Communication: Standard surface hopping predicts incorrect scaling for Marcus' golden-rule rate: The decoherence problem cannot be ignored

Brian R. Landry and Joseph E. Subotnik[a)]
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA

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We evaluate the accuracy of Tully's surface hopping algorithm for the spin-boson model for the case of a small diabatic coupling parameter (V). We calculate the transition rates between diabatic surfaces, and we compare our results to the expected Marcus rates. We show that standard surface hopping yields an incorrect scaling with diabatic coupling (linear in V), which we demonstrate is due to an incorrect treatment of decoherence. By modifying standard surface hopping to include decoherence events, we recover the correct scaling ($\sim V^2$). © *2011 American Institute of Physics*. [doi:10.1063/1.3663870]

Modeling photo-induced nonadiabatic reactions has become increasingly popular in recent years due to a variety of interesting possible applications in the fields of alternative energy and electronics. Although quite a few algorithms exist for modeling nonadiabatic dynamics,[1–3] surface-hopping methods are arguably the most widely used because they are inherently simple and computationally efficient.[4–7] By treating the nuclei classically while maintaining the quantum character of the electrons, surface-hopping algorithms make a reasonable assumption—nuclei are much heavier and, therefore, behave more classically than electrons—and this assumption leads to dramatic computational savings.

Even though Tully's standard fewest switches surface-hopping (FSSH) method is widely used today, there still remain open questions as to its overall validity, and new benchmarking examples are certainly needed. While most publications have so far focused on calculating detailed balance properties or inelastic scattering cross sections,[8–11] we will instead address the question of rates,[6,12,13] which is crucial for modeling photo-induced experiments. In so doing, we can critically evaluate the long-time behavior of surface-hopping algorithms, where nuclei visit regions of nonadiabatic coupling repeatedly and any failures of FSSH should be obvious. In particular, multiple curve crossings in time typically lead to an amplification of the decoherence failures of surface-hopping and a growth in the inconsistency between electronic amplitudes and the active adiabatic surface populations.[13–16] Thus, if they are present, we might expect to see evidence of decoherence problems in our results. Lastly, to make our evaluation even more strenuous, we will focus on model Hamiltonians where the diabatic coupling is small and the adiabatic basis may not be the most natural. Because FSSH is usually propagated on adiabatic surfaces, this will further test the limits of the standard Tully algorithm.

Unfortunately, there are few exact quantum results we can compare against when evaluating nonadiabatic rates from surface-hopping. In the case of small diabatic couplings, however, the essential result is Marcus theory,[17] whose predictions have been verified experimentally many times for cases of electron transfer. In this communication, our goal is very simple: to recover Marcus theory using surface-hopping approaches applied to the spin-boson model. The spin-boson model has been used often in the past for studying coupled diabatic surfaces (e.g., Refs. 6,12,18–21) and, through perturbation theory on a small diabatic coupling V, one can derive analytically the celebrated high-temperature Marcus expression[22]

$$k = \frac{2\pi |V|^2}{\hbar\sqrt{4\pi E_r kT}} \exp\left(-\frac{(E_r - \epsilon_0)^2}{4E_r kT}\right). \quad (1)$$

Here, E_r is the reorganization energy, ϵ_0 is the energy difference between the minima of the diabatic states (i.e., the driving force), and kT is the temperature. For our purposes, Eq. (1) has two crucial features: (i) The expected transition rate is proportional to the square of the diabatic coupling $|V|^2$; (ii) as a function of ϵ_0, the expected rate should be peaked when the driving force equals the reorganization energy.

In seeking to match Marcus theory (Eq. (1)), we will show below that standard FSSH dynamics fails qualitatively. Although FSSH dynamics do correctly predict a peak in rate as a function of driving ϵ_0, our striking conclusion is that the FSSH algorithm does not recover the correct scaling (in V); FSSH rates scale as V instead of V^2. Moving forward, we will invoke the well-known decoherence approach of Rossky and co-workers to collapse the electronic amplitude when appropriate,[14,15,23–39] and having done so, we will show that one now recovers the correct V^2 scaling. Thus, this work highlights the true significance of the decoherence problem: surface-hopping cannot recover the Marcus rates of the simplest possible nonadiabatic system without an adjustment for decoherence. With this correction, however, it does seem to work well. The implications of these results are profound and will be discussed in the final section.

