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Chemical Reaction Computations Using the Quantum-Potential Method

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We apply the quantum potential approach in quantum mechanics to compute reaction times in the H–H_2 collinear collision. The latter is obtained from the wave function of the system that is obtained by numerically integrating the time-dependent Schrädinger equation using the split-operator scheme. The equations of motion for the quantum trajectory are integration using a fourth-order Runge-Kutta scheme and possible applications to other situations are discussed.

1. INTRODUCTION

The time-dependent study of such processes as molecular scattering and photodissociation dynamics can be performed using many numerical methods (Kosloff, 1988) that essentially consist in the integration of the time-dependent Schröedinger equation

$$i\,\frac{\partial\psi}{\partial t} = H\psi \tag{1}$$

where $H = H_0 + V$ is the system Hamiltonian, including the interactions among electrons and nuclei in the molecule(s). Here and in the following we use atomic units. Since even a molecule with a small number of atoms possesses a great number of electrons, this is a very difficult problem to deal with directly. The simplest approach is to use the Bohr–Oppenheimer approximation where the nuclei of the atoms are supposed to move in a

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potential energy surface that corresponds to the electronic energy for a given fixed position of the nucleus, resulting in a problem with fewer less degrees of freedom and that can be solved with present-day computers, at least for molecules with a small number of atoms, typically three or four (Bowman and Wang, 1994). Many properties can be computed using these techniques, such as reaction probabilities and photodissociation cross sections (Schinke, 1993).

In photodissociation dynamics one useful property is the dissociation time, defined as the interval of time required for the dissociation fragments to move apart so that they do not interact with each other. This is important, for instance, in the interpretation of electronic spectra from a dissociating triatomic molecule where one needs to know the proportion of electrons emitted from the original molecule and by the diatomic fragment (Naves de Brito *et al.*, 1997). Nevertheless some care must be taken as the molecule wave packet has a spatial spreading and therefore it is not clear when the interaction fragments leave the mutual interaction region. One way to avoid this problem is to use the expectation values of the positions of the fragments as reference, but even if this expectation value is outside the interaction region, the wave packet may still be spreading over it. For a critical review of the problem see Landauer and Martin (1994) and references therein.

In this paper we propose to overcome these difficulties by using the quantum potential method initially introduced by Bohm (1952; Dewdney and Hiley, 1982) as an alternative to the Copenhagen interpretation of quantum mechanics, but having essentially the same experimental predictions. This method is envisioned here not as an alternative theory, but as a computation technique that gets rid of the ambiguity in the definition of dissociation and reaction times in molecules in accordance with quantum mechanics. Simply speaking, that approach considers a quantum system as having a well-defined trajectory moving under the action of the usual interaction potential plus a “quantum potential” derived from the wave function of the system. Quantum properties are then computed from ensemble averages over many possible trajectories of the system.

Our approach is used to compute the reaction time in the $H–H_2$ collinear reaction. It is a very well known system and suited as a standard for our calculations. The paper is structured as follows: In Section 2 we briefly explain the main points in the quantum potential method and in Section 3 present the numerical methods used to compute the quantum trajectories while propagating the wave function of the system. Section 4 is dedicated to the application to the $H–H_2$ system, and some concluding remarks follow in Section 5.

2. THE QUANTUM POTENTIAL APPROACH

In this section we present Bohm's quantum potential approach (Bohm, 1952) for a one-particle system. The generalization for an N-particle system is straightforward and will not be presented for the sake of brevity.

The wave function is written in polar coordinates in the complex plane as

$$\psi(\mathbf{r}, t) = A(\mathbf{r}, t)e^{iS(\mathbf{r},t)} \tag{2}$$

where $\mathbf{r}$ stands for all coordinates needed to describe the molecule, and A is the amplitude and S the phase of ψ. Inserting Eq. (2) in (1) and taking the real and complex parts yields the equations

$$-\frac{(\nabla S)^2}{2M} + V - \frac{1}{2M}\frac{\nabla^2 A}{A} = 0 \tag{3}$$

where M is the mass of the particle, and

$$\frac{\partial A^2}{\partial t} + \nabla \cdot \left(A^2 \frac{\nabla S}{M}\right) = 0 \tag{4}$$

