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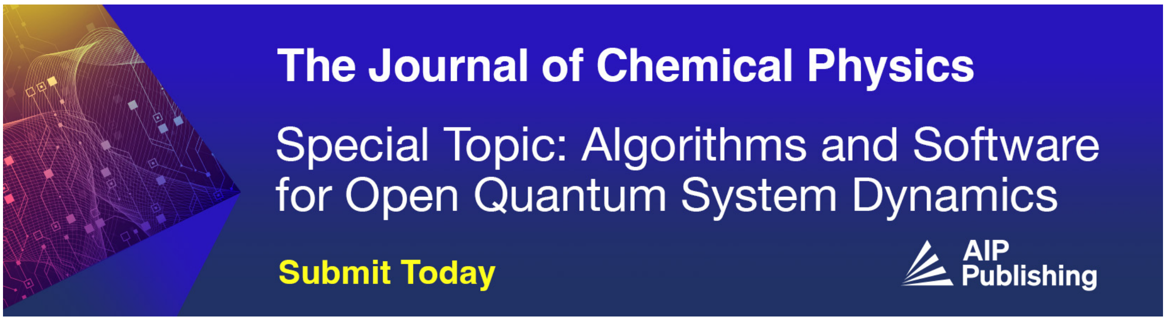

Modeling nonadiabatic dynamics with degenerate electronic states, intersystem crossing, and spin separation: A key goal for chemical physics

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ABSTRACT

We examine the many open questions that arise for nonadiabatic dynamics in the presence of degenerate electronic states, e.g., for singlet-to-triplet intersystem crossing where a minimal Hamiltonian must include four states (two of which are always degenerate). In such circumstances, the standard surface hopping approach is not sufficient as the algorithm does not include Berry force. Yet, we hypothesize that such a Berry force may be crucial as far as creating chiral induced spin separation, which is now a burgeoning field of study. Thus, this Perspective highlights the fact that if one can generate a robust and accurate semiclassical approach for the case of degenerate states, one will take a big step forward toward merging chemical physics with spintronics.

I. INTRODUCTION

The field of nonadiabatic dynamics is rich and well traversed. Dating back to the basic Marcus/Hush/Bixon/Jortner theory of electron transfer,[1–3] chemists have continuously explored how electron transfer and electronic dynamics are intimately intertwined with nuclear motion and nuclear relaxation. Nowadays, there is immense literature on coupled electronic-nuclear (or so-called "nonadiabatic") dynamics;[4–6] there are efficient codes for solving exactly certain classes of nonadiabatic harmonic problems, i.e., spin-boson problems;[7,8] there are even a few semiclassical algorithms for propagating nonadiabatic systems such that a seasoned chemist can sometimes look at a given Hamiltonian and predict dynamics at room temperature. Yet, in this Perspective, we will argue that many questions remain within the realm of nonadiabatic dynamics, especially at the intersection with spin chemistry. In particular, much of the progress cited above may need to be adjusted to account for nonadiabatic dynamics in the presence of multiple, *degenerate* electronic states.

A. What we understand so far: Semiclassical nonadiabatic dynamics with real-valued, non-degenerate electronic Hamiltonians

In order to understand the nature of semiclassical nonadiabatic dynamics, consider a typical Hamiltonian of the form $\mathbf{H} = \mathbf{H}^{el} + \frac{\mathbf{P}^2}{2M}$, where $\mathbf{H}^{el}$ is the electronic Hamiltonian and $\frac{\mathbf{P}^2}{2M}$ is the nuclear kinetic energy. In order to propagate the Hamiltonian in time, we must propagate both the electronic and nuclear degrees of freedom. Usually, propagating the electronic dynamics is the easy part. Given that electrons move so much faster than do nuclei, for almost[9] all standard nonadiabatic approaches today, one propagates the electronic degrees of freedom using a predetermined nuclear position and velocity,

$$\dot{c}_j = \frac{-i}{\hbar}\epsilon_j c_j - \sum_k \frac{\mathbf{P}}{M}\cdot \mathbf{d}_{jk} c_k. \qquad (1)$$

Here, $\mathbf{d}(\mathbf{R})$ is the matrix of derivative couplings, $d^{\alpha}_{jk} = \left\langle \Phi_j \middle| \frac{\partial}{\partial R_\alpha} \Phi_k \right\rangle$, that captures how the adiabatic states $\{|\Phi_j(\mathbf{R})\rangle\}$ change with nuclear position. The adiabatic states are the eigenstates of the electronic Hamiltonian $[\mathbf{H}^{el}(\mathbf{R})|\Phi_j(\mathbf{R})\rangle = \epsilon_j(\mathbf{R})|\Phi_j(\mathbf{R})\rangle]$, and the electronic wavefunction is expressed in the adiabatic representation $[|\Psi(t)\rangle = \sum_j c_j(t)|\Phi_j(\mathbf{R}(t))\rangle]$.

