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Letter

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Does Nonadiabatic Transition State Theory Make Sense Without Decoherence?

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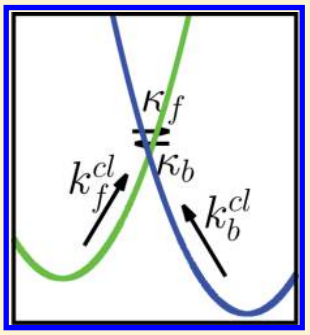
ABSTRACT: We analyze thermal rate constants as computed with surface hopping dynamics and resolve certain inconsistencies that have permeated the literature. On one hand, according to Landry and Subotnik (*J. Chem. Phys.* **2012**, *137*, 22A513), without decoherence, direct dynamics with surface hopping overestimates the rate of relaxation for the spin-boson Hamiltonian. On the other hand, according to Jain and Subotnik (*J. Chem. Phys.* **2015**, *143*, 134107), without decoherence, a transition state theory with surface hopping underestimates spin-boson rate constants. In this Letter, we resolve this apparent contradiction. We show that, without decoherence, direct dynamics and transition state theory should not agree; agreement is guaranteed only with decoherence. We also show that, even though the effects of decoherence may be hidden for isoenergetic reactions, these decoherence failures are exposed for exothermic reactions. We believe these lessons are essential when interpreting surface hopping papers published in the literature without any decoherence corrections.



Fewest switches surface hopping (FSSH) is one of the most popular methods to include nonadiabatic effects into classical simulations.[1,2] Over the past 20 years, there has been a flurry of activity regarding the computation of thermal rate constants within the FSSH formalism, either by directly monitoring the decay of reactant populations[3−6] or using transition state theory (TST), as popularized by Hammes-Schiffer and Tully (HST).[7−17] For reactions with large barriers, where a direct simulation is computationally unfeasible, a TST formalism is particularly desirable.

Recently,[17] we benchmarked TST-FSSH over a broad range of parameters for the spin-boson model. We found that, if we included decoherence, a combination of transition state theory and surface hopping recovers Marcus theory both in the adiabatic and nonadiabatic limits. Otherwise, without decoherence, TST-FSSH did not agree with Marcus theory. The data in ref 17 suggest that TST-FSSH should be an ideal tool for calculating the rates of rare nonadiabatic events for most Hamiltonians. However, that being said, we now find two pernicious contradictions in the literature *a propos* of surface hopping and decoherence.

The first contradiction regards under what circumstances a decoherence correction is needed. For roughly 20 years, Rossky,[18−21] Hammes-Schiffer,[22,23] and Truhlar[24−28] have argued that decoherence corrections are necessary to account for coherent wavepackets feeling different forces on different surfaces and thereafter bifurcating. In the context of rate theory, Landry and Subotnik[5] have shown that, without a decoherence correction, the FSSH algorithm will overestimate the relaxation rate and the final rate will scale incorrectly with the diabatic coupling. The reasoning in ref 5 is that a rate constant corresponds to the long-time decay of an initially prepared nonequilibrium population and, without a decoherence correction, artificial memory builds up in the FSSH amplitudes.[4−6] That being said, historically, several research groups have studied the symmetric spin-boson model with large reorganization energies[29−31] and found that FSSH nearly matches exact results. Why should this be so? This contradiction has not been resolved in the literature and leads to question #1: *Are the decoherence arguments in ref 5 incomplete? If so, when is decoherence essential for extracting surface hopping rates? If not, why does the symmetric spin-boson model seemingly not require a decoherence correction?*

A second contradiction in the literature regards the qualitative difference in rate constants computed with direct simulations or with TST formalism. According to refs 5, 6, without decoherence, direct FSSH dynamics predicts electron transfer rate constants that are much too large compared with exact dynamics. According to ref 17, however, if one uses a TST version of FSSH dynamics (again, without decoherence), one finds rate constants that are too slow compared with exact dynamics. Thus, one is left with question #2: *Assuming that decoherence is necessary for an accurate rate, but was often missing historically for most calculations, how should we interpret previously published rates in the literature that ignored decoherence? Will these rates be too large or too small in general?*

The motivation for this article is to resolve these questions using simple numerical examples. By comparing standard FSSH results (without decoherence) with augmented-FSSH (A-FSSH)[5] (which includes decoherence), we will show that exothermicity emerges as a factor that can cloak the cumulative effects of decoherence (which are always present but sometimes hidden). We will also show that, when interpreting surface hopping rates published in the literature without any decoherence corrections, the reader can usually estimate

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whether such rates are too large or too small simply by examining the specifics of how that rate was extracted.

