

Numerical Simulations of Free Radical Dynamics

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Given for one instant an intelligence which could comprehend all the forces by which nature is animated and the respective situation of the beings who compose it—an intelligence sufficiently vast to submit these data to analysis—it would embrace in the same formula the movements of the greatest bodies of the universe and those of the lightest atom; for it, nothing would be uncertain and the future, as the past, would be present to its eyes.—Laplace.

I. INTRODUCTION

Simulating chemical reactions in the condensed phase involves the parallel computation of the concerted quantum dynamics of breaking and formation of chemical bonds with the simultaneous response and influence of the surrounding media. In many systems it is not entirely possible to treat all of the motions quantum mechanically without resorting to various levels of approximation. One approach which has proven to be quite powerful in a wide range of scenarios is to partition the full system into interacting subsystems according to whether the dynamics in the subsystem is predominantly classical-like or if the dynamics must necessarily be treated quantum mechanically. Such partitionings are motivated by the simple observation that quantum mechanical effects are typically localized to only a few specific types of motions typically along some chosen reaction coordinate. The remaining motions, i.e. those of the surrounding media, can largely be regarded as classical. Thus, partitioning the extended system into interacting quantum and classical subsystems allows one to study the details of a condensed phase quantum phenomena while retaining a detailed description of the response and influence of a complicated molecular media in its full dimensionality. Consequently, the level of description afforded by mixed

quantum/classical treatments and the relative computational efficiency of the method has allowed a synergistic interaction between theory and experiment since experiments can be used to validate theoretical models which in turn have provided a number of valuable mechanistic insights.

Current quantum chemical methods have proven to be quite adequate in providing structural and dynamical information for radicals in the gas phase and inert matrices. In these circumstances, quantum computations have provided a direct link between experimental spectroscopic investigations limited chiefly by the level of sophistication needed to obtain accurate structures, spin dependent properties such as hyperfine interactions, and higher order properties such as hyperpolarizabilities.

In the condensed phase, the story is quite different. In order to perform molecular dynamics of the solvent molecules, we need to provide accurate empirical solvent-solvent and solute-solute interaction potentials [1,2]. However, empirical models cannot accurately reproduce many important modifications induced by the solute on the electronic structure of the solvent molecules. Consequently, the use of simple fixed point charge models for the solvent ignores the polarization response of the solvent molecules to changes in the electronic structure of the solute. Mixed approaches have been developed, in which a Monte Carlo simulation of the solvent was coupled to a quantum mechanical description of the solute, however, to date these have been performed at the Hartree-Fock level due to the computational overhead required to sample a statistically meaningful number of solvent configurations [3,4]. Furthermore, the representation of the solvent molecules by simple point charge models neglects many important polarization induced effects when computing the electronic structure of the solute.

Solvent models have been developed in which the solvent is treated as a polarizable dielectric continuum [5–8]. While the use of dielectric continuum models has a long history, the latest generation of models are extremely sophisticated and include such features as realistic solute cavities and exact description of the electrostatic problem [9–11]. Such Polarizable Continuum Models (PCM) have been included in the Gaussian/94 (G94) [12] package allowing an accurate extension of a variety of quantum chemical approaches (including HF, MP2, CC, and DFT) to condensed phase problems. Such fully *ab initio* approaches are

currently accurate enough to interpret experimental hyperfine splittings and permit an unbiased assessment of the role of electronic, vibrational, and solvation effects in determining the observed result [10]. The success of these models open the possibility for studying a number of large biologically important radical species in their natural aqueous environment.

Ab initio molecular dynamics methods, especially the Density Functional Theory-Molecular Dynamics (DFT-MD) methods introduced by Carr and Parrinello [13–15] (CP) have been highly successful in describing a variety of chemical phenomena in the condensed phase [15–17]. The CP method avoids the necessity of providing semi-empirical pseudopotentials for the molecular forces by solving the Kohn-Sham equations for the electronic density for a given nuclear configuration. The molecular dynamics are then solved under the Born-Oppenheimer approximation in which the nuclei move under the Hellmann-Feynman forces computed by the DFT calculation. Additional quantum effects in the nuclear motion, such as energy level quantization and barrier tunneling, can be introduced through path integral dynamics [18,19]. While this method is useful in determining mechanistic details of many chemical reactions, electronic transition due to the non-adiabatic motion of the nuclei cannot be properly include due to the fact the Kohn-Sham equations are not guaranteed to be convergent variationally for states other than the electronic ground state. Thus, all nuclear dynamics are confined to the ground adiabatic potential energy surface. For a large number of systems of chemical importance, this level of description is sufficient. However, for many systems, sudden changes in the solute quantum state play pivotal roles in determining the dynamics of the reaction.

Quantum-classical simulations overcome many fundamental shortcomings associated with both classical molecular dynamics (MD) and the quantum chemical methods mentioned above. Foremost amongst the assumptions in both MD and quantum chemistry is that all the dynamics occur on a single potential energy surface under the Born-Oppenheimer approximation. Quantum mechanical effects arising from tunneling and dynamical interference effects and discrete energy levels are completely absent in classical MD. These effects become significant particularly in low temperature systems containing hydrogen atom motions and for computing various time-dependent spectroscopic observables. The restriction of the dynamics to a single Born-Oppenheimer potential surface is another serious limita-

tion. For each non-degenerate electronic state of the many-atom system there is a distinct Born-Oppenheimer potential energy surface parameterized by the positions of all the atoms. When a transition between electronic states occurs, the forces acting on the atoms may change dramatically. Thus the proper and self consistent incorporation of these effects is crucial to describing a wide host of chemical dynamical effects, many of which are important to free radical dynamics. [20]

Electronically non-adiabatic processes play a surprisingly ubiquitous role in chemical reaction dynamics for a wide number of systems including photosynthesis, polymeric chain-reactions, photodissociation, and electron transfer reactions. and various aspects which must be considered in order to simulate such processes for a condensed matter system. Foremost amongst the goals of this chapter is to present the quantum-classical methodology as a useful method of simulating these processes in the condensed phase, to discuss some of the subtle aspects of non-adiabatic dynamics which we have demonstrated to be important considerations, and to present some of our recent results obtained using these methods.

We consider here a system composed of a few important degrees of freedom which include any reaction coordinate we care to choose coupled to a much larger number of degrees of freedom which we shall refer to as the bath. We shall treat the motions of the system using quantum mechanics and motions in the bath via classical mechanics. The quantum motions may be, for example, nuclear motions, as in the hydrogen transfer reaction, electronic degrees of freedom as in the case of an electron transfer reaction or non-radiative relaxation process, a combination of the two, and so forth. One important class of motions of chemical interest which are inherently quantum mechanical in nature are transitions between discrete electronic states. Since the nuclear positions and velocities of all the molecules in the system determine the electronic states and the transition amplitudes between the states and the states and transition amplitudes in turn influence the the forces governing the trajectories, any mixed quantum classical theory must treat self-consistently the classical and quantal degrees of freedom.

The aqueous electron, nature's simplest radical anion, provides an ideal test case system for the methods which we shall develop below. Many of the dynamical features present in this system have analogues in other systems in which energy quantization, non-radiative

energy transfer, and other quantum effects play important roles. The aqueous electron is one of the very few important chemical systems which can be described more or less exactly without resorting to various levels of quantum chemical approximations. Thus, it provides a unique testcase for a variety of dynamical theories.

The remainder of this chapter is organized as follows: we first present a general overview of classical molecular dynamics and Monte-Carlo methods. This is aimed as a general overview of the use of molecular simulation methods. As a part of this overview, we discuss recent developments in *ab initio* molecular dynamics, in particular the density functional theory methods developed by Carr and Parrinello. We then focus our discussion on nonadiabatic simulations. We present the formal details of quantum/classical dynamics and highlight two important considerations which are necessary to address: the treatment of interaction force and the treatment of the phase coherence between the quantum and classical subsystems. We then move on to show results of simulations based upon these methods focusing primarily upon the role that quantum decoherence plays in determining the survival timescale of an excited electronic state using the aqueous electron as a prototypical system, highlighting the interplay which has evolved between theoretical and experimental studies of this system over the past few years. Finally, we conclude with a discussion of future directions we and others are undertaking to apply the methods discussed here to a variety of other systems.