The difficult part of nonadiabatic dynamics is the feedback mechanism, whereby the fast electronic motion induces changes in the much-slower nuclear motion. Nowadays, there are two standard paradigms for incorporating such feedback and establishing equations of motion for the nuclei:

1. The oldest technique is mean-field theory.[10] Mean-field theory stipulates that one moves with the mean-field or average force,

$$\dot{\mathbf{P}} = -\left\langle \Psi \middle| \frac{\partial \mathbf{H}^{el}}{\partial \mathbf{R}} \middle| \Psi \right\rangle = -\sum_j \frac{\partial \epsilon_j}{\partial \mathbf{R}} |c_j|^2 + \sum_{jk} (\epsilon_j - \epsilon_k) \mathbf{d}_{jk} c_j c_k^*. \quad (2)$$

   Equations (1) and (2) are the so-called Ehrenfest equations of motion. Today, there are effectively many variations of the Ehrenfest inspired equations above. For instance, these same equations can be derived by a Meyer–Miller–Stock–Thoss (MMST) transformation[11–13] or by the Poisson bracket mapping equation (PBME) approximation to the quantum–classical Liouville equation (QCLE).[14,15] In general, one theme of semiclassical quantum dynamics is that, in many contexts, one can simulate nonadiabatic dynamics by propagating the Ehrenfest equations of motion but sampling over the correct initial conditions in phase space so as to simulate the correct initial wavepacket and then windowing the results.[16]
2. Apart from mean-field theory, the other standard approach to nonadiabatic dynamics today is surface hopping.[17] According to Tully's fewest switches surface hopping (FSSH) algorithm,[18] one propagates the electronic degrees of freedom according to Eq. (1) but propagates nuclear degrees of freedom along one "active" adiabatic surface, denoted λ,

$$\dot{\mathbf{P}} = -\frac{\partial \epsilon_\lambda}{\partial \mathbf{R}}. \quad (3)$$

   In order to account for electronic transitions, one switches between active adiabatic surfaces stochastically. Note that when an electronic transition occurs, one must rescale momenta in the direction of the derivative coupling, $\mathbf{d}$. All downward transitions are allowed, but for upward transitions, one must have enough kinetic energy; otherwise, the transition is forbidden.

Using these two approaches, over the last few decades, theoretical chemists have learned a great deal about the nature of quantum dynamics in the presence of a classical bath. Beyond designing improved algorithms [e.g., partial linearized density matrix (PLDM) and[19,20] *ab initio* multiple spawning (AIMS)[21–23]], theoretical chemists have used the Ehrenfest and FSSH paradigms to answer some of the most interesting problems in theoretical chemistry including the following:

1. The nature of detailed balance. Neither FSSH or Ehrenfest dynamics satisfies detailed balance exactly. That being said, on account of forbidden hops, FSSH dynamics can recover detailed balance approximately,[24,25] usually with a small error. Standard Ehrenfest dynamics cannot recover detailed balance at all, but this problem can be remedied if either one applies a windowing scheme in the proper basis[26] or presumably if one collapses Ehrenfest dynamics to adiabatic states.[27,28]
2. The nature of decoherence. Neither FSSH or Ehrenfest dynamics can correctly capture key elements of decoherence, i.e., the way wavepackets separate after going through a nonadiabatic curve crossing. In general, it is now appreciated that for either algorithm, one must collapse the relevant amplitude $\vec{c}$ to the correct adiabatic state following such a crossing. If one can apply such a decoherence correction correctly, both algorithms are dramatically improved; often FSSH can then achieve quantitative accuracy for scattering problems.[29]
3. The nature of rate theory and activated nonadiabatic processes. Assuming that one can treat decoherence correctly,[30] one can construct meaningful theories of chemical reaction rates with either Ehrenfest[31] or surface-hopping[32,33] dynamics. Both of these methods can be employed to calculate slow thermal rate processes.

As should be clear from the discussion above, over the last 60 years, many advances have been made as far as understanding the nature of nonadiabatic dynamics. Indeed, the modern chemist can run *ab initio* semiclassical atomistic calculations of electron and/or energy transfer for realistic systems that are not too large[34,35] and thereby learn how nuclear motion can either promote or frustrate electronic transitions. For the most part, one would not necessarily be wrong to claim that the biggest impediment to simulate nonadiabatic dynamics today is the problem of electronic structure—which is perhaps why the U. S. Department of Energy has put forth so many resources in recent years to calculate electronically excited states energies and gradients.[36]

Despite this rosy outlook, however, the seasoned reader may note that one key element is entirely missing from the analysis presented above: spin degrees of freedom and more generally degenerate states. Marcus theory does not address spin; Marcus's key realization was that electrons could give and take energy from a bath of nuclear motion, and so spin did not enter his formulation.[37] Thus, one can wonder: Is spin merely a bystander during the electron transfer process? Or during relaxation after photoexcitation? This question has been taken up recently by several leading chemists, especially Mai *et al.*[38] and Granucci *et al.*[39] who have focused on intersystem crossing (ISC) dynamics with spin–orbit coupling (SOC) between a singlet and a triplet. In this Perspective, we will argue that the presence of spin–orbit coupling and/or degenerate systems dramatically increases the complexity of nonadiabatic dynamics in not subtle ways that fundamentally reflect new and very rich physics and that modeling nonadiabatic dynamics with spin degrees of freedom and/or electronic degeneracy represents a key opportunity for future discovery in physical chemistry.

II. THEORY: WHAT WE DO NOT UNDERSTAND

A. Two-state nonadiabatic dynamics with complex-valued Hamiltonians

The simplest electronic Hamiltonian that goes beyond the standard photochemical problems described above (and that cannot easily be treated by surface hopping or Ehrenfest) is of the following form:

$$\mathbf{H}^{el}(x,y) = A\begin{pmatrix} -\cos(\theta(x)) & \sin(\theta(x))e^{iWy} \\ \sin(\theta(x))e^{-iWy} & \cos(\theta(x)) \end{pmatrix}, \\ \theta \equiv \frac{\pi}{2}(\mathrm{erf}(Bx)+1). \tag{4}$$

$\mathbf{H}^{el}$ in Eq. (4) reflects a system with one electron that can occupy two-electronic states $\{|a\uparrow\rangle, |b\uparrow\rangle\}$ with spin–orbit coupling. In principle, the full Hamiltonian should also include the $\{|a\downarrow\rangle, |b\downarrow\rangle\}$ states (and be four dimensional), but here we assume that there is no coupling between the $|\uparrow\rangle$ and $|\downarrow\rangle$ states. Note that $\mathbf{H}^{el}$ is complex-valued because the spin–orbit coupling operator is complex-valued, and we assume that the system includes an odd number of electrons [such that the time-reversal operator($\mathbf{T}$) satisfies $\mathbf{T}^2 = -\mathbf{I}$]. Mead showed 40 years ago[40] that in such a case, the Hamiltonian cannot be made real.

