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ABSTRACT

We propose a "backtracking" mechanism within Tully's fewest switches surface hopping (FSSH) algorithm, whereby whenever one detects consecutive (double) hops during a short period of time, one simply rewinds the dynamics backward in time. In doing so, one reduces the number of hopping events and comes closer to a *truly* fewest switches surface hopping approach with independent trajectories. With this algorithmic change, we demonstrate that surface hopping can be reasonably accurate for nuclear dynamics in a multidimensional configuration space with a complex-valued (i.e., not real-valued) electronic Hamiltonian; without this adjustment, surface hopping often fails. The added computational cost is marginal. Future research will be needed to assess whether or not this backtracking correction can improve the accuracy of a typical FSSH calculation with a real-valued electronic Hamiltonian (that ignores spin).

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I. INTRODUCTION

Fewest switches surface hopping (FSSH)[1] is a popular brand of nonadiabatic dynamics due to its low cost, decent accuracy, and straightforward implementation.[2] For the most part, the algorithm is able to model branching ratios for molecular Hamiltonians and recover reasonable time scales of electronic relaxation, all while thermal equilibrium with detailed balance is maintained more or less.[3,4] As such, the algorithm is widely used today to simulated photo-excited dynamics,[5] electron transfer[6,7] and transport,[8] and passage through conical intersections;[9,10] Tully's original article[1] is cited more than 150 times each year, and software interfaces for FSSH dynamics are now widely available.[11]

Of course, the FSSH algorithm does have some well-known failures, especially the issue of decoherence: The original algorithm did not account fully for wavepacket separation.[12] That being said, over the past two decades, many researchers have investigated the decoherence problem, and a range of solutions have been presented that can largely solve this problem in practice.[2,13–26] Another problem with FSSH is the issue of recoherences[27]—FSSH cannot model wavepacket separation followed by wavepacket recombination. This subtle, truly quantum effect is (for the most part) unsolvable by any classical algorithm; the hope has always been that such subtle effects can often be ignored for many practical problems, especially in the condensed phase.

Now, one case of interest is entirely missing from the discussion above: the case of complex-valued (i.e., not real-valued) Hamiltonians. Such Hamiltonians arise when one allows for spin–orbit interactions, and in such a case, it is well known[28] that for a system with an odd number of electrons, the electronic Hamiltonian cannot be made real-valued. Furthermore, recently, the suggestion has been made[29–31] that nonadiabatic effects arising from spin–orbit interactions can lead to spin-separation and may well be responsible for the perplexing chiral induced spin-selectivity (CISS) effect that has been reported by Waldeck and Naaman and co-workers.[32–34] For this reason, one would like to model coupled nuclear-spin dynamics with FSSH. As designed by Tully, however, the original FSSH was not conceived with complex-valued Hamiltonians in mind. After all, one of the signature ideas of surface hopping is the notion of momentum rescaling: Whenever a hop is accepted within the FSSH algorithm, one rescales momentum in the direction of the derivative coupling $\boldsymbol{d}$ (which, therefore, is required to be real-valued). Hence, one must wonder: For a complex-valued Hamiltonian, how should one choose the necessarily *real-valued* direction of momentum rescaling? Re($\boldsymbol{d}$)? Im($\boldsymbol{d}$)? Some linear combination? With this quandary in mind, in a recent article, we made a preliminary exploration of complex FSSH dynamics.[35] Our preliminary conclusions

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were that, for some problems, FSSH could be reasonably accurate if (i) one guessed the correct rescaling direction and (ii) one explicitly included Berry force[36,37] effects. That being said, the data in Ref. 35 also demonstrated that if the Berry force effects were large enough, FSSH usually just failed entirely. At the time, we assumed that such failures were simply the result of error building up within an imperfect semi-classical algorithm.

In this communication, we will actually show that, within the context of multi-dimensional nonadiabatic dynamics with complex Hamiltonians, sometimes the failures of FSSH do not arise from any intrinsic quantum features, but rather just the presence of too many consecutive (or double) hops back and forth occurring in a region of nonadiabatic coupling. Moreover, we will prove that, at least within a small test set of model problems, this FSSH error can usually be corrected by "backtracking," i.e., moving trajectories backward in time if certain criteria are met. This solution requires a negligible computational cost while leading to more accurate electronic branching ratios and far more accurate nuclear momenta. Moreover, although we have come upon this non-Markovian adjustment to surface hopping as a necessary correction for simulating dynamics with a complex-valued Hamiltonian, it is possible that this subtle algorithmic change will be effective for *multi-dimensional real-valued* electronic Hamiltonians as well.

