Non-Born-Oppenheimer molecular dynamics of Na···FH photodissociation

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The accuracy of non-Born-Oppenheimer (electronically nonadiabatic) semiclassical trajectory methods for simulations of “deep quantum” systems is reevaluated in light of recent quantum mechanical calculations of the photodissociation of the Na···FH van der Waals complex. In contrast to the conclusion arrived at in an earlier study, semiclassical trajectory methods are shown to be qualitatively accurate for this system, thus further validating their use for systems with large electronic energy gaps. Product branching in semiclassical surface hopping and decay-of-mixing calculations is affected by a region of coupling where the excited state is energetically forbidden. Frustrated hops in this region may be attributed to a failure of the treatment of decoherence, and a stochastic model for decoherence is introduced into the surface hopping method and is shown to improve the agreement with the quantum mechanical results. A modification of the decay-of-mixing method resulting in faster decoherence in this region is shown to give similarly improved results.


I. INTRODUCTION

Molecular dynamics (i.e., classical trajectory) simulations have found widespread use throughout chemistry and biology for elucidating reaction mechanisms, identifying important product species, modeling energy transfer, and simulating ensembles. Qualitative, and sometimes quantitative, insights may be gained from such simulations so long as certain quantum effects (tunneling, zero point motion, electronic transitions, etc.) do not dominate the dynamics. There have been several efforts to generalize molecular dynamics simulations to include quantum effects while retaining the computational efficiency and simplicity of the classical trajectory framework, and the present work focuses on one such generalization, namely, the incorporation of coupled electronic states and transitions between them.

Traditional molecular dynamics simulations are restricted to a single Born-Oppenheimer electronic state (typically, the ground electronic state), and they are therefore unable to treat a variety of interesting chemical phenomenon, such as diabatic charge transfer reactions, photodissociation, internal conversion, intersystem crossing, chemiluminescence, and most reactions of electronically excited species. Several so-called “non-Born-Oppenheimer” molecular dynamics (NBOMD) methods have been developed that incorporate electronic state changes into molecular dynamics simulations, including the trajectory surface hopping,1–5 spawning,6–8 and decay-of-mixing9–12 classes of methods. These methods rely on classical trajectories to describe the nuclear motion of the system, and they differ from one another in their treatments of the electronic motion and in their prescriptions for how the nuclear and electronic degrees of freedom are coupled to one another.

Because there is no unique way to couple quantum and classical subsystems, practical semiclassical descriptions of quantum mechanical events are necessarily somewhat ad hoc. It is therefore desirable to attempt to quantify the errors associated with the additional assumptions and approximations used by the various NBOMD methods to model electronic transitions. This kind of analysis is further motivated by direct dynamics simulations of non-Born-Oppenheimer systems,13–17 where the cost associated with the evaluation of the nuclear forces may prohibit studies of the sensitivity of results to the various implementations of NBOMD methods that have been proposed.

A series of systematic studies of the accuracy of several NBOMD methods was recently carried out, and the results are summarized in a review.18 These tests included several model two-state atom-diatom reactive systems featuring three kinds of surface couplings: weak interactions, avoided crossings, and conical intersections. Quantum mechanical calculations were performed for several different initial conditions and for several variants of each system type, and the results of a total of 17 test cases were used to evaluate various implementations of the trajectory surface hopping and decay-of-mixing methods. For the best methods, average errors in branching probabilities and final internal energies were found to be only 20%–40%. Errors in this range are similar to those found in tests of single-surface trajectory simulations,19 and we may conclude from these studies that, for these NBOMD methods, the treatment of the electronic transition is not a significant additional source of error. (It is important to note that these errors refer to specific implemen-
tations of the surface hopping and decay-of-mixing methods, which are the result of several refinements; many implementations of the surface hopping and other semiclassical formalisms have significantly larger errors, thus emphasizing the importance of these systematic tests and refinements.)

In another test of several semiclassical trajectory methods, the photodissociation of the collinear NaFH van der Waals complex was simulated using a model two-state set of coupled analytic potential energy surfaces. In that study, quantum mechanical calculations predicted the almost exclusive formation of the Na(3s)+HF product fragments and a half life of 172 ps for the photoexcited van der Waals complex (exciplex). The NBOMD methods, on the other hand, predicted NaF+H to be the dominant product channel with exciplex half lives ranging from 0.7 to 170 ps. This severe failure of the trajectory-based methods was attributed to the deep quantum nature (i.e., the large electronic energy gap) of the NaFH system. The disagreement of the quantum and semiclassical dynamics calculations was very troubling.

