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On Surface Hopping and Time-Reversal

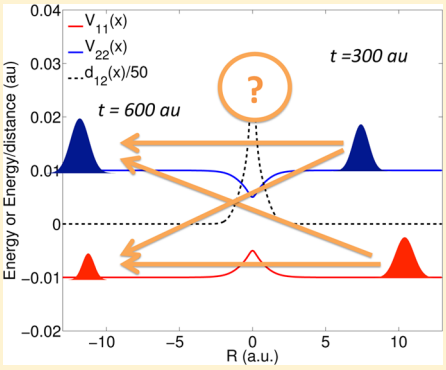
Joseph E. Subotnik*,† and Young Min Rhee‡,§

†Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

‡Center for Self-assembly and Complexity, Institute for Basic Science (IBS), Pohang 790-784, Korea

§Department of Chemistry, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

ABSTRACT: While individual Tully-style fewest switches surface hopping (FSSH) trajectories are stochastic and cannot be inverted in time, it is possible to reverse in time the dynamics of a swarm of FSSH trajectories. Here we show exactly how to invert such dynamics, and we investigate the stability of such time-reversed surface hopping dynamics. We demonstrate that FSSH trajectories can be inverted successfully for short time periods, but the time-reversed dynamics become unstable for long times with multiple hopping events. We argue that this instability of FSSH going backward in time can be correlated with the stability of the FSSH algorithm going forward in time.



INTRODUCTION

Over the years, Tully's fewest switches surface hopping algorithm (FSSH[1,2]) has been a popular choice for propagating nonadiabatic dynamics for two basic reasons. (i) First, the FSSH algorithm is usually accurate enough (and often very accurate). In 2008, Schmidt and co-workers showed that FSSH obeys detailed balance approximately,[3,4] and more recent work has explored how one can derive[5] the FSSH algorithm approximately from the quantum classical Liouville equation (QCLE)[6−10] and calculate arbitrary observables starting from arbitrary initial conditions.[11] (ii) Second, and just as importantly, the FSSH algorithm is very computationally efficient, whereby some physical observables can be predicted with only hundreds of trajectories. The latter feature has been essential given the urge to run calculations nowadays with ab initio on-the-fly potential energy surfaces.[12,13]

Despite the positive attributes above, several negative features of FSSH are also known. First, only a few years after the FSSH algorithm was introduced, Rossky and co-workers showed[14] that the FSSH algorithm does not correctly model decoherence events, i.e., the bifurcation of two wavepackets on different electronic surfaces. A great deal of research has investigated this failure.[15−29] Second, and certainly not surprisingly given the first failure, the FSSH algorithm also cannot properly handle recoherences, i.e., two separate wave packets coming together and interfering.[5,30]

Besides the two failures listed above, there is a third failure of surface hopping that has been discussed now and again in the literature,[2] namely the time-irreversibility of the FSSH algorithm. FSSH trajectories are stochastic and, thus, almost by definition, if we reverse all momenta, change the sign of i, and run FSSH trajectories backward, we will not recover our initial conditions. By contrast, Ehrenfest dynamics are smooth and time reversible, as has been emphasized in the literature, in the context of Meyer−Miller dynamics[31] and the related Poisson bracket mapping equation dynamics.[32−34] Given the close connection between time reversibility, Boltzmann's H-Theorem, and detailed balance,[35] one might expect that Ehrenfest dynamics would recover equilibrium populations more accurately than FSSH dynamics, but, in fact, the opposite is true. FSSH dynamics predict population ratios that are exponential in the energy gap (and close to Boltzmann), while Ehrenfest dynamics predict polynomial population ratios (that overestimate high energy states).[3,4] Thus, there are cases where one might want to propagate a swarm of trajectories forward and backward in time,[36] and the inability to invert FSSH backward in time is a negative feature of the algorithm.

Furthermore, in a recent publication[37] we showed that, for a swarm of FSSH trajectories in a closed environment, the purity (and entropy) of the swarm grows in time, even though, according to true quantum dynamics, a pure state should remain pure forever.[35] This lack of "total entropy conservation" is another consequence of the time-irreversibility failure of the FSSH algorithm.

