Proton transfer in solution: Molecular dynamics with quantum transitions

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We apply "molecular dynamics with quantum transitions" (MDQT), a surface-hopping method previously used only for electronic transitions, to proton transfer in solution, where the quantum particle is an atom. We use full classical mechanical molecular dynamics for the heavy atom degrees of freedom, including the solvent molecules, and treat the hydrogen motion quantum mechanically. We identify new obstacles that arise in this application of MDQT and present methods for overcoming them. We implement these new methods to demonstrate that application of MDQT to proton transfer in solution is computationally feasible and appears capable of accurately incorporating quantum mechanical phenomena such as tunneling and isotope effects. As an initial application of the method, we employ a model used previously by Azzouz and Borgis to represent the proton transfer reaction $AH-B \Rightarrow A^-H^+B$ in liquid methyl chloride, where the $AH-B$ complex corresponds to a typical phenol-amine complex. We have chosen this model, in part, because it exhibits both adiabatic and diabatic behavior, thereby offering a stringent test of the theory. MDQT proves capable of treating both limits, as well as the intermediate regime. Up to four quantum states were included in this simulation, and the method can easily be extended to include additional excited states, so it can be applied to a wide range of processes, such as photoassisted tunneling. In addition, this method is not perturbative, so trajectories can be continued after the barrier is crossed to follow the subsequent dynamics.

I. INTRODUCTION

Molecular dynamics involves the numerical solution of the classical mechanical equations of motion of an ensemble of interacting atoms or molecules. This method has been shown to be an extremely valuable tool for obtaining insights into chemical behavior in many kinds of systems, including isolated molecules, biopolymers, liquids, and surfaces. The greatest virtue of molecular dynamics is that the classical mechanical equations of motion can be solved easily enough that the method can be applied to systems containing a large number of degrees of freedom. A fundamental limitation of molecular dynamics, of course, is that atoms actually obey quantum mechanical as opposed to classical equations of motion. Zero-point motion, quantum interferences, quantized energy levels, and tunneling are absent in classical mechanics. The importance of quantum mechanical effects on chemical rate processes has been documented experimentally for a great many systems, particularly at low temperatures and those involving hydrogen atoms.

Unfortunately, a fully quantum mechanical version of molecular dynamics for systems of many degrees of freedom is not likely to be practical in the near future, so classical mechanical molecular dynamics will continue to be the workhorse for many years to come. It is important, therefore, to develop ways to incorporate quantum mechanical effects, at least approximately, into molecular dynamics simulations. This may be feasible, for example, in situations for which only one or a few degrees of freedom exhibit significant quantum effects. In such cases, an improvement to classical mechanics alone might be achieved by treating the few selected degrees of freedom quantum mechanically, while treating the rest of the degrees of freedom by classical mechanical degrees of freedom must be treated self-consistently, i.e., each should have an effect on the other. Moreover, the assumption that the quantum degrees of freedom are "adiabatic" is inadequate in many cases, so quantum transitions must be incorporated into the dynamics. A number of methods for doing this have been proposed. With the exception of Ref. 13, which addresses vibrational relaxation, all of these so-called "surface-hopping" methods have been applied to date to processes for which the quantum degrees of freedom are electronic and all atoms move classically. Surface hopping in that case refers to quantum transitions among different electronic states. In the present paper we describe our efforts to apply one of these methods to a case where the adiabatic approximation is assumed to be valid for electrons, but where one of the atoms (a hydrogen atom) may display quantum behavior. In this case, surface hops will refer to quantum transitions among vibrational-like levels of the hydrogen in a potential dictated by the positions of the classical atoms. Thus we generalize the name of the method, "molecular dynamics with electronic transitions," to "molecular dynamics with quantum transitions" (MDQT).

We apply MDQT to proton transfer in solution, which has been studied using various other methods. The specific system that we examine here is a model for the intramolecular reaction $AH-B \Rightarrow A^-H^+B$ in liquid methyl chloride, constructed and studied by Azzouz and Borgis. We use essentially the same parameters as Azzouz and Borgis, who chose them to represent a typical OH-N asymmetrical hydrogen bonded complex. This is a stringent test of the method because it is a problem that has many degrees of freedom and in which both quantum zero-point energy and quantum tunneling may play significant roles. Zero-point motion is difficult to incorporate accurately into an otherwise classical mechanical framework. Tunneling is also a very
challenging problem.\textsuperscript{25} While there exist a host of "tunneling corrections"\textsuperscript{26} to classical rates,\textsuperscript{26} they do not provide a way to continuously follow a trajectory from one side of the energy barrier to the other if it has insufficient energy to surmount it classically. (Exceptions to this are the methods of Valone \textit{et al.}\textsuperscript{27} and of Makri and Miller.\textsuperscript{28})

Following the terminology of Hynes, Borgis, and others,\textsuperscript{17,19} proton transfer can be classified as either adiabatic or nonadiabatic, and different computational procedures are used in the different regimes. The MDQT method we propose should apply, in principle, to both regimes, as well as to cases intermediate between these extremes. To clarify the terminology, we assume throughout this paper that the dynamics is electronically adiabatic, i.e., the motion of the atoms is governed by a single electronic Born--Oppenheimer potential energy hypersurface. Reaction barriers or tunneling barriers are frequently associated with a change in electronic configuration as the system traverses the barrier. In such cases there may exist a complementary low-lying excited electronic state in the vicinity of the top of the barrier. In this study we do not consider the possibility of electronic transition to such an excited state, although the MDQT approach could include this process if it were significant. Throughout the remainder of this paper, the terms adiabatic, diabatic and nonadiabatic refer to the quantum dynamics of the hydrogen atom, used in analogy to the more usual electronic situation.

We start with a Born--Oppenheimer separation of the hydrogen atom from that of all other atoms. The coordinates of all of the classical atoms are fixed at some position, \(\mathbf{R}\), and we compute the eigenstates and eigenenergies of the hydrogen atom subject to the potential dictated by the fixed classical atoms. Figure 1 is a schematic one-dimensional illustration of potential curves for hydrogen atom motion at three different configurations of the classical coordinates. In Fig. 1(a), the reactant side exhibits a deeper potential well, so the ground state hydrogen atom wave function will be localized almost completely on the reactant side, and the first excited state on the product side, as illustrated by solid and dashed lines. The reverse is true in Fig. 1(c); the ground state corresponds to products and the first excited state to reactants. When the classical coordinates are positioned so that they produce nearly symmetrical potential wells, Fig. 1(b), then the lowest two hydrogen atom eigenstates will have almost equal reactant and product character, with the lower and upper eigenstates displaying approximately even and odd symmetry, respectively. The energy difference between the two lowest adiabatic eigenstates when the potential wells are approximately symmetrical is called the "tunnel splitting" and is proportional to the tunneling rate between reactants and products.