Approach. We investigate the spin-boson Hamiltonian, one of the most well studied model systems for electron transfer, and for simplicity we choose a quantum Brownian oscillator spectral density.[17,32] This model is defined as a two-level quantum system coupled to a single, primary classical harmonic oscillator and, in turn, the latter is coupled ohmically to a harmonic bath. Because the harmonic bath is Ohmic, all dynamics can be modeled through a Langevin equation, whereby the two-level quantum system plus primary mode experience a Markovian friction, which is characterized by a single parameter η. The parameters for this potential for this letter are mass m_0 = 1836 au, the frequency of primary mode ω_0 = 200 cm^{-1}, the reorganization energy λ = 6375 or 8499 cm^{-1}, temperature k_BT = 400 cm^{-1}, friction η/ω_0 = 1,10, and driving force ϵ = 400 or 1600 cm^{-1}; the diabatic coupling is varied as V_c = 25, 50, 100 cm^{-1}. These parameters were chosen to make sure that (a) the system is in the normal, as opposed to the inverted, regime ($\epsilon < \lambda$); (b) all transitions are by nonadiabatic, as opposed to adiabatic, mechanism ($V_c^2 < \hbar\omega\sqrt{\lambda k_BT}$); and (c) nuclear motion can be considered classical ($k_BT > \hbar\omega$). The reorganization energy and driving force are chosen together such that the diabatic barrier height $V_d^{\ddagger}$ is 1400 cm^{-1}.

We consider the left well as corresponding to the reactants, and the right well as corresponding to the products. We report the transmission coefficient κ given by

$$\kappa = \frac{k_f}{k_{TST}^f} \tag{1}$$

where k_f is the forward rate constant, and the forward transition state theory estimate is defined as

$$k_{TST}^f = \frac{\omega_0}{2\pi} e^{-\beta V_d^{\ddagger}} \tag{2}$$

$$= 0.18 \text{ ps}^{-1} \tag{3}$$

Here β is the inverse temperature. The transmission coefficient (κ) can be computed using either direct or TST methods, as we now discuss.

Direct Dynamics. For direct simulations, the initial conditions for each trajectory are chosen from a classical Maxwell–Boltzmann distribution around the left minima. Thereafter, the decay of the population of the reactants is monitored, and fit to an exponential to obtain the total rate constant

$$k_{tot} = k_f + k_b \tag{4}$$

where k_f and k_b are the forward and the backward rate constants, respectively. The forward rate constant k_f is then extracted as

$$k_f = k_{tot}\frac{1}{1 + e^{-\beta\epsilon}} \tag{5}$$

(Note that, in all simulations—with or without decoherence—the long time reactant and product populations obey detailed balance approximately, justifying eq 5.) For reasons that will be clear below, it will be helpful to analyze the effects of the back-reaction (from the right well back to the left well). To that end, we can reduce the contribution from the back-reaction in two ways: either (a) increasing the exothermicity $\epsilon = 4k_BT$ or (b) terminating trajectories once they reach the right minima. In the second case, for trajectories that are terminated once they reach the product minima, we set $k_f = k_{tot}$.

For V_c = 25 cm^{-1}, trajectories are evolved for 500 ps; for V_c = 50 and 100 cm^{-1}, the trajectories are evolved for 100 ps. In all cases, an average over 4000 trajectories is taken with an integration time step of 0.02 fs. Early time transient behavior (particularly for FSSH calculations) was not included in the exponential fit for the computation of the rate constant.

Transition State Theory. TST estimates of the rate constant are calculated following the algorithm presented in ref 17, which is very similar to the original Hammes-Schiffer and Tully (HST) algorithm[7] with only two meaningful differences: (a) backward propagation is performed solely on the ground adiabatic surface, and (b) all trajectories are weighted based on the Boltzmann distribution of the ground potential energy surface. As shown in ref 17, with proper treatment of decoherence and frustrated hops, we find that the TST-A-FSSH transmission coefficients agree quite well with direct simulations across a broad range of parameters and, when applicable, also with Marcus theory and the numerically exact hierarchical equations of motion (HEOM) with Debye spectral density.[33−38] For the present TST calculations, we average over 20 000 trajectories to compute the transmission coefficient, with an integration time step of 0.02 fs.