Reversed FSSH Trajectories. With this background in mind, in the present article, we want to ask a very simple question: even though individual FSSH trajectories are not time-reversible, and even though the entropy of a swarm of FSSH trajectories grows in time, is it not possible to reverse the entire FSSH algorithm backward in time? In other words, even though one individual FSSH trajectory is stochastic and cannot be propagated backward, can a swarm of trajectories be

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propagated backward in time? More generally, what would it mean to run FSSH dynamics "backwards in time"?

Almost 20 years ago, Hammes-Schiffer and Tully showed how to perform this type of time-reversed calculation in practice for one particular problem.[38] Namely, for the case of a rare, nonadiabatic crossing event (where we know the initial state of the system at time $t = -\infty$ and want to compute a transmission function), ref 38 suggested that we construct trajectories that go backward in time, and then reweight those trajectories so as to estimate the probabilities of forward propagating FSSH reaching the crossing point. For the Hammes-Schiffer/Tully (HST) scheme, reweighting is essential: some proposed trajectories will presumably take on zero weight. The HST scheme will be exact in the limit that all backward-moving trajectories are considered and reweighted (with arbitrary hopping) *and provided we know the initial state at time* $t = -\infty$.

In the present article, our goal is to invert FSSH dynamics in time without making any assumption about the system at earlier times. As an example, consider the cartoon of an avoided crossing in Figure 1 (known as Tully model problem no. 1).

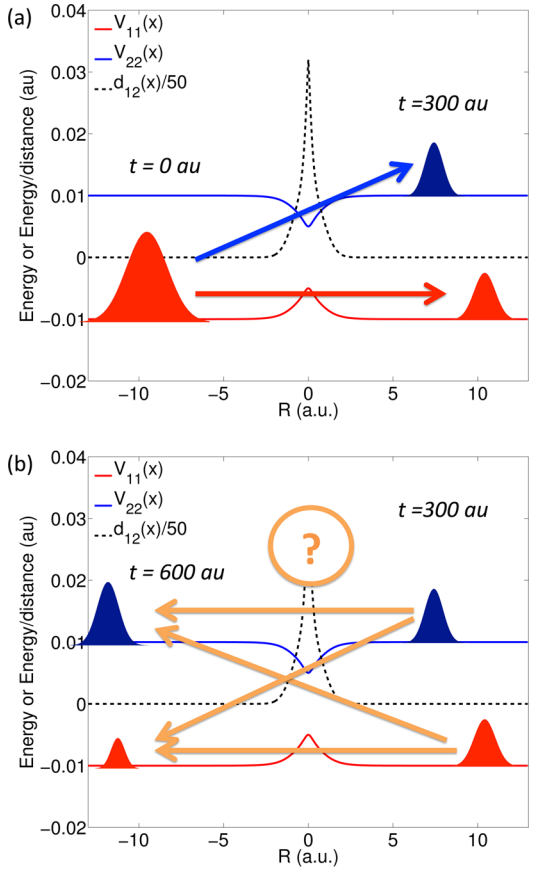

Figure 1. A schematic diagram of reversing the FSSH algorithm. In part a, beginning at time 0, we start with an incoming wavepacket on the lower adiabat, and this adiabat subsequently goes through a crossing and branches into 2 wavepackets over a time span of $\Delta t = 300$ au. In part b, if we can invert FSSH dynamics going backward in time, the two resulting wavepackets must go backward through the crossing region again and recombine into one wavepacket.

We imagine that we have initialized (at $t = 0$) a surface hopping calculation incoming on the ground state from the left and the wavepacket has just passed through the avoided crossing at time $t = 300$. At this juncture, our swarm of FSSH trajectories represent two wave packets, one on each electronic surface. If we switch the momenta of each individual trajectory from $\vec{P}$ to $-\vec{P}$, and send the particles backward in time, would we predict that these two wavepackets came originally from one single wavepacket that bifurcated? Or would we predict that there were two wavepackets that came together and interfered? Running straightforward FSSH dynamics backward in time cannot answer this question because FSSH is not time-reversible.

We will show below that the FSSH algorithm *can* be reversed in time but only at the cost of numerical instability and poor convergence as the number of hopping events grows. Thus, such reversed calculations are not feasible for long time calculations. Nevertheless, such inversions are allowed in principle, and they are possible for very short times.