Subsequently, a new set of collinear quantum mechanical calculations has been carried out and these new results differ significantly from the previous ones. Furthermore, the decay-of-mixing method was not tested in the earlier study, and several refinements of the trajectory surface hopping method have since been developed. The goal of the present study is to reevaluate the accuracy of the best NBOMD methods for the NaFH system in light of the new set of quantum mechanical calculations.

In the course of the present evaluation, we highlight the important role of the treatment of decoherence in developing accurate semiclassical trajectory methods.

II. THEORY

Potential energy matrix. A full-dimensional diabatic representation of the two lowest-energy electronic states of NaFH has been presented previously. The ground and first-excited adiabatic potential energy surfaces may readily be obtained from the diabatic surface fit by diagonalizing the diabatic potential energy matrix, and the nonadiabatic coupling is assumed to result entirely from the diabatic-to-adiabatic transformation. This surface fit was obtained using a database of adiabatic energies computed using high-level electronic structure theory methods at more than 1530 geometries. Minor refinements were made in a subsequent publication, and the resulting surface fit (called NaFH–B) was used in the new quantum mechanical calculations and is used here.

Initial conditions. For each simulation, 5000 semiclassical trajectories were initiated in the ground vibrational state of the collinear NaFH van der Waals well of the ground adiabatic electronic state using quasi-classical initial conditions and harmonic frequencies for the two nuclear degrees of freedom. This procedure resulted in a distribution of initial coordinates and momenta with internal energies close to the harmonic estimate of the zero point energy. For the collinear NaFH van der Waals well of the NaFH–B surface fit, the harmonic frequencies are 4115 and 103 cm⁻¹, and the harmonic zero point energy is 0.26 eV. The quasi-classical procedure resulted in a distribution of the initial internal energies with an average of 0.27 eV (relative to the bottom of the van der Waals well) and a standard deviation of 0.03 eV.

Each trajectory in the ensemble was then instantaneously promoted to the excited adiabatic electronic state with white light. The average photon energy (i.e., the average adiabatic energy gap) for the initial ensemble of trajectories was 1.9±0.1 eV, and the average total energy was 2.1±0.1 eV relative to the Na(3s)+HF asymptote at its classical equilibrium.

Trajectory surface hopping. For a given classical path, the electronic motion (i.e., the change in the electronic state populations as a function of time) may be readily obtained by integrating the solution to the time-dependent electronic Schrödinger equation. For a two-state system, the time dependence of the electronic population $P_1$ of the ground state is given by (we consider the adiabatic representation exclusively in this article)

$$\dot{P}_1 = -2 \text{Re}(a_{12}^* \mathbf{v} \cdot \mathbf{d}),$$

where $a_{12}$ is the electronic coherence of states 1 and 2, $\mathbf{v}$ is the nuclear velocity of the trajectory, $\mathbf{d}$ is the nonadiabatic coupling vector, and variables in bold denote vectors in the nuclear degrees of freedom.

In the trajectory surface hopping simulations, trajectories are propagated in a single electronic state, and this single-surface propagation is interrupted by sudden surface switches or hops. The quantum mechanical populations $P_1$ are used to determine the location of the surface switches according to the “fewest switches” (FS) prescription of Tully, which was formulated such that, in the limit of degenerate electronic states and for a single set of initial conditions, (1) the relative populations of the ensemble of classical trajectories in the electronic states are equal to the quantum mechanical populations $P_1$ and (2) the number of surface switches is minimized. For more general cases, frustrated hopping and the divergence of the ensemble of independent trajectories lead to a breakdown of this internal consistency, as discussed below and in detail elsewhere.

When a surface hop is requested by the FS algorithm, the kinetic energy of the trajectory is adjusted along the nonadiabatic coupling vector such that the total energy of the trajectory is conserved. If such an adjustment is not possible (i.e., if the energy due to the momentum component along the nonadiabatic coupling vector is less than the electronic energy gap and if the trajectory is hopping to a higher-energy electronic state), the hop is declared “frustrated.” Frustrated hops have been shown to have serious implications for the accuracy of trajectory surface hopping methods in some cases, and we have previously considered several prescriptions for dealing with them.