This communication is structured as follows: In Sec. II, we review the FSSH algorithm for both real-valued and complex-valued electronic Hamiltonians. We then explain why standard FSSH fails for multi-dimensional complex dynamics as a motivation for introducing the backtracking adjustment. In Sec. III, we present some simulation results for the simplest two-dimensional (2-D) complex-valued electronic Hamiltonian, which will demonstrate the efficacy of the backtracking adjustment—especially in the limit of large Berry forces. In Sec. IV, we discuss further the notion of backtracking, making connections to other related algorithms, and hypothesizing about the notion of backtracking for *real-valued* electronic Hamiltonians. We conclude in Sec. V. Henceforward, as far as notation, we will denote all multidimensional nuclear vectors with bold characters, i.e., $\boldsymbol{p}$.

II. METHOD

A. FSSH review

We begin by briefly reviewing the normal FSSH algorithm, as well as its extension to systems with complex-valued electronic Hamiltonians. For a more complete description, many references are available.[12,38,39]

Within a FSSH simulation, each trajectory is assigned an "active" adiabatic surface j. The nuclear degrees of freedom are propagated adiabatically along a given adiabatic surface, while the electronic part is evolved according to the electronic Schrödinger equation,

$$\begin{aligned} \dot{\boldsymbol{r}} &= \boldsymbol{p}/m, \\ \dot{\boldsymbol{p}} &= -\nabla E_j(\boldsymbol{r}), \\ \dot{c_k} &= -\frac{iE_k(\boldsymbol{r})c_k}{\hbar} - \sum_l \frac{\boldsymbol{p}\cdot\boldsymbol{d}_{kl}(\boldsymbol{r})c_l}{m} \text{ for } k = 0, 1, \ldots. \end{aligned} \tag{1}$$

Here, E_k (E_j) is the kth (jth) potential energy surface, and $\boldsymbol{d}_{kl}$ is the derivative coupling between surfaces k and l. To account for nonadiabaticity, according to Tully,[1] at each time step, an FSSH trajectory should switch from one adiabatic surface (j) to another surface (k) with probability

$$\begin{aligned} P_{j\to k} &= \max\left[0, -2\mathrm{Re}\left(\left(\frac{\boldsymbol{p}}{\boldsymbol{m}}\cdot\boldsymbol{d}_{kj}\right)\frac{\rho_{jk}}{\rho_{jj}}\Delta t\right)\right], \\ \rho_{lm} &\equiv c_l c_m^*. \end{aligned} \tag{2}$$

If a hop is attempted, one must rescale the trajectory's nuclear momentum along a certain direction to conserve the total system energy. We note that an attempted hop upward may be frustrated if the nuclear momentum is too small to accommodate the change in potential energy.[2,40]

B. FSSH nuances that are highlighted with complex-valued electronic Hamiltonians

Now, for a real-valued Hamiltonian, the rescaling direction is unambiguously the direction of the derivative coupling $\boldsymbol{d}_{jk}$. This choice can be justified semiclassically through a scattering approach[41] as well as through a simple reading of the quantum–classical Liouville equation.[42–44] However, for the case of a complex-valued Hamiltonian—for example, what one might encounter with spin-orbit coupling—the situation becomes far more difficult because the rescaling direction is not straight-forward to discern. The equations are necessarily more involved, and we are unaware of a rigorous assignment of the rescaling direction nor have we been able to construct such an assignment ourselves. In practice, to date,[35] we have investigated two different approaches including (i) a vector that depends on the momentum ($Re\sum_{k\neq j}\left[\boldsymbol{d}_{jk}\frac{\boldsymbol{p}\cdot\boldsymbol{d}_{kj}}{m}\right]$) and (ii) other intuitive (but *ad hoc*) vector quantities that depend only on the electronic Hamiltonian.

