FH + H \qquad (R5)$$
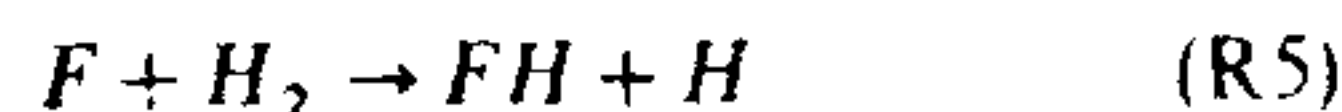
also showed that $\langle P^R \rangle$ was strongly dependent on the topological features of the PES. Sathyamurthy *et al*[22] were able to demonstrate the utility of cubic splines to interpolation of ab initio PESs by showing that results on a splinefitted surface were identical with those obtained on the original analytic surface. Thareja and Satyamurthy[23] have recently used the TDQM approach in testing the quality of an analytic fit to the ab initio PES for the reaction (R2). When different fits were obtained for the same original ab initio surface, the fit that led to the same $\langle P^R \rangle$ as on the SLTH was taken to be the best.

In addition to yielding P^R at different levels of resolution, the time-evolution method provides a valuable insight into the detailed nature of the collision dynamics. Typical 3D perspective plots of $|\Psi|^2$ in configuration space at different time intervals give a pictorial representation of the reactants transforming into products and the resulting picture can be compared directly with a plot of a family of trajectories "Structures" in these plots reveal the complexity of the dynamics and are indicative of indirect collisions. Using the FFT algorithm, Kosloff and Kosloff[24] investigated the conditions for complex formation in $H^+ + H_2$ and its isotopic analogs for which the PES has a deep potential well in it.

From a knowledge of $\Psi(r, t)$, quantal flux patterns could be drawn, in analogy with the fluid flow in classical hydrodynamics. Plots of the quantal probability flux vector

$$j(r, t) = \frac{\hbar}{\mu} \operatorname{Im}[\Psi^*(r, t) \nabla \Psi(r, t)]$$

were made by MW[7] and quantum whirlpools were identified. These have been investigated subsequently by Hirschfelder[25] who described them as quantized vortices around wavefunction nodes.

3.2 Collision-induced dissociation processes

In contrast to the formidable problems faced by the time-independent approach in studying CID processes, the time-dependent approach is applicable to the CID problem with as much ease as for the exchange reaction. Ford *et al*[26] reported the first TDQM results for the reaction of the type

$$A + BC \rightarrow A + B + C \qquad (R6)$$
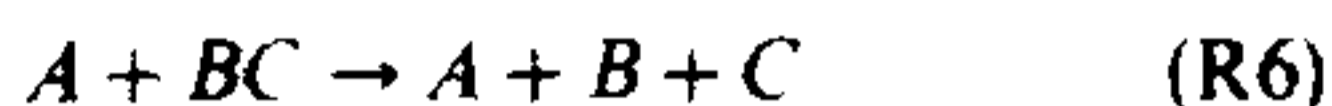
using a model potential. Subsequently Kulander[11] reported the results for the reaction

$$H + H_2 \rightarrow H + H + H \qquad (R7)$$
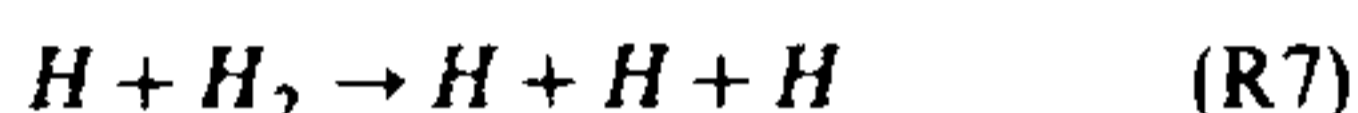
on a LEPS surface. Leforestier *et al*[12,27,28] have studied a variety of model CID reactions over a wide range of energies. By deconvoluting $\langle P^R \rangle$ to obtain the energy dependence of P^R for a CID process, they have been able to obtain information on the threshold behaviour, vibrational enhancement and inhibition and their dependence on E_{trans}. They have shed further light on the dynamical nature of CID processes by plots of $|\Psi|^2$ and j at different time intervals.

3.3 Spectroscopy of the transition state

Recently, we[13] have made use of the TDQM approach to predict the wings to the Lyman-α absorption line in $H + H_2$ collisions by obtaining the time averaged $|\Psi|^2$ values and relating them to absorption intensity. Work is in progress in using this approach in predicting the emission spectrum for the H_3^* system and spectra of transition states for a few other systems. The approach thus promises to be an effective tool in the emerging area of 'spectroscopy of the transition state'.

3.4. Gas-surface scattering

Atom-surface scattering plays a vital role in the investigation of solid surface properties. The rapid advancement in the recent past on the experimental side of the atom-surface encounters pose a challenge to theoretical models. Time-independent quantal calculations have not become practicable yet. Classical and semi-classical methods have been used extensively in simulating the experimental results. But they are of limited validity. For the first time Agrawal and Raff[14] showed that the time-dependent approach could be used to study gas-surface scattering by representing an incident atom by a wavepacket and using the explicit integration method for the time evolution of the system. Yinnon and Kosloff[29] have been able to compute scattering intensities, resonance strengths and other attributes using the FFT algorithm. Gerber *et al*[30] have used the same approach to study the scattering of He atom from a Cu surface with isolated Ar impurities. Kosloff and Cerjan[31] have studied the desorption and scattering of a He atom from W and Pt surfaces using the same method.

4. CONCLUDING REMARKS

The TDQM approach to reactive scattering has been receiving considerable attention, of late. It scores over the time-independent approach in that there is no need for construction of channel hamiltonians and matching of the wavefunctions. There is no increase in the complexity of the problem or the computational time requirement with an increase in the total energy of the system. As a matter of fact, there is a reduction in the computer time with an increase in energy-analogous to the classical approach. In contrast to the time-independent approach in which P^R has to be computed for different E_{trans} and v and averaged over the appropriate distributions in order to calculate state-selected and overall rate constants, the TDQM method could be made to yield them directly by a suitable choice of initial Ψ. Also, the deconvolution methods have made it possible to obtain in a single calculation P^R over a wide range of E_{trans}.

The time is not far off when the time-dependent approach could be used with much more ease than its time-independent analog in predicting rate observables for reactions in three dimensions.

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