II. EXCESS ELECTRON AS A PROTOTYPICAL FREE RADICAL SYSTEM

The solvated electron provides perhaps the simplest example of electronic dynamics in the condensed phase. Aqueous electrons are of particular importance since they play a prominent role in the broad area of radiation chemistry of water. In spite of intensive experimental and theoretical study since identification of the hydrated electron over 30 years ago, many dynamical features of electron solvation have remained incompletely understood, largely due to the extremely fast timescales on which electronic relaxation occurs [21]. Newly developed femtosecond spectroscopic techniques are now providing glimpses of the details of condensed phase electronic dynamics. From a theoretical standpoint, the aqueous electron is an ideal test case for new condensed phase theories. Recent theoretical advances in treating

condensed phase electronic dynamics [22–26] has led to an exceptional interplay between theory and experiment, helping to unravel many subtle dynamical aspects of this system.

While excess aqueous electrons are often prepared in conjunction with chemical reactions and charge transfer reactions in H₂O, experimental preparation of the electron in neat water can be accomplished by direct photoionization of water. Following injection into the water, the electron typically has 2.0 to 2.5 eV of excess energy which must be absorbed by the water as the electron is solvated. Initially, the electron is delocalized in a continuum band of energy levels. However, the electron rapidly localizes into one of three nearly degenerate p-state and subsequently relaxes to an s-state where it is further solvated by the surrounding water molecules. This fully solvated species exists until scavenged by impurities in the system (typically on the order of a few hundred ns for ultra-pure water). The kinetics of the localization process has been extensively studied both theoretically and experimentally.

The fully solvated electron can be regarded as a particle in a hard roughly prolate spheroidal cavity formed by the surrounding water molecules. The first “solvation shell” of water molecules is an octahedral structure with hydrogen atoms on the vertices with an average e-/O radius of $\approx 3.2 \text{ \AA}$. In the fully solvated state, the water molecules in the surrounding shells arrange themselves as to maximize the hydrogen bonding network. The first excited states of this system are p-states lying roughly 1.7 eV above the ground state which are split due to slight asymmetry of the shell of water molecules about the electron. The energy gap between the s and p states and the energies of the p states are modulated by fluctuations in the local solvent structure.

In the simulations which we shall discuss through the course of this chapter, we assume that the electron has been prepared in a equilibrated s-state and subsequently promoted into one of the p-states when the s-p energy gap becomes 1.7 eV simulating the effect of the 720 nm laser excitation pulse used in the experiments performed by the Barbara and co-workers. The relaxation mechanism following excitation is given by



Following promotion into one of the p-states at $t = 0$, the system is no longer in equilibrium and solvent water molecules move to accommodate the new distribution of electronic charge and partially solvates the p-state on a timescale, t_1 . During this time, the s-p energy gap to

narrows from 1.7 eV to $\omega_{sp} \approx 0.5$ eV. As the energy gap narrows, the non-radiative transition probability back to the ground state increases and is maximized around avoided crossings. Thus, measurements of the excited state lifetime reflect both the non-radiative decay of the state as well as the solvation/relaxation dynamics of the surrounding media. The solvation dynamics of this system have been extensively studied by Schwartz and Rossky. The excited state solvation response, defined as the normalized autocorrelation function of the s-p energy gap following excitation,

$$S(t) = \left\langle \frac{\omega_{sp}(t) - \omega_{sp}(0)}{\omega_{sp}(\infty) - \omega_{sp}(0)} \right\rangle, \quad (2)$$

indicates a rapid ≈ 24 fs inertial Gaussian component which makes up roughly 40% of the response followed by a much slower 240 fs exponential decay which makes up the remainder. Following the non-radiative $p \rightarrow s$ transition, the new s-state (e_s^*) is no longer in equilibrium and the water solvent molecules respond to resolvate the electron. Figure 1 shows the results of two typical runs following preparation in the excited state.

An important puzzle concerning the non-adiabatic dynamics of the hydrated electron has been the surprising lack of a sizable isotope effect on the non-adiabatic transition rate. [27,28] Estimating the non-radiative coupling between the excited and ground state using Fermi's Golden Rule

$$k_{10} \propto |\vec{v} \cdot \langle \psi_0 | \vec{\nabla} \psi_{ex} \rangle|^2 \quad (3)$$

shows that the nuclear velocities, \vec{v} , play a direct role in determination of the non-adiabatic transition rate. Since the fastest nuclear velocities in D₂O (the D's) are classically $\sqrt{2}$ times slower than those in H₂O (the H's) while the other factors (the electron-water interaction potential, the quantum force on the nuclei, etc.) remain the same, the expectation is that non-adiabatic transition rates should be roughly half as large in D₂O compared to H₂O. Indeed, mixed quantum-classical simulations have suggested isotope effects of factors of 2 – 4 for the electronic transition rate in this system. [29–31] Experiments, however, have found at most a modest difference in the non-adiabatic transition rate for electrons photo-injected into H₂O versus D₂O, [32–34] and at most a 15% isotopic effect have been extracted from femtosecond spectroscopic studies of photoexcited equilibrium electrons. [28,35] This disparity between theory and experiment comes as a surprise given the level of sophistication of the

theories and their ability to match experiment on many other aspects of the system. This has caused us to re-evaluate the quantum-classical methodology and examine the various approximations used to derive the method, which we shall describe in detail in the following section.

III. QUANTUM-CLASSICAL METHODOLOGY

A. Non-adiabatic Dynamics

Due to the fundamental role that dynamical process play in chemical reactivity, there is a large body of literature devoted to extracting dynamical information from computer simulations for both adiabatic and non-adiabatic dynamics. [23,24,36–44] As discussed above, it is not computationally feasible to treat a condensed phase dynamical system fully quantum mechanically while retaining a molecular level description of the dynamics; it is, however, entirely possible to simulate the physics of interest by treating a select few degrees of freedom quantum mechanically while treating the remainder classically. The general prescription goes as follows: write the total Hamiltonian in terms of “quantum” and “classical” contributions,¹

$$H_{tot} = H_Q(x, R) + \frac{P^2}{2m} + V_C(R), \quad (4)$$

where $H_Q(x, R)$ is the Hamiltonian for just the quantum variables, x , parameterized by the classical coordinates, R . The other are the classical kinetic energy and the solvent-solvent potential interaction, $V_C(R)$, which is independent of the quantum subsystem. The quantum subsystem is propagated in concert with the classical particles using the time dependent Schrödinger equation, (note: we set $\hbar = 1$ throughout)

¹Rigorously, one should start from fully quantum realization of the system and introduce mixing between the electronic and vibrational motions through the application of the vibrational kinetic energy operator on the electronic wavefunction to arrive at these equations. C. f. M. Born and K. Haug, *Dynamical Theory of Crystal Lattices*, (Oxford Univ. Press, 1954).

$$i \left[\frac{\partial}{\partial t} + \sum_{\mu} \dot{R}_{\mu} \frac{\partial}{\partial R_{\mu}} \right] \psi(x; R, t) = H_Q(x, R) \psi(x; R, t), \quad (5)$$

where the summation is over all classical coordinates. Here we have used the chain rule of differentiation to decompose the the total time differential, to show explicitly the “non-adiabatic coupling term”: $\dot{R} \nabla_R \psi(x; R, t)$. Under the Born-Oppenheimer approximation, the quantum subsystem is assumed to respond much faster than the timescale set by the motion of the classical particles. When this is the case, the non-adiabatic coupling term can be ignored and the classical particles evolve on the adiabatic potential energy surfaces defined by solving the time independent Schrödinger equation at each classical configuration, R , for the adiabatic state

$$H_Q(R, t) |\phi_n(R(t))\rangle = \varepsilon_n(R, t) |\phi_n(R(t))\rangle. \quad (6)$$

Under the adiabatic approximation, the classical particles evolve under

$$m \ddot{R}_{\mu}(t) = - \frac{\partial}{\partial R_{\mu}} (\varepsilon_n(R(t)) + V_C(R(t))). \quad (7)$$

Thus, the coupling between solvent and solute are those predicted by the Hellmann-Feynman theorem

$$\begin{aligned} F_{\mu}^Q(R(t)) &= - \frac{\partial}{\partial R_{\mu}} \langle \phi_n(R(t)) | H_Q(R(t)) | \phi_n(R(t)) \rangle \\ &= - \frac{\partial \varepsilon_n(R(t))}{\partial R_{\mu}}. \end{aligned} \quad (8)$$

When the non-adiabatic coupling becomes significant, such as at an avoided crossing of the adiabatic energy surfaces, the classical motion can induce transitions in the quantum subsystem. As the classical particles move away from regions of strong non-adiabatic coupling, the classical particles must evolve on a given adiabatic surface. This asymptotic condition introduces a twist on the classical dynamics since the classical particles must “switch” surfaces during the course of a quantum transition. Various computational schemes have been developed which incorporate this switching aspect into the classical dynamics. Perhaps the most straightforward scheme is the “surface hopping algorithm” pioneered by Tully [38,40] subsequently incorporated in the work of Webster, Friesner, and Rossky [23,24] and of Coker and coworkers [37,43,45,46]. The general feature of all these algorithms is that the classical

particles stochastically “switch” between quantum states according to a criteria determined by the quantum transition probability between the initial and final quantum states over a given time interval. Thus, over the course of a simulation, a switching trajectory emerges as the quantum system hops between the various quantum states tracing out a path through state space.