Besides the question of hops between surfaces, there is another hiccup to using FSSH in the presence of a complex-valued Hamiltonian. In the limit of slow adiabatic nuclear dynamics, because of the changing phase of the adiabatic electronic states,[28,45,46] nuclei moving on surface j experience what Berry[36] has called a geometric magnetic field of the form

$$\boldsymbol{F}_j^B = 2\hbar Im\sum_{k\neq j}\left[\boldsymbol{d}_{jk}\frac{\boldsymbol{p}\cdot\boldsymbol{d}_{kj}}{m}\right]. \tag{3}$$

Note that the Berry force above will diverge to infinity in the nonadiabatic limit, e.g., at a conical intersection. The standard FSSH dynamics do not include this built-in magnetic field during propagation, and so Eq. (3) must be included when we extrapolate FSSH to the case of complex-valued electronic Hamiltonians.

In the end, from the discussion above, one finds that, in a spatial region of strong nonadiabaticity, provided that there is a complex-valued electronic Hamiltonian, there are two competing factors: (i) a strong magnetic field whose magnitude and direction depend on the adiabatic surface and (ii) a strong desire to switch adiabatic surfaces. The effects are clearly not compatible with each other. To better understand the exact problem, consider the following situation, as visualized in Fig. 1. We imagine a wavepacket approaching an avoided crossing for which the Berry force is very strong. Suppose that according to FSSH, one should hop from state 1 to state 0

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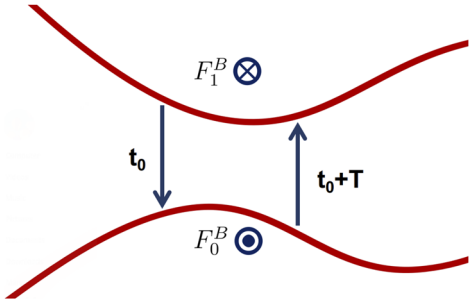


FIG. 1. A visualization of the consecutive (or double) hopping situation. A trajectory first switches from adiabat 1 to adiabat 0 at t_0 and then switches back quickly from adiabat 0 to adiabat 1 at $t_0 + T$. During the time period $[t_0, t_0 + T]$, according to the standard FSSH, the trajectory responds to Berry force F_0^B. However, according to FSSH with backtracking, during this time period, the trajectory will respond instead to Berry force F_1^B (and, also during this time period, no hops will be allowed to surface 0).

at time t_0 and then hop back from state 0 to state 1 at time $t_0 + T$. In such a case, during the time interval $[t_0, t_0 + T]$, FSSH dynamics will move a nuclear trajectory along adiabat 0 with the corresponding Berry force F_0^B. However, because of the subsequent hop back up to surface 1, one could reasonably argue that this is the wrong physics. Instead, during the time interval $[t_0, t_0 + T]$, one should really move a nuclear trajectory along adiabat 1 with the corresponding Berry force F_1^B. Thus, FSSH dynamics are set up for failure because of the presence of too many hops back and forth.

C. Backtracking correction

If the analysis is qualitatively correct, there should be a simple fix to the FSSH algorithm worth exploring. If the problem is indeed the presence of too many hops back and forth, why not just correct trajectories that hop more than once within a short time period?

In practice, this notion leads to what we will refer to as "backtracking." Within such a backtracking approach, one makes the following change to the FSSH algorithm: Suppose that the trajectory hops from state j to state k at time t_0, and attempts to hop back (no matter whether frustrated or not) from state k to state j after a short time period T (so that $t_0 + T$ is the time of the second hop). In such a case, we will rewind (i.e., bring back) the trajectory to its original position, momentum, electronic amplitude, and adiabatic surface (j) just before the initial hop at time t_0. Furthermore, we will then forbid this trajectory from hopping to state (k) within the next period of time T. Obviously, this backtracking prescription requires the definition of "a short time period," but to that end, the energy gap is the perfect criterion. Thus, we will rewind a hop if we find that time T for a consecutive (double) hop satisfies

$$T < \frac{2\pi\hbar}{\Delta\tilde{E}}. \tag{4}$$

Here, $\Delta\tilde{E}$ is the maximum energy gap as encountered by the trajectory after the initial hop from j to k at time t_0. In other words, after every FSSH hop (say, from j to k), one needs to keep track of the maximum energy gap $|E_j - E_k|$ (as a function of time) that the trajectory experiences.

The backtracking mechanism above will clearly eliminate some redundant double hops between surfaces within the FSSH algorithm. Moreover, in a moment, we will show that by eliminating such redundant hops, one clearly corrects the FSSH algorithm for the case of complex-valued electronic Hamiltonians, finding far more accuracy than was possible heretofore. We will discuss the broader possibilities and potential dangers of backtracking in Sec. IV.