The most well-defined way to formulate a dynamical method that treats the classical particles and the quantum hydrogen motion in a self-consistent way is to invoke the adiabatic assumption (the Born--Oppenheimer approximation), i.e., to require that the hydrogen atom be restricted to its ground vibration-like state at all times. An adiabatic simulation will then proceed as follows. At each time increment, the eigenenergy and eigenfunction of the lowest hydrogen atom vibrational state and the resulting Hellmann–Feynman forces on the classical particles are computed. These forces are then used to propagate the classical particles via classical mechanics through one time increment. The process is then repeated to map out a complete trajectory. This procedure has been applied to proton transfer reactions in solution by Borgis \textit{et al.}\textsuperscript{17} and Laria \textit{et al.}\textsuperscript{18} In their simulations, the energy separation of the ground and excited hydrogen vibrational states was sufficiently large to prevent significant population of the excited state, so the adiabatic assumption appears valid. This will be the case in proton transfer situations when the potential energy barrier is small or nonexist-
ent, so that the tunnel splitting is large and the tunneling rate essentially instantaneous. This corresponds to the strong coupling limit of proton transfer as formulated by Bell, and the adiabatic approach provides an accurate way to incorporate tunneling and zero-point corrections in this limit.

If the tunneling barrier is relatively large then the tunnel splitting will be small, and quantum transitions between the lowest two states may become probable. It is this case for which MDQT is essential. For example, since the first excited state of Fig. 1(c) corresponds to the hydrogen in the reactant state, the effect of a quantum transition from the ground state to the first excited state as the system evolves from Figs. 1(a) to 1(c) is that proton transfer does not occur. Thus nonadiabatic transitions generally reduce the proton transfer probability. Since the tunneling rate depends on the energy splitting between the ground and excited states, including both states is crucial to properly describe tunneling. Only the ground state enters in the adiabatic approximation, however, so the adiabatic method contains no information at all about the tunneling rate. If the adiabatic method is applied to a case where the tunnel splitting is small, then the computed rate will be too large. This can be seen from Fig. 1. No matter how high the barrier, if a solvent fluctuation takes the system from a configuration like Fig. 1(a) to one like Fig. 1(c), then the adiabatic assumption will demand that a reaction occur, and the ground state wave function suddenly switches from reactant to product character. This sudden change of character of the wave function is nonphysical since the wave function cannot respond instantaneously. Nonadiabatic transitions correct this nonphysical behavior by allowing for a transition to the excited state, thereby retaining reactant character in Fig. 1(c). As discussed below, the MDQT method introduces transitions with the probabilities required to reproduce the correct tunneling rate and does so self-consistently with the classical motion.

In cases where the tunnel splitting is so small that the probability of a nonadiabatic transition is nearly unity (the diabatic limit), then the probability of proton transfer can be computed perturbatively. An advantage of the MDQT method proposed here is that it can be used in both adiabatic and diabatic limits, as well as in the intermediate regime. This is crucial for proton transfer where the barrier height depends sensitively on the separation of donor and acceptor. The same system will generally display both adiabatic and nonadiabatic behavior in different regions of configuration space. As discussed below, even in cases for which the adiabatic pathway dominates, the adiabatic method may fail because nonadiabatic transitions may be required to turn off nonphysical tunneling in nonadiabatic regions. Another advantage of MDQT is that it is not perturbative, so trajectories can be continued after the barrier is crossed to evaluate reactivity. Nonadiabatic transitions may be required to turn off nonphys-

II. METHODS AND RESULTS

In this section we discuss the methods we have developed for applying MDQT to proton transfer. In subsection A, we present the model system and the associated interaction potentials. In subsection B, we discuss the adiabatic molecular dynamics method, and in subsection C, we present the method by which we include quantum mechanical transitions (MDQT). Subsection D is an outline of the specific nonadiabatic molecular dynamics scheme we have applied here. We discuss the calculation of the rate constants for proton transfer and present our results in subsections E and F.

A. Azzouz–Borgis model

The model system we are using to study proton transfer is essentially the same as that used by Azzouz and Borgis. The proton transfer reaction is $\text{AH} \rightarrow \text{B} \rightarrow \text{A}^+ \rightarrow \text{H}^+ + \text{B}$. We are treating the proton coordinate quantum mechanically, as is essentially the same as that used by Azzouz and Borgis. Since the model constrains the complex $\text{AH} \rightarrow \text{B}$ to be linear, the position of $\text{H}$ can be represented by a one-dimensional variable $r$, which is the distance between $\text{A}$ and $\text{H}$ in the complex. We are treating the proton coordinate quantum mechanically, as will be discussed in the next subsection. In this subsection we discuss the interaction potentials for the system.

The solvent–solvent interaction $V_{SS}(\mathbf{r})$ is in the form of intermolecular site–site Lennard-Jones and Coulomb potentials. We use the TIPS (transferable intermolecular potential functions) format, where the interaction $\epsilon_{mn}$ between solvent molecules $m$ and $n$ is a sum of interactions between sites $i$ and $j$ on $m$ and $n$, respectively:

$$
\epsilon_{mn} = \sum_i \sum_j \left[ q_i q_j e^{2/r_{ij}} + A_{ij} A_{ji} r_{ij}^{-2} - C_{ij} C_{ji} r_{ij}^{-6} \right].
$$

For methyl chloride, the methyl group is reduced to a single atomic site, and the distance between the methyl and chloride groups is fixed at 1.781 Å. The TIPS parameters were...
TABLE I. TIPS parameters for methyl chloride; used for solvent–solvent interaction.

<table>
<thead>
<tr>
<th>Site</th>
<th>$q$ (e)</th>
<th>$A^2$ (kcal Å$^{12}$ mol$^{-1}$)</th>
<th>$C^2$ (kcal Å$^{4}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>0.25</td>
<td>$7.95 \times 10^6$</td>
<td>2750</td>
</tr>
<tr>
<td>Cl</td>
<td>-0.25</td>
<td>$5.25 \times 10^6$</td>
<td>2950</td>
</tr>
</tbody>
</table>

obtained from Bigot et al.$^{30}$ and are given here in Table I. These parameters have recently been used for extensive studies of liquid methyl chloride.$^{31}$

The hydrogen-bonding interaction (and repulsion between A and B) within the $A\cdots B$ complex is given by

$$V_{HB}(R_{AB};r) = b e^{-aR_{AB}}+D_A \left[ 1 - \exp \left( -\frac{n_A(r-d_A)^2}{2r} \right) \right] + c D_B \left[ 1 - \exp \left( -\frac{n_B(r-d_B)^2}{2(r-R_B-r)} \right) \right],$$

where $R_{AB}=|\mathbf{R}_A - \mathbf{R}_B|$. This gas-phase H-bonding potential is discussed in detail by Azzouz and Borgis.$^{16}$ The parameters we have used are given in Table II and correspond closely to Model II in Ref. 16. The potential is shown for $R_{AB}=2.7$ Å in Fig. 2. The masses of A and B are $m_A=93$ and $m_B=59$, which correspond to the masses of phenol and trimethylamine, respectively.