Equation (4) represents a standard avoided crossing in the x-direction but with two twists.

- First, for the Hamiltonian in Eq. (4), the adiabatic potential energy surfaces are completely flat; a simple calculation shows that the eigenvalues of $\mathbf{H}^{el}$ are $\pm A$ (Fig. 1). That being said, note that the effective Landau–Zener parameter[41] is $\frac{2\pi A}{\hbar B v}$ (where v is the velocity of a trajectory in the reactive x-direction). Thus, one can use Eq. (4) to model many different nonadiabatic regimes (adiabatic, nonadiabatic, high-friction, etc.) by modifying A (the energy gap), B (the inverse length scale for the crossing), or v (the nuclear momentum). At the same time, one can also ignore the fact that different adiabatic surfaces usually have different forces (e.g., one electronic state might be repulsive and the other attractive). In the end, using Eq. (4), one can isolate physical effects as induced by the complex-valued nature of the diabatic coupling and especially the parameter W; such effects are not usually considered within the standard nonadiabatic dynamics problems.
- Second, although the magnitude of the diabatic coupling $\sin(\theta(x))$ changes only as a function of x, the phase of the diabatic coupling is modulated in the y-direction by a parameter W—which makes the problem nontrivially two-dimensional. Note that because $\mathbf{H}^{el}$ is complex-valued, the derivative couplings are also therefore complex-valued.[42–45] This twist implies that one cannot use Tully's standard surface hopping approach to model dynamics through the curve crossing in Eq. (4); after all, FSSH posits that electronic hops should accompany momentum rescaling in the direction of $\mathbf{d}$[46]—which is impractical if $\mathbf{d}$ is complex-valued.

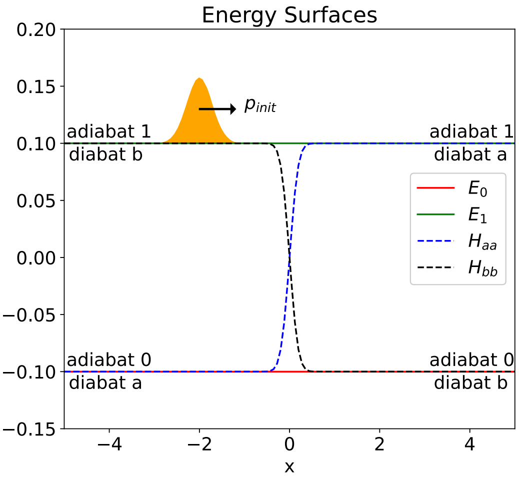

FIG. 1. The potential energy surfaces corresponding to Eq. (4). Note that the adiabatic curves are completely flat such that according to surface hopping,[18] one would predict that an incoming wavepacket on the upper adiabat should transmit 100%; this prediction is not correct because of Berry's force.

In Fig. 2, we plot scattering results from Ref. 47. By comparing exact data (black) against Tully's standard FSSH (blue), we see that FSSH fails miserably for this problem. After all, consider transmission along the upper surface for the $A = 0.10$ case [Fig. 2(c)]. Here, if we initialize with $p_x = p_y = 8$, the exact total transmission on the upper adiabat is close to 0%. That being said, because Tully's FSSH algorithm moves along adiabatic surfaces—and because those adiabatic surfaces are flat—Tully's FSSH algorithm predicts 100% transmission. Standard FSSH fails miserably.

1. Abelian Berry curvature and force

In order to understand why FSSH fails, one can turn to Berry's 1993 paper on geometric magnetism.[49] There, Berry showed that when the derivative coupling becomes complex, adiabatic motion on surface j follows an effective, so-called "geometric" magnetic field of the form

$$\boldsymbol{F}_j^{mag} = 2\hbar \mathrm{Im}\sum_{k\neq j}\left[\boldsymbol{d}_{jk}\left(\frac{\boldsymbol{P}}{m}\cdot\boldsymbol{d}_{kj}\right)\right]. \tag{5}$$

For $\mathbf{H}^{el}$ in Eq. (4), this expression becomes (on the lower adiabat 0 and the upper adiabat 1) $\boldsymbol{F}_j^{mag} = (-1)^j \frac{\hbar W}{2m}\frac{\partial\theta}{\partial x}\sin(\theta)(P^y, -P^x)$. Note that the Berry forces are equal and opposite in magnitude and the direction for the lower and upper adiabats and the magnitude of the Berry force is proportional to the parameter W. Currently, very little is known from *ab initio* calculations about the size of W for realistic molecules; however, it is known that near certain conical intersections, the effective size of W can be very large.[50]

Berry's force is completely missing from Tully's FSSH algorithm. Nevertheless, the exact data (in Fig. 2) make it clear that Berry force is real and, within a certain parameter regime, has