THEORY AND ALGORITHM

Standard FSSH. Inverting FSSH dynamics in time is, in fact, quite straightforward. (Below, we will restrict ourselves to the case of two electronic states.) Before giving the reversed algorithm, for easier comparison between the two, we remind the reader of the basic rules for FSSH:

1. Initialize all trajectories with the correct electronic amplitudes ($\vec{c}$), position ($\vec{R}$) and momentum ($\vec{P}$), and active adiabatic surface $\lambda = 1, 2$ corresponding to the physical initial conditions.

2. Compute $\vec{c}(t + \Delta t)$ by propagating the time-dependent electronic Schrödinger equation,

$$\frac{dc_j}{dt} = \frac{-i}{\hbar}\sum_k H_{jk}c_k - \sum_{k\alpha} d^{\alpha}_{jk}c_k\frac{P^{\alpha}}{M^{\alpha}} \tag{1}$$

where H is the adiabatic electronic Hamiltonian and $\vec{d}$ is the matrix of derivative couplings.

3. Compute $\vec{R}(t + \Delta t)$ and $\vec{P}(t + \Delta t)$ by propagating the nuclei classically along adiabat λ:

$$\dot{R}^{\alpha} = \frac{P^{\alpha}}{M^{\alpha}} \tag{2}$$

$$\dot{P}^{\alpha} = F_{\lambda}(\vec{R}) \tag{3}$$

4. Check that a hop is energetically allowed by computing the rescaled momentum. For a two state problem, if $\lambda = j$, the rescaled momentum on state k ($\vec{P}_k$) is $\vec{P}_k = \vec{P} + \epsilon\vec{d}$, where

$$\sum_{\alpha}\frac{(P^{\alpha}_k)^2}{2M^{\alpha}} + V_{kk} = \sum_{\alpha}\frac{(P^{\alpha})^2}{2M^{\alpha}} + V_{jj} \tag{4}$$

If $\vec{P}_k$ is complex (so a hop is not allowed), return to step 2.

5. If $\vec{P}_k$ is real (so a hop is allowed), calculate the probability of hopping. If $\lambda = j$, the probability of hopping from state j to state k is

$$\gamma^{j\to k}_{\text{hop}} = \Gamma\left[\frac{2P^{\alpha}}{M^{\alpha}}\frac{Re(d^{\alpha}_{jk}(\vec{R})c_kc_j^*)}{c_jc_j^*}dt\right] \tag{5}$$

where Γ represents the positive projector:

$$\Gamma[x] = \Theta[x]\cdot x = \begin{cases} x & x > 0 \\ 0 & x < 0 \end{cases} \tag{6}$$

Θ is a Heaviside function.

6. Generate a random number $\zeta \in [0, 1]$. If $\gamma^{j\to k}_{\text{hop}} > \zeta$, set $\lambda = k$ and return to step 2.

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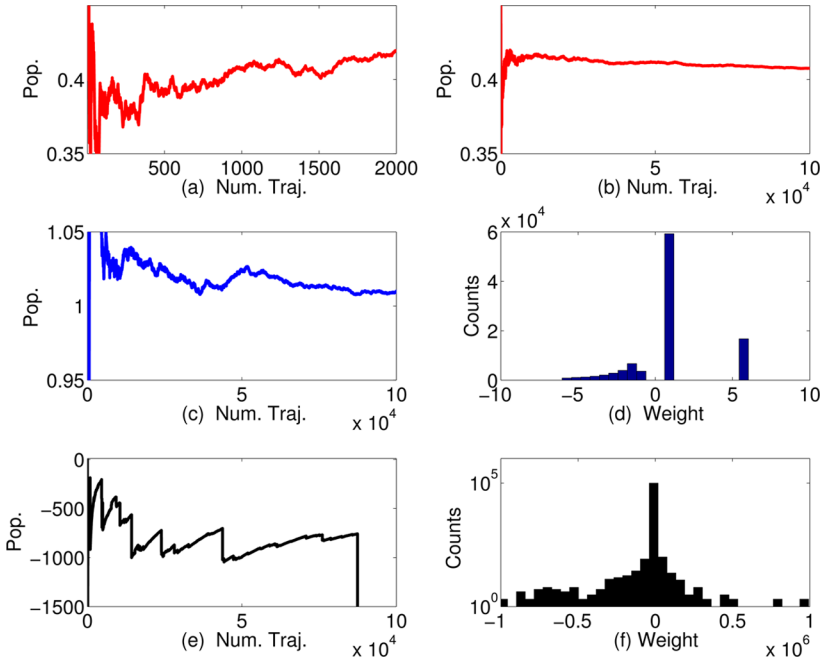