The interaction of the solvent with the complex, $V_{CS}(R;r)$, is the same as that used in Ref. 16 and consists of both a Lennard-Jones and a Coulomb part. The Lennard-Jones part $V_{LJ}(\mathbf{R})$ involves the interaction of the A and B groups of the complex with the methyl and chloride groups of each solvent molecule. The Lennard-Jones parameters are chosen to be identical for all of these site–site interactions: $\sigma=3.5$ Å and $\epsilon=200$ K. The Coulombic part $V_C(\mathbf{R};r)$ involves the interaction between the charges on the solvent molecules (given in Table I) and the r-dependent point charges $e_a(r)$ assigned to A, H, and B of the complex

$$e_a(r) = [1-f(r)]e_a^e + f(r)e_a^i, \quad \alpha = A, H, B,$$

$$f(r) = \frac{1}{2} \left[ 1 + \frac{r-r_0}{\sqrt{(r-r_0)^2+l^2}} \right],$$

where $r_0=1.43$ Å and $l=0.125$ Å. The reactant, covalent state is defined by $e_A^e=0.5e$, $e_H^e=+0.5e$, $e_B^e=0$, and the product, ionic state is defined by $e_A^i=-e$, $e_H^i=+0.5e$, $e_B^i=+0.5e$.

As in Ref. 16, the simulations described in this paper were performed using periodic boundary conditions$^9$ for a system of 255 solvent molecules and one $A\cdots B$ complex in a cube with sides of length 28 Å (i.e., density $p=0.012$ Å$^{-3}$). Our simulations were run at a temperature of 247 K, which is essentially the same as the temperature of 249 K used in Ref. 16. The Lennard-Jones potential for the solvent–solvent and the solvent–complex interactions was spherically truncated at $R_c=13.8$ Å and shifted accordingly. The Coulombic potential for the solvent–solvent and solvent–complex interactions was smoothly truncated to zero at $R_c=13.8$ Å using a function $T(R_{ij})$ given by Steinhauser:$^{32}$

$$T(R_{ij}) = \begin{cases} 1, & R_{ij} < R_T, \\ 0, & R_{ij} > R_c, \end{cases}$$

where $R_T$ is the distance between the centers of two interacting neutral molecules and $R_T=0.95R_c$.

Note that in the gas-phase H-bonding potential shown in Fig. 2, the well with minimum at $r\approx 1.0$ represents the reactant, covalent state $AH\cdots B$, and the well with minimum at $r\approx 1.6$ represents the product, ionic state $A^-H^+B$. The Coulomb part of the interaction of the solvent with the complex $V_C(\mathbf{R};r)$ stabilizes the ionic form of the complex much more than the covalent form, so the product well in Fig. 2 is lowered more than the reactant well in the presence of the solvent. Thus for some configurations of the classical coordinates, the potential energy of the system as a function of the quantum coordinate $r$ qualitatively resembles the curves in Fig. 1, where the reactant and product wells are nearly symmetric. These are the situations where tunneling may occur.

B. General simulation scheme for adiabatic treatment

As mentioned above, we treat the proton coordinate $r$ quantum mechanically and the other coordinates $\mathbf{R}$ classically, and we separate the protonic motion from the slower

![FIG. 2. Gas-phase H-bonding potential, $V_{HB}(R_{AB};r)$, within $AH\cdots B$ complex for $R_{AB}=2.7$ Å.](image-url)
classical motions in the system. In this subsection, we discuss the simulation scheme for an adiabatic treatment, where we assume that the Born–Oppenheimer approximation is valid so the proton always remains in a single state. In other words, we assume that the proton can instantaneously adapt to the classical coordinates. In the next two subsections, we extend this scheme for a nonadiabatic treatment, where we allow the proton to make transitions among quantum mechanical states, i.e., where we no longer invoke the Born–Oppenheimer approximation.

The Schrödinger equation for the proton at a given configuration \( R \) of the classical coordinates is

\[
\begin{align*}
\hat{H}_p(R;r)\Psi_n(R;r) &= \left( -\frac{\hbar^2}{2m_p} \nabla_r^2 + V_{CB}(R;r) \right) \Psi_n(R;r) \\
&= \epsilon_n(R) \Psi_n(R;r),
\end{align*}
\]

where \( \hat{H}_p \) is the proton Hamiltonian and \( m_p \) is the mass of the proton. Then the Hamiltonian for the classical particles is

\[
\hat{H}(R) = -T + V_\text{class}(R) + \epsilon_n(R),
\]

where \( T \) is the kinetic energy of all of the classical particles. Thus the equations of motion for the classical particles with masses \( m_i \) are

\[
\begin{align*}
m_i \ddot{\mathbf{r}}_i &= -\nabla_{\mathbf{r}_i} V_\text{class}(\mathbf{r}_i) - \epsilon_n(R) \\
&= -\nabla_{\mathbf{r}_i} V_\text{class}(\mathbf{r}_i) - \nabla_{\mathbf{r}_i} \langle \Psi_n | \hat{H}_p | \Psi_n \rangle \\
&= -\nabla_{\mathbf{r}_i} V_\text{class}(\mathbf{r}_i) - \langle \Psi_n | \nabla_{\mathbf{r}_i} \hat{H}_p | \Psi_n \rangle,
\end{align*}
\]

where the brackets denote integration over only the quantum mechanical coordinate \( r \). We have used the Hellmann–Feynman theorem\(^3\) for the last equality, which involves the Hellmann–Feynman forces

\[
\langle \Psi_n | \nabla_{\mathbf{r}_i} \hat{H}_p | \Psi_n \rangle = \int dr \ \Psi_n^* (\mathbf{r};r) \nabla_{\mathbf{r}_i} \hat{H}_p (\mathbf{r};r) \Psi_n (\mathbf{r};r).
\]

Note that the subscript \( n \) denotes the quantum mechanical state of the proton, which in this subsection we will take to be the ground state, \( n=0 \).

The general simulation scheme for the adiabatic treatment is as follows. First, the Schrödinger Eq. (5) is solved for the ground state for a given classical configuration. Then, using the ground state wave function to calculate the Hellmann–Feynman forces given in Eq. (8), the classical equations of motion [Eqs. (7)] are integrated to obtain a new classical configuration. This procedure is repeated until the simulation is terminated according to a criterion discussed below. In the remainder of this subsection, we discuss the details of our implementation of this procedure.