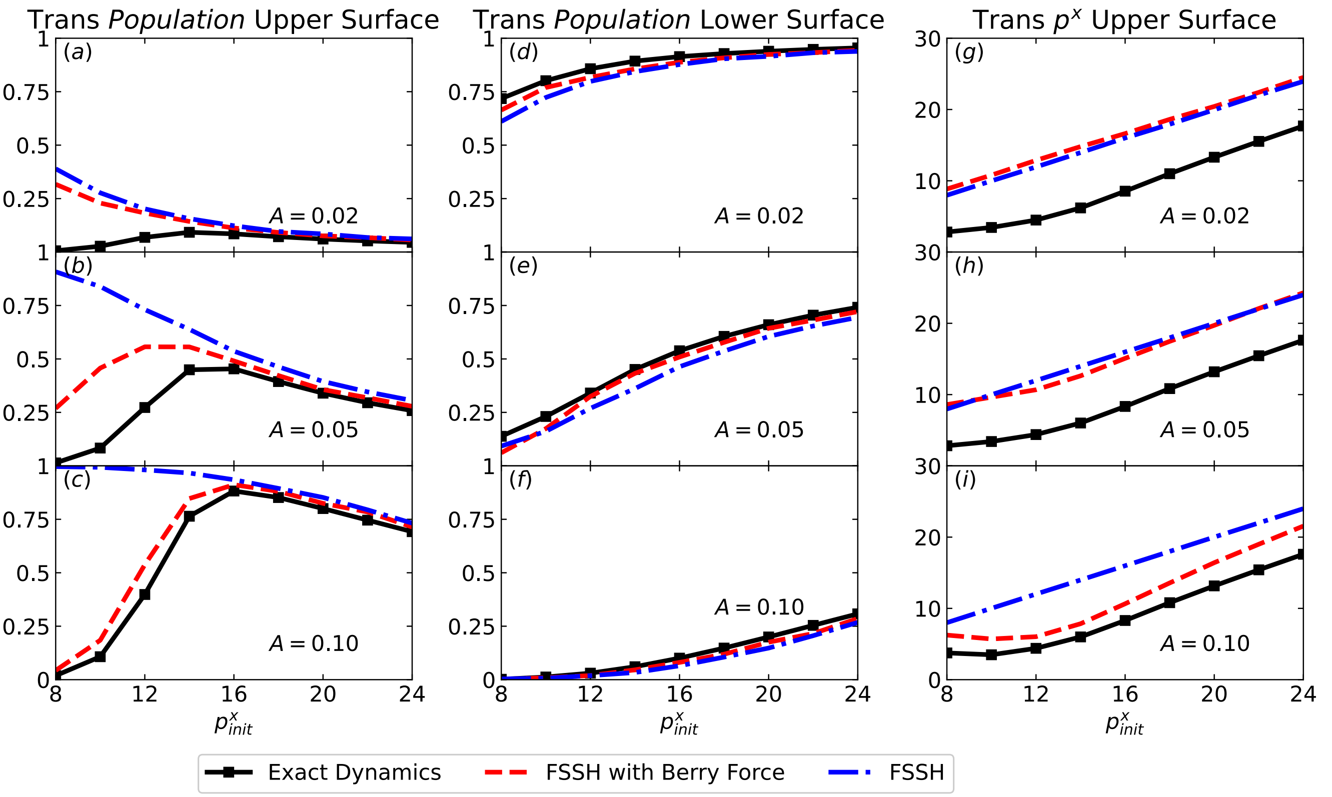

FIG. 2. Transmitted populations on the upper [(a)–(c)] and lower adiabatic surfaces [(d)–(f)] as a function of initial incoming momentum, p_x. In [(g)–(i)], we plot the average momentum in the x-direction $\langle p_x \rangle$ that emerges on the upper adiabat. Here, $W = 5$ [in Eq. (4)], and for initial conditions, we set $p_y = p_x$. We plot three different values of the parameter A, which should lead to adiabatic conditions (A = 0.10), diabatic conditions (A = 0.02), or something in between (A = 0.05). We plot exact dynamics (black), standard FSSH data (blue), and FSSH with Berry force (red). Overall, standard FSSH fails dramatically here; FSSH with Berry force performs much better. If one introduces a scheme to minimize the number of hops (so-called "backtracking"), one can do even better[48]—though this latter approach is so far not general (data from Refs. 47 and 48).

significant consequences. To that end, in Ref. 47, we proposed including Berry force in an *ad hoc* manner: within the context of Tully's FSSH algorithm, when propagating dynamics on adiabatic state j, we propose that each trajectory should feel a total force equal to the Born–Oppenheimer force $\mathbf{F}_j^{BO} = -\frac{\partial \epsilon_j}{\partial \mathbf{R}}$ plus the Berry force $\mathbf{F}_j^{mag}$,

$$\mathbf{F}_j^{FSSH\text{-}Berry} = \mathbf{F}_j^{BO} + \mathbf{F}_j^{mag}. \tag{6}$$

As shown in Fig. 2, inclusion of Berry force can lead to a very large correction and results that are closer to exact. In fact, for the adiabatic case ($A = 0.10$), Berry-corrected FSSH is accurate. That being said, Berry-corrected FSSH still fails in the nonadiabatic limit ($A = 0.02$).

In the future, even for systems with two electronic states, developing improved FSSH protocols will be essential. Recently, we proposed one such protocol (so-called "backtracking"), which was designed to minimized hops and can sometimes achieve improved branching ratios (e.g., see the results in Fig. 2). Nevertheless, this approach is not yet general and likely will need to be adjusted to handle more realistic Hamiltonians, e.g., when the adiabatic surfaces are not flat as in Eq. (4).

B. Nonadiabatic dynamics with degeneracy (real-valued or not): Intersystem crossing

One of the most interesting features of ISC is the existence of highly degenerate states. Consider the simplest process: a singlet converting to a triplet. Formally, this transformation requires at least four states since the triplet is (obviously) triply degenerate. The need for a four-state model implies that simple two state models (like Marcus theory[37,51]) need not necessarily be applicable. Interestingly, over the last ten years or so, even though there has been a great deal of research into the nature of ISC dynamics, theorists have mostly avoided the question of degeneracy. For instance, in their pioneering article on FSSH with ISC,[39] Persico *et al.* made progress by reducing singlet–triplet dynamics to a 2 × 2 Hamiltonian, thus ignoring all Berry phase effects. Mai *et al.*[38,52] and Curchod *et al.*[53] have allowed for degeneracy when propagating the electronic Schrödinger equation but have not considered the effect of Berry force when propagating nuclear dynamics.

