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Self-consistent time-dependent, Hartree-Fock calculation for a reactive molecular collision

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We report the first calculations on a molecular collision system using a fully self-consistent time-dependent Hartree-Fock (TDHF) method. The nuclear motion is treated classically with the forces determined by the time propagating electronic charge density. The electronic state is generated using a finite-difference TDHF calculation. We present results including a typical reactive trajectory, a corresponding time evolution of the electronic energy, and density plots of the molecular wave function evolving through the collision.

Finite difference and finite element solutions to the time-dependent Schrödinger equation or the time-dependent, Hartree-Fock (TDHF) equations have provided very accurate results for atomic collision processes at medium- and high-collision energies.[1] There have been many applications in the fields of nuclear collisions,[2] electronic collisions,[3] and molecular dynamics.[4] The calculations using one of these methods which we report here are unique in two respects. It is the first application of finite-difference techniques for TDHF in a molecular collision problem and secondly, it is an application to a range of collision energies (a few eV) in which the nuclear degrees of freedom cannot be treated trivially. Here the forces on the nuclei, determined by the instantaneous electronic charge density, are large enough that a simple straight line or Coulomb trajectory is inappropriate. In addition, since we are studying a molecular collision problem, we must be able to treat reactive trajectories in which the incident and scattered particles are different. Thus in our calculations we solve self-consistently for the time evolution of the electronic wave function in the field of the scattering nuclei whose motion, in turn, is governed by the electronic state.

The system we have chosen to study is the collision between a proton and a hydrogen molecule. This system is important from an experimental point of view. In H plasmas the cross sections for these collisions will affect the concentrations of the different ionic species and may be important in determining the vibrational state distribution of H_2, which is a crucial parameter in the kinetics leading to H^- production.[5] Theoretically, this system is also important because its collisions are known to be highly nonadiabatic. Due to the strong interaction between the lowest two adiabatic electronic states, no accurate collision calculation can ignore the influence of the first excited state.

Since the system has only two electrons, it is in many respects the simplest polyatomic molecule and its adiabatic potential energy surfaces have been determined very accurately.[6] The lowest surface is strongly attractive and the first excited state is strongly repulsive. These two states are degenerate or have avoided crossings for some internuclear geometries in the entrance and exit channels. Due to the deep well in the lower surface, a *very* large number of quantum states are energetically accessible, although most of them are closed asymptotically. For this reason a full quantum-mechanical calculation for collisions in three dimensions is not possible. However, semiclassical methods have been used successfully.[7] Also, a quantum-mechanical calculation does exist for the collinear system.[8] Therefore we decided that a suitable test case for our method would be to consider collisions in this system with the constraint that all three nuclei lie on a straight line. The possible consequences of such collisions are represented by the following equations:

$$H^+ + H_2 \rightarrow H^+ + H_2 \ , \tag{1}$$

$$H^+ + H_2 \rightarrow H + H_2{}^+ \ , \tag{2}$$

$$H^+ + H_2 \rightarrow H_2{}^+ + H \ , \tag{3}$$

$$H^+ + H_2 \rightarrow H_2 + H^+ \ . \tag{4}$$

The first two of these represent nonreactive collisions which result in the exchange of translational and internal (vibrational) energy or charge. The last two represent the various final states in a reactive collision.

We will briefly outline the calculational details and then present illustrative results from a single trajectory. The singlet electronic wave function is written in the Hartree approximation as

$$\Psi(\vec{r}_1, \vec{r}_2, t) = (1/\sqrt{2})\Phi_1(\vec{r}_1,t)\Phi_1(\vec{r}_2,t)(\alpha_1\beta_2 - \beta_1\alpha_2) \ , \tag{5}$$

where the spatial orbital satisfies the usual TDHF equation

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\Phi(\vec{r},t) &= h\Phi(\vec{r},t) \\ &= \left[-\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{2}\int\frac{d\vec{r}\,'\rho(\vec{r}\,',t)}{|\vec{r}-\vec{r}\,'|} - \sum_{\lambda=1}^{3}\frac{e^2}{|\vec{r}-\vec{X}_\lambda|}\right]\Phi(\vec{r},t) \ . \end{aligned} \tag{6}$$

Expressing this wave function in cylindrical coordinates, (R,z,ϕ), which are appropriate for collinear nuclear geometries, we have

$$\Phi(\vec{r},t) = R^{-1/2}\chi(R,z,t)e^{im\phi} \ , \tag{7}$$

where for the relevant molecular Σ state, $m=0$.