The Schrödinger Eq. (5) was solved by expanding the wave function in a set of normalized basis functions

\[
\Psi_n(R;r) = \sum c_{in}(R) \phi_i(r).
\]

The basis functions were of the form of the solutions for a quantum mechanical simple harmonic oscillator\(^3\)

\[
\phi_i(r) = 2^{-m'2 \pi^{1/4} (m')^{-1/2} \alpha^{1/2} H_m[\alpha(r-r_0)]} \times \exp[\alpha^2 (r-r_0)^2/2],
\]

where \( m \) is an integer, \( H_m(x) \) is a Hermite polynomial, and the index \( i \) on the basis function represents a pair of values for \( m \) and \( r_0 \). We used a total of 6 basis functions, consisting of two sets of 3 basis functions (\( m=0 \rightarrow 5 \)). One set of six basis functions was centered at \( r_0=1.0 \text{ Å} \), and the other set was centered at \( r_0=1.6 \text{ Å} \), so there were six basis functions approximately centered at the minimum of each well in the gas phase potential shown in Fig. 2. All 12 basis functions had \( \alpha=7.732 \text{ Å}^{-1} \), which corresponds to a proton oscillating harmonically with a frequency of \( \omega=2000 \text{ cm}^{-1} \).

If we substitute the expansion in Eq. (9) into Eq. (5), then we get the standard eigenvalue problem

\[
H c = \epsilon c,
\]

where \( H \) is a Hamiltonian matrix with elements

\[
H_{ij} = \int dr \ \phi_i(r) \hat{H}_p (r;r) \phi_j(r)
\]

and \( S \) is an overlap matrix with elements

\[
S_{ij} = \int dr \ \phi_i(r) \phi_j(r).
\]

We calculated \( H_{ij} \) and \( S_{ij} \) numerically using Simpson’s method\(^5\) with 33 points evenly spaced over a region from \( r=0.6 \text{ Å} \) to \( r=2.0 \text{ Å} \). We solved the eigenvalue problem by symmetrically orthogonalizing the basis set to obtain a transformed eigenvalue equation

\[
H' c' = \epsilon c',
\]

solving for \( c' \) and \( \epsilon \) by diagonalizing \( H' \), and then back transforming \( c' \) to get \( c \).\(^6\) We used the EISPACK\(^7\) software package for the diagonalization of the matrix \( H' \).

After solving the Schrödinger equation, we calculated the Hellmann–Feynman forces in Eq. (8) using the same numerical integration method as we used to calculate \( H_{ij} \) and \( S_{ij} \). Given these forces, we used the RATTLE\(^8\) algorithm, which is based on the velocity Verlet algorithm, to integrate the equations of motion [Eqs. (7)] while constraining the intramolecular bond lengths of the solvent molecules.

C. Nonadiabatic methods

In this subsection we discuss the MDQT method by which we incorporated quantum mechanical transitions into the molecular dynamics scheme discussed in the previous subsection. We used the method introduced in Ref. 11. With this method, the proton remains in a single state, except for the possibility of sudden switches from one state to another that occur in infinitesimal time. We first outline the algorithm used to determine when such a switch will occur, and then we present the details of our implementation of this algorithm.

We assume that the classical coordinates follow some (not necessarily classical) trajectory \( R(t) \), where \( t \) is time.
Then the Hamiltonian $H_\rho(R;r)$ is a time-dependent operator, depending on time through $R(t)$. We now define a wave function $\Phi(R,r,t)$ that describes the quantum mechanical state at time $t$, and we expand this wave function in terms of the orthonormal Born–Oppenheimer wave functions $\Psi_n(R;r)$ described in Sec. II B

$$\Phi(R,r,t) = \sum_n C_n(t) \Psi_n(R;r).$$

where $C_n(t)$ are complex-valued expansion coefficients. If we substitute Eq. (15) into the time-dependent Schrödinger equation and perform some algebraic manipulations, we get

$$i\hbar \dot{C}_k = \sum_j C_j(V_{kj} - i\hbar \dot{R} \cdot \mathbf{d}_{kj}),$$

where

$$V_{kj}(R) = \langle \Psi_k(R;r)|H_\rho(R;r)|\Psi_j(R;r)\rangle,$$

and the nonadiabatic coupling vector $\mathbf{d}_{kj}(R)$ is defined as

$$\mathbf{d}_{kj}(R) = \langle \Psi_k(R;r)|\nabla_R \Psi_j(R;r)\rangle.$$

Again the brackets denote integration over only the quantum mechanical coordinate $r$. Equations (16) are integrated numerically, simultaneously with integration of the trajectory $R(t)$, to obtain the amplitudes $C_j$ of each quantum mechanical state at a given time $t$. We use the information contained in these amplitudes in order to determine whether or not the proton should switch from one state to another at a given time $t$.

The “fewest switches” algorithm presented in Ref. 11 correctly apportions trajectories among states according to the quantum probabilities $|C_j(t)|^2$ with the minimum required number of quantum transitions. According to this algorithm, the probability of switching from the current state $k$ to all other states $j$ during the time interval between $t$ and $t + \Delta$ is

$$g_{kj} = \frac{b_{kj}(t + \Delta)\Delta}{a_{kk}(t + \Delta)} ,$$

where

$$a_{kj} = C_k C_j^*$$

and

$$b_{kj} = 2\hbar^{-1} \text{Im}(a_{kj}^* V_{kj}) - 2 \text{Re}(a_{kj}^* \dot{R} \cdot \mathbf{d}_{kj}).$$

If $g_{kj}$ is negative, it is set equal to zero. Note that $a_{kk}$ is the population in state $k$. We also point out that Eq. (19) is valid only for $\Delta$ small enough to satisfy the following conditions:

$$a_{kk}(t) = a_{kk}(t + \Delta),$$

$$a_{kk}(t + \Delta) - a_{kk}(t) = a_{kk}(t + \Delta)\Delta.$$

Later in this subsection we will discuss methods for calculating $g_{kj}$ when $\Delta$ is so large that these conditions are not satisfied.

In order to determine whether a switch to any state $j$ will occur, a uniform random number, $\xi$, $0 < \xi < 1$, is selected at each time step in the trajectory. For example, if $k = 1$, a switch to state 2 will occur if $\xi < g_{12}$, a switch to state 3 will occur if $g_{12} < \xi < g_{12} + g_{13}$, etc. If a switch to a different state $k'$ does occur and if $\epsilon_j(R) = \epsilon_j'(R)$, then the velocities must be adjusted in order to conserve total energy. According to Ref. 11, the adjustment should be made to the component of velocity in the direction of the nonadiabatic coupling vector $\dot{R} \cdot \mathbf{d}_{kj}(R)$ at the position of the transition $R$. Later in this subsection we will discuss methods for making this velocity adjustment. If $\epsilon_j(R) > \epsilon_j(R)$ and the velocity reduction required is greater than the component of velocity to be adjusted, then the switch does not occur (the transition is classically forbidden), and the component of velocity in the direction of the nonadiabatic coupling vector is reversed.

This switching procedure ensures that, for a large ensemble of trajectories, and ignoring the difficulties with classically forbidden states, the fraction of trajectories assigned to any state $k$ at any time $t$ will equal the quantum probability $|C_k(t)|^2$. In the remainder of this subsection, we discuss the details of our implementation of this algorithm.