Some, but not all, frustrated hops arise from an incorrect treatment of electronic decoherence, as discussed below. The fewest switches with time uncertainty (FSTU) method has been developed to deal with a source of frustrated hops, namely, those associated with tunneling, that does not arise from an incomplete treatment of electronic decoherence. A
trajectory may attempt to hop into a classically forbidden region of an excited electronic state associated with the tail of the quantum mechanical probability distribution. The FSTU method is a simple modification of the FS method that allows the trajectory to effectively tunnel into the excited electronic state by allowing the trajectory to hop some (short) time before or after the time of the frustrated surface hop. The maximum uncertainty in the hopping time is limited by the energy the trajectory would have been required to borrow to hop at the location of the frustrated hop and the time-energy uncertainty relationship.

In tests of the FSTU method on systems with weakly coupled electronic states, the FSTU method was shown \(^{30}\) to be dramatically more accurate than the unmodified FS method, thus demonstrating the importance of tunneling surface hops for some systems. For more strongly coupled systems, the FSTU method, on average, gives similar results to the unmodified FS method.

The FSTU method (by design) does not eliminate all frustrated hops. The remaining frustrated hops may be attributed to the breakdown of the independent trajectory approximation when using Eq. (1) to compute the electronic state populations and are treated using the \(\nabla V\) prescription. \(^{31}\) Specifically, if the target electronic surface is repulsive in the direction of the nonadiabatic coupling vector, then the nuclear momentum along the nonadiabatic coupling vector is reversed. Otherwise, the nuclear momentum is unchanged. In this way, the frustrated trajectory instantaneously feels a force associated with the target electronic state. This strategy was previously shown \(^{31}\) to be (slightly) more accurate than simply ignoring all frustrated hops and several other prescriptions.

Decay of mixing. Motivated in part by the problems associated with frustrated hopping in trajectory surface hopping simulations, as well as a desire to develop a trajectory based method with the results approximately independent of the choice of electronic representation, the decay-of-mixing methods were developed.\(^ {9-11}\)

In these methods, trajectories are propagated on a mean-field potential energy surface, which is a representation-independent weighted average of the potential energy surfaces. The weights are obtained by integrating the solution to the time-dependent Schrödinger equation, with terms added to force the system to "demix" as trajectories leave regions of coupling. In this way, trajectories are propagated without surface hops, the potential energy surface is continuous, electronic transitions occur by smoothly varying the weights associated with the electronic states, and trajectories tend toward quantized electronic states away from regions of coupling. Furthermore, when the effect of the demixing terms is small and when the electronic state coupling is large, the nuclear motion is independent of the choice of electronic representation.

In the present study, we test the coherent switches with decay of mixing (CSDM) method,\(^ {11}\) which was found to be the most accurate semiclassical trajectory method tested in our recent review.\(^ {18}\) A mixed state CSDM trajectory stochastically demixes to a quantized pure state with a first-order decay time constrained so that demixing does not occur when the momentum in the nonadiabatic coupling direction is insufficient to support the required accompanying energy transfer and so that it is greater than or equal to the fastest electronic time scale in the system. The most systematically studied form for the first-order decay time is given (for a two-state system) by

\[
\tau = \frac{\hbar}{\Delta V \left(1 + \frac{E_0}{T_S}\right)},
\]

where \(\Delta V\) is the difference in the adiabatic electronic energies, \(E_0\) is a parameter, and \(T_S\) is the kinetic energy associated with the component of the momentum where energy is being added or removed as the trajectory demixes. The parameter \(E_0\) was previously \(^{18}\) set to the value 0.1 \(E_0\) (1 \(E_0\) = 27.21 eV), which was shown to give good results for several systems.

The electronic state toward which the trajectory demixes is determined by a fewest-switches criterion based on a locally coherent set of electronic state populations.\(^ {11}\)

Analysis of the products. Each trajectory was integrated until one atom was separated from the other two by at least 15 Å. The final electronic state and molecular arrangement could therefore be assigned unambiguously, and product branching probabilities were obtained by counting trajectories. Semiclassical trajectories violating the zero point energy requirement may finish the simulation in the excited state \(\text{Na}(3p)+\text{HF}\) product channel. The probability of this outcome is small (less than 1%), and this channel is not considered further.