Methods: We calculated transition rates between the left and right diabatic harmonic wells of the spin-boson model using standard Tully surface-hopping.[4] In the relevant basis for transitions, the diabatic basis $\{|\Xi_l\rangle, |\Xi_r\rangle\}$, the spin-boson

a)Author to whom correspondence should be addressed. Electronic mail: subotnik@sas.upenn.edu.

Hamiltonian is

$$H = \begin{pmatrix} \frac{1}{2}m\omega^2 x^2 + Mx & V \\ V & \frac{1}{2}m\omega^2 x^2 - Mx - \epsilon_0 \end{pmatrix}, \quad (2)$$

where m is the mass of the particle and M can be expressed in terms of the reorganization energy as $M = \sqrt{E_r m\omega^2/2}$.

In order to follow the standard Tully algorithm, carrying out all surface-hopping dynamics in an adiabatic basis, we diagonalized Eq. (2) giving the adiabatic energy surfaces

$$E_{1,2}(x) = \frac{1}{2}m\omega^2 x^2 - \frac{\epsilon_0}{2} \mp \sqrt{\left(\frac{\epsilon_0}{2} + Mx\right)^2 + V^2} \quad (3)$$

with E_1 taking the top (i.e., minus) sign and the derivative coupling

$$d_{12}(R) = \frac{1}{2}\frac{MV}{(Mx + \epsilon_0/2)^2 + V^2}. \quad (4)$$

The eigenvectors of the Hamiltonian (2) give the adiabatic states in terms of the original diabatic states

$$|\Phi_i(x)\rangle = f_i(x)|\Xi_l\rangle + g_i(x)|\Xi_r\rangle \quad (5)$$

for $i = 1$ or $i = 2$, where

$$f_{1,2}(x) = \sqrt{\frac{1}{2} \mp \frac{1}{2}\frac{Mx + \epsilon_0/2}{\sqrt{(Mx + \epsilon_0/2)^2 + V^2}}}, \quad (6)$$

$$g_{1,2}(x) = \mp\sqrt{\frac{1}{2} \pm \frac{1}{2}\frac{Mx + \epsilon_0/2}{\sqrt{(Mx + \epsilon_0/2)^2 + V^2}}}. \quad (7)$$

For this problem, we were interested in the transition rates between and, therefore, populations on diabatic states rather than adiabatic states. Thus, even though all calculations were carried out in an adiabatic basis, it was necessary to convert a trajectory on one adiabatic surface into a probability of being on one of the diabatic surfaces. To do this, we used the coefficients $f_i(x)$ and $g_i(x)$ together with the following interpretation: if one is moving along the bottom (active) adiabatic surface corresponding to $|\Phi_1(x)\rangle$, we assume that the probability of being on the left diabat is $|f_1(x)|^2$ and the probability of being on the right is $|g_1(x)|^2$. The probabilities are set analogously for the upper adiabat.

Contact with a thermal bath was modeled by adding a random force ξ and friction term γ yielding a form of Langevin dynamics, following the work of Tully and Beeman.[40,41] The nuclear trajectories move on the adiabatic surfaces given by Eq. (3) with the additional forces due to the bath. The total force on the nuclear degree of freedom is, therefore,

$$F = -\frac{dE_i(x)}{dx} - \gamma p + \xi, \quad (8)$$

where i is the label of the active surface that the trajectory is moving on and ξ is a Markovian Gaussian random force with standard distribution $\sigma = \sqrt{2\gamma mkT/dt}$ (with time step dt). For the discrete integration of these equations of motion, the Markov property means that the random force at each time step is uncorrelated with the random force at the previous time step.