First we discuss the integration of Eqs. (16) to obtain the amplitudes $C_j$ of each state. Note that in the adiabatic (Born–Oppenheimer) representation,

$$V_{kj}(R) = \epsilon_k(R) \delta_{kj},$$

where $\delta_{kj}$ is the Kronecker delta function and $\epsilon_k(R)$ has already been obtained from the solution of the Schrödinger Eq. (5). For numerical convenience, we introduce the following new variables:

$$C_j = C_j \exp(i \int_0^t dt' V_{00}/\hbar).$$

Then we can rewrite Eqs. (16) in terms of these new coefficients

$$i\hbar \dot{C}_k - \dot{C}_k(V_{kk} - V_{00}) - i\hbar \sum_j C_j \dot{R} \cdot \mathbf{d}_{kj}.$$

We used the fourth-order Runge–Kutta numerical integration method to integrate Eqs. (26) from $t$ to $t + \Delta$, where $\Delta$ is the step size for the integration of the classical equations of motion [Eqs. (7)] discussed in the previous subsection. We point out that the new coefficients $\dot{C}_j$ contain all of the information necessary for the switching algorithm, so we do not ever have to calculate the original coefficients $C_j$.

Moreover, use of the chain rule gives

$$\left( \Psi_k \frac{\partial \Psi_j}{\partial t} \right) = \dot{R} \cdot \mathbf{d}_{kj}(R),$$

so the nonadiabatic coupling $\dot{R} \cdot \mathbf{d}_{kj}$ can be evaluated numerically using a finite difference method to evaluate the derivative of the wave function with respect to time. Hence, we do not need to calculate the nonadiabatic coupling vector explicitly to compute the coefficients $\dot{C}_j$. Using this method, it is straightforward to derive the following:

$$\left[ \dot{R} \cdot \mathbf{d}_{kj}(t + \Delta/2) \right] \approx \frac{1}{2\Delta} \left[ \langle \Psi_k(t)|\Psi_j(t + \Delta)\rangle - \langle \Psi_k(t + \Delta)|\Psi_j(t)\rangle \right].$$
Thus we can calculate $V_{kk} = \epsilon_k$ at each classical time step, and we can calculate the nonadiabatic coupling $\mathbf{R} \cdot \mathbf{d}_{kj}$ halfway between each classical time step. The fourth-order Runge-Kutta numerical integration method, however, requires that we obtain values for $V_{kk}$ and for the nonadiabatic coupling at other times. Moreover, it is often necessary to use a smaller time step $\delta t \ll \Delta$ for the integration of Eqs. (26) than is required to integrate the classical equations of motion [Eqs. (7)]. Since the most computationally expensive part of the simulation is the calculation of the classical forces, i.e., evaluation of $-\nabla_{\mathbf{R}} V_{SS}(\mathbf{R})$, it is important for $\Delta$ to be as large as possible. Thus we used a smaller time step $\delta t \ll \Delta$ for the integration of Eqs. (26), which required us to obtain values for $V_{kk}$ and for the nonadiabatic coupling at many intermediate times between $t$ and $t+\Delta$. We used a simple linear interpolation and extrapolation scheme to obtain these values at intermediate times. For example, we interpolated between $\epsilon_k(t)$ and $\epsilon_k(t+\Delta)$ to determine the necessary intermediate values of $\epsilon_k = V_{kk}$. Similarly, we interpolated and extrapolated from $[\mathbf{R} \cdot \mathbf{d}_{kj}](t-\Delta/2)$ to $[\mathbf{R} \cdot \mathbf{d}_{kj}](t+\Delta/2)$ in order to get the necessary values of the nonadiabatic coupling vector between $t$ and $t+\Delta$.

Next we discuss the calculation of the switching probabilities $g_{kj}$. Recall that Eq. (19) is only valid if the conditions in Eqs. (22) and (23) are satisfied. In general, we found that the largest time step $\Delta$ capable of integrating the classical equations was often too large to satisfy these conditions. As mentioned above, however, for computational efficiency $\Delta$ should be as large as possible. So we used the following alternative method to calculate $g_{kj}$. Maintaining the "fewest switches" criterion, it is straightforward to derive the following:

$$g_{kj} = \frac{\int_{t}^{t+\Delta} dt \ b_{jk}(t)}{a_{kk}(t)},$$

where, in our case,

$$b_{jk}(t) = -2 \text{Re}(\tilde{C}_j(t) \tilde{C}_k^*(t) [\mathbf{R} \cdot \mathbf{d}_{kj}](t)).$$

The numerator of Eq. (29) can be numerically integrated simultaneously with the integration of Eqs. (26) using the time step $\delta t$. This requires very little extra computation since the quantities in Eq. (30) must be calculated at all relevant intermediate times during the integration of Eqs. (26).

We emphasize that if we were forced to decrease the classical time step $\Delta$ in order to calculate the amplitudes of the states [Eqs. (26)] or to calculate the switching probabilities [Eq. (29)], the computational expense of the simulations would increase substantially. Using the methods described above, however, we typically used values of $\delta t = 0.001 \Delta$ without significantly increasing the computational expense.

Now we discuss the method of adjusting the velocities to maintain energy conservation if a switch occurs. Recall that for a switch from state $k$ to $k'$, the adjustment should be made to the component of velocity in the direction of the nonadiabatic coupling vector $\mathbf{d}_{kk'}(\mathbf{R})$, which is defined in Eq. (18). We can calculate this vector using the off-diagonal Hellmann–Feynman expression

$$\nabla_{\mathbf{R}} \langle \Psi_k(\mathbf{R};r) | H_p(\mathbf{R},r) | \Psi_{k'}(\mathbf{R};r) \rangle$$

$$= -0 - \langle \Psi_k(\mathbf{R};r) | \nabla_{\mathbf{R}} H_p(\mathbf{R},r) | \Psi_{k'}(\mathbf{R};r) \rangle$$

$$= -[\epsilon_{kk'}(\mathbf{R}) - \epsilon_{kk'}(\mathbf{R})] \langle \Psi_k(\mathbf{R};r) | \nabla_{\mathbf{R}} \Psi_{k'}(\mathbf{R};r) \rangle,$$

which leads to

$$\mathbf{d}_{kk'}(\mathbf{R}) = \frac{\langle \Psi_k(\mathbf{R};r) | \nabla_{\mathbf{R}} H_p(\mathbf{R},r) | \Psi_{k'}(\mathbf{R};r) \rangle}{\epsilon_{kk'}(\mathbf{R}) - \epsilon_{kk'}(\mathbf{R})}$$

for $k \neq k'$. Note that $\mathbf{d}_{kk} = 0$ for orthonormal wave functions $\Psi_n(\mathbf{R};r)$.