III. RESULTS

For our model problem, we will work with the same 2-dimensional complex-valued Hamiltonian as studied in Ref. 35. This model assumes flat (i.e., constant) adiabatic potential energies such that one can cleanly isolate the effect of switching surfaces. In the xy plane, we imagine an avoided crossing in the x-direction modulated by a diabatic coupling that changes sign in the y-direction,

$$\begin{aligned} H &\equiv A\begin{bmatrix} -\cos\theta & \sin\theta e^{i\phi} \\ \sin\theta e^{i\phi} & \cos\theta \end{bmatrix}, \\ \theta &\equiv \frac{\pi}{2}(erf(Bx)+1), \\ \phi &\equiv Wy. \end{aligned} \tag{5}$$

We set $B = 3.0$ a.u., and we fix the mass of the incoming particle as $m = 1000$ a.u. For this model problem, we have already established empirically[35] that the optimal direction for momentum rescaling is simply the x-direction. Note, however, that the effect of backtracking as described below should be consistent using other rescaling schemes as well. For instance, for the case that we rescale in the direction $Re\left[\boldsymbol{d}_{jk}\frac{\boldsymbol{p}\cdot\boldsymbol{d}_{kj}}{m}\right]$, we show similar results in the supplementary material.

We imagine an incoming wavepacket arriving from the left on the upper adiabatic surface in the form of a Gaussian, $\Psi(\boldsymbol{r},0) = \exp\left(-\frac{(x+3)^2}{4\sigma_x^2} - \frac{y^2}{4\sigma_y^2} + i\boldsymbol{p}_0\cdot\boldsymbol{r}\right)|u\rangle$, where $|u\rangle$ represents the upper adiabatic electronic state and $\sigma_x = \sigma_y = 0.5$. Note that, asymptotically, the diabats and adiabats are equivalent in the limit $x \to -\infty$ such that this initialization is easy to implement. As far as initializing our FSSH dynamics, all trajectories are sampled from the Wigner conditions corresponding to $\Psi(\boldsymbol{r}, 0)$, i.e., positions are sampled from a Gaussian distribution centered $x_0 = -3$, $y_0 = 0$ with standard deviations $\sigma_x = \sigma_y = 0.5$ and momenta are sampled from Gaussian distribution centered at $\boldsymbol{p}_0$ with standard deviations $\sigma_{p_x} = \sigma_{p_y} = 1$. We study three choices for the energy gap A: 0.02, 0.05, and 0.1. For a given velocity, when A is large, we expect adiabatic dynamics; when A is small, we expect nonadiabatic dynamics.

At the end of each FSSH simulation, we extract scattering populations as well as the average momentum on each adiabatic surface. As far as the exact dynamics are concerned, we propagate that all dynamics use the fast Fourier transform technique[47] on a 2D grid using the same grid parameters as in Ref. 35.

In Fig. 2, we begin our analysis by plotting the transmitted population and momentum distribution results on each adiabatic

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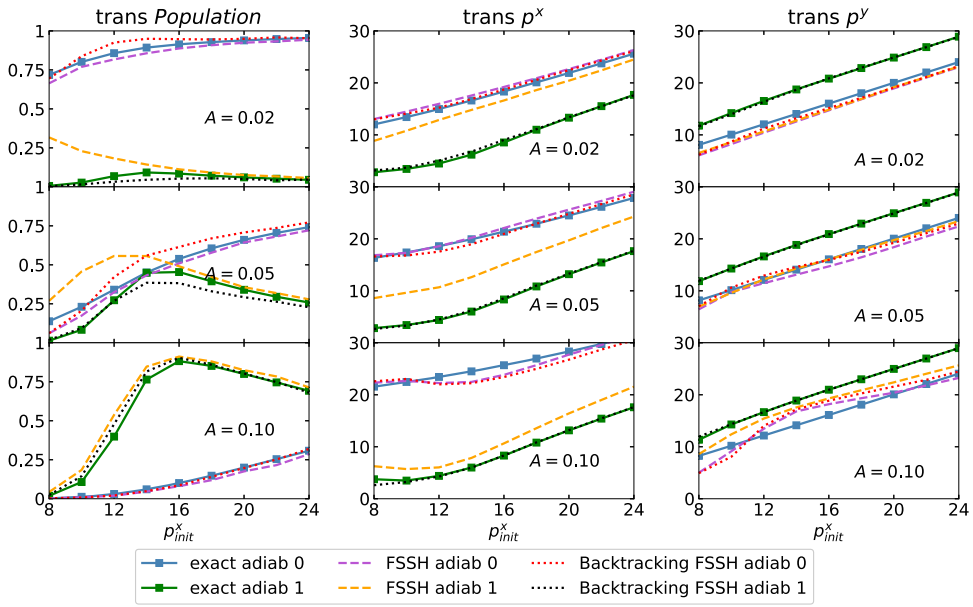