For our initial conditions, we chose a Boltzmann distribution of nuclear positions and momenta in the left diabatic well,

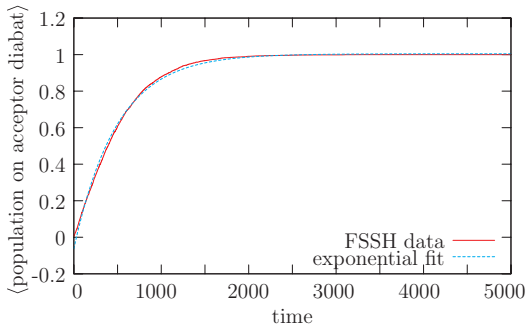

FIG. 1. Sample of the ensemble averaged population data as a function of time and exponential fit, $\langle \text{pop}(t)\rangle = a\exp(-kt) + b$.

with the corresponding electronic amplitude, and we sampled an average of 5000 distinct FSSH trajectories each with a time step of $dt = 2.5$ (in atomic units). As a function of time, we plotted both (i) the average population on the right diabatic surface and (ii) the average trajectory position; this information was then fit to an exponential function to determine a transition rate (see Fig. 1). Some of the data showed transient non-exponential behavior at short times, but such phenomena were not significant enough to substantially influence the rates. As a rule, we found the same rate according to average population and average position to within our statistical noise. As a result, we show below only the rates from average population.

For the surface-hopping trajectories with decoherence, we collapsed the electronic wave function whenever the trajectory crossed the minimum of a diabatic well while moving away from the crossing point. More explicitly, for the normal Marcus regime each time the position of a trajectory crossed $x = \pm M/m\omega^2$ while moving on the lower adiabatic surface headed away from the crossing region, the electronic wavevector was set to $\binom{1}{0}$ putting all the probability density on the lower surface. For the inverted regime, simple collapses occurred on the upper surface for $x = -M/m\omega^2$ and the lower surface for $x = M/m\omega^2$. This collapsing criterion is closely related to the ideas of Fang and Hammes-Schiffer.[14] The reasoning is quite sensible: once a trajectory is far from the crossing region, wave packets on the upper and lower surfaces should separate. Then there is no longer a possibility to hop, and the particle should "forget" that it was ever in the crossing region (to be discussed more later). More elaborate approaches for decoherence have been proposed (e.g., Ref. 15, and see references therein). The relevant parameter ranges that were used are given in Table I, all in atomic units, adapted from Hammes-Schiffer.[6] Results are independent of mass (we chose $m = 1$).

Results: The results of our calculations are shown in Figs. 2 and 3. In Fig. 2, we plot the rate as a function of driving force ϵ_0 for a variety of different frictional (γ) values. In many respects, this figure suggests that surface-hopping does quite well. Most importantly, FSSH correctly predicts a peak in the rate as a function of ϵ_0, and that peak is centered at $\epsilon_0 = E_r$, as it should be. Furthermore, from our data it would appear that, as a function of γ, our calculations can be

TABLE I. Parameters and ranges used for FSSH (atomic units, $\hbar = 1$).

Parameter	Range
E_r	2.39×10^{-2}
kT	9.5×10^{-4}
ϵ_0	$1.5 \times 10^{-2} - 3.0 \times 10^{-2}$
V	$1.49 \times 10^{-5} - 2.28 \times 10^{-4}$
ω	3.5×10^{-4}
γ	$1.875 \times 10^{-5} - 2.4 \times 10^{-3}$

interpreted in terms of Kramer's theory. According to Kramer's theory, the transition rate should be small for small γ in the under-damped limit, increase and level off at the transition state regime for moderate γ, and then decrease in the over-damped limit as γ gets very large.[22] Fig. 2 shows that is approximately what we find (at least near the top of the curve) using the standard FSSH algorithm; around $\gamma = 0.0006$, our system is in the transition state regime, and the rate is independent of γ just as in Marcus theory. As a side note, in the under-damped limit, the peak in ϵ_0 shifts to a value less than E_r.