The velocities should be adjusted as if they were subjected to a force in the direction of the nonadiabatic coupling vector. Recall, however, that for the classical molecular dynamics [integration of Eqs. (7)], we are using Cartesian coordinates with constraints on the intramolecular solvent bonds. Thus in addition to the nonadiabatic coupling force, a constraint force must be applied to the velocities to ensure that the adjusted velocities satisfy the derivatives of the constraints, i.e., that the adjusted velocities do not have any components in the direction of the solvent intramolecular bonds. We applied this constraint force using a method equivalent to the velocity part of the RATTLE algorithm.

Using this method, the new velocities $\mathbf{R}'$ can be calculated as follows:

$$\dot{\mathbf{R}}' = \dot{\mathbf{R}} - \gamma_{kk'} \mathbf{d}_{kk'}(\mathbf{R})/m_i,$$

where $i$ indicates a site on a molecule and $m_i$ is the mass of the group at site $i$.

In order to account properly for the constraint forces on the solvent molecules of our model system, we define

$$\mathbf{d}_{kk'}^i(\mathbf{R}) = \mathbf{d}_{kk'}(\mathbf{R}) - g_{ij} \mathbf{R}_{ij},$$

where $i$ and $j$ indicate the two groups on a particular solvent molecule,

$$\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j,$$

and

$$g_{ij} = R_{ij} (d_{kk'}^i/m_i - d_{kk'}^j/m_j)/[\mathbf{d}_{jj}^i(m_i^{-1} - m_j^{-1})].$$

Note that $\mathbf{d}_{kk'}^i(\mathbf{R}) = \mathbf{d}_{kk'}^j(\mathbf{R})$ if $i$ represents a site on the AH–B complex since no constraints are imposed on the complex.

In order to maintain energy conservation, we define

$$\gamma_{kk'} = b_{kk'} + \sqrt{b_{kk'}^2 + 4a_{kk'} [\epsilon_k(\mathbf{R}) - \epsilon_{kk'}(\mathbf{R})]}, \quad b_{kk'} < 0$$

and

$$\gamma_{kk'} = b_{kk'} - \sqrt{b_{kk'}^2 + 4a_{kk'} [\epsilon_k(\mathbf{R}) - \epsilon_{kk'}(\mathbf{R})]}, \quad b_{kk'} \geq 0$$

where

$$a_{kk'} = \frac{1}{2} \sum_i m_i^{-1} |\tilde{d}_{kk'}^i|^2.$$
and
\[ b_{kk'} = \sum_i \hat{\mathbf{R}}_i \cdot \mathbf{d}_{kk'}. \]  
(41)

Note that a switch can occur only if
\[ b_{kk'}^2 + 4a_{kk'}[\epsilon_k(R) - \epsilon_{k'}(R)] \geq 0. \]  
(42)

Otherwise, there is not enough velocity in the direction of the nonadiabatic coupling vector to maintain energy conservation. In this case, the system remains in the initial quantum state, and we just reverse the component of velocity in the direction of the nonadiabatic coupling vector.\(^{39}\) i.e., we change the velocities according to Eq. (33) with \[ \gamma_{kk'} = b_{kk'}/a_{kk'}. \]

D. Outline of method for nonadiabatic dynamics

In this subsection we outline the method we used to perform the nonadiabatic dynamics.

**Step 1.** Initialize coefficients \( \tilde{C}_j \) and choose state \( k. \) [We always started with the total population in the ground state \( (k=0), \) so we set \( \tilde{C}_0 = 1.0 \) and set all other coefficients to zero.] Initialize nonadiabatic coupling. (We took two adiabatic steps to obtain the nonadiabatic coupling necessary for the extrapolation scheme discussed above.) Solve the Schrödinger equation for the current configuration \( \mathbf{R}(t_0) \) to obtain \( \Psi_n(t_0) \) and \( \epsilon_n(t_0). \) In the following steps, \( t_0 = 0, \) and \( s \) is an integer representing the current time step.

**Step 2.** Using \( \Psi_k(s-1)\Delta \) to evaluate the Hellmann–Feynman forces [Eq. (8)\], integrate the equations of motion [Eqs. (7)\] from \( t = (s-1)\Delta \) to \( t = s\Delta \) using a time step of \( \Delta \) to obtain a new configuration \( \mathbf{R}(s\Delta). \)

**Step 3.** Solve the Schrödinger Eq. (5) for this configuration to obtain \( \Psi_n(s\Delta) \) and \( \epsilon_n(s\Delta) \) for all states \( n \) included in the calculation. (We report results below for simulations including 2 states and 4 states.)

**Step 4.** Use Eq. 28 to calculate \( [\hat{\mathbf{R}} \cdot \mathbf{d}_{ij}] (s\Delta - \Delta/2) \) for all included states \( j. \)

**Step 5.** Integrate the coefficient equations [Eqs. (26)\] from \( \tilde{C}_j(s-1)\Delta \) to \( \tilde{C}_j(s\Delta) \) for all included states \( j \) using a time step of \( \delta \leq \Delta. \) Simultaneously, numerically integrate \( f(t) \Delta dt \) \( b_{jk}(t), \) where \( b_{jk}(t) \) is defined in Eq. (30), for all included states \( j \) using a time step of \( \delta. \)

**Step 6.** Use Eq. (29) to calculate the switching probabilities \( g_{kj} \) for all included states \( j. \)

**Step 7.** Generate a random number and determine whether a switch to any state \( j \) should be invoked according to the switching probabilities \( g_{kj}. \)

**Step 8.** If no switch should occur, go back to Step 2. If a switch from \( k \) to \( k' \) should occur, calculate the nonadiabatic coupling vector using Eq. (32) and use this to calculate the velocity adjustment necessary to conserve energy [Eqs. (38)–(41)\]. If the required velocity reduction is greater than the component of velocity to be adjusted [i.e., Eq. (42) is not satisfied], no switch occurs, so reverse the velocity component along the nonadiabatic coupling vector and go back to Step 2. Otherwise, adjust the velocities using Eq. (33), switch states (set \( k = k' \)), and go back to Step 2.

F. Calculating rate constants

In this subsection, we discuss how we calculated rate constants for the reaction \( AH-B\rightarrow A^-+H^+B \) in liquid methylene chloride. The system is defined to be a reactant if the classical coordinates are reactant stabilizing and the hydrogen atom is in its ground state. Similarly, it is defined to be a product if the classical coordinates are product stabilizing and the hydrogen atom is in its ground state. We determine whether the classical coordinates are reactant or product stabilizing by the value of \( \langle \mathbf{r} \rangle_0 = \langle \Psi_0 | \mathbf{r} | \Psi_0 \rangle. \) For the purposes of defining a reactive event, the system is reactant stabilizing if \( \langle \mathbf{r} \rangle_0 < 1.05 \) and product stabilizing if \( \langle \mathbf{r} \rangle_0 > 1.62. \) Then a reactive event is defined to occur if the system starts as a reactant and becomes a product. We found that the rate constant is insensitive to the exact numbers used to define reactant and product stabilizing.