FIG. 2. Transmitted populations and momenta distribution as a function of initial incoming momentum, p_x. Here, $W = 5$, and for initial conditions, we set $p_y = p_x$. For this dataset, although backtracking results are slightly worse than the original FSSH algorithm for population at intermediate momenta $p_0 \in [16, 20]$ for the case $A = 0.05$, overall the process of backtracking makes a huge improvement as far the momentum results for all incoming conditions. In particular, backtracking leads to a dramatic improvement in the population results at low momentum for the case $A = 0.02$. Overall, backtracking is clearly essential for capturing the qualitative shapes of the branching ratios and accurate momentum distributions.

surface as a function of initial momentum, p_x. For parameters, we let $W = 5$ [which reflects how important the complex-valued nature of the Hamiltonian will be (i.e., how strong the Berry force will be)], and we choose $p_y = p_x$. For this Hamiltonian and this set of initial conditions, the Berry force in Eq. (3) will tend to promote reflection. We plot the transmitted populations on the different adiabatic states, as well as the x and y momenta (state-resolved) on the different adiabatic states. We begin our analysis by studying the $A = 0.02$ and $A = 0.05$ cases, which correspond to the more nonadiabatic flavor of dynamics. Here, we find that (as was found in Ref. 35) the standard FSSH (with Berry force included) misses a large portion of reflected population. In particular, note the erroneous yellow curve (FSSH adiab 1) for $A = 0.02$ at low incoming momentum ($A = 0.02$). By contrast, as soon as we add backtracking, the overall error appears minimized, both as far as populations and momentum distribution for both surfaces; the corrections to the momentum distribution are quite noteworthy. To understand the underlying dynamics here, note that when the particles move along adiabat 1, the underlying

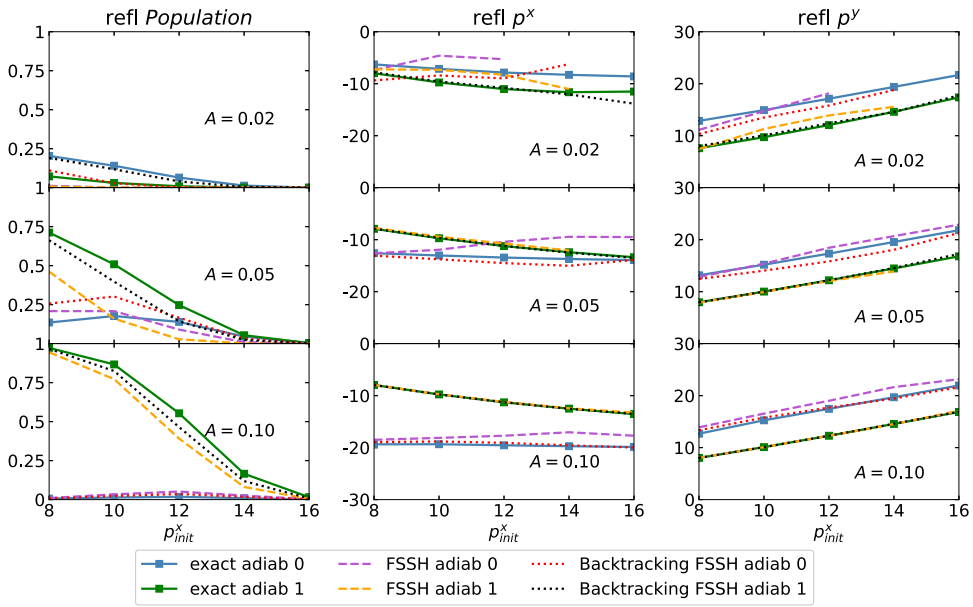


FIG. 3. Reflected population and momenta distribution as a function of initial p_x. Here, $W = 5$, and for initial conditions, we set $p_y = p_x$. For this dataset, backtracking again largely fixes the errors of the standard FSSH algorithm, especially the outgoing momenta. As far as the population results are concerned, backtracking slightly outperforms the standard FSSH when $A = 0.10$ and slightly underperforms when $A = 0.05$. Most interestingly, when $A = 0.02$, backtracking predicts roughly the correct amount of reflection, while the standard FSSH does not predict any reflection. However, strangely, FSSH with backtracking apparently inverts the reflection on adiabats 0 and 1. This bizarre failure will be discussed in Sec. IV.