We present results for two different frictional regimes: moderate and strong friction.

Moderate Friction Regime. For the case of moderate friction, we set η/ω = 1. Figure 1 shows the results. Clearly, we see differences in the transmission coefficients computed using A-FSSH (red lines, including decoherence) versus using FSSH (blue lines, without decoherence). Furthermore, for FSSH calculations, direct and TST calculations do not agree. We now systematically discuss these results.

Linear or Quadratic Scaling with V_c for Direct FSSH Dynamics. We first address the issue of scaling of the rate constants with diabatic coupling. According to Figure 1 (panels b and c), direct dynamics FSSH rate constants scale linearly with V_c whenever there is a large exothermicity ($\epsilon = 4k_BT$) or a small exothermicity ($\epsilon = k_BT$), provided that trajectories are terminated upon reaching the right minima. From this data, we may hypothesize that direct FSSH rate constants scale linearly (and incorrectly) with V_c when there is no significant back reaction.

To further investigate this hypothesis, we consider a smaller driving force, $\epsilon = k_BT$, with standard FSSH dynamics (i.e., no termination). In such a case, according to Figure 1*a*, the scaling of the direct dynamics FSSH rate constant is no longer linear, but actually much closer to quadratic—which would be correct. For the moment, we are unsure[39] as to the exact scaling of these rate constants with V_c, but the direct FSSH data is unambiguously better for smaller driving forces. This improvement and lowering of the rate constant can be interpreted as a consequence of a back-reaction. After all, consider a trajectory that starts in the left minima, eventually reaches the top of the barrier, chooses not to hop upward (with a small probability), and then relaxes into the right minima. Later, this same trajectory will emerge from the product well, eventually revisit the dividing surface, and then with a large probability—because there was no decoherence correction—the trajectory will relax into the reactant well while remaining on the ground adiabat. This behavior must occur because, for the entirety of its journey (without a decoherence correction), this FSSH trajectory will hold an electronic amplitude that corresponds to the donor

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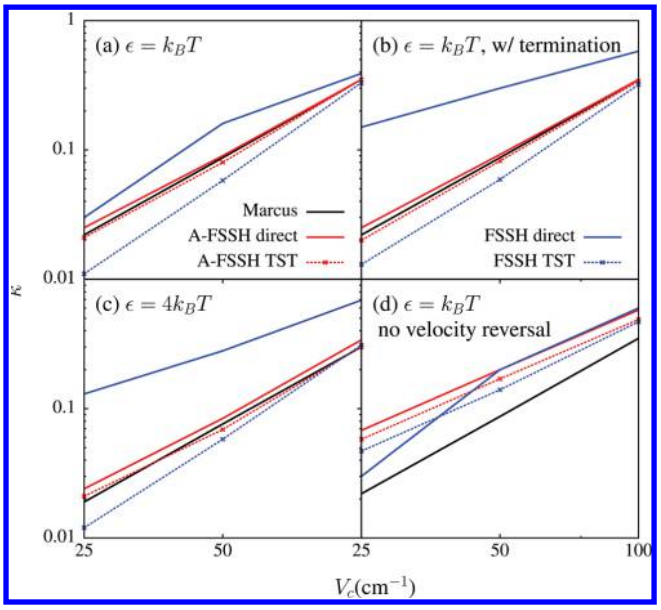

Figure 1. Transmission coefficient κ as a function of diabatic coupling V_c in the moderate friction regime ($\eta/\omega = 1$). For all cases, solid black line refers to the Marcus results (which are nearly exactly the same as Fermi's Golden Rule results). Solid and dotted red lines refer to direct and TST A-FSSH results (which include decoherence), respectively, and solid and dotted blue lines refer to direct and TST FSSH results (which ignore decoherence), respectively. ϵ characterizes the driving force (or asymmetry) of the spin-boson Hamiltonian. (a) $\epsilon = k_BT$, (b) $\epsilon = k_BT$, with trajectories terminated on reaching the minima of the right well, (c) $\epsilon = 4k_BT$, and (d) $\epsilon = k_BT$ with no velocity reversal on encountering frustrated hops. A-FSSH results are clearly consistent with Marcus theory, while FSSH results are sensitive to the Hamiltonian, dependent on the exact algorithm, and usually erroneous.