We use standard finite difference techniques to solve the time evolution of the wave function, χ, in two spatial dimensions. The second derivatives are evaluated using a three-point difference formula and the time integration is performed using the Peaceman-Rachford alternating directions implicit method.[9]

The nuclei, to a very good approximation, are treated classically. The classical equations of motion include forces due to the internuclear repulsions and the field due to the instantaneous electronic density.

$$\frac{d\vec{x}}{dt}=\vec{v} \tag{8}$$

$$\frac{d}{dt}M\vec{v}=-\vec{\nabla}_x\left(\left\langle\Phi(\vec{r},t)\left|h+\sum_{i=1}^{3}\sum_{j>1}^{3}\frac{e^2}{|\vec{x}_i-\vec{x}_j|}\right|\Phi(\vec{r},t)\right\rangle\right) . \tag{9}$$

The initial conditions consist of the target H_2 molecule at a particular internuclear separation and a vibrational velocity corresponding to one of the eigenfunctions of the previously determined diatomic potential. The initial electronic state is the static Hartree-Fock solution on the finite difference grid for the H_2 molecule at the chosen H_2 bond distance. The incident proton is at a large ("asymptotic") distance from the molecule with an initial velocity in the direction of the diatomic axis. The electronic wave function evolves one step in time according to the instantaneous nuclear positions. Then we evaluate the forces on the nuclei and propagate the classical equations of motion one time step. We iterate this procedure until the nuclear trajectory reaches the asymptotic region where the final state of the system is determined. Thus we obtain a completely self-consistent time-evolving representation of the collision event. In a full calculation, to determine the final-state distributions for a given initial collision energy and vibrational level, we average over the vibrational phase as in a standard classical trajectory calculation.[10]

The results of these calculations are of two types. First, from a full calculation we can obtain the usual final-state distributions; the average charge-transfer and reaction probabilities and the average vibrational energy in the resulting diatomic. We also obtain for each trajectory, as in any time-dependent calculation, the time evolution of all the various parameters that characterize the colliding system. We have the trajectory of the nuclei, the time evolution of the electronic density, and the expectation values of any other interesting operators such as the electronic energy, momenta, etc. Here we show as examples three figures. First, in Fig. 1 is shown the trajectory for the collision. As can be seen, this particular trajectory is reactive since it moves from the region where R_1 is small to the final state where R_2 is small. This system is known to be highly reactive in the few-eV energy range[7,8] so that the trajectory shown here can be assumed to be typical. In Fig. 2 we show the time evolution of the expectation value of th electronic Hamiltonian. Also shown at a number of points is the static Hartree-Fock energy for the corresponding internuclear configuration. Finally, in Fig. 3 we show density plots of our electronic wave function at various times during the collision. By projecting this wave function at the final time onto molecular eigenstates (which must include the translation factors so that the atomic or molecular orbital will follow the nuclei), we can obtain transition probabilities.

The major attraction of the TDHF method is that since the wave function evolves in time partially in response to its own changing charge density it does include some degree of correlation and therefore is better than a static Hartree-Fock (SHF) wave function. Also, since the electronic wave function responds dynamically to the nuclear motions, nonadiabatic effects are included implicitly. This is especially important for many-electron systems where accurate application of the standard perturbed stationary state method[11] is not well defined. In essence, our translation factors[12] and switching functions[12] are built in; the electrons are free to

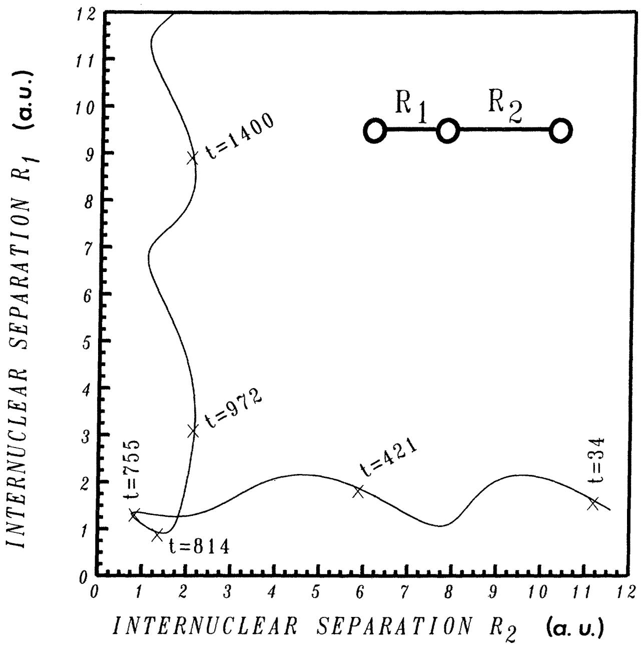

FIG. 1. Trajectory for initial vibrational level $v=2$ and a relative kinetic energy of 3 eV. Time is in atomic units.