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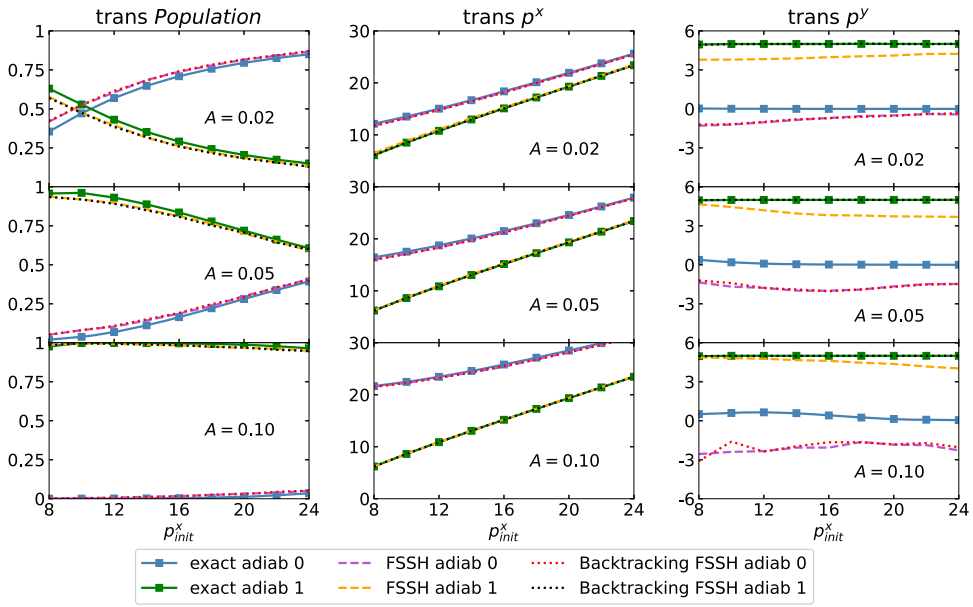


FIG. 4. Same as Fig. 2, but with initial $p_y = 0$. Here, both algorithms recover accurate transmission probabilities, but only inclusion of the backtracking adjustment yields accurate outgoing momentum distributions.

Berry force is in the direction of reflection. However, when the particles move along adiabat 0, the underlying Berry force is in the direction of transmission. Obviously, if a particle hops twice, the particle will feel dramatically different forces, leading to confusion and incorrect outgoing probabilities (i.e., too much transmission). By contrast, by backtracking, one forces the trajectories to hop as few times as possible and one does recover the correct probability of transmission.

Now, if one looks carefully, one does note that backtracking does slightly degrade the accuracy of the population data at intermediate momenta, especially in the case $A = 0.05$. Nevertheless, qualitatively, the dynamics are clearly improved overall with backtracking. Furthermore, turning to the case $A = 0.10$, we find that while the standard FSSH alone can correctly predict population distribution, the inclusion of backtracking slightly improves the population results and strongly improves the momentum results.

Next, in Fig. 3, we turn our attention to the case of reflection for the same conditions as above. For the cases $A = 0.05$ and $A = 0.10$, FSSH with backtracking agrees with the exact results better than does the standard FSSH, especially for the momentum distribution. Interestingly, for the $A = 0.02$ case, we notice that FSSH does not agree with the exact dynamics but rather shows a strange inversion: While exact dynamics predict that the reflected population on adiabat 0 is larger than the reflected population on adiabat 1, FSSH with backtracking predicts the opposite (i.e., FSSH predicts that the reflected population on adiabat 1 is larger than the reflected population on adiabat 0) with both magnitudes switched. This FSSH failure will be analyzed in Sec. IV as one potential pitfall of the method. Overall, though, it is clear that as compared with the standard FSSH, backtracking clearly leads to strong improvements. After all, in the limit $A = 0.02$, the standard FSSH does not predict any reflection at all.