Figure 2. Data for Tully problem no. 1.[1] The particle begins on the lower adiabat at $R = -0.5$ au and $P = 30$ au. (a−d) A particle starts on the lower adiabat at $R = -0.5$ at time $t = 0$. (a, b) FSSH probabilities to be on the lower adiabat at $t = 300$ as a function of the number of trajectories. Notice the quick convergence of FSSH. (c) R-FSSH probabilities to be on the lower adiabat at $t = 600$ as a function of the number of trajectories. Note that R-FSSH can invert the dynamics successfully (as the population converges to 1), but the convergence is slower. (d) A histogram of the trajectory weights for the simulation of length $\Delta t = 600$ au. (e, f) A particle starts on the lower adiabat at $R = -5$ at time $t = 0$. (e) R-FSSH probabilities to be on the lower adiabat at $t = 6000$ as a function of the number of trajectories. Note that R-FSSH is completely unstable. (f) A histogram of the trajectory weights for a simulation of length $\Delta t = 6000$ au.

Reversed FSSH (R-FSSH). Now, the only time-irreversible piece of the FSSH algorithm is the stochastic hop between surfaces (step 6). Thus, suppose that in our simulation, at time t, we have $N_1(\vec{R}, \vec{P}_1, \vec{c}, t)$ particles at position $(\vec{R},\vec{P}_1)$ with electronic amplitude $\vec{c}$ moving along surface 1, and that we have $N_2(\vec{R}, \vec{P}_2, \vec{c}, t)$ particles at position $(\vec{R},\vec{P}_2)$ with electronic amplitude $\vec{c}$ moving along surface 2. (Here, $\vec{P}_1$ and $\vec{P}_2$ are matching, rescaled momenta from eq 4 above.) Suppose, furthermore, that, at $(\vec{R}, \vec{P}_1, \vec{c})$, there is a positive probability γ to hop from surface 1 to surface 2, a probability $g = 1 - \gamma$ to remain on surface 1, and a zero probability to hop from surface 2 to surface 1. In terms of a master equation, if we consider a swarm of trajectories, these probabilities can be summed up by

$$\begin{pmatrix} N_1(\vec{R}, \vec{P}_1, \vec{c}, t + \Delta t) \\ N_2(\vec{R}, \vec{P}_2, \vec{c}, t + \Delta t) \end{pmatrix} = \begin{pmatrix} g & 0 \\ \gamma & 1 \end{pmatrix} \begin{pmatrix} N_1(\vec{R}, \vec{P}_1, \vec{c}, t) \\ N_2(\vec{R}, \vec{P}_2, \vec{c}, t) \end{pmatrix} \tag{7}$$

Thus, Tully's algorithm can be inverted according to

$$\begin{pmatrix} N_1(\vec{R}, \vec{P}_1, \vec{c}, t) \\ N_2(\vec{R}, \vec{P}_2, \vec{c}, t) \end{pmatrix} = \frac{1}{g} \begin{pmatrix} 1 & 0 \\ -\gamma & g \end{pmatrix} \begin{pmatrix} N_1(\vec{R}, \vec{P}_1, \vec{c}, t + \Delta t) \\ N_2(\vec{R}, \vec{P}_2, \vec{c}, t + \Delta t) \end{pmatrix} \tag{8}$$

The mathematics above, corresponds to the following reverse FSSH algorithm:

1. Initialize all trajectories appropriately at time t and give every trajectory a weight $w = 1$.

2. Compute $\vec{c}(t - \Delta t)$ by propagating the time-reversed electronic Schrödinger equation,

$$\frac{dc_j}{dt} = \frac{-i}{\hbar} \sum_k H_{jk} c_k + \sum_{k\alpha} d^{\alpha}_{jk} c_k \frac{P^{\alpha}}{M^{\alpha}} \tag{9}$$

$$c_j(t - \Delta t) \approx c_j(t) - \frac{dc_j}{dt} \Delta t$$

Note the changes in sign compared with eq 1.

3. Compute $\vec{R}(t - \Delta t)$ and $\vec{P}(t - \Delta t)$ by propagating the nuclei classically along adiabat λ.

4. If the active surface is $\lambda = j$, compute the corresponding momentum on surface k $(\vec{P}_k)$ according to eq 4. If P_k is complex (so that a hop is not allowed energetically), return to step 2.