In mixed quantum-classical simulations, we assume that the nuclear motion of at least a few degrees of freedom can be treated via classical mechanics and that the evolution of remaining degrees of freedom can be treated via quantum mechanics parameterized by the classical variables. The coherent evolution of the reduced density matrix along a given classical trajectory, $\rho(R)$, is given by the Liouville equation

$$i\frac{d\rho(R(t))}{dt} = [H_Q(R(t)), \rho(R(t))]. \quad (9)$$

Here, the density matrix, $\rho(R(t))$, is defined along a single trajectory, $R(t)$ as

$$\rho(R(t)) = |\psi(R(t))\rangle\langle\psi(R(t))|, \quad (10)$$

where $|\psi\rangle$ is the solution of the time dependent Schrödinger equation. In the basis of adiabatic eigenstates this becomes

$$\rho(R(t)) = \sum_{ij} \rho_{ij}(R(t)) |\phi_i(R(t))\rangle\langle\phi_j(R(t))|, \quad (11)$$

with the time evolution of each component given by

$$i\dot{\rho}_{ij} = (\varepsilon_i\delta_{jk} - i\dot{R}d_{ik})\rho_{kj} - \rho_{ik}(\varepsilon_i\delta_{ik} - i\dot{R}_\mu d_{kj}^\mu). \quad (12)$$

where ε_i are the adiabatic energies computed for a given point along the path, d_{ij}^μ is a component of the non-adiabatic coupling vector

$$d_{ij}^\mu = \langle\phi_i(R(t))|\frac{\partial}{\partial R_\mu}|\phi_j(R(t))\rangle, \quad (13)$$

and $\{|\phi_j(R(t))\rangle\}$ are the adiabatic eigenstates of the quantum Hamiltonian at configuration $R(t)$.

Over a short time interval δt , we can construct the probability for making a quantum mechanical transition from an initial state $|\phi_i(t)\rangle$ to a final state $|\phi_f(t + \delta t)\rangle$ writing

$$\begin{aligned}
P_{ij}(t_o + \delta t, t_o) &= |\langle \phi_j | \exp(-i \int_{t_o}^{t_o + \delta t} ds H(s)) \phi_i \rangle|^2 \\
&= \int_{t_o}^{t_o + \delta t} dt \frac{\dot{\rho}_{jj}(t)}{\rho_{ii}(t)} \\
&\approx \delta t \frac{\dot{\rho}_{jj}(t)}{\rho_{ii}(t)}
\end{aligned} \tag{14}$$

The first line is the definition of a quantum transition probability. The second and third lines are obtained by solving the equations of motion for the density matrix over a short time period which gives the probability of switching from state i to j by the rate of change of the population of the final state weighted by the population of the initial state integrated over the short time interval. Using this we can write

$$P_{ij}(t; \delta t) = \delta t \frac{-2\text{Re} \left\{ \rho_{ji}(t) \dot{R}(t) \langle \phi_i | \frac{\partial}{\partial x} | \phi_j \rangle \right\}}{\rho_{ii}(t)}. \tag{15}$$

These probabilities are computed at each time step over the course of the simulation and determine whether or not the classical degrees of freedom will continue to evolve on the present energy surface or if they must switch energy surfaces due to a non-adiabatic transition in the quantum degrees of freedom. This particular approach for computing the quantum transition probability has the desired advantage that it minimizes the number of switches between states all the while maintaining the correct statistical distribution of state populations at all times. [40]

In the Molecular Dynamics with Quantum Transitions (MDQT) algorithm [40,42], the classical variables switch suddenly between the adiabatic potential surfaces at the switching times. Such abrupt changes in the potential energy when an electronic transition does occur causes a change in the total energy of the system. In the MDQT method, the velocity of the classical variables are modified in order to properly conserve energy [40] by randomly rescaling the velocity vectors of the classical particles along the direction of non-adiabatic transition vector such that the transition energy is transferred from the quantum to the classical degrees of freedom (or vice versa) in such a way that the total energy of the system is conserved. We shall next discuss a theory in which the trajectories move on an effective potential which changes smoothly as the quantum state evolves from the initial to final state over a finite time interval.

1. Solvent-Solute Coupling in the Presence of Quantum Transitions

When a quantum transition does occur, the forces coupling the quantum system to the solvent change to reflect the new electronic state. This change is often dramatic, especially in transitions between an excited state and the ground electronic state. For example, in the case of an excess electron in H₂O, the first excited state is a p-state while the ground state is a roughly spherical s-state. Furthermore the partially solvated p-state occupies a much larger solvation cavity than the ground state for the same solvent configuration. Thus, both the shape and spatial distribution of the electron changes suddenly as the result of an electronic transition. Consequently, the forces coupling the electron to the solvent change suddenly as well. A proper description of the solvent-solute coupling must accommodate these sudden changes.

A further consideration is the fact that the total energy of the system must be conserved. Any energy involved in making a transition in the quantum state must be absorbed or transferred to the solvent continuously throughout the transition. In the case of an excess e⁻ in H₂O, the p-s transition dumps roughly 0.5 eV of electronic energy into the solvent. This energy must be accommodated by the solvent translational, librational, and vibrational motions in a time scale of a few femtoseconds.

Along a given path, $R(t)$, the partial quantum transition amplitude between an initial and final quantum state, $|i(R_i)\rangle$ and $|f(R_f)\rangle$ respectively, is given by

$$\begin{aligned} T_{if}[R(t)] &= \langle f(R_f) | e^{-i \int_{t_i}^{t_f} ds H_Q[R(s)]} | i(R_i) \rangle e^{+iS[R(t)]} \\ &= U_{if}[R(t)] e^{+iS[R(t)]}, \end{aligned} \quad (16)$$

where $U_{if}[R(t)]$ is the transition amplitude for the quantum subsystem and $S_C[R(t)]$ is the classical action computed along the path $R(t)$, i.e.

$$S_C[R(t)] = \int_{t_i}^{t_f} dt \left\{ \frac{m}{2} \dot{R}(t)^2 - V_C(R(t)) \right\}. \quad (17)$$

We are calling this a *partial* amplitude here in the sense that this represents the full transition amplitude along one Feynman path taken by the solvent or bath degrees of freedom. Indeed, the full quantum transition probability of starting in some initial solvent/solute state $|i(t_o)\rangle$ ending up in a given final solvent/solute quantum state, $|f(t_f)\rangle$, at some time t_f is computed

by summing over all possible Feynman paths, $R(t)$, taken by the solvent between initial and final solvent configurations, R_i and R_f , and with initial and final electronic states, $|i(R_i)\rangle$ and $|f(R_f)\rangle$ respectively. I.e.

$$\begin{aligned} K_{fi}(R_f, R_i; t) &= \int \mathcal{D}R(t) T_{if}[R(t)] \\ &= \int \mathcal{D}R(t) \langle f(R_f) | e^{-i \int_{t_i}^{t_f} ds H_Q[R(s)]} | i(R_i) \rangle e^{+i S_C[R(t)]} \end{aligned} \quad (18)$$

The transition amplitude for the quantum subsystem, $U_{if}[R(t)]$, is a complex functional of $R(t)$. We can obtain a semiclassical approximation for the combined system/bath propagator, $K_{fi}(R_f, R_i; t)$ on the assumption that the magnitude of $U[R]$ varies much more slowly than its phase along a given path. Expanding the phase to second order in the classical paths \tilde{R} yields the variational equation

$$\delta \left(\hbar \text{Im} \ln U_{if}(\tilde{R}) + S_C(\tilde{R}) \right) = 0. \quad (19)$$

The variation of the electronic propagator is given by

$$\delta U_{if}[R] = -\frac{i}{\hbar} \int_{t_i}^{t_f} ds \langle f(t_f) | U(t_f, s) \delta H_Q U(s, t_i) | i(t_i) \rangle. \quad (20)$$

Using this, we arrive at the ‘‘classical’’ equations of motion for the saddle point trajectories, \tilde{R} .