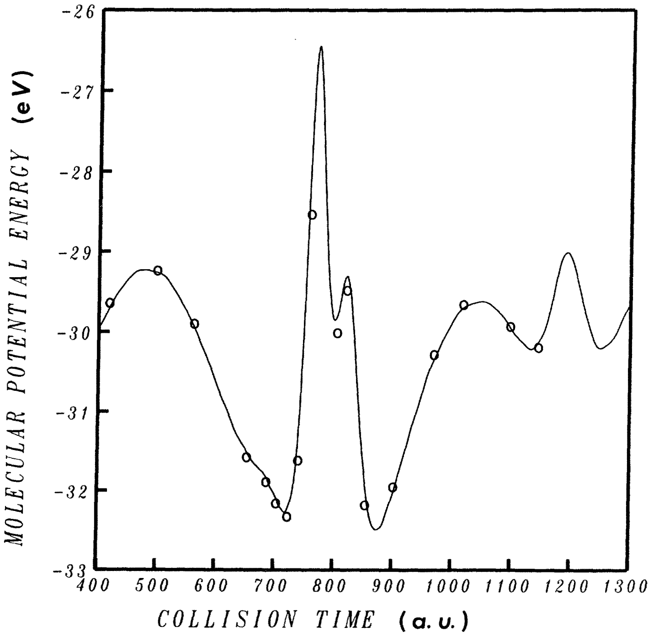

FIG. 2. Time-dependent expectation value of molecular potential energy. Circles denote static Hartree-Fock energies for the relevant internuclear geometries.

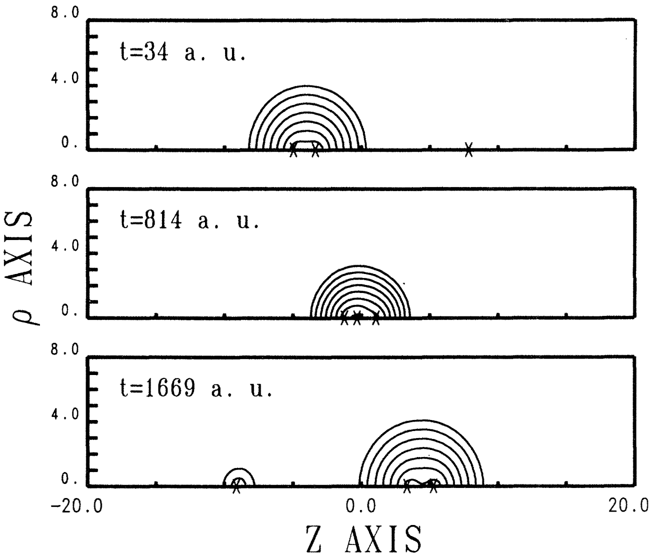

FIG. 3. Density contours near beginning, middle, and end of collision. Contours separated by $\sqrt{10}$. The ×'s denote the positions of the protons.

flow where the equations drive them and are not restricted to the space of a preselected basis set. The most significant limitation of the method is the restriction to a single configuration. It is well known that a single configuration SHF wave function cannot properly describe the electronic state of two open-shell fragments for large interfragment separations, whereas at smaller internuclear separations the SHF wave function becomes much more accurate, particularly for strongly bound (covalent) molecular states. The TDHF wave function, having more flexibility than the static solution, is expected to be even more accurate for all internuclear separations, so we expect that our TDHF wave function provides a good representation of the electronic state in this system. This flexibility is illustrated by the fact that the time-dependent expectation value of the electronic Hamiltonian can lie below the SHF ground-state energy indicating the presence of correlation and, at other times during the collision, lie above it, which indicates the presence of the excited-state components (see Fig. 2). Thus our method uses an approximate wave function whose very simple form makes it easy to include nonadiabatic effects in a straightforward manner. This is not the case for the standard expansion in terms of adiabatic molecular states.

The calculations we have reported here illustrated the feasibility of this method. The subtleties involved in extracting reaction and charge-exchange probabilities from a full calculation, including several trajectories to average over the initial vibrational phase, are beyond the scope of this Brief Report. We only indicate that since the TDHF equations are nonlinear, we do not have a linear superposition of asymptotic states. Thus although our wave function has components of the excited electronic states, obtaining state-to-state transition probabilities is more difficult than in a traditional quantum-mechanical calculation. An understanding of these problems and the generation of more complete results will be subjects of future work.

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