5. Calculate both possible hopping rates that one would have found in the *forward* direction, $\gamma^{1\to2}$ and $\gamma^{2\to1}$, according to eq 5. Only one of these rates can be positive.

6. If $\gamma^{a\to b} > 0$, define $\gamma \equiv \gamma^{a\to b}$ and $g = 1 - \gamma$.

(a) If $\lambda = a$, generate a random number, $\zeta \in [0, 1]$

i. If $\zeta < (\gamma/(1 + \gamma))$, there is a hop; set $\lambda = b$. The weight of this trajectory (w) is multiplied by $-(1 + \gamma)/g$. Continue to step 2.

ii. Otherwise, there is no hop. The weight of this trajectory (w) is multiplied by $(1 + \gamma)/g$. Continue to step 2.

(b) If $\lambda = b$, there will be no hop. The weight for this trajectory is unchanged. Continue to step 2.

At the end of all R-FSSH trajectories, to compute an observable, every trajectory must be weighted by w.

The above algorithm is somewhat tricky to understand physically. Suppose we have a FSSH trajectory going forward in time with $\gamma = \gamma^{1\to2} > 0$ at time $t_0 - \Delta t$ and with $\lambda = 2$ at time t_0. In theory, there are two possibilities for reversing this trajectory, from t_0 backward to $t_0 - \Delta t$. On the one hand, this trajectory could have come from $\lambda = 1$ with a forward probability γ (i.e., with a hop); on the other hand, this trajectory also could have

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come from $\lambda = 2$ with unit forward probability (i.e., without a hop). The mathematics of R-FSSH then suggests (perhaps counterintuitively) that, as we moved backward in time, we remain on $\lambda = 2$ with unit probability (i.e., we do not reweight). However, we also subtract $-\gamma/g$ times the population on surface 1 from the total population on surface 2, which ensures that the population on surface 2 is reduced at time $t_0-\Delta t$ (relative to time t_0). In other words, some of the trajectories on surface 1 at time t_0 will hop to surface 2 at time $t_0-\Delta t$, but with negative probability weighting. Recall that g is the conditional probability that we stay on surface $\lambda = 1$ after a forward hop.

Finally, for a trajectory with $\lambda = 1$ at time t_0, we can also remain on the same surface ($\lambda = 1$) and conservation of probability requires that we reweight such trajectories by $1/g$.[39]

RESULTS

We have coded up the reversed fewest switches surface hopping (R-FSSH) algorithm above to investigate its effect and usefulness. Our model of choice will be Tully's avoided crossing problem,[1] shown in Figure 1. We have performed the following calculation:

1. We initialize a set of trajectories at $R = -0.5$ on the lower adiabatic surface, with incoming momentum $P = 30$ au.
2. We propagate trajectories going forward with FSSH for a time period $\Delta t = 300$ au. The particle mass is 2000 au.
3. We reverse all momenta ($P \rightarrow -P$).
4. We run R-FSSH trajectories backward in time for 300 au.
5. We compute the population on the lower adiabatic state by averaging over trajectories with proper reweighting. If the calculation has succeeded, the probability should be 1.

In Figure 2, parts a and b, we show the probability of being on the lower surface as a function of time after running FSSH for the first $\Delta t = 300$ au. In part a, we show convergence of the FSSH algorithm with 2000 trajectories; in part b, we show convergence after 10^5 trajectories. FSSH converges quite well; after 10^5 trajectories, according to FSSH, only $40.7 \pm 0.1\%$ or so of the wavepacket remains on the lower adiabat. After 2000 trajectories, the FSSH algorithm computes a population of 41.8%.

In Figure 2c, we show the probability of being on the lower adiabat at time $t = 600$ au after running reversed R-FSSH trajectories for $\Delta t = 300$ au. As must be true, one finds that the probability is converging to 1, as it must, but R-FSSH converges slower compared to FSSH. In part d, we plot a histogram of the weights of all trajectories. Indeed, we find weights as big as ± 7, which explains the slower R-FSSH convergence.