The delay time \(t_d\) for each trajectory was defined as

\[
t_d = t_f - r_f/v_f,
\]

where \(r_f\) and \(v_f\) are the final center of mass separation and relative velocity, respectively, of the fragments, and \(t_f\) is the total time of the trajectory. The semiclassical trajectory prediction for the half life of the photoexcited complex was taken as the median delay time obtained from the ensemble of 5000 trajectories.

Decoherence. Decoherence is defined here in the context of semiclassical trajectories to be the phenomenological decay of the off-diagonal elements of the electronic density matrix \([a_{12}\text{ in Eq. (1)}]\) due to imagined nuclear wave packets propagating in the different electronic states having different average velocities, which leads, after some time, to their dephasing and the separation of their centers and diminished overlap. A complete treatment of decoherence is difficult, especially when one insists upon methods based on independent trajectories, such as the methods considered here. Discussions of decoherence in the context of semiclassical trajectories have been given elsewhere.\(^ {9-12,29,32-37}\)

A simple modification of the FSTU method is proposed here to demonstrate the effect that decoherence has on the present system. Prior to a surface hop the system is assumed to evolve coherently as in FSTU. At a surface hop at time \(t_s\), the system begins to decohere with a first-order rate coefficient given by
where $\mu$ is the reduced mass of the system (with both coordinates scaled to the same reduced mass), and $\Delta F$, $\Delta V$, and $\Delta \rho$ are the differences in the forces, potential energies, and nuclear momenta for the two electronic states; only the components of the forces and momenta in the direction of the nonadiabatic coupling vector are considered. The average nuclear momentum $\bar{\rho}$ for the two electronic states is evaluated using the nuclear momentum of the trajectory for the currently occupied state, and the momentum for the electronic state that is not currently occupied is obtained in the same way as the momentum is adjusted at a surface hop. If there is not enough energy for such an adjustment, the momentum for the excited state is set to zero. Equation (4) was derived by considering the short time behavior of the overlap of wave packets traveling in different electronic states.

At some time $t$ later along the trajectory, the probability that the trajectory will have decohered is given by

$$P(\Delta t) = \exp(-\Delta t/\tau),$$

(5)

where $\Delta t = t - t_0$. This probability is checked against a random number, and, when a decoherence event is called for, the electronic state populations are reinitialized to the currently occupied electronic state. At every attempted surface hop, whether or not it is successful, $t_0$ and $\tau$ are reset. We denote this implementation of stochastic decoherence (SD) in the FSTU model as FSTU/SD.

We emphasize that reinitializations may not be suitable for more complicated systems, where a system may experience successive regions of coupling and where phase information needs to be retained between the regions. In the present system, as discussed in the next section, this model is useful for demonstrating the important role that decoherence plays in determining the outcome of FSTU semiclassical trajectory simulations.

Demixing in the CSDM method includes an explicit treatment of decoherence as defined above as the decay of the off-diagonal elements of the electronic state density matrix. Demixing also includes so-called “algorithmic decoherence” where the diagonal elements of the electronic state density matrix are modified to force a mixed state CSDM trajectory into a quantized pure electronic state. Because of this algorithmic decoherence, the CSDM demixing time must become large as $T_s$ becomes small, and the formula given by Eq. (2) therefore differs from the decoherence time given by Eq. (4). We will discuss the relative magnitudes of the two expressions for the decoherence time [Eqs. (2) and (4)] for the NaFH system in Sec. III.

### III. RESULTS AND DISCUSSION

Product branching probabilities and half lives $t_{1/2}$ of the photoexcited collinear Na···FH exciplex were computed using the CSDM, FSTU, and FSTU/SD semiclassical trajectory methods, as discussed above, and the results are summarized in the first three rows of Table I. [For these CSDM calculations, we used the previous recommended value of $E_{00}$ = 0.1 $E_h$ in Eq. (2).] Also shown in Table I are the quantum mechanical results from Refs. 20 and 24. The more recent set of quantum mechanical results differs markedly from those reported in Refs. 20–22, and these new results are in much better agreement with the NBOMD results.