At first glance, one might presume that degeneracy need not be important for semiclassical nonadiabatic dynamics. After all, on the one hand, why should standard surface hopping care about degenerate states? Degenerate states have the same adiabatic forces, and so the presence of parallel surfaces would not seem to be a road block. On the other hand, Ehrenfest dynamics are optimal when surfaces have similar forces; again, the presence of degeneracy should not be problematic. Indeed, Levine and Fedorov had success working with variants of Ehrenfest dynamics applied to problems with dense manifolds of electronic states.[54] Nevertheless, one must wonder: If one finds indistinguishable degenerate states (that preclude any meaningful derivative coupling), can the entire FSSH ansatz really be correct? As it turns out, we will now show that surface hopping can dramatically fail in the presence of degeneracy—*even for a real-valued Hamiltonian with an even number of electrons and time-reversal symmetry*. This conclusion also sheds light on the FSSH failures for the two-state, complex-valued Hamiltonian problem above since the two-state Hamiltonian can be viewed as a subsystem in a degenerate four-state system (see the Appendix).

To begin our analysis, consider the extension of the electronic Hamiltonian in Eq. (4) to a four state model (in order to account for a singlet–triplet crossing). The corresponding electronic Hamiltonian for ISC can be written down (in the basis $|s\rangle, |t_{+1}\rangle, |t_0\rangle, |t_{-1}\rangle$) as

$$\mathbf{H}^{\mathrm{ISC}} = A\begin{pmatrix} \cos\theta(x) & \frac{1}{2}\sin\theta(x)e^{-iWy} & \frac{i}{\sqrt{2}}\sin\theta(x) & \frac{1}{2}\sin\theta(x)e^{iWy} \\ \frac{1}{2}\sin\theta(x)e^{iWy} & -\cos\theta(x) & 0 & 0 \\ \frac{-i}{\sqrt{2}}\sin\theta(x) & 0 & -\cos\theta(x) & 0 \\ \frac{1}{2}\sin\theta(x)e^{-iWy} & 0 & 0 & -\cos\theta(x) \end{pmatrix}, \tag{7}$$

where, as above, $\theta \equiv \frac{\pi}{2}(er(\mathrm{B}x) + 1)$. Equation (7) corresponds to a naive crossing between a singlet and a triplet. Note that through a trivial (constant) change of basis with

$$\mathbf{U} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & 0 & i & 0 \\ 0 & \frac{1}{i\sqrt{2}} & 0 & -\frac{1}{i\sqrt{2}} \end{pmatrix}, \tag{8}$$

this Hamiltonian can be made entirely real,

$$\tilde{\mathbf{H}}^{\mathrm{ISC}} = A\begin{pmatrix} \cos\theta(x) & \frac{1}{\sqrt{2}}\sin\theta(x)\cos(Wy) & \frac{1}{\sqrt{2}}\sin\theta(x) & \frac{1}{\sqrt{2}}\sin\theta(x)\sin(Wy) \\ \frac{1}{\sqrt{2}}\sin\theta(x)\cos(Wy) & -\cos\theta(x) & 0 & 0 \\ \frac{1}{\sqrt{2}}\sin\theta(x) & 0 & -\cos\theta(x) & 0 \\ \frac{1}{\sqrt{2}}\sin\theta(x)\sin(Wy) & 0 & 0 & -\cos\theta(x) \end{pmatrix}. \tag{9}$$

The adiabatic energies corresponding to Eq. (7) [or equivalently, Eq. (9)] are plotted in Fig. 3(c). The largest and smallest eigenvalues of H are flat: $E_1 = -A$ and $E_4 = A$. The middle two eigenvalues ($E_{2,3}$) are doubly degenerate. Because the Hamiltonian can be made entirely real, one might presume that the Berry force [from Eq. (5)] must be zero. Nevertheless, such a prediction is incorrect. To see this fact, consider the case where a wavepacket is incoming along the singlet state as shown in Fig. 3(a). At low velocities, one finds a very interesting result: if the wavepacket approaches the crossing at $x = 0$ in a perpendicular fashion, the incoming wavepacket splits into four daughter wavepackets: there is some reflection on the $|s\rangle$ state, the $|t_1\rangle$ transmits upward with $P_y = +W$, the $|t_0\rangle$ transmits straight across with $P_y = 0$, and the $|t_{-1}\rangle$ transmits downward with $P_y = -W$ [see Fig. 3(b)].