$$m \ddot{\tilde{R}}(t) = -\text{Re} \left\{ \frac{\langle f(R_f) | U(t_f, t) \nabla H_Q U(t, t_i) | i(R_i) \rangle}{\langle f(R_f) | U(t_f, t) | i(R_i) \rangle} \right\} - \nabla V_C. \quad (21)$$

(We shall drop the tilde for now on.) This is basically Newton’s equations of motion. Thus, the semiclassical estimate for the force contribution between the quantum and classical degrees of freedom is given by [47]

$$F_Q[R(t)] = -\text{Re} \left\{ \frac{\langle f(R_f) | U(t_f, t) \nabla H_Q U(t, t_i) | i(R_i) \rangle}{\langle f(R_f) | U(t_f, t) | i(R_i) \rangle} \right\}. \quad (22)$$

This force is a functional of the trajectory which we are trying to calculate over the course of a simulation and must be solved iteratively. In other words, we guess a path and a set of end points, compute the quantum wavefunction for the new configuration, propagate the initial wave forward in time and the final wave back in time to a set of intermediate times to compute the forces for a new path and continue with this cycle until either the

procedure satisfies some convergence criteria or one simply runs out of patience or CPU time. This semiclassical/stationary phase description of the coupling between the quantum and classical variables is a central feature in the quantum/classical stationary phase surface hopping methods developed by Webster, Friesner, and Rossky (WFR) [23,24,41]. While providing an exact semi-classical description of the forces coupling the quantum and classical subsystems, the computational overhead required to iteratively determine the classical path can be quite large, especially if there are two or more paths with nearly identical action or if the time interval is taken to be too large. This creates considerable computational overhead since the motion of all of the solvent species must be determined variationally rather than through a propagative scheme, such as the Verlet algorithm.

Furthermore, when we specify the initial and final states of the quantum solute, we are in effect imposing a quantum measurement on the solute which destroys coherence in the quantum subsystem. In the algorithm developed by Webster, Friesner, and Rossky (WFR), this “computational coherence timescale” is chosen to be identical to the timescale required to accurately compute the fastest motions in the solvent. Later developments by Coker and co-workers [37,43,45,46] and later by Bittner and Rossky [36,48–50] have allowed for full retention and partial retention of coherence.

2. Treating the phase coherence between the solvent and solute subsystems: Consistent Histories Formulation

In both the MDQT and WFR/SP approaches, the classical switching path can be written as a time ordered sequence of events,

$$R^\alpha(t) = \{R_{\alpha_0}^{\alpha_0}, \dots, R_j^{\alpha_j}, \dots, R_n^{\alpha_n}\} \tag{23}$$

in which superscript α_j denotes the switching outcome at time-step j and $\alpha_0 = i$ corresponding to our choice of the initial quantum state. Two such paths are shown schematically in Fig. 1 where we plot the eigenenergy of the occupied state along the path as a function of time for an aqueous electron following laser excitation. Changes in the quantum state imply that there is a corresponding sudden change in the forces exerted on the classical particles

over the course of its evolution. The result is that different sequences of switching events will lead to rapidly diverging paths.

Each path of the quantum subsystem will have associated with it a unique classical path characterizing the slight differences in the bath dynamics arising from the slight differences in the forces from different quantum paths. These slight differences in the bath dynamics mean that bath trajectories will be divergent even on a very short time scale. The result of this is that the off-diagonal elements of the quantum density matrix will be rapidly diminished as the various bath paths diverge. Thus, coherence in the quantum subsystem is lost due to the slight differences in the bath dynamics for each quantum path. We now explore the issue of phase coherence between the solvent and solute subsystems. Our approach is based upon a novel interpretation of quantum mechanics introduced by Griffiths [51], Omnès [52,53], and Gell-Mann and Hartle [54–56] over roughly the past 10 years. This interpretation of quantum mechanics, termed “consistent” or “decoherent” histories, has generated a great deal of attention in the field of quantum cosmology [57–60].

Let us consider the evolution of an initial quantum state $|i(R_o)\rangle$, taken as an adiabatic eigenstate of the quantum mechanical Hamiltonian for initial bath (or classical) configuration R_o , along a switching path, $R^\alpha(t)$. During each time interval, we determine whether or not a quantum transition has occurred according to a stochastic switching criteria as discussed above, modify the classical dynamics accordingly, and record the outcome of each switching attempt.

We can write the reduced quantum transition probability for a mixed quantum-classical system as

$$\begin{aligned} P_{if}(t_f) &= \left\langle \sum_{\{R^\alpha(t), R^\beta(t)\}} T_{if}[R^\alpha(t)] T_{if}^\dagger[R^\beta(t)] \rho_i(R_o) \right\rangle_{\circ}, \\ &= \left\langle \sum_{\{R^\alpha(t), R^\beta(t)\}} U_{if}[R^\alpha(t)] \rho_i(R_o) U_{if}^\dagger[R^\beta(t)] e^{i(S[R^\alpha] - S[R^\beta])} \right\rangle_{\circ}, \end{aligned} \quad (24)$$

where $\rho_i(R_o)$ is the probability density of being in the initial state. The average, $\langle \dots \rangle_{\circ}$, is taken over initial configurations, and the sum is over pairs of switching paths

$$\{R^\alpha(t), R^\beta(t) | R^\alpha(0) = R_o, R^\beta(0) = R_o\} \quad (25)$$

which start at the initial configuration, R_o , with the quantum state in the initial state and

end at any final configuration with the quantum state in state $|f\rangle$ at t_f .

Notice that this definition of the transition probability no longer involves a single path. In fact, the transition probability depends upon all other alternative paths which could ultimately lead to the final state. When the sequence of switching events for a pair of paths, $R^\alpha(t)$ and $R^\beta(t)$ are identical, the contribution from the classical action will vanish and the quantum transition probability along a given path is given simply by

$$P_{if}(t) = \left\langle \sum_{\{R^\alpha(t)\}} |U_{if}[R^\alpha(t)]|^2 \rho_i(R_o) \right\rangle. \quad (26)$$

which is identical to the transition probability we write in the previous section. Applying the assumption of Eq. 26 to a switching path implies that the coherences between the quantum states are not damped by the bath. This can lead to the overestimation of the non-adiabatic transition rates as demonstrated in Ref. [36].

When transitions do occur, we must consider the phase interference between the various alternative switching pathways. At short times following a switch, there will be a significant contribution from the phase interferences between two alternative paths with similar histories and the total transition probability is the sum over the partial transition amplitudes for each pathway. [61] However, at longer times following a switch, the action difference between two paths will be very large so that the phase interferences will be added destructively, leaving a sum over incoherent transition probabilities. In short, there will be considerable phase coherence between paths with similar histories but little or no phase coherence between paths with dissimilar histories. The timescale over which we must explicitly consider quantum interference effects between alternative pathways is the *quantum decoherence time*.

Recently we demonstrated that quantum decoherence effects can be consistently incorporated into mixed quantum-classical systems by recognizing that restricting the quantum evolution to given classical pathways is equivalent to making a series of quantum measurements on the total system. [36,48,49] The classical path sequence shown in Eq. 23 and illustrated in Fig 1 is an example of a quantum mechanical history. Along this history, the time evolution operator for the quantum system can be written equivalently as a time ordered sequence of alternating quantum projection operators and unitary evolution operators

$$\hat{C}[R^\alpha(t)] = \hat{U}_n \hat{P}^{\alpha_{n-1}} \dots \hat{U}_1 P^{\alpha_1} \hat{U}_o \quad (27)$$

where the projections at each time interval are members of complete sets representing the total set of possible hopping outcomes,

$$\sum_{\alpha_i} \hat{P}^{\alpha_i} = 1, \quad (28)$$

and

$$\hat{U}_n = e^{-i \int_{t_{n-1}}^{t_n} ds H[R^\alpha(s)]} \quad (29)$$

is the unitary evolution operator for the quantum wavefunction along a segment of the switching path. Every time we “roll the dice” to determine the next quantum state along the switching path, we need to apply the projection operator \hat{P} to the quantum wavefunction.