Noting that $A = \psi\psi^*$, we see that Eq. (4) states the conservation of total probability. Now we define the quantum potential by

$$Q(\mathbf{r}) \equiv -\frac{1}{2M}\frac{\nabla^2 A}{A} \tag{5}$$

and Eq. (3) takes the form

$$-\frac{(\nabla S)^2}{2M} + V + Q = 0 \tag{6}$$

which is the Hamilton–Jacobi equation for a particle in a potential $V + Q$. The equations of motion are then given by

$$M\frac{dv}{dt} = -\nabla V - \nabla Q \tag{7}$$

Also, as in the usual Hamilton–Jacobi theory in classical mechanics, the momentum of the particles is related to S by the relation

$$p = \nabla S \tag{8}$$

Due to its simpler form Eq. (8) is preferred in a practical situation instead of Eq. (7). It is possible to show that quantum mechanical predictions can be recovered by performing an average over an ensemble of trajectories.

3. NUMERICAL METHODS

The time-dependent Schrödinger equation (1) has the formal solution

$$\psi(t) = e^{-iHt}\,\psi(0) \tag{9}$$

The evolution operator in (9) can be approximated using the split-operator approximation of Feit and Fleck (Feit *et al.*, 1982; Feit and Fleck, 1982) in the Schrödinger picture (Araújo Sousa *et al.*, 1995) for a small time step Δt by

$$e^{-iH\Delta t} = e^{-iH_0\Delta t/2}\,e^{-iV\Delta t}\,e^{-iH_0\Delta t/2} + \mathcal{O}(\Delta t^3) \tag{10}$$

and is therefore a second-order method (i.e., correct up to order two in Δt).

For three collinear identical atoms the Jacobi coordinate system given in Fig. 1 is better suited. The H_2 distance is denoted by R and the distance from the hydrogen atom to the center of mass of the diatom is denoted by r. The kinetic energy Hamiltonian is then given by

$$H_0 = -\frac{1}{2\mu_1}\frac{\partial^2}{\partial r^2} - \frac{1}{2\mu_2}\frac{\partial^2}{\partial R^2} \tag{11}$$

where the reduced masses are given by $\mu_1 = 2m/3$ and $\mu_2 = m/2$ and m is the mass of atomic hydrogen. The wave function is represented in an equally spaced grid of points and the action of the operator H_0 on ψ is obtained using the Fourier pseudo-spectral method of Kosloff and Kosloff (1983). Then Eq. (8) is solved using a fourth-order Runge-Kutta method. Once the quantum potential is computed in the grid used to represent the wave function, its value at the trajectory is obtained by interpolation.

As a by-product we obtain a method for the determination of the eigenfunctions of a given potential energy surface using a propagation in complex time, the so-called relaxation method (Kosloff, 1988). Its main advantage is to yield the wave function in the same numerical grid used in the propagation.

4. APPLICATION TO THE COLLINEAR H–H_2 REACTION

The initial condition is chosen such that the H_2 molecule is in its lowest vibrational state $\phi_0(R)$ (obtained using the relaxation method) and the H atom in a state described by the Gaussian function

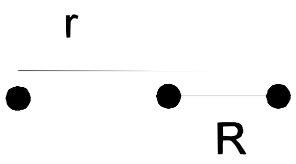

Fig. 1. Jacobi coordinates.

$$g(r) = (2\pi\delta^2)^{-1/4}\, e^{-(r-r_0)^2/4\delta}\, e^{-ik_0 r} \tag{12}$$

with average momentum k_0, width δ, and centered at $r = r_0$. The wave function of the H–H_2 system at $t = 0$ is then given by $\psi(R, r, 0) = \phi_0(R)g(r)$.