We used a classical time step of \( \Delta = 0.01 \) ps except for in the crossing region, where we used a smaller time step of \( \Delta = 0.001 \) ps to obtain more accurate values for the nonadiabatic coupling and the energy splittings between states. Thus when the trajectory entered the crossing region from the reactant stabilizing region at a time \( t, \) defined to be when \( \langle \Psi_0(t-\Delta) | \mathbf{r} | \Psi_0(t-\Delta) \rangle < 1.2 \) \( \mathbf{A} \langle \langle \Psi_0(t) | \mathbf{r} | \Psi_0(t) \rangle \rangle, \) we returned to the previous classical step, \( \mathbf{R}(t-\Delta), \) and decreased the time step so that \( \Delta = 0.001 \) ps. If, after no fewer than ten steps, the trajectory returned to the reactant region and no switches to higher states had occurred yet for this trajectory, the time step was increased so that \( \Delta = 0.01 \) ps again. At all times, the coefficient time step \( \delta \) remained the same: \( \delta = 10^{-5} \) ps.

Moreover, in order to eliminate nonphysical coherence in the coefficients, we set the magnitude of the coefficient of the current state \( k \) equal to one and the magnitude of all other coefficients equal to zero (i.e., \( \tilde{C}_k = 1 \) and \( \tilde{C}_j = 0, j \neq k \) whenever \( \langle \Psi_k(t-\Delta) | \mathbf{r} | \Psi_k(t-\Delta) \rangle < 1.62 \) \( \mathbf{A} \langle \langle \Psi_0(t) | \mathbf{r} | \Psi_0(t) \rangle \rangle \) or \( \langle \Psi_k(t) | \mathbf{r} | \Psi_k(t) \rangle \) \( < 1.05 \) \( \mathbf{A} \langle \langle \Psi_0(t-\Delta) | \mathbf{r} | \Psi_0(t-\Delta) \rangle \rangle \) for \( k \neq 0. \)

To obtain initial conditions, we generated ten different ground state configurations (consisting of \( \mathbf{R} \) and \( \tilde{C}_0 \) \) in the reactant stabilizing region that were equilibrated to 247 K. From these configurations we could generate different trajectories by producing a random Gaussian distribution of velocities with an approximate temperature of 247 K, and then scaling the velocities to have the same kinetic energy as that associated with the original velocities.

In order to facilitate comparison between rate constants calculated by the adiabatic and the nonadiabatic methods, we started the adiabatic and nonadiabatic trajectories from the same configurations. We then calculated the adiabatic and nonadiabatic trajectories simultaneously until a switch from the ground state to an excited state or a velocity reversal occurred in the nonadiabatic trajectory, or a reactive event occurred. If a switch or velocity reversal occurred, then we continued both trajectories separately until for each one either a reactive event occurred or the system returned to reactants. This procedure was repeated until at least 100 reactive events were achieved for both the adiabatic and the nonadiabatic trajectories. We calculated the adiabatic (nonadiabatic) rate constant by adding up the number of reactive
TABLE III. Rate constants obtained from simulations using adiabatic and nonadiabatic methods including the lowest two and the lowest four quantum states for the transfer of hydrogen (H) and deuterium (D).

<table>
<thead>
<tr>
<th>Simulation method</th>
<th>No. states</th>
<th>$k$ (s$^{-1}$) for H</th>
<th>$k$ (s$^{-1}$) for D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adiabatic</td>
<td>2</td>
<td>$1.8 \times 10^{11}$</td>
<td>$1.7 \times 10^{11}$</td>
</tr>
<tr>
<td>Nonadiabatic</td>
<td>2</td>
<td>$0.77 \times 10^{11}$</td>
<td>$0.20 \times 10^{11}$</td>
</tr>
<tr>
<td>Adiabatic</td>
<td>4</td>
<td>$1.9 \times 10^{11}$</td>
<td>$1.7 \times 10^{11}$</td>
</tr>
<tr>
<td>Nonadiabatic</td>
<td>4</td>
<td>$0.78 \times 10^{11}$</td>
<td>$0.20 \times 10^{11}$</td>
</tr>
</tbody>
</table>

Events for the adiabatic (nonadiabatic) trajectories and dividing this number by the total time for all adiabatic (nonadiabatic) trajectories. We repeated this procedure replacing the hydrogen with deuterium to calculate the kinetic isotope effect.

F. Results

The results we obtained by following the procedure presented in this section and including only the two lowest quantum states are presented in the first two rows of Table III. Note that the nonadiabatic proton transfer rate constant is 2.3 times smaller than the adiabatic proton transfer rate constant. This number is small but statistically significant. Moreover, the result that including quantum transitions decreases the rate constant agrees with the physical discussion in Sec. I. Note also that, within our statistical uncertainties, there is no kinetic isotope effect for the adiabatic method. A kinetic isotope effect of 3.9 was found for the nonadiabatic method. In the adiabatic case, proton transfer occurs whenever the solvent stabilizes the product side so that it is lower in energy than the reactant side, as shown in Fig. 1(c). Thus deuterium and hydrogen behave virtually identically. (The difference in zero-point energies does not appear to significantly affect the dynamics in this case.) When quantum transitions are included, the rate constant is smaller for deuterium than for hydrogen since tunneling is slower for deuterium, i.e., the deuterium energy levels are closer together so the probability of a quantum transition is greater for deuterium than for hydrogen. Thus all of these results appear to be qualitatively correct.

Azzouz and Borgis studied essentially the same proton transfer reaction using both a Landau–Zener curve-crossing approach, with which they obtained a value of $7.8 \times 10^{9}$ s$^{-1}$ for the rate constant with a kinetic isotope effect of 46, and a path-integral centroid approach, with which they obtained a value of $10.5 \times 10^{9}$ s$^{-1}$ for the rate constant with a kinetic isotope effect of 40. Our results do not agree well with these results, but since we used very different methods, further study is necessary to find the source of the discrepancy.

In order to shed some light on this discrepancy, we determined an approximate lower limit for the nonadiabatic rate constant that would be obtained using any surface-hopping approach. We simulated 50 adiabatic reactive events, where Eqs. (26) were integrated throughout the trajectories but no switches were allowed. We found that the average final ground state population, which is the probability of an adiabatic reactive event, was 0.26 for hydrogen and 0.05 for deuterium. Thus, even if every nonadiabatic branch were nonreactive, including nonadiabatic transitions can reduce the adiabatic rate constant by at most a factor of 3.8 and 20 for hydrogen and deuterium, respectively. Using our results for the adiabatic proton transfer rate constants given in the first row of Table III, we calculated that the lower limits of the nonadiabatic rate constants are $0.47 \times 10^{11}$ s$^{-1}$ and $0.09 \times 10^{11}$ s$^{-1}$ for hydrogen and deuterium, respectively, which are considerably higher than the results of Azzouz and Borgis but lower than our results. We point out that in our case this lower limit was not obtained because even after a nonadiabatic transition, a reactive event could occur before the system returned to reactants. This suggests that the major source of the discrepancy between the results of Azzouz and Borgis and our results is not due to our treatment of nonadiabatic transitions.