In general the projection operators in Eq. 28 are any operator acting on the Hilbert space of the quantum subsystem. In practice, we have found the Gaussian form to be useful.

$$\hat{P}_i(Q) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(\hat{Q}-Q)^2/2} \quad (30)$$

where \hat{Q} is a bounded operator in the Hilbert space of the quantum system with eigenvalues $\{Q_j\}$. Later we shall define \hat{Q} in terms of the coupling between the quantum and classical variables. The parameter α serves as the range of values which are projected out by \hat{P} . When acting on the quantum density matrix \hat{P} acts under the trace operation,

$$\begin{aligned} \hat{P}\rho &= \left(\frac{\alpha}{\pi}\right)^{1/2} \int dQ e^{-\alpha(\hat{Q}-Q)^2/2} \hat{\rho} e^{-\alpha(\hat{Q}-Q)^2/2} \\ &= e^{-\alpha(Q_i-Q_j)^2/4} \rho_{ij}. \end{aligned} \quad (31)$$

Thus, when $\alpha \rightarrow \infty$, \hat{P} projects out all of the adiabatic eigenstate and full coherence between the states is retained. On the other hand, taking $\alpha = 0$ means that we project out only the state determined by the random switching event killing off any coherences between the eigenstates.

In our approach, we use the decoherence timescale to set a characteristic time interval between subsequent applications of the projection operators. During this interval, transition amplitudes are added coherently according to the rules of quantum mechanics. Application of the projection operators destroys the coherences and we are left with transition probabilities which are then added according to the rules of standard probability theory. Within our approach, Eq. 24 is rewritten as

$$\begin{aligned}
P_{i \rightarrow f}(t) &= \left\langle \sum_{R^\alpha(t)} \langle f_n | \hat{C}[R^\alpha(t)] \rho_i(R_o) \hat{C}^\dagger[R^\alpha(t)] | f_n \rangle \right\rangle_o \\
&= \left\langle \sum_{R^\alpha(t)} \langle f_n | \hat{U}_n \hat{P}^{\alpha_{n-1}} \dots \hat{P}^{\alpha_1} \hat{U}_1 \rho_i \hat{U}_1^\dagger \hat{P}^{\alpha_1} \dots \hat{P}^{\alpha_{n-1}} \hat{U}_n^\dagger | f_n \rangle \right\rangle_o, \tag{32}
\end{aligned}$$

where $|f_n\rangle = |f(R^{\alpha_n})\rangle$ is the final quantum state at the end of path $R^\alpha(t)$.

When the time intervals between “measurements”, $\delta t_n = t_n - t_{n-1}$, are members of a Poisson distribution, the probability of maintaining coherence over a given interval, δt_n , is

$$\pi(\delta t) = \int_0^{\delta t} dt \frac{e^{-t/\tau}}{\tau} = 1 - e^{-\delta t/\tau}, \tag{33}$$

and τ is the characteristic decoherence timescale. Under these conditions, the time evolution of the quantum density matrix over the short time step δt is given as

$$\rho(t + \delta t) = \left(1 - \frac{\delta t}{\tau}\right) \rho(t) + i \frac{\delta t}{\tau} [H_Q, \rho] + \frac{\delta t}{\tau} \hat{P} \rho. \tag{34}$$

Taking the limit of $\delta t \rightarrow 0$ yields the master equation for the quantum density matrix

$$\begin{aligned}
\dot{\rho} &= i[H_Q, \rho] - \frac{1}{\tau}(\rho - \hat{P}\rho), \\
&= \mathcal{L}\rho - \frac{1}{\tau}(\rho - \hat{P}\rho). \tag{35}
\end{aligned}$$

Using the Gaussian projector above,

$$\begin{aligned}
\dot{\rho}_{ij} &= i[H_Q, \rho]_{ij} - \frac{1}{\tau}(\rho_{ij} - [\hat{P}\rho]_{ij}), \\
&= [\mathcal{L}\rho]_{ij} - \frac{1}{\tau}(1 - \exp[-\alpha(Q_i - Q_j)^2/4])\rho_{ij}. \tag{36}
\end{aligned}$$

The first term contains the Liouvillian of the system, $\mathcal{L} = i[H_Q, \]$. Evolution of the quantum system under this term alone is unitary and non-dissipative. The second term introduces *quantum decoherence* into the dynamics of the quantum subsystem due to the series of projections described above. The coherences originally in the quantum subsystem decay due to the series of weak measurements imposed by the environment.

Both $\hat{C}[R^\alpha(t)]\rho_i(R_o)\hat{C}^\dagger[R^\alpha(t)]$ in Eq. 32 and the density matrix in Eq.36 is a functional of only a *single* classical trajectory as opposed to a sum over pairs of trajectories as in Eq. 24. Where did the other paths go? It turns out that all pairs of paths are still included in these equations, except that we periodically “prune” the paths which branch away from the main

bundle of paths at either the switching times (when we determine a quantum transition to have occurred) or when we have determined that a “measurement” has occurred by randomly making the density matrix diagonal through application of the projection operators or by smoothly diminishing the off diagonal coherence using the master equation. Both methods are formally equivalent.

When the quantum system is coupled linearly in \hat{Q} to a bath of oscillators, the fluctuations in the quantum system become proportional to the ability of the bath to dissipate energy. Under such conditions for a Markov bath, the relation is [62]

$$\frac{\alpha}{4\tau} = \frac{2m\gamma_0 kT}{\hbar^2}, \quad (37)$$

where γ_0 is the dissipation constant. One can then relate decoherence in the quantum system to fluctuations in the harmonic bath through the fluctuation-dissipation theorem. In essence, our decoherence ansatz is entirely consistent with other theories of quantum dissipation. In other theories of quantum relaxation, such as the spin-boson model [63,64], master equations such as the Redfield relaxation theory [65–69], or Liouville space methods [70], both decoherence and dissipation are treated implicitly through effective equations of motion, thus losing the molecular level information about the relaxation dynamics. In our treatment, dissipation is included *explicitly* through the classical molecular dynamics of the condensed phase medium, thus retaining a molecular level description. Quantum decoherence is treated implicitly in order to avoid summing over alternative pairs of classical paths.

3. Decoherence Timescales

Because our formalism relies upon an *a priori* knowledge of the decoherence time scale for the given system, we desire a molecular level theory of the process, allowing access to a measure of the quantum decoherence timescale. In developing a theory of quantum decoherence we introduced parameters which characterize the decay of coherences due to differences in the dynamics of the bath for each possible quantum state. Here we shall make use of the projection operator to solidify that concept and determine how one can go about obtaining a measure of the coherence time and length scales from realistic mixed quantum/classical simulations.

Let us consider the effect of coarse graining over a few timesteps. At the initial time t_o , we select the initial state of the total system to be a pure state given by $|\Psi_o(R_o)\rangle$. Now, evolve $|\Psi_o\rangle$ to time t_1 under the time dependent Hamiltonian $H(R(t))$ where $R(t)$ is a classical path and resolve the final state in a basis of eigenstates $\{|\phi_\alpha^1\rangle\}$ of $H(R(t_1))$.

$$|\Psi_1(R_1)\rangle = \sum_{\alpha_1} c_{\alpha_1} |\phi_{\alpha_1}^1(R_1)\rangle. \quad (38)$$

Next, we project this state into coarse grained sets by writing

$$\sum_{\alpha_1} c_{\alpha_1} |\phi_{\alpha_1}^1(R_1)\rangle = \sum_{\Delta_1} \sum_{\alpha_1 \in \Delta_1} c_{\alpha_1} |\phi_{\alpha_1}^1(R_1)\rangle. \quad (39)$$

As a result of the projection, there is little or no phase coherence between the various eigenstates composing this set. Since each adiabatic eigenstate defines a different adiabatic potential which the classical path may follow from this point in time until the next time step, each adiabatic state will define a unique coarse grained path or “branch” for the classical evolution. Select a branch using some selection criteria and propagate the state under the Hamiltonian, $H(R_1(t))$, where $R_1(t)$ is a classical trajectory along a given branch labeled by the sequence of adiabatic potential surfaces followed by the trajectory. We accumulate these as an indication of the history of choices made along the path. Again at time t_2 , resolve the new state at t_2 in a basis of eigenstates of $H(R_1(t_2))$ and select a new branch for the classical dynamics

$$\sum_{\alpha_1 \in \Delta_1} c_{\alpha_1} |\phi_{\alpha_1}^1(R_1)\rangle \mapsto \sum_{\Delta_2} \sum_{\alpha_2 \in \Delta_2} c_{\alpha_2} |\phi_{\alpha_2}^{2\Delta_1}(R_{21})\rangle. \quad (40)$$

Iterating the procedure once again to time t_3 yields the total quantum state of the system/bath along a particular trajectory.

$$\sum_{\alpha_2 \in \Delta_2} c_{\alpha_2} |\phi_{\alpha_2}^{2\Delta_1}(R_{21})\rangle \mapsto \sum_{\Delta_3} \sum_{\alpha_3 \in \Delta_3} c_{\alpha_3} |\phi_{\alpha_3}^{3\Delta_2\Delta_1}(R_{321})\rangle. \quad (41)$$

One can begin to see the conceptual underpinnings of the decoherent histories approach to quantum mechanics. At each level of coarse graining, the evolution of the classical variables branches into different possible histories where each branch indicates evolution along a different adiabatic potential surface. The evolution of the total quantum state depends very much upon the particular history, $\{\Delta_n, \Delta_{n-1}, \dots\}$, selected at each time step.