The conclusion from Fig. 3 is that even though the Berry force expression in Eq. (5) can be made zero for each state, a nuclear wavepacket that undergoes ISC will split into three daughter wavepackets, and *each daughter wavepacket will move along a trajectory that is dictated by the spin of that wavepacket*. This is a blatant violation of the Born–Oppenheimer approximation and suggests that one can achieve spin-selective reaction rate constants (without an external magnetic field) and spin separation. Clearly,

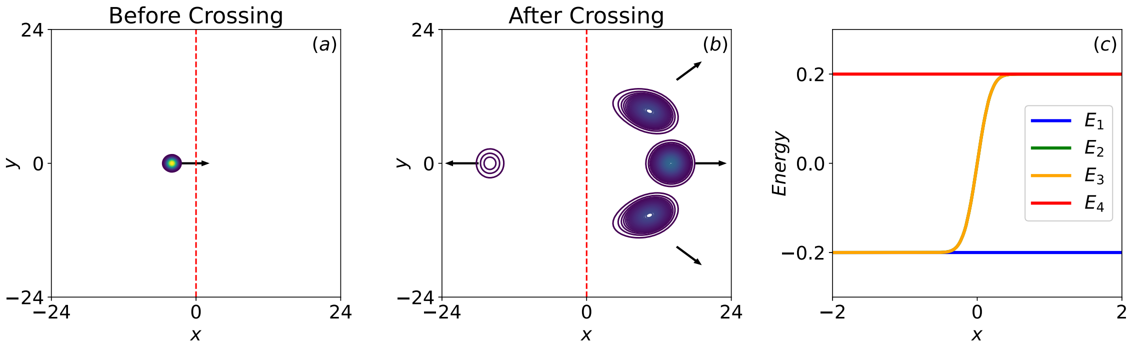

FIG. 3. Exact wavepacket data for the dynamics associated with the four-state model in Eq. (7), corresponding to a singlet–triplet ISC event. (a) A wave packet approaches a crossing at $x = 0$ along the singlet manifold. (b) The wavepacket reflects on the singlet and splits into three daughter wavepackets that transmit along the triplet manifold (with spin up deflecting upward, spin down deflecting downward, and spin zero not deflecting at all). (c) A zoomed-in plot of the adiabatic surfaces. For this model problem [Eq. (9)], there is clearly a very strong Berry force effect, even though the Hamiltonian can be made real. Unfortunately, from the perspective of the adiabatic surfaces in (c), it is not obvious how Berry forces emerge [and yield the dynamics in (b)]; *in fact, such spin-dependent nuclear motion is completely neglected by standard FSSH dynamics*.

the dynamical implications of Berry phase (i.e., generalizations of Berry force) are far more complicated in the presence of degenerate states; the Berry-corrected surface hopping algorithm from Sec. II A [which relies on Eq. (5)] will obviously fail to yield the correct dynamics.

1. Non-Abelian Berry curvature and force

Within the electronic structure community, going back to the work of Wilczek and Zee,[55] it is known that for the case of multiple, degenerate electronic bands, the nature of Berry phase becomes far more complicated. To better understand the case of many states, note that the Berry force in Eq. (5) is usually written down as

$$\mathbf{F}_j^{mag} = \boldsymbol{\Omega}_j \cdot \mathbf{P}, \tag{10}$$

where $\boldsymbol{\Omega}_j$ is the Berry curvature,

$$\Omega_j^{\alpha\beta} = \frac{\partial}{\partial R_\alpha} d_{jj}^{\beta} - \frac{\partial}{\partial R_\beta} d_{jj}^{\alpha}. \tag{11}$$

The crucial point about the curvature in Eq. (11) is that if one modifies the sign or phase of adiabat j, $|\Phi_j(\mathbf{R})\rangle \rightarrow \left|\Phi_j(\mathbf{R})e^{ig(\mathbf{R})}\right\rangle$, the quantity $\Omega_j^{\alpha\beta}$ is unchanged.

Now, more generally, for a set of degenerate states, one requires a measure of the curvature of the degenerate subspace: how does the entire degenerate subspace change as a function of $\mathbf{R}$? To make progress, one requires a curvature that is invariant to the transformation,

$$\begin{pmatrix} |\Phi_1(\mathbf{R})\rangle \\ |\Phi_2(\mathbf{R})\rangle \end{pmatrix} \rightarrow \begin{pmatrix} U_{11}(\mathbf{R}) & U_{12}(\mathbf{R}) \\ U_{21}(\mathbf{R}) & U_{12}(\mathbf{R}) \end{pmatrix} \begin{pmatrix} |\Phi_1(\mathbf{R})\rangle \\ |\Phi_2(\mathbf{R})\rangle \end{pmatrix}, \tag{12}$$

where $\mathbf{U}$ is an arbitrary, complex-valued unitary matrix. As is well known,[56] even though Eq. (11) does not suffice, there is an appropriate "non-Abelian" Berry curvature tensor of the form,

$$\Omega_{jk}^{\alpha\beta} = \frac{\partial}{\partial R_\alpha} d_{jk}^{\beta} - \frac{\partial}{\partial R_\beta} d_{jk}^{\alpha} - \sum_l \left(d_{jl}^{\alpha} d_{lk}^{\beta} - d_{jl}^{\beta} d_{lk}^{\alpha} \right). \tag{13}$$

Clearly, the Berry tensor with two or more electronic indices [$\Omega_{jk}^{\alpha\beta}$ in Eq. (13)] is much more complicated than the simple Berry curvature with one index [$\Omega_j^{\alpha\beta}$ in Eq. (11)]. In particular, the semiclassical meaning of the Berry curvature is simple for one electronic state (say *j*): one needs only to apply a built-in magnetic field along state *j* in Eq. (10). However, there is no such simple dynamical interpretation of the multi-state ("non-Abelian") Berry curvature tensor in Eq. (13). With multiple electronic states, one must realize an effective magnetic field that depends on the coherences between multiple electronic states. For a better understanding of ISC dynamics within a surface hopping algorithm, one will require a significant generalization of the semiclassical result in Eq. (10).