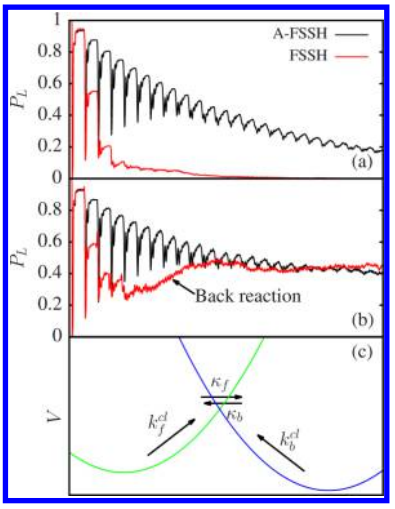

Figure 2. Decay of the reactant population P_L with time for constant energy trajectories (without friction) for (a) $\epsilon = 4k_BT$ and (b) $\epsilon = k_BT$, with $V_c = 50\ \mathrm{cm}^{-1}$. (c) Schematic of the various time scales associated with the reaction; the diabatic potential energy surfaces are shown in green (for reactant) and blue (for product) lines. Here k_f^{cl} (k_b^{cl}) is the classical forward (backward) rate constant, and κ_f (κ_b) is the forward (backward) transmission coefficient. These rate constants will likely not be constant in time without decoherence. Moreover, detailed balance requires that true dynamics should satisfy $\kappa_f = \kappa_b$; this equality holds approximately with A-FSSH. However, if decoherence is not included, κ_b can sometimes be as large as unity, leading to the spurious back-reaction shown in panel b.

diabat (rather than acceptor diabat) and hop accordingly. Thus, after only a few crossings, one should expect forward transitions from reactant-to-product will occur with a small nonadiabatic transmission coefficient while the backward product-to-reactant transitions follow a larger adiabatic transmission coefficient. If the driving force is small enough, this bizarre state of affairs will tend to reduce the total FSSH rate constant, such that the final results are close to the Marcus values (see Figure 1). Note, though, that this agreement is an extreme example of cancellation of errors: direct dynamics FSSH rate constants will be completely unreliable as soon as there is a large exothermicity.

To demonstrate this interpretation conclusively, we have run a set of constant energy simulations (without friction). A schematic view is given in Figure 2c. We choose the initial position of the trajectory to be the left minima, the initial velocity to be positive, and the total energy to be equal to the diabatic barrier height ($1400\ \mathrm{cm}^{-1}$). The diabatic coupling is chosen as $V_c = 50\ \mathrm{cm}^{-1}$ so that the adiabatic barrier height is $1350\ \mathrm{cm}^{-1}$. The decay of the population in the left well P_L (computed by averaging over 2000 trajectories) is shown in Figure 2a,b, both for the case of (a) large exothermicity ($\epsilon = 4k_BT$) and (b) small exothermicity ($\epsilon = k_BT$). While the A-FSSH decay is consistently exponential for both large and small exothermicities, the FSSH decay shows nonexponential behavior in both cases. In particular, for the case of small exothermicity (Figure 2b), note the increase in P_L at roughly 1 ps because of the spuriously large back-reaction discussed above.

In the end, to answer Question #1: The decoherence arguments of ref 5 are not incomplete; decoherence should be applied always on top of FSSH calculations, both for isoenergetic and exothermic reactions. However, for isoenergetic reactions (including the symmetric spin-boson model), FSSH rates do happen to recover the nearly correct rate constant without a decoherence correction by a fortuitous coincidence. For a more general endothermic or exothermic reaction, however, surface hopping should fail entirely without decoherence.

Direct versus TST Dynamics. Second, we compare direct dynamics versus transition state theory. Note that, while the direct and TST A-FSSH calculations are in agreement, no such agreement exists for FSSH calculations in Figure 1: direct FSSH rates are too large while TST FSSH rates are too small.