Finally, we have also run simulations for the case of initialization with $p_y = 0$. In Fig. 4, we plot only transmission results, as these initial conditions do not predict any reflection. From these figures, it is clear that FSSH with backtracking and standard FSSH both yield the correct populations, but (as above) only backtracking yields the correct outgoing momenta.

Overall, the data here are clear: By including backtracking, FSSH can (at least qualitatively) recover exact data; without backtracking, the standard FSSH will encounter large problems if the Berry force is large and momenta are small.

IV. DISCUSSION: FUTURE POSSIBILITIES AND POTENTIAL CAVEATS

The data above have demonstrated that, with the inclusion of backtracking, the accuracy of the FSSH algorithm can be improved, sometimes dramatically. For the case of a complex-valued Hamiltonian with large Berry forces, as we conjectured in Sec. II C, the basic problem of FSSH is that one does not know when to hop. Indeed, one can find multiple hops, back and forth, between the same pair of surfaces. Presumably, in one dimension, such effects should not be important, and in preliminary test data (not shown), we have found that backtracking makes no difference when studying one dimensional test cases, e.g., the original Tully model problems from Ref. 1. Nevertheless, in many dimensions, if the forces are very different on the different surfaces, it is clear that a transient hop can dramatically affect the overall course of a simulation, sending trajectories in very incorrect directions in the meantime and ruining the premise of an FSSH calculation. Of course, the problem above need not be limited to complex-valued electronic Hamiltonians. For real-valued electronic Hamiltonians, different adiabatic surfaces should also have very different forces. Hence, one must wonder whether a backtracking correction will be helpful when

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running FSSH dynamics in general; this poses one very interesting avenue for future research.

Now, while we hope that the backtracking approach posed here will appeal to many theorists/computationalists, we are aware that, in practice, this approach may also appear unsettling. After all, the backtracking procedure proposed above involves going backward in time in a very non-Markovian sense. If this approach is unsettling, we must mention that the notion of rewinding a trajectory backward is hardly new. As far back as Preston and Tully's first paper on surface hopping,[48] one operated under the premise that one could find a crossing and then step backward to initialize hops just as the crossing point. Similarly, more recently, Martinez *et al.* consistently used a rewinding of sorts when running *ab initio* multiple spawning (AIMS):[49–51] within AIMS, when one finds regions of nonadiabatic coupling, one must always rewind a trajectory with spawned basis functions to a time before the crossing occurs. In this sense, one might think of the present backtracking approach as another step in the direction of merging FSSH and AIMS. Finally, within the context of FSSH dynamics, Truhlar and co-workers previously proposed the notion of fewest switches with time uncertainty[39,52] (FSTU), whereby a frustrated hop at time t_0 will be activated at time $t_0 + T$ if T is small enough. Although FSTU and backtracking have different goals in mind, there is clearly a parallel between both the approaches in the sense that both introduce some new non-Markovian effects.

Now, the implications above are exciting, and yet given the success of Tully's standard algorithm and the fact that we are now proposing to add a new non-Markovian element into the original FSSH algorithm, one must also be cautious before incorporating such a backtracking correction within bread and butter calculations.