III. WHY ARE NONADIABATIC DYNAMICS WITH DEGENERACY SO IMPORTANT

A. Intersystem crossing dynamics

ISC is one of the primary relaxation channels in photo-excited systems. Because of antisymmetry and exchange, the lowest lying molecular excited states are usually triplets.[57] Thus, as far as understanding spin conversion, ISC is dictated by nuclear–electronic dynamics not thermodynamics, and today there is an intense push to understand: what is the probability of ISC and what is the time scale for ISC? A slew of theoretical chemists either have investigated or are currently investigating such questions with various techniques—including surface hopping in (both spin-diabatic and spin-adiabatic basis sets)[38,39,52,53,58–63] and *ab initio* multiple spawning.[53,64–66] However, by default, all of these techniques invoke standard nuclear motion along adiabatic surfaces and do not include the effects of Berry force. As a result, the literature has not accurately addressed whether or not spin polarization emerges concurrently with ISC, and yet this would also seem to be a key question for future research—which brings us to the recent observations of chiral induced spin selectivity (CISS).

B. Chiral induced spin selection (CISS)

As shown by Göhler *et al.*, the original CISS effect was detected by the following scenario: Imagine that one shines light on a gold (Au) surface coated with (chiral) double stranded DNA (dsDNA). If one measures the spin of the electrons ejected, one finds a spin preference for one spin orientation vs another (all relative to the principle axis of the dsDNA).[67] Over the years, it has been shown that this effect is not limited to dsDNA on gold: the effect occurs for various molecules or materials.[67–78] The basic molecular model of CISS effect is shown in Fig. 4: somehow or another (and the underlying physics remain debated), an electron undergoing chiral transmission has a fundamental spin preference.

Understanding CISS is important because of the enormous number of possible applications in biology and engineering science.[79] For instance, on the science side, spin selectivity has been observed for electron transfer in photosystem I, raising the possibility that CISS may well play a role in the efficiency of this key enzyme.[80] On the technology side, if one can understand and manipulate systems that display CISS, there is the possibility of creating very small (<40 nm) spintronic logic devices that function through the application of magnetic fields.[81] Finally, a recent study of water splitting on nanoparticles found that the presence of chiral ligands can nearly double the exchange current[82,83] which suggests a role for using spin-dynamics to construct efficient electrochemical pathways.

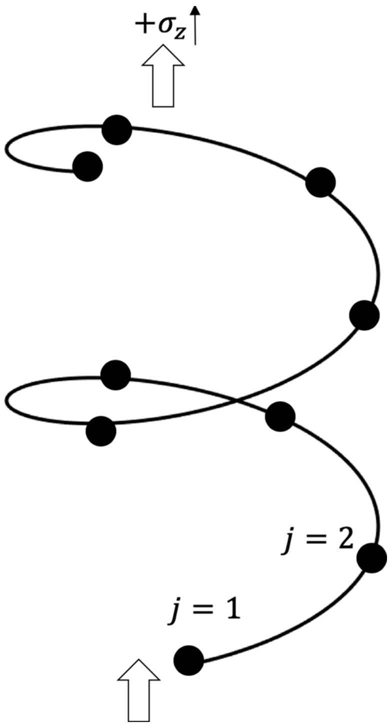

FIG. 4. A schematic model of the original CISS effect. The principle axis of the chiral potential is in the z direction. Despite the small differences between spin up and spin down electronic states, experimentally an electron moving through a chiral potential is found to have a probability of transmission that strongly depends on its spin (σ_z). One must wonder whether this spin-dependence is tied to nuclear motion and Berry force effects.

Now, a multitude of theories have been proposed to explain the CISS effect.[79,84–98] Approaches include (i) tight-binding atomistic simulations (where one assumes Rashba-like SOC)[86–90] as well as (ii) solid state calculations, whereby one investigates transport in the context of band theory with SOC and a chiral potential.[79,92–95] However, while these frameworks successfully predict spin polarization in certain conditions, the fundamental physical force behind CISS is not yet fully understood. Two essential items remain not fully explained:

1. The magnitude of the observed spin polarization is not yet consistent with theory. For most atomistic calculations, a SOC much larger than a free carbon atom (several meV) is required for theory to match experiment. For some models,[79,94] one must also require the energy of the incoming electron to be comparable to the SOC gap; yet, experimentally, CISS is observed for systems with thermal energy much larger than SOC values.[67–69,99]
2. Most CISS models have not included incoherent charge transport effects, even though studies have shown that electron transfer in DNA has a large incoherent component.[100–103]

With these limitations in mind, we have a different perspective as to the physical origins of CISS: even though no definitive isotope experiment has yet been demonstrated, we will contend that *CISS may arise when nuclear motion becomes entangled with spin-dependent electronic dynamics*. In Ref. 104, for a simple 2D model system, we showed that nuclear motion can lead to quantitative and qualitative differences in spin-dependent transmission if a system lacks spatial inversion (e.g., chiral systems) and that spin polarization can be as large as ≈10% for parameters that are not too exaggerated relative to commonly accepted electronic-based models of CISS.[86,88] Although our simulations from Ref. 104 assumed an electronically closed systems with an odd number of electrons, the discussion in Sec. II B makes clear that the same effects can arise (and can even be magnified), provided that one has several degenerate electronic states (e.g., a singlet–triplet crossing). Moreover, recently we have demonstrated that spin polarization can arise even for very small spin–orbit coupling—provided that there is a conical intersection nearby to amplify the Berry force.[50] Finally, as will be discussed below in Sec. IV C, spin-polarization in the condensed phase should be enhanced when a system is out of equilibrium so that frictional forces do not damp away all Berry phase effects; indeed, for a typical CISS experiment, spin-polarization does increase dramatically far away from equilibrium (i.e., with high voltage).[68,69,72,78,99] Altogether, one must wonder: Is nuclear motion and the breakdown of Born–Oppenheimer perhaps the physical force underlying CISS (an idea which is now also being pursued independently by Fransson[105])?