To understand this disagreement, consider the two different algorithms. On one hand, for direct dynamics (without decoherence), a set of trajectories (starting in the reactant minimum) are followed as long as it takes until thermal equilibrium is achieved so that most trajectories sit in the product well. These direct calculations require long simulations—long enough for thermal fluctuations to activate many barrier crossings so that, after many failed attempts, most trajectories finally switch diabats and relax into the product basin. Because the FSSH electronic amplitudes become inaccurate at long times, these repeated crossings will lead to incorrect FSSH statistics. More precisely, the direct FSSH rate constants will be too large because, after multiple crossings, the electronic amplitudes will undergo artificial interferences.[4]

On the other hand, for TST calculations, one initializes trajectories at the crossing point with the appropriate

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amplitudes, and trajectories are terminated when they are stabilized in either the reactant or the product minima. These trajectories can be quite short. Moreover, as discussed in ref 17, to recover the TST-FSSH rate constants at moderate friction, one must usually allow for only one recrossing of the dividing surface. Thus, the *multiple* recrossing problem is mostly absent for TST-FSSH, and TST-FSSH rate constants should scale nearly correctly and not be too far off. In fact, as shown in ref 17, a rule of thumb would be that TST-FSSH rate constants are smaller than the exact rate constant by a factor of 2 in the limit of small diabatic couplings; this factor of 2 arises because FSSH trajectories do not capture full contributions from excited state dynamics.

Thus, we can now answer Question #2: Without decoherence, there is no guarantee that FSSH rates as extracted with direct dynamics will agree with FSSH rates as extracted from transition state theory. When interpreting previously published literature that ignored decoherence, one should expect that FSSH rates will be too large when calculated with direct dynamics (due to the multiple recrossing problem); and FSSH rates will be slightly too small when calculated with TST (due to a neglect of excited state dynamics).

Finally, we mention that both of the problems above are resolved with decoherence: there is no multiple recrossing problem, and excited state dynamics are treated correctly. As such, with decoherence, direct A-FSSH and TST-A-FSSH both make predictions that are very close to the correct answer.

Strong Friction Regime. It is informative to study the results above for the case of strong friction ($\eta/\omega = 10$). Table 1 shows

Table 1. Transmission Coefficients in the Strong Friction Regime ($\eta/\omega = 10$) for Different Values of V_c: 25 cm^{-1}, 50 cm^{-1}, and 100 cm^{-1}[a]

		25 cm^{-1}	50 cm^{-1}	100 cm^{-1}
$\epsilon = k_BT$	A-FSSH	0.019 (0.027)	0.082 (0.081)	0.19 (0.19)
	FSSH	0.024 (0.022)	0.096 (0.076)	0.21 (0.19)
	HEOM[b]	0.023	0.080	0.21
$\epsilon = 4k_BT$	A-FSSH	0.024 (0.025)	0.075 (0.075)	0.22 (0.19)
	FSSH	0.036 (0.022)	0.14 (0.086)	0.24 (21)
	HEOM	0.021	0.077	0.22

[a]Direct dynamics results are outside parentheses; TST results are within parentheses. Hierarchical equations of motion (HEOM) data can be considered exact. [b]The numerically exact hierarchy equations of motion calculations are performed using the open source software PHI.[37,38] The details of computation are provided in ref 17.

the results for the strong friction regime, where the effects of decoherence are now apparently smaller. In the case of $\epsilon = k_BT$, which has a significant back reaction, the rates computed using FSSH (without decoherence) are roughly the same as the numerically exact HEOM results. In the case of $\epsilon = 4k_BT$, which has no significant back reaction, FSSH results (without decoherence) shows larger (but not very large) deviations from the HEOM results. For all cases, the A-FSSH results are close to the HEOM results.

For the case of large exothermicity, Table 1 and Figure 1 can be interpreted in the context of the Straub–Berne formalism[40] (which is equivalent to Zusman[41] and Rips–Jortner[42] expressions). According to this formalism, the transmission coefficient κ should be given by

$$\kappa^{-1} = \kappa_{na}^{-1} + \kappa_{ad}^{-1} - 1 \quad (6)$$

where κ_{na}^{-1} and κ_{ad}^{-1} are interpreted as the number of recrossings for nonadiabatic and adiabatic paths, respectively. For small V_c, in the strong friction regime considered here ($\eta/\omega = 10$), $\kappa_{na} \ll \kappa_{ad}$, and thus we expect $\kappa \sim \kappa_{na}$ and no dependence on the friction. Indeed, for A-FSSH calculations (with decoherence), we find such behavior, and we emphasize that A-FSSH also agrees with the HEOM results and Marcus theory for $V_c = 25$ cm^{-1}. That being said, for FSSH calculations in the limit of weak diabatic coupling and strong friction, $\kappa_{na} \simeq \kappa_{ad}$ and thus increasing the friction does lower the final FSSH rate, almost as if the reaction were adiabatic. (Of course, according to eq 6, A-FSSH and FSSH will necessarily give the same reaction rate for very large friction as the reaction becomes dominated by the adiabatic pathway.) This argument explains the partial convergence of results in Table 1.