- First, one potential cause for concern is the question of whether or not incorporating backtracking will eventually ruin the surface-amplitude consistency of surface hopping. In other words, the premise of surface hopping has always been that there will be a hypothetical equivalence between the fraction of particles on adiabat j and the square of the jth amplitude, $|c_j|^2$; to test whether backtracking introduces problems, future work will need to investigate detailed balance.
- Second, one might also wonder how decoherence corrections interface with backtracking? After all, when amplitude-surface consistency is broken, FSSH tends to need a decoherence correction.[53]
- Third, one can also ponder whether backtracking introduces any meaningful correction (at all) in the presence of friction? In such a case, is it possible that there will be no consecutive (double) hops within a small window? If so, would that mean that the standard FSSH would work better or worse? Usually, FSSH works best with friction,[44] but would that be true with complex-valued Hamiltonians?
- Fourth, in this article, we have dealt with the state of affairs when there are only two electronic states; one must ask how to generalize this approach to the case of many electronic states. Presumably, one would simply backtrack or rewind after consecutive (double) hops between any pair of states, but this simple interpretation will need to be checked.
- Fifth, for the present article, we have dealt exclusively with the case whereby the initial wavepacket is on the excited state and we have worried about the case that we hop down to the ground state at time t_0 and we hop back up at a time $t_0 + T$. What if the opposite were to occur, and we were to start on the ground state and then first hop up and then hop down? Would the physics of backtracking be any different? On this point, an interesting nuance arises. After a double hop is detected between times t_0 and $t_0 + T$, according to the procedure outlined above, we rewind the trajectory to time t_0 and do not allow any additional hops until time $t_0 + T$. The rational for this "no-hopping period" is that during this time period, the particle will traverse the crossing region. Yet, because of momentum rescaling, in the absence of friction, a trajectory will necessarily pass through the crossing region with a different velocity depending on whether or not it traverses along the higher or lower adiabatic state: in particular, the velocity along the excited state should be smaller than the velocity along the ground state by a simple energy-conservation argument. Thus, one might wonder if the "no-hopping time period" should be different for up-down vs down-up consecutive (double) hops? Should up-down double hops be matched with shorter no-hopping periods, while down-up double hops should be matched with longer no-hopping periods? To this end, in the supplementary material, we plot the results for the model above using a no-hopping period of $2T$, and we show that the scattering results do actually improve with such an increased no-hopping period. In short, if one decides to walk down that path, there may be room for some optimization or parameterization of the backtracking algorithm.
- Finally, backtracking cannot solve all of FSSH's problems. In particular, as described in Ref. 27, the recoherence problem in FSSH certainly remains and is not addressed by backtracking. Moreover, as the reflection data show in Fig. 3 ($A = 0.02$), if the Berry force is large enough, backtracking cannot match exact data for reflection branching ratios. To better understand this figure, note that the FSSH data are easy to interpret. According to FSSH, if a trajectory moves along adiabat 1, one reflects; if a trajectory moves along adiabat 0, one transmits. Therefore, following the standard intuition, FSSH with backtracking predicts that most trajectories that reflect will be on the upper diabat. By contrast, in order to explain the exact reflection data in Fig. 3 ($A = 0.02$) heuristically, one must surmise that the optimal semiclassical trajectories must depend very sensitively on the exact location of the hopping: If the incoming wavepacket stays on adiabat 1 just long enough so that it begins to reflect, then the wavepacket hops at just the right time, presumably, one will recover the exact branching ratios with more reflected population on adiabat 0. In practice, however, it appears that FSSH with backtracking is still simply too crude to recover this effect using a "no-hopping" rule for time T. Hence, one may ask: Is it clear when backtracking can salvage FSSH and when FSSH is unsalvageable?

All of these questions need to be addressed in the future.

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V. CONCLUSION

In summary, we have proposed incorporating a simple backtracking adjustment inside the FSSH algorithm, whereby whenever one encounters consecutive hops (back and forth) within a short time window, one simply rewinds the trajectory to the first hop and then proceeds without any hopping for some prescribed period of time. For our purposes, we have guessed that a short time window can be chosen as the inverse of the adiabatic energy gap. With this ansatz, we have shown that such a backtracking approach eliminates consecutive (double) hops for a trajectory going through a region with a strong derivative coupling. We have also shown that incorporating backtracking can lead to strongly improved results for multidimensional scattering calculations with complex-valued Hamiltonians, where the urge to hop is incompatible with a Berry force, which leads to big problems for the standard FSSH approach. However, if we invoke backtracking, we can indeed recover reasonably accurate branching ratios and outgoing momentum distributions. With regard to computational cost, the backtracking adjustment requires only a marginal expense and the dynamics are completely stable.

Looking forward, there are many tests ahead for this non-Markovian adjustment to the FSSH algorithm. We will need to run many multi-dimensional applications and model problems to learn exactly when consecutive (double) hops emerge as a gross problem for FSSH dynamics: Do these problems arise only for complex-valued Hamiltonians or also for real-valued Hamiltonians? We will also need to investigate whether or not the present backtracking approach proves to be a robust solution to the consecutive (double) hop problem, i.e., is it possible the present case is just too easy to solve? Answering these questions should yield very useful information (and intuition) about the nature of nonadiabatic molecular dynamics going forward and perhaps form a fundamental adjustment to the standard FSSH algorithm.

SUPPLEMENTARY MATERIAL

See the supplementary material for the scattering results for different rescaling directions as well as different definitions of the "no-hopping" time period.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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