In other words, when we allow the classical variables to switch between adiabatic potentials at a particular time as the result of a electronic transition, the evolution of the electronic system becomes dependent upon when the transitions actually occur.

Quantum coherence between alternative states is lost as the overlap between the alternatives decays. We can provide an estimate for the rate at which coherence is lost considering the short time evolution of the reduced density matrix along a given path. For example at time t_3 , the reduced density matrix is given by

$$\begin{aligned} \rho^{3\Delta_2\Delta_1}(R_{321}(t_3)) &= \sum_{\Delta_3\Delta'_3} \sum_{\alpha_3 \in \Delta_3} \sum_{\beta_3 \in \Delta'_3} c_{\alpha_3} c_{\beta_3}^* \\ &\times |\phi_{\alpha_3}^{3\Delta_2\Delta_1}(R_{321})\rangle \langle \phi_{\beta_3}^{3\Delta_2\Delta_1}(R_{321})|. \end{aligned}$$

To estimate the overlap between alternative branches for times $t > t_3$ we assign to the bath coordinates at time t_3 Gaussian wavepackets centered at the instantaneous phase space positions of the bath variable, $|G(R, P)\rangle$. In other words, we write

$$|\phi_{\alpha_3}^{3\Delta_2\Delta_1}(R_{321})\rangle = |\phi_{\alpha_3}^{3\Delta_2\Delta_1}\rangle |G(R_{321}, P_{321})\rangle. \quad (42)$$

Next, we make the approximation that we can decouple the evolution of the quantum system from the evolution of the bath over a short time period and allow the path to begin to branch in to R_{321} and $R_{3'21}$.

$$\begin{aligned} \rho^{3\Delta_2\Delta_1}(R_{321}(t > t_3)) &= \sum_{\Delta_3\Delta'_3} \sum_{\alpha_3 \in \Delta_3} \sum_{\beta_3 \in \Delta'_3} c_{\alpha_3}(t) c_{\beta_3}^*(t) \\ &\times |\phi_{\alpha_3}^{3\Delta_2\Delta_1}(R_{321})\rangle \langle \phi_{\beta_3}^{3\Delta_2\Delta_1}(R_{3'21})| \\ &\times J_{\alpha_3\beta_3}(R_{321} - R_{3'21}; t). \end{aligned} \quad (43)$$

$J_{\alpha_3\beta_3}(R_{321} - R_{3'21}; t)$ is the overlap integral between paths. The decoherence time can thus be determined by the timescale at which this vanishes.

Let us approximate $J_{\alpha_3\beta_3}(t)$ using Gaussian coherent state wavepackets which follow the classical evolution of the alternative paths. Under this approximation, and to lowest order in time the overlap decays as (We drop the 321 and 3'21 notation and take $R = R_{321}$ at time t_3 and consider times $t \geq t_3$).

$$J_{\alpha\beta}(R; t) = \exp \left[-\frac{t^2}{4m\omega} (F^\alpha(R) - F^\beta(R))^2 \right] \quad (44)$$

where $F^\alpha(R)$ and $F^\beta(R)$ are the instantaneous quantum forces acting on the classical particles as the path bifurcates along the various adiabatic potentials. (Note: that we are implicitly summing over all particles in the system in the exponent of this equation.) The width of the Gaussian, ω , is left arbitrary for the time being. Thus, a rough estimate of the quantum decoherence time at a given configuration is given by the decay width of $J_{\alpha\beta}(t)$, [36,48]

$$\tau_D = 2 \frac{\sqrt{m\omega}}{F^\alpha - F^\beta}. \quad (45)$$

Finally, averaging over an ensemble of configurations, we obtain the “average coherence decay”

$$\langle J(t) \rangle = \int dR P(R) \exp \left[-\frac{t^2}{4m\omega} (F^\alpha(R) - F^\beta(R))^2 \right], \quad (46)$$

where $P(R)$ is the probability distribution function for configuration R .

Such quantities are easily computable in mixed quantum/classical simulations and provide a convenient measure for coherence times in simulations. We shall later use this measure to assess the choice of decoherence times in simulations of the dynamics of an excess electron in ordinary and heavy water. [48] The coherence time for one bath configuration will be quite different than the coherence time for another configuration. However, one can envision a case in which quantum transitions occur only when the classical variables are in a few rare configurations. In this case a global decoherence time would not provide an accurate measure of the decoherence timescale. As we shall demonstrate next, even small changes in the decoherence timescale can have profound effects on both the quantum and the classical evolution.

4. Coherence Times For Physical Systems

We can estimate the decay of quantum coherence for the hydrated electron from Eq. 46 with information available from excited state simulations. For the present example, the initial state i is the equilibrium excited state of the hydrated electron, and the final state j is the ground state of the electron. For the widths of the frozen Gaussians, we chose

$$4m\omega = 6mkT \quad (47)$$

which results from rigorous analysis of the non-adiabatic transition rate between displaced harmonic oscillators in the high temperature limit, [29,30] and also allows for direct comparison to the earlier calculations of Neria and Nitzan. [29,30] To compute the average decoherence decay we constructed ensemble of excited state configurations by assuming that the system was equilibrated at times past 1 ps after being prepared in the excited state. n We chose 20 configurations at 25-50 fs intervals from each of 5 individual trajectories for a total of 100 configurations. Details of these simulations are given in the Appendix.

The results of this calculation are shown as in Fig. 2. For the hydrated electron the coherence decays in a roughly Gaussian manner, and a Gaussian fit to the decay has a variance of ≈ 3.1 fs. Another estimate of the decoherence time is found in the area under the curve, which for this example is 2.8 fs. This result is in good agreement with previous calculations using a different model for the hydrated electron, [29,30] and demonstrates *a posteriori* justification for the hypothesis of a ≈ 1 fs coherence time in the earlier non-equilibrium simulations. We also note that the rapid decoherence of this system provides *a posteriori* justification for the short time approximation used to estimate $\langle J(t) \rangle$. We find that the exponential is typically dominated by only 5 to 10 nuclei which are the closest to the bulk of the electronic charge density. This makes sense from the stance that the largest difference in force between the two surfaces will be for nuclei in positions where the charge density, is large on one surface and small on the other.

We also show the coherence decay curve for an excited electron in D₂O computed similarly. The coherence decay in D₂O is qualitatively similar to that in H₂O, only for D₂O the approximate Gaussian decay time is ≈ 4.6 fs (versus ≈ 3.1 fs for H₂O) and the area under the curve is 4.1 fs (versus 2.8 fs for H₂O).

The longer coherence time in heavy water compared to light water arises predominantly from the difference in mass in the choice of the Gaussian width. For classical H₂O and D₂O, the probability of a given nuclear configuration is the same. Static ensemble properties for the two fluids should be identical since the ensembles contain identical nuclear configurations with equal statistical weights. ² Since the electronic Hamiltonian for the solvated electron

²This is true for classical water models. When quantum mechanical effects are properly included,

is identical for both heavy and light water, the static ensemble averaged potential energy difference and the difference in Hellmann-Feynman forces on the two surfaces will also be identical for the two fluids. Thus, the only differences in the evaluation of the coherence decay for the two fluids is through the mass term that enters through the Gaussian width. Since the nuclear overlap part of the coherence decay depends on the sum over nuclei, the mass change leads to the net slower decay of coherence in D₂O versus H₂O. In fact, for the purposes of evaluating $J(t)$ for the solvated electron in D₂O, the H₂O simulations would suffice.

The different coherence decay times in the two solvents play a direct role in determining the isotope effect on the overall non-adiabatic transition rate. In simplified terms, to determine the non-adiabatic transition rate before quantum coherence has decayed, non-adiabatic transition *amplitudes* should be added; after the decoherence interval, memory of the complex phases is lost and non-adiabatic transition *probabilities* should be added.