We also performed the procedure presented in this paper including the four lowest quantum states, which is very straightforward and not significantly more computationally expensive than including only two states. As shown in Table III, the results were the same within the statistical error as those where we included only the two lowest states. We observed only one transition to the third state and no transitions to the fourth state during these simulations. We also observed, however, that the quantum probabilities of the third and fourth excited states quite often became as large as 0.09 and 0.04, respectively, and in a few rare instances became as large as 0.25. Thus, there is a non-negligible probability of a transition to the third or fourth state, although the effect on the final reaction rate is insignificant.

The results discussed in this subsection show that for this proton transfer model, inclusion of nonadiabatic transitions reduced the calculated rate constant by factors of 2.3 and 8.5 for hydrogen and deuterium, respectively. While these are not major corrections, they are significant and dominate the isotope effect. At lower temperatures for this system, nonadiabatic corrections will become much more important as the rate becomes increasingly controlled by tunneling. Even for the conditions of the present simulation, however, the inclusion of nonadiabatic transitions may be crucial for properly portraying the reaction pathway. As discussed above, the adiabatic approximation can produce nonphysical passage across a tunneling barrier irrespective of the height of the barrier. In situations such as the present one in which the barrier height depends significantly on the other (classical) coordinates, the adiabatic approximation may allow reaction to occur for high-barrier configurations that should be unimportant. Inclusion of nonadiabatic transitions corrects this deficiency in a consistent way, even in situations such as the present one that exhibit regions of both adiabatic and nonadiabatic behavior.

III. DISCUSSION

This paper presents an initial demonstration of the feasibility of the application of MDQT to proton transfer reactions in solution. In order to implement this approach, we developed several new numerical methods, which were discussed in the previous section. For example, we developed a method for using multiple time steps so that the complex coefficients (which determine the populations of the states)
can be integrated with a smaller time step than the classical equations of motion. This allows a larger time step to be used for integration of the classical equations of motion throughout the simulation, which is important in order for these simulations to be computationally feasible. We also developed efficient numerical methods for calculation of the nonadiabatic coupling, the probability of hopping from one state to another, the nonadiabatic coupling vector, and the appropriate adjustment to the velocities after a hop to conserve energy.

We applied all of these new methods to a particular model of proton transfer in solution. The results of our simulations appear reasonable in that including quantum transitions decreases the rate constant, as expected when tunneling is not instantaneous. Moreover, when quantum transitions are included, replacing hydrogen with deuterium decreases the rate constant, as expected since tunneling of deuterium is slower, i.e., the deuterium energy levels are closer together so the probability of quantum transitions is larger. We performed the simulations including both two and four quantum states in order to emphasize the computational ease with which more than two states can be included. For this model, however, we found that two states were adequate to describe the dynamics. Furthermore, our results show that nonadiabatic effects are not very important for this model at this temperature, although the effects are more significant for deuterium than for hydrogen. Nonadiabatic effects will typically be more important for problems with large barriers (and thus smaller splittings) and low temperatures. In these cases, the rates of proton transfer will be much slower, so our direct method of calculating the rate constants will be computationally infeasible. Instead, methods for infrequent events, such as umbrella sampling or constrained reaction coordinate dynamics, must be used in conjunction with MDQT to study such systems.

There are two main limitations of the method presented in this paper. The first is that the time step must be large enough so that simulations of the proton transfer process are computationally feasible. In general, the time step for molecular dynamics simulations must be chosen small enough to accommodate the fastest degree of freedom. For a classical simulation of proton transfer, this degree of freedom is the vibration of the proton, and a very small time step must be chosen. For an adiabatic quantum mechanical simulation, a larger time step can be chosen. For a nonadiabatic quantum mechanical simulation, however, the complex coefficients must be integrated in parallel with the classical equations of motion, and the phase factor of the complex coefficients oscillates with a frequency similar to that of the classical vibration of the proton. Thus this requires a time step as small as that required for classical simulations of proton transfer. Since the complex coefficients need to be integrated only in the regions of strong nonadiabatic coupling, however, the time step can be as large as that for adiabatic quantum mechanical simulations during the majority of the simulation, as long as the time step is decreased in the regions of strong nonadiabatic coupling. Moreover, for the simulations presented in this paper, we implemented a multiple time step scheme that allowed us to use a large time step throughout the simulations. The second limitation of this method is that the number of states (and the associated number of basis functions) included must be small enough so that the calculation of the quantum mechanical energies and wave functions is computationally feasible. For the model studied in this paper, we showed that including only the two lowest states was adequate, and we found that the quantum mechanical part of the simulation was much faster than the calculation of the classical forces. Overall, the MDQT calculation proved far less time consuming in this case than a full classical mechanical simulation of the same system in which the time step was dictated by the hydrogen vibration.

The Azzouz–Borgis model we employed for this study was chosen, in part, because the quantum mechanics is simple; the hydrogen atom moves only in one dimension along the line of centers of the A and B groups. In other applications it may be necessary to treat all three hydrogens degrees of freedom quantum mechanically. This will significantly increase the computational effort for calculating the quantum mechanical energies and wave functions. As shown by Laria et al., however, this may still be computationally quite feasible. It is also likely that a three-dimensional quantum particle will require inclusion of many quantum states in the MDQT simulation, but this is straightforward and computationally tractable.

The method presented in this paper has a combination of attributes that makes it advantageous over existing methods. It enables proton transfer in solution to be simulated using full molecular dynamics for a large number of classical degrees of freedom while treating a small number of degrees of freedom (i.e., the hydrogen motion) quantum mechanically. The quantum mechanical and classical degrees of freedom are treated self-consistently, with no ad hoc tunneling corrections imposed. Quantum mechanical phenomena such as zero-point motion, tunneling, and isotope effects are incorporated into the full-scale molecular dynamics simulations. Since this method is not perturbative, trajectories can be continued after the barrier is crossed. Moreover, this method can be used in both adiabatic and diabatic limits, as well as in the intermediate regime, with no prior assumptions about which regime is applicable. This is particularly important for proton transfer, since the barrier height depends on the separation of the donor and acceptor so a single system can display both adiabatic and nonadiabatic behavior in different regions of configuration space. Finally, this method can easily be extended to include more than two states, so it can be applied to a wide range of processes, such as photoassisted tunneling and vibrational relaxation.

S. Hammes-Schiffer and J. C. Tully: Proton transfer in solution 4667


The component of velocity in the direction of the nonadiabatic coupling vector is reversed in this case because there is insufficient momentum to overcome the “Pechukas force” that takes the system from one state to another. This change of sign of the velocity, which is a basic element of the MDET and MDQT methods, was inadvertently omitted in the original description of the method in Ref. 11.