One striking conclusion of Fig. 2 is that standard FSSH grossly overestimates the transition rate in this problem. To understand why this is so, we studied the effect of changing V. In Fig. 3, we show the surprising fact that, for small V, FSSH predicts the incorrect scaling as a function of V. More specifically, FSSH predicts the transition rate should scale as V rather than V^2. In the same figure, we also show that adding decoherence by collapsing the wavefunction recovers V^2 dependence for small V. For the larger values of V both surface-hopping methods give a slope of around 1, which corresponds to linear scaling in V. Thus, for the algorithm with decoherence, there is a clear transition from adiabatic to diabatic parameter regimes, and this transition moves the transition rate from V to V^2 scaling. For the standard FSSH, however, the scaling remains linear for the our entire range of V. These

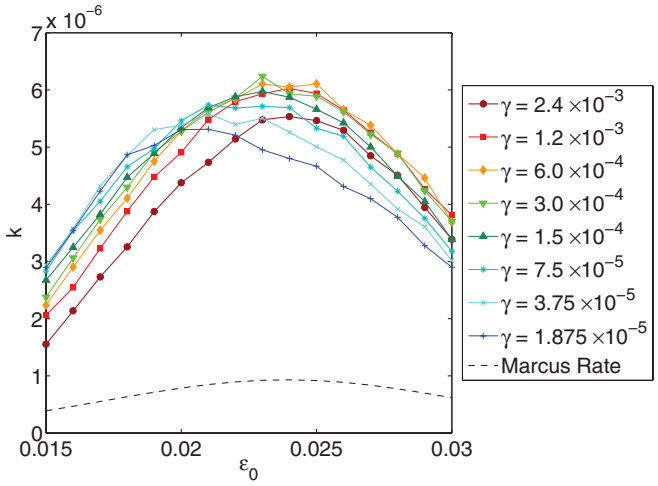

FIG. 2. Rates for various values of friction coefficient γ calculated using standard FSSH. Note that as γ is decreased from the over-damped limit the rates increase and level off. This γ regime gives the standard transition state theory rates. As γ is decreased further the rates decline again reaching the under-damped limit. $V = 5 \times 10^{-5}$.

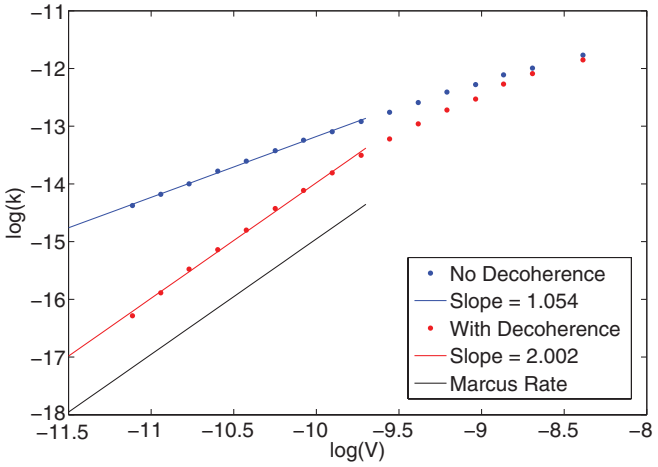

FIG. 3. Log-log (base e) plot of the rate k as a function of diabatic coupling V for $\epsilon_0 = 0.015$ in the normal Marcus regime. A plot for $\epsilon_0 = 0.033$ in the inverted regime is nearly identical. The Marcus expression is expected to fail for large V and is only plotted for the regime in which we expect it to hold. $\gamma = 0.0024$, slightly in the over-damped regime.

scaling arguments hold in the transition state regime and the over-damped regime (we have not checked the under-damped regime).

According to Fig. 2, FSSH predicts the qualitatively correct form for the rate constant as a function of driving force, ϵ_0, with a turnover near $\epsilon_0 = E_r$. This is an encouraging development, as it was shown recently that ring polymer molecular dynamics does not predict an inverted regime.[42] To explain why FSSH succeeds in this regard, consider the following. Because the FSSH algorithm propagates all dynamics in an adiabatic basis, in either the normal or the inverted regime there is a barrier to move from the left to the right well. Accordingly, the decay rate should be nearly optimized when the avoided crossing is at the bottom of the diabatic curve on the left (i.e., the barrierless regime). In this sense, the FSSH algorithm reproduces the correct physical picture.