5. Effect of Decoherence on Quantum Transition Rates

One of the primary effects of electronic coherence loss can be observed in the evaluation of the switching probabilities. If we approximate the short time evolution of the density matrix as

$$\rho_{ij}(t + \delta t) \approx \exp \left\{ -\frac{\delta t}{\tau} \left[1 - \exp \left(-\alpha(F_i - F_j)^2/4 \right) \right] \right\} \rho_{ij}(t), \quad (48)$$

and substitute this into the non-adiabatic switching probability given above, one obtains

$$\begin{aligned} \tilde{P}_{ij}(\delta t) \approx & \exp \left\{ -\frac{\delta t}{\tau} \left[1 - \exp \left(-\alpha(f_i - f_j)^2/4 \right) \right] \right\} \\ & \times \int_t^{t+\delta t} ds \frac{-2\text{Re}\{\rho_{ij}\dot{R}_\mu\langle\phi_i|\partial_\mu\phi_j\rangle\}}{\rho_{ii}}. \end{aligned} \quad (49)$$

This predicts that one should see a change over from non-adiabatic dynamics to adiabatic dynamics as the coherence timescale becomes very small. Thus, even in this relatively simple

H₂O and D₂O have slightly different properties due to differences in the spatial dispersion of the H and D nuclei. C. f. G. S. Delbuono, P. J. Rossky, J. Schnitker, J. Chem. Phys. **95**, 3728 (1991).

model of coherence loss, it is readily apparent that decoherence due to the coupling to an external environment generally tends to suppress quantum effects and increases the degree of adiabaticity in the quantum subsystem [36].

As one can see from the last set of equations, one can estimate the effect of coherence loss on the quantum transition probability given a coherence timescale and the quantum transition amplitudes for a given system. Recall that the origin of this equation is that the classical degrees of freedom (the bath) make a series of quantum measurements on the system at random time intervals. Thus we can write the non-adiabatic transition probability between states i and j as a function of the measurement timescale τ as

$$P_{ij}(\tau) = \frac{1}{Q} \sum_N \frac{1}{\tau} w_N(\tau, n\Delta t) \left| \sum_{n=1}^{\tau} T_{ij}^{(N)}(n\Delta t) \right|^2. \quad (50)$$

Here, $T_{ij}^{(N)}(n\Delta t)$ is the quantum transition amplitude at the n^{th} timestep starting from the N^{th} configuration. In other words, to compute this quantity, we propagate the quantum subsystem coherently over a coherence time picked from a distribution of possible coherence times. During this interval we sum over amplitudes. At the end of the interval, coherences between states are killed off and we sum over probabilities. The outer summation is over starting configurations and $w_N(\tau, n\Delta t)$ is the statistical weight for a given configuration to have a coherence time of τ . These are normalized by Q . The time step, Δt is taken as the shortest timestep used to propagate the equations of motion for the system. For the case of the electron in H₂O and D₂O, this $\tau = 1$ fs throughout.

In Fig. 3, we plot the estimated lifetime of the electron in the excited state as a function of coherence timescale for both solvents. The solid lines, labeled “fixed” refer to using a single coherence time interval in evaluating Eq.50, i.e. $w_N(\tau, n\Delta t)/Q = \theta(\tau - n\Delta t)$. The curves labeled “Poisson” refer to lifetimes computed using a Poisson distribution of coherence time intervals.

$$w_N(\tau, n\Delta t)/Q = \exp(-n\Delta t/\tau)/\tau \quad (51)$$

Both curves track each other quite well. For a 1 fs coherence time, these lifetimes correspond to ≈ 550 fs for H₂O and ≈ 850 fs for D₂O. The magnitude of these rates agree reasonably with the rates reported in earlier simulations [26,71,72] and the roughly 2:1 simulated isotope

effect is reproduced as well. While non-adiabatic transitions typically occur from configurations with higher than average transition probabilities, these configurations are reasonably rare that the average transition probability determined here provides a reasonable estimate of the non-equilibrium population dynamics.

We can now use the coherence timescales estimated above to provide an estimate of the excited state survival times. For equal coherence times of 1 fs, which was the original assumption in the simulations by Schwartz and Rossky, the survival probabilities in Fig.3 predict roughly a 2:1 isotope effect. However, when we use the decoherence times computed above, we find that the $\approx 50\%$ difference in coherence times yields an estimation of the lifetimes which are identical to within 10%. Furthermore, the lifetimes and estimated isotope effect agree remarkably with the experimental values reported by Barbara. These results are summarized in Table 1. This provides a clear demonstration that quantum decoherence plays a direct and key role in the electronic dynamics of this system.

B. Decoherence in Quantum MD Simulations

Quantum decoherence can be also be incorporated into non-adiabatic quantum MD simulations through either the projection operator method or the master equation theory discussed above. In the statistical limit, both methods give identical results. [36] The computational algorithm given below uses the projection operator approach (Eq.32) with the coherence time intervals chosen from a Poisson distribution with characteristic time scale $\tau_D = 3.1fs$ as derived from our estimates of the coherence time scale for an electron in H₂O when the excited state is nearly solvated. This time scale was estimated by computing the average decay time of the overlap of frozen Gaussian vibrational wavefunctions evolving on different adiabatic potential energy surfaces by sampling a large number of nearly equivalent excited state configurations. Also note that this method can be used for both the MDQT method and the WFR/SP methods since we assume that the treatment of the quantum-classical forces is independent of coherence retention. The consistent histories algorithm proceeds as follows:

1. Determine coherence interval from Poisson distribution of possible intervals with char-

acteristic time scale τ_D .

2. Propagate the quantum wavefunction over this time scale while self consistently evolving the classical degrees of freedom. At the end of each dynamical time step $h \leq \tau_D$, determine the switching path followed by the classical variables using the stationary phase algorithm developed by Webster, *et al.* [23,24] modified such that coherence in the quantum wavefunction is maintained over the entire coherence interval. We also note that the stationary phase switching path is determined in a piece-wise continuous fashion by selecting intermediate quantum states every dynamical time step. This is to avoid the computational overhead of computing variationally the stationary phase trajectory over relatively long time intervals. So long as τ_D is no longer than a few dynamical time steps, this approximation should not be too extreme; however, certain pathological cases can be invented in which this approximation does break down.
3. If either a switch occurs in the time interval or we reach the end of the interval, the quantum wavefunction is collapsed using the projection operators discussed above.
4. Repeat.

In Fig. 4 we plot the switching times from the excited state to the ground state for a total of 23 simulation runs. The starting configurations were generated by performing a 35 ps simulation in which the electron was prepared in the ground state and 16 initial configurations were chosen whenever the energy difference between the ground state and one of the p-like excited states become resonant with the excitation laser (1.7 eV). [35,28,73] These starting configurations were identical to configurations used previously by Schwartz and Rossky in their work on this system. [26,71,72] Following the initial excitation, the system was allowed to evolve. During this time, the energy gap between the p-states and the s-state narrowed to $\approx 0.5eV$ as the excited state was solvated by the surrounding water molecules. The simulation continued until a switch from the excited state to the ground state was recorded. Immediately after the switch, the energy gap between the occupied ground state and the first excited state widened dramatically as the solvent responded to the new electronic state. The average and median switching times from these simulations are compiled in Table 2.

In order to test the sensitivity of the switching times to the choice of sequence of coherence intervals, five configurations were “recycled” by using different random number sequences for the coherence time intervals to generate different switching paths starting from the same initial configuration. For each such pairs of paths, the classical dynamics were identical up until the earlier switching time when one of the paths switched from the excited state to the ground state. However, since the coherences between the different quantum states were killed off at randomly different times for each path, each path sampled a different probability distribution function for making a switch at each MD time step. Hence any correlations between switching times resulting using the same initial configuration reflect correlations in the distribution of coherence time intervals. Given that there is typically a 100 fs time difference between pairs of data (in one case a 530 fs difference) which is roughly 1/3 of the average survival time scale of the excited state, we find very little correlation between the switching times originating from the same initial configuration.