Frustrated Hops. While we have shown above that decoherence must be included to recover Marcus theory, ref 17 demonstrates that, in order to recover Marcus theory, one also requires a correct treatment of frustrated hops. Thus, for the computations above, upon encountering a frustrated hop, we have reversed velocity in an approach similar to the "VV" approach of Jasper and Truhlar[43] (see ref 16 for more details). One might wonder: Is velocity reversal somehow related to decoherence?

To address this point, in Figure 1d, we show one set of results where the velocity is not reversed. Note that, without velocity reversal, surface hopping rate constants are substantially (and incorrectly) larger than exact rate constants. Furthermore, the results are relatively independent of whether decoherence is included or not. Thus, to zeroth order, we may conclude that the question of frustrated hops can be decoupled from the question of decoherence.

Foundations of TST and Decoherence. Before concluding, there is one abstract point we would like to emphasize about TST. In classical mechanics, a TST rate constant is the flux of reactive trajectories crossing a dividing surface at thermal equilibrium. For FSSH trajectories, because decoherence is not included, such a TST rate constant is meaningless. After all, at thermal equilibrium, the FSSH electronic amplitudes are completely random and, hence, the set of equilibrium trajectories that go from the reactant nuclear basin to product nuclear basin do not satisfy any constraints on their electronic amplitudes. As such, this set of trajectories is unrelated to any well-defined initial electronic state, and these trajectories cannot be used for a physical rate constant; a naive implementation of TST-FSSH would correspond to choosing the electronic amplitudes randomly and would result in useless rate constants. Thus, it is important to realize that the TST-FSSH algorithm from ref 17 (as well as the HST algorithm[7]) does *not* correspond to a standard equilibrium TST theory. Instead, one should consider the TST-FSSH estimates in Figure 1 as corresponding to a short time fit to nonequilibrium direct FSSH dynamics assuming initialization in the reactant electronic state and assuming velocity equilibration at the transition state.

In other words, without decoherence, the foundations of TST are absent, and transition state theory must be formulated very carefully. Luckily, these nuances disappear as soon as decoherence is included correctly. At equilibrium, according to the A-FSSH algorithm, the electronic amplitudes are effectively set to (1,0) or (0,1) in each basin (reactant or product) for the models above. As such, the TST-A-FSSH rate constant will be equal to the equilibrium flux of trajectories from reactant to

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product. Thus, with decoherence, we expect direct A-FSSH and TST-A-FSSH will always agree, as can be seen in Figure 1.

In the end, the conclusions of this Letter are as follows. First, the accuracy of the standard FSSH algorithm (without decoherence) is highly sensitive to exothermicity. On one hand, direct FSSH will predict a grossly inaccurate rate (with an incorrect scaling law) for highly exothermic electron transfer reactions. On the other hand, FSSH will often predict reasonable lifetimes and rates for isoenergetic reactions. That being said, this latter success of the FSSH algorithm for the isoenergetic case is entirely coincidental (and such coincidences have been isolated previously for gas phase scattering problems as well).[44] In general, one should not expect much accuracy from FSSH rates as calculated without decoherence; in fact, as a practical matter, using FSSH one often finds erroneous nonexponential populations as a function of time (which can preclude extracting a rate in the first place).

Second, we have discussed two distinct ways of extracting rate constants with surface hopping trajectories: (*i*) direct dynamics from an initially prepared state, and (*ii*) a TST formalism based on backward and forward propagation. We have shown that these two formalisms must agree only with decoherence. Without decoherence, these two formalisms will not agree in general: direct dynamics rates will be too large, and TST rates will be too small in the regime of weak electronic coupling and moderate friction. In general, we have argued that naively applying nonadiabatic transition state theory without a decoherence correction to surface hopping would be nonsensical.

Third, we have shown that, while an incorrect treatment of forbidden hops can significantly impact rate constants, velocity reversal is effectively decoupled from the problem of decoherence, and should be treated separately.

We expect that these conclusions will be very general across a broad range of Hamiltonians. Looking forward, because decoherence corrections are easily available nowadays (e.g., ref 5) and because these corrections are both crucial and effective in the context of transition state theory, we anticipate that surface hopping can and will be used often in the future to estimate rates of thermally activated, i.e. rare, nonadiabatic events.

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Notes

The authors declare no competing financial interest.

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