Finally, in Figure 2e,f, we show results for a simulation that is ten times longer (i.e., $\Delta t = 6000$ au) starting at $R = -5$. In this case, the particle has the chance to hop up and down within the window of the simulation. As shown in Figure 2e, the predicted R-FSSH population is chaotic and totally unphysical, and the weights of each trajectory can be astronomically large (part f). Obviously, the R-FSSH inversion cannot be used in practice for all but very short times.

DISCUSSION AND CONCLUSIONS

We have shown that the FSSH algorithm can be inverted in time in principle, but that such inversion is numerically unstable with multiple hopping events. On the one hand, these results are interesting in principle; they remind us that, even though it is stochastic, the surface hopping algorithm is in fact invertible. On the other hand, these results are disappointing because inverting FSSH trajectories could be very useful (but such reversal is impossible in practice). To that end, several comments are now in order.

First, the instability of R-FSSH is obviously the result of trajectories acquiring unbounded, positive, or negative weights. While the exact form of the weights in reverse FSSH dynamics is the direct consequence of the forward FSSH hopping rate (in eq 6), such unstable weights would also be needed to invert any classical stochastic dynamics. After all, any classical master equation is of the form:

$$\begin{pmatrix} A_1(t+\Delta t) \\ A_2(t+\Delta t) \end{pmatrix} = \begin{pmatrix} a & 1-b \\ 1-a & b \end{pmatrix} \begin{pmatrix} A_1(t) \\ A_2(t) \end{pmatrix} \tag{10}$$

and the matrix inverse is

$$\begin{pmatrix} a & 1-b \\ 1-a & b \end{pmatrix}^{-1} = \frac{1}{a+b-1} \begin{pmatrix} b & b-1 \\ a-1 & a \end{pmatrix} \tag{11}$$

From this point of view, FSSH is just like any other rate equation: FSSH increases entropy (just like any other master equation), and FSSH can be inverted only with negative weighting schemes (again, just like any other master equation).

Second, recall that Feynman path integrals require trajectories with *bounded* complex weights, while the quantum classical Liouville equation requires trajectories with bounded real weights (but these weights can be both positive and negative). Both methods are time reversible, but both are numerically unstable for long times forward or backward. Consider now that the Tully FSSH algorithm provides an approximate solution to the QCLE that is stable (compared with the standard momentum-jump solution).[8,40,41] From this comparison, one might conclude that one basic trade-off for the FSSH algorithm is that what FSSH achieves going forward in time, FSSH loses going backward in time. After all, on the one hand, FSSH achieves quick convergence going forward in time because all trajectories have a simple, positive weight that does not change in time. However, to invert FSSH trajectories, one requires weights that can be positive or negative *and* unbounded. As such, R-FSSH is *more unstable* than Feynman path integrals and QCLE momentum-jump trajectories. (This likely explains why no one has previously inverted FSSH trajectories as we do here.)

Third and finally, it is worth mentioning that adding decoherence on top of FSSH trajectories (which is known to increase long time accuracy[15,18,42]) results in dynamics that are completely unreversible for a swarm of trajectories. Thus, again, there would appear to a be natural trade-off between, on the one hand, achieving convergent, accurate dynamics in the forward direction and, on the other hand, losing the ability to run dynamics in the reverse direction.

In conclusion, in this paper we have shown that, in principle, a swarm of FSSH trajectories can be inverted, but we have also shown that such a reversed algorithm is neither efficient nor stable in practice for long times with greater than one hopping event. From these results, we have argued that the FSSH algorithm achieves its combination of accuracy and efficiency in the positive time direction at the expense of the difficulty of inverting trajectories backward in time. The same argument could also be made for the multiple-spawning algorithm[43,44] if only a limited number of basis functions are available (though, it should be emphasized, multiple spawning does not increase the entropy of the total universe[37]).

Looking forward, it will be interesting to analyze the consequences of these statements with regards to rare event sampling

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and whether the R-FSSH inversion scheme can be of any use for very short time dynamics (i.e., dynamics with only one hopping event). After all, in principle, the R-FSSH protocol is limited only by the number of hops and not by the exothermicity of the process. Thus, for a downhill trajectory from a transition state to the reactant basin (for which a downward electronic transition is converted into thermal energy), inversion and rare-event sampling up to and over the barrier might theoretically be possible but only if the nonadiabatic crossing space is extremely localized and there is at most one hop.

AUTHOR INFORMATION

Corresponding Author

*E-mail: subotnik@sas.upenn.edu.

Notes

The authors declare no competing financial interest.

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