The half lives predicted by the FSTU and CSDM semiclassical methods are 0.85 and 0.76 ps, respectively, which are in good agreement with the new quantum mechanical result (0.42 ps). The association of a single lifetime to describe the decay of the exciplex is not appropriate for this system, as the distribution of delay times predicted by the FSTU and CSDM methods is not well modeled by a single exponential, as shown in Fig. 1, where $F_d$ is the fraction of trajectories having delay times greater than $t$. Therefore, the factor of ~2 overestimation of the quantum mechanical half life of the exciplex does not necessarily indicate poor performance on behalf of the NBOMD methods. A more detailed study of the distribution of delay times would be required to more quantitatively assess the accuracy of the NBOMD methods, and such an analysis is not pursued here. The key point is that the significant (factor of 250!) discrepancy obtained earlier is no longer a cause for concern in light of the new quantum mechanical results.

The new quantum mechanical results predict the almost exclusive formation of NaF+H, in contrast to the previous quantum mechanical results and are in qualitative agreement with the FSTU and CSDM results. Again, the conclusion given previously, that NBOMD methods may be qualita-
The successful upward hops are distributed throughout the region associated with the van der Waals and exciplex wells. The frustrated hops, however, are mainly localized at extended H–F separations near the line of avoided crossings. The nonadiabatic coupling is largest perpendicular to the line of crossings, i.e., along the H–F stretching motion. The majority (~80%) of frustrated hops in this region are reflected (via the $\nabla V$ prescription) back into the interaction region and are (at least temporarily) prevented from exiting into the NaF+H product channel. These frustrated hops clearly have a significant effect on the predicted branching ratio, and the source of these frustrated hops is identified next.

In the classical path formulation [Eq. (1)], a single nuclear velocity $v$ is associated with the electronic motion in both electronic states. This assumption is valid in the limit of degenerate electronic states but is a serious source of concern for more general cases. For collinear NaFH, the adiabatic energy gap is 0.8–1.6 eV near the exciplex, which is large relative to the total energy of the system in the present simulations (~2.1 eV), resulting in significant differences in the nuclear velocities in the two electronic states. Furthermore, the ground and excited state surfaces have qualitatively different shapes in the region associated with the line of avoided crossings: the ground state surface proceeds over a small barrier to form the NaF+H products, whereas the excited state surface is repulsive. One would expect a divergence of wave packets traveling on the two surfaces in this region, resulting in a damping out of the electronic coherences and a corresponding reduction in the rate of population transfer. In the classical path formalism, this physical picture would translate into a damping out of $a_{12}$ near the line of avoided crossings and a reduction in the number of attempted surface hops as the system exits the NaF+H product channel. The association in Eq. (1) of a single velocity and, over time, a single trajectory with the electronic motion of the ground and excited electronic states, however, fails to properly account for the electronic decoherence associated with divergent trajectories, and this failure is the source of the unphysical hopping attempts near the line of avoided crossings.

Using the FSTU/SD method we obtain ensemble-averaged decoherence times [from Eq. (4)] of 1.8±0.3 fs at the first surface hop (ensemble-averaged decoherence and demixing times are the reciprocal of the mean value of $\tau^{-1}$, which correctly corresponds to the average relaxation rate, not the average relaxation time, and the quoted width of the distribution corresponds to one standard deviation of $\tau^{-1}$). This time scale is somewhat shorter than the average time between the first forward surface hop and the next attempted surface hop in the FSTU simulation (~3 fs), and frustrated hopping is therefore significantly reduced in the FSTU/SD simulation, where 83% of trajectories finish the simulation without attempting a second surface hop. (Recall that in the FSTU simulation, only 20% of trajectories finished the simulation without attempting a second surface hop.) The FSTU/SD product branching fractions are in excellent agreement with the new set of quantum mechanical results, as shown in Table I, and the half life of the exciplex is also reduced, improving agreement with the quantum me-
chemical results. These results strongly suggest that the treatment of decoherence plays a significant role in obtaining quantitative results for systems with large energy gaps and significant coupling to classically forbidden regions of excited electronic states.

In order to test the sensitivity of the FSTU/SD scheme to $\tau$, we varied it. A lower bound on the decoherence time is given by

$$\tau = \hbar / \Delta V,$$

which corresponds to the fastest time scale in the system. FSTU/SD simulations using Eq. (6) resulted in ensemble-averaged decoherence times of $\sim 0.5$ fs, which are approximately four times shorter than those obtained using Eq. (4). The results of the simulation, however, were largely unchanged, with $P_{\text{FSTU+SD}} = 4.0$ and $t_{1/2} = 0.49$ ps.