Nevertheless, Fig. 3 shows clearly that FSSH predicts the incorrect scaling as a function V and that this failure results from a lack of decoherence. The conceptual error in the FSSH model is straightforward here. When a wave packet approaches the coupling region, it bifurcates. One daughter wave packet relaxes into each diabatic well, and these daughter wave packets behave independently and no longer interact with one another. But in standard FSSH, even for a trajectory that should represent one of a pair of separating daughter wave packets, an individual FSSH trajectory is never adjusted so as to account for this separation in space. Instead, each FSSH trajectory has an infinite memory, leading to scenarios where FSSH is effectively modeling separated wave packets as coherent superpositions. Thus, the next time a particle approaches an avoided crossing, one will find incorrect branching ratios. To correct FSSH, it is necessary to collapse the electronic amplitude, so that when the corresponding two wave packets are far apart, each trajectory has an amplitude that matches the active surface.

To understand the problem more mathematically, consider that Marcus theory can be derived by assuming that we have a classical oscillator on the left diabatic surface that

approaches an avoided crossing with some frequency, and with each crossing event, the particle changes diabatic surfaces according to the Landau-Zener transition probability (which scales as V^2).[22] From this valid point of view, each crossing event is statistically independent and one finds a rate proportional to V^2. When performing FSSH dynamics, however, each trajectory moves through the avoided crossing several times before relaxing into the right well. After each pass through the coupling region, the electronic amplitude becomes more and more nonsensical and inconsistent, and the probability to hop begins scaling as V. To show this, suppose we start on the left electronic state. Up to some unknown phases, for each crossing event, the electronic propagator is

$$\mathbf{U} \approx \begin{pmatrix} 1 & -\theta V \\ \theta V & 1 \end{pmatrix}, \tag{9}$$

where θ is a proportionality constant given by Landau-Zener. Specifically, $|\theta|^2 = 2\pi/\hbar\dot{x}|F_b - F_a|$, where F_a and F_b are the forces from the two diabatic surfaces and the expression is evaluated at the crossing point. On the one hand, if the initial wave packet is $\binom{1}{0}$, the final electronic state is $\approx \binom{1}{\theta V}$, so the change in population on the upper surface is $\theta^2 V^2$. On the other hand, if the initial wave packet is $\binom{\alpha}{\beta}$, the final electronic state is $\approx \begin{pmatrix} \alpha - \beta\theta V \\ \beta + \alpha\theta V \end{pmatrix}$, so that the change in population on the upper surface is $|\beta + \alpha\theta V|^2 - |\beta|^2 \sim V$. Thus, the cumulative effect of this incorrect electronic amplitude is that the transition rates increase as V, ultimately leading to an incorrect rate constant.

To conclude, our results highlight the importance of adding decoherence to surface hopping algorithms. Without decoherence, one can calculate erroneously large decay rates for photo-excited molecules ($\sim V$ instead of $\sim V^2$ scaling). With decoherence, however, we have shown that one recovers the correct scaling. Thus, our research emphasizes the urgent need for efficient methods for incorporating decoherence within FSSH trajectories. Unfortunately, the simple collapsing criterion discussed above is not usually applicable because (i) it cannot be used near the peak of the Marcus curve $\epsilon_0 = E_r$, where the avoided crossing region is near the minimum of one diabatic curve; (ii) this criterion is only well suited for one-dimensional model Hamiltonians where we can identify unique minima and crossing points. More generally, we introduced recently an augmented-FSSH algorithm (A-FSSH) (Ref. 15) for treating decoherence without any parameters in the context of FSSH trajectories, and our next project will be to test the A-FSSH algorithm in the context of this spin-boson problem. In the end, the spin-boson problem is clearly a fertile test system for nonadiabatic algorithms, and in an upcoming paper, we will examine the complicated relationship between solvent effects, nuclear frequencies, surface hops, and decoherence in more detail including the shifts in Fig. 2. For now, this much is already clear: without correctly treating decoherence, computational chemists should be very wary when modeling nonadiabatic rate constants using the standard FSSH algorithm in the limit of curve crossings with small diabatic couplings.

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