The incoming H atom can then collide with the H_2 molecule and be reflected back (nonreacting channel) or react with one of the hydrogen atoms in the diatom and eject the other hydrogen atom (reacting channel). The reaction time is defined as the time between the instant of time the incoming H atom enters the interaction region and the ejected atom leaves it. Comparing the LSTH interaction energy for H_2 as a function of the distance of its center of mass to the third hydrogen atom, we conclude that the interaction between H and H_2 is significant for $R < 4.5$ a.u. We choose an ensemble of equally spaced points in the region where the initial condition is significantly different from zero. Some of these points will correspond to no reaction due to a potential energy barrier in the interaction potential $V(r, R)$. Here we use the LSTH potential (Siegbahn and Liu, 1978; Truhlar and Horowitz, 1978). The remaining points will overcome the potential barrier and the reaction time is computed as an average over these points with a weight factor given by $|\psi(t = 0)|^2$. Usually the points ahead of the wave function (which means initial conditions lying in a point in front of the Gaussian function, i.e., with smaller r) will react and those behind it (initial condition with greater r) will not react. This same fact has been discussed by Dewdney and Hiley (1982) in a one-dimensional square barrier problem.

In the numerical computation we chose a grid with 256 × 256 points with a spatial range of 6.5 a.u. in each coordinate. The parameters in the Gaussian in Eq. (12) are $r_0 = 5.2$, $\delta = 0.35$, and $k_0 = 5.82$. The packet is then propagated using the split-operator method. Figure 2 shows a trajectory in the reaction channel for a total integration time of 400 a.u.

Some trajectories entering the reaction channel are given in Table I with their reaction time. Other points in the ensemble simply were reflected back by the potential barrier in the LSTH potential. The total number of trajectories in the ensemble required for the convergence of the reaction time is 3000. The average reaction time computed as explained above is 1330.25 a.u. The individual reaction times for some initial conditions are shown in Table I. In Fig. 1 we show the reaction time as a function of the coordinate r for R fixed at the maximum of the ground-state vibrational state of H_2.

5. CONCLUDING REMARKS

We showed how to use the quantum potential theory of Bohm to define reaction times in a quantum mechanical system, avoiding the intrinsic ambiguity in its definition in the usual approach to quantum mechanics. Reaction

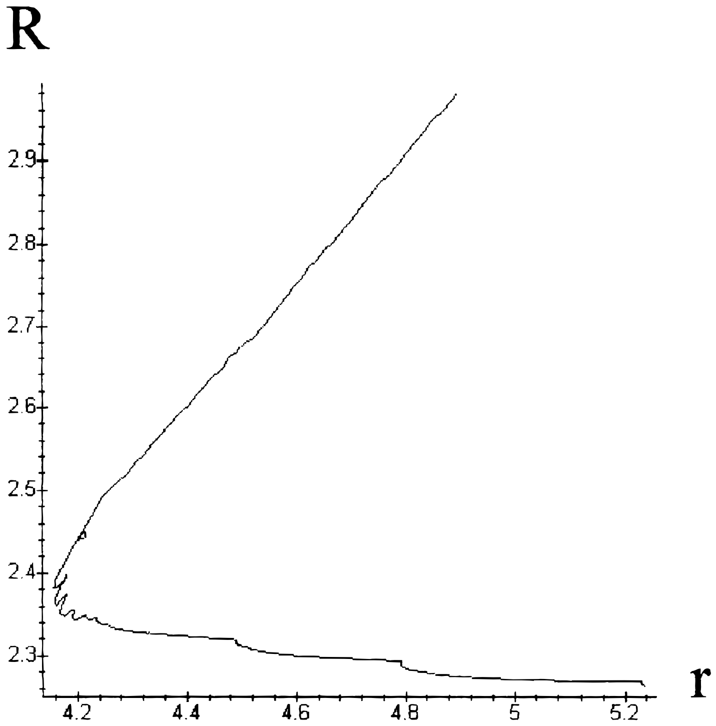

Fig. 2. Trajectory entering the reaction channel.

Table I. Points in the Reaction Channel

R	*r*	Reaction time
4.7051	1.4102	1308.5
4.7051	1.4615	1360.0
4.7564	1.3589	1396.5
4.7564	1.4102	1328.5
4.7564	1.4615	1299.0
4.7564	1.5128	1377.0
4.8076	1.3589	1477.5
4.8076	1.4102	1373.5
4.8076	1.4615	1342.5
4.8076	1.5128	1385.5

rates can also be easily computed simply by summing the statistical weights of the trajectories entering the reaction channel. This approach is entirely consistent with the predictions of quantum mechanics and can also be used to compute dissociation times in molecules with three or more atoms. This is particularly useful for interpreting emission spectra from the original molecule and the dissociation fragments. A three-dimensional calculation is in course and will be published elsewhere.

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