We emphasize that the description of decoherence as occurring by stochastic reinitializations of the quantum mechanical state populations is an incomplete model of the true dynamics, although it has been very successful for a diverse range of systems. The FSTU/SD method presented here is similar to the method recently employed by Granucci and Persico, which would likely give very similar results for the present system. Furthermore, when frustrated hops are simply ignored in the FSTU simulations, the predicted results are $P_{\text{FSTU}} = 5.2$ and $t_{1/2} = 0.66$ ps, which are in good agreement with the quantum results. Therefore, the collinear Na2-HF system alone does not allow for a definitive evaluation of various methods proposed for the treatment of decoherence in trajectory surface hopping calculations.

Next, we consider the treatment of decoherence in the CSDM simulations. The CSDM ensemble-averaged decomposing times [Eq. (2)] evaluated at the locations of the first surface hop for the ensemble of FSTU trajectories are 1.2$\pm$0.4 fs and are in good agreement with those obtained using Eq. (4); this indicates that Eq. (2) with $E_0 = 0.1 E_h$ predicts physically meaningful decoherence times for the excited-state complex. Over the course of a CSDM trajectory, Eq. (2) oscillates between $\sim 0.7$ fs [close to the lower limit given by Eq. (6)] and arbitrarily large values associated with small values of $T_1$. Small values of $T_1$ may be related to demixing toward classically forbidden regions of the excited electronic state, an analog of the problem of frustrated hopping in trajectory surface hopping simulations. The formula for the CDSM demixing time effectively turns off decoherence ($\tau \rightarrow \infty$) as the system approaches these classically forbidden regions, whereas one expects fast decoherence near the line of avoided crossings based on the divergence of wave packets traveling in the two electronic states, as discussed above.

Although the previously parametrized value of $E_0 = 0.1 E_h$ gives decoherence times consistent with those obtained using Eq. (4), we tested decreasing $E_0$ in Eq. (2) by a factor of 10 or 100 to observe the empirical effect of doing so. Smaller values of $E_0$ systematically lower $\tau$ but also reduce the effect of small $T_1$ in determining the overall dynamics, and we found that the results improved significantly. The CSDM method with $E_0 = 0.01$ and 0.001 $E_h$ predicts $P_{\text{CSDM}} = 9.1$ and 6.2, respectively, and in both cases $t_{1/2}$ is predicted to be 0.4 ps, in excellent agreement with the quantum mechanical results. We infer from these results that the CSDM method with Eq. (2) and the originally recommended value of $E_0$ may suffer from a problem similar to that encountered in the FSTU method due to an improper treatment of decoherence in regions of coupling to energetically forbidden excited electronic states. We note that in previous tests, the CSDM method with $E_0 = 0.1 E_h$ was shown to perform better on average than all of the other NBOMD methods tested, including the FSTU method, with average errors of only 25%. Furthermore, the results of the CSDM simulations were found to be relatively insensitive to $E_0^1$, although values smaller than 0.05 $E_h$ were not previously considered.

For both the FSTU and CSDM methods, the present analysis supports the view that improved treatments of decoherence should be included in semiclassical trajectory calculations if quantitative predictions are desired, and it motivates further work on the best way to do so.

IV. CONCLUSIONS

Exciplex half-lives and product branching ratios for the photodissociation of collinear Na2-HF are predicted by two types of semiclassical trajectory methods and in both cases are found to be in good agreement with a recent set of quantum mechanical results. In contrast to the conclusion given in a previous letter, we find that semiclassical trajectory methods may be confidently used to model “deep quantum” systems featuring large adiabatic energy gaps.

The present system also highlights the need for more accurate treatments of decoherence in trajectory-based descriptions of systems with coupled electronic states if quantitative predictions are desired. The use of the fully coherent classical path equation and the independent trajectory approximation to describe the electronic motion results in unphysical attempted surface hops in regions where the excited electronic state is energetically inaccessible, and the results of the trajectory surface hopping simulations are sensitive to the treatment of these frustrated hops. The incorporation of a stochastic model for decoherence largely eliminates the unphysical frustrated hops and results in near quantitative predictions of the quantum mechanical results. Similarly, the CSDM method with the previously preferred value of the parameter in the decoherence time predicts coherent motion in regions of the surface associated with energetically forbidden electronic states, and increasing decoherence in this region by decreasing the decoherence-time parameter is shown to significantly improve the results.

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