As the excited state is solvated by the surrounding water molecules, the energy gap between the excited state and the ground state narrows to its equilibrium value. Furthermore, from first order perturbation theory, we expect that the electronic transition rate to be inversely proportional to the magnitude of the energy difference between initial and final states. Thus, a simple model for the excited state survival probability can be written as

$$\frac{\partial P(t)}{\partial t} = -\frac{k_{\text{eq}}}{\tilde{\omega}(t)} P(t) \quad (52)$$

subject to the initial condition $P(0) = 1$. Here, k_{eq} is the non-adiabatic transition rate for the solvated excited state and $\tilde{\omega}(t)$ is the average energy gap normalized to the average energy gap of the solvated excited state. $\tilde{\omega}(t)$ is related to the solvation response $S(t)$ by

$$\tilde{\omega}(t) = \frac{\langle\omega_o\rangle S(t) + \langle\omega_{\text{eq}}\rangle(1 - S(t))}{\langle\omega_{\text{eq}}\rangle}. \quad (53)$$

In Fig. 5, we plot $\tilde{\omega}(t)$ using the fit to the solvation response function generated by our simulations. These fits are nearly identical to those obtained by Schwartz and Rossky. [31,25,26,71] At short times, when $\tilde{\omega}(t) > 1$, the non-adiabatic transition rate will be small since the energy gap is large. At long times $\tilde{\omega}(t) \rightarrow 1$ as the energy gap relaxes to its equilibrium value. Thus, k_{eq} is the exponential decay constant of the excited state population once the excited state is fully solvated.

The solution of Eq. 52 is the one parameter family of curves given by

$$P(t) = \exp\left(-k_{\text{eq}} \int_0^t \frac{ds}{\bar{E}(s)}\right) P(0). \quad (54)$$

Using a non-linear fitting procedure, we fit our data to this model to obtain an estimate of the equilibrium non-adiabatic lifetime of 241 fs with a $\chi^2 = 1.707$. A plot of our data superimposed on this fit is given in Fig. 4. Interestingly enough, our data does not fit this simple model as nicely as the data given by Schwartz and Rossky. This suggests that the longer coherence times used in this study imparts a non-trivial memory dependency into the survival probability which is inadequately captured in Eq. 52.

As expected, the lifetimes reported here (Table 2) are consistently shorter than the lifetimes reported by Schwartz and Rossky in which a constant 1 fs coherence time scale throughout their simulations, thus emphasizing the profound sensitivity of these simulations to the coherence time scale. Furthermore, our results are consistent with the estimated lifetimes estimated above.

IV. DISCUSSION

In this chapter we have briefly described the results of our work towards a molecular level description of quantum relaxation phenomena. Here we have focused exclusively upon the role that transient quantum mechanical coherences between the solvent and the solute play in the electronic relaxation of an excited solute species. In mixed quantum-classical computer simulations, fundamental assumptions about the decay of these coherences produce direct manifestations on the computed quantum mechanical transition rates and must be included consistently in order to make realistic predictions and comparisons. [36,48]

We have focused our attention primarily upon electronically non-adiabatic processes and various aspects which must be considered in order to simulate such processes for a condensed matter system. In most quantum-chemical calculations, the fundamental assumption is that the nuclear dynamics are well within the Born-Oppenheimer approximation and that breakdowns in this approximation are rare and unusual events. However, in nature the opposite is largely true. Non-adiabatic events occur in a number of important chemical processes including the process of vision and photosynthesis, predissociation, photodissociation, charge

transfer, spin-quenching, and charge transfer reactions of which free radical chemistry is a vital component.

The computational algorithm, based upon the so-called consistent histories interpretation of quantum mechanics, provides both the molecular level underpinnings of quantum decoherence and the computational means for properly including decoherence effects in non-adiabatic quantum-molecular dynamics simulations. According to the rules of ordinary quantum mechanics, a quantum system will evolve into a coherent superposition of alternative states. In our decoherence theory, this coherence is dissipated due to the differences in the forces exerted on the bath by alternative states involved in the superposition. Thus, on short scales, a quantum system in a bath will obey the rules of ordinary quantum mechanics and evolve into a coherent superposition of states, whereas on longer time scales, the coherences between states are diminished and the quantum system must be described as statistical (i.e., incoherent) mixture of states. As the quantum system interacts continuously with the bath, coherences between states are continuously created by non-adiabatic coupling and damped by the divergence in the bath dynamics induced by the system-bath coupling.

This subtle interplay between coupling and decoherence and the subsequent dependency of transition rates on the decoherence time scale has profound implications for a variety of condensed phase chemical dynamics including: internal conversion and internal vibrational energy redistribution (in which the bath is comprised of all the modes of the molecules except for the one mode of interest), electronic energy transfer between molecules or different parts of the same molecule, and charge transfer reactions including proton and electron transfer. In these latter examples, both the condensed phase environment and the internal motions of the molecules act as a bath which couples the quantum states together. The decay of quantum coherence, which depends upon the frequencies and populations of the bath modes coupled to the quantum system will determine the extent to which the non-adiabatic coupling can act to allow the chemical reaction to proceed. Changes in the spectral density due to isotopic changes in the bath can have a substantial impact on non-adiabatic chemical dynamics [48,49]. Furthermore, the decay of quantum coherence can determine the adiabaticity for a chemical reaction.

Perhaps the two major lacunae in our theory of decoherence is the explicit dependency

upon an *a priori* estimate of the coherence time scale and the fact that this time scale remains fixed throughout the calculation. As mentioned above, we estimated this time scale by computing the average decay time of the overlap of a product of Gaussian coherent states evolving on different adiabatic potential energy surfaces. In this estimate, the individual widths of the coherent state wavefunctions centered about the initial phase space points of the classical nuclei are set to be proportional to the thermal DeBroglie wavelength of each nuclei. Although physically realistic for a variety of situations, this does leave the coherence *length scale* (i.e. the widths) as an adjustable parameter. While the effects of changing the coherence length scale over a broad range have not been systematically studied, results from our previous work demonstrate that the non-adiabatic transition is quite sensitive to changes in the coherence time scale and hence will be sensitive to changes in the coherence length scales. Furthermore, as the bath explores various regions of the quantum potential energy surface, the force differences which give rise to the decay of the quantum coherences should vary from one configuration to the next. [48] Current progress is underway towards obtaining both the coherence length and time scale during the course of the non-adiabatic simulation *ab initio* by examining the quantum mechanical fluctuations of the bath particles about their stationary phase paths.

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Tables

TABLE I. Summary of experimental and theoretical estimates of the nonradiative lifetime of an excess electron in H₂O and D₂O. The first two rows are experimental results from Gauduel and Barbara and the remainder are theoretical estimates. All theoretical numbers reported are for relaxation from an *equilibrated* first excited state of the electron in either solvent. See text for details regarding the differences in the theoretical values.

	H ₂ O (fs)	D ₂ O(fs)	D ₂ O/H ₂ O
Gauduel <i>et al.</i> (Ref. [27])	240	250	1.04
Kimura <i>et al.</i> (Ref. [28])	310 ± 80	310± 80	1.0
Neria and Nitzan (Ref. [30])	220	800	≈ 4
Schwartz and Rossky (Ref. [31])	450	850	≈ 2
1fs Coherence ^a	550	850	1.55
Present Estimate ^b	310 - 285	345 - 334	1.11 - 1.17

^a 1.0 fs coherence time for both H₂O and D₂O.

^b Estimated lifetime ranges correspond to estimated ranges of the coherence time for both solvents. H₂O: 2.8 -3.1 fs. D₂O: 4.1-4.6 fs. (c.f. Fig 2.)

TABLE II. Excited state lifetimes for the aqueous electron. (SR= Schwartz and Rossky, J. Chem. Phys. **101** 6902 (1994). SBPR = Schwartz, Bittner, Prezhdo, and Rossky, J. Chem. Phys. **104** 4942 (1996)). The coherence times used in each study are listed in parentheses.

	Present (3.1 fs)	SR (1 fs)	SBPR (2.8-3.1 fs) ^(a)
Median	338 fs	630	—
Average	384	730	—
Equilibrium	234	450	310-270

(a.) Only Equilibrium lifetimes considered.

Figure Captions

FIG. 1. Energy levels and occupations for two trajectories starting from identical water configurations. The occupied state as a function of time is indicated by + and \diamond for the two trajectories.

FIG. 2. Overlap function averaged over 100 equilibrated excited state configurations for H₂O and D₂O.

FIG. 3. Effective Excited State Lifetimes vs. Quantum Decoherence Time. Shown for both H₂O and D₂O are estimates of the excited state lifetimes using the estimates of the quantum coherence timescales. As discussed in the text, we estimate the coherence times to be 2.8-3.1 fs for H₂O and 4.1-4.6 fs for D₂O. The corresponding lifetimes are 310 - 285 fs and 345-334 fs for H₂O and D₂O respectively. The experimental range of 310 ± 80 fs is from Ref. [28]. See text for details.

FIG. 4. Distribution of switching times following initial excitation for e⁻/H₂O. Diamonds (\diamond) represent the switching times from the simulations. Superimposed curves are the results of a Gaussian fit (B) and a kinetic model (C).

FIG. 5. Plot of the normalized energy gap between the ground and occupied excited state following initial excitation.