IV. WHAT DOES THE FUTURE HOLD

A. New adiabatic approaches: Within or without the quantum classical Liouville equation

The QCLE is the natural starting point for deriving semiclassical theories of nonadiabatic dynamics. For a two-state model, e.g., for the $\mathbf{H}^{el}$ in Eq. (4), if we define A_{ij}^W to be the partial Wigner transform over the nuclear degrees of freedom, the QCLE reads as follows:

$$\frac{\partial}{\partial t}A_{11}^W(R,P,t) = \sum_\alpha \frac{2P^\alpha}{M^\alpha}\mathrm{Re}\big(A_{12}^W d_{21}^\alpha\big) - \sum_\alpha \frac{P^\alpha}{M^\alpha}\frac{\partial A_{11}^W}{\partial R^\alpha} - \sum_\alpha F_{11}^\alpha \frac{\partial A_{11}^W}{\partial P^\alpha} - \sum_\alpha \mathrm{Re}\left(\frac{\partial A_{12}^W}{\partial P^\alpha}F_{21}^\alpha\right) \tag{14}$$

and

$$\frac{\partial}{\partial t}A_{12}^W(R,P,t) = \frac{-i}{\hbar}(V_{11}-V_{22})A_{12}^W - \sum_\alpha \frac{P^\alpha}{M^\alpha}d_{12}^\alpha\big(A_{22}^W - A_{11}^W\big) - \sum_\alpha \frac{P^\alpha}{M^\alpha}\frac{\partial A_{12}^W}{\partial R^\alpha} - \sum_\alpha \frac{1}{2}\big(F_{11}^\alpha + F_{22}^\alpha\big)\frac{\partial A_{12}^W}{\partial P^\alpha} - \sum_\alpha \frac{1}{2}F_{12}^\alpha\left(\frac{\partial A_{11}^W}{\partial P^\alpha} + \frac{\partial A_{22}^W}{\partial P^\alpha}\right). \tag{15}$$

As shown by Kapral[106] and by us,[107] Tully's FSSH algorithm can be partly justified by comparison against the QCLE. Such a comparison clarifies how decoherence is missing from FSSH[27,28,108–121] and how FSSH can be generalized to simulate light-driven molecular dynamics.[122] Thus, in order to produce an accurate, practical, and generalized surface hopping approach, one would like to derive a series of appropriate quantum–classical approaches for complex-valued and/or degenerate Hamiltonians.

Now, there has been some progress made so far in this regard. In Ref. 123, we proved that the physics of the Berry force in Eq. (5) are contained in the QCLE. Such a conclusion was made by making the adiabatic approximation, whereby one solves for the coherence elements A_{12} by assuming that damping is much faster than any nuclear motion. This assumption leads to

$$A_{12}^W \equiv \frac{\sum_\alpha i\hbar \frac{P^\gamma}{M^\gamma}d_{12}^\gamma\big(A_{22}^W - A_{11}^W\big)}{V_{11}-V_{22}} + \sum_\alpha \frac{i\hbar}{2}d_{12}^\alpha\left(\frac{\partial A_{11}^W}{\partial P^\alpha} + \frac{\partial A_{22}^W}{\partial P^\alpha}\right). \tag{16}$$

Next, by plugging Eq. (16) into Eq. (14), one can derive adiabatic dynamics on surface 1 with a Berry force,

$$\frac{\partial}{\partial t}A_{11}^W(R,P,t) = -\sum_\alpha \frac{P^\alpha}{M^\alpha}\frac{\partial A_{11}^W}{\partial R^\alpha} - \sum_\alpha F_{11}^\alpha\frac{\partial A_{11}^W}{\partial P^\alpha} + \sum_{\alpha,\beta} 2\hbar\,\mathrm{Im}\left(d_{21}^\beta \frac{P^\alpha}{M^\alpha}d_{12}^\alpha\right)\frac{\partial A_{11}^W}{\partial P^\beta}, \tag{17}$$

where one recognizes [from Eq. (5)] $F_1^{mag,\beta} = \sum_\alpha 2\hbar \mathrm{Im}\Big(d_{21}^\beta \frac{P^\alpha}{M^\alpha}d_{12}^\alpha\Big)$. For additional details, see Ref. 123. Note that before Ref. 123, it was not at all obvious that the Berry force needs to arise from the QCLE. After all, given that the Berry force [in Eq. (5)] is proportional to $\hbar$, whereas the QCLE ignores all terms of order $\mathcal{O}(\hbar)$ and higher, it was not clear whether or not the physics of Berry force ($\mathbf{F}^{mag}$) are contained within the structure of the QCLE [and if not, one would require an altogether different dynamical starting point (beyond the QCLE)]. The fact that the physics underlying $\mathbf{F}^{mag}$ is already contained within the QCLE should give one hope of establishing a rigorous, generalized, and practical surface hopping algorithm.

Nevertheless, there is a caveat: the derivation of the Berry force within the QCLE[123] relies on implementing the adiabatic limit. The most important question still remains: Can one derive a meaningful surface hopping approach that includes the Berry force in the *nonadiabatic* limit, where there will be a balance between the Berry force and electronic transitions? Can we systematically derive a surface hopping algorithm to account for degeneracy starting from the QCLE?

B. A role for Ehrenfest dynamics

While this Perspective has largely assumed a surface hopping perspective of nonadiabatic dynamics, the reader should note that the QCLE can also be transformed into Ehrenfest dynamics if one maps electronic states to harmonic oscillators.[14] Traditionally, the disadvantage of Ehrenfest dynamics has been a lack of branching[18] and a lack of detailed balance.[24] That being said, much of this failure can be ameliorated by improved sampling and windowing[16,26] or enforced branching.[124] Moreover, we have found that Ehrenfest dynamics can account for Berry force in a mean-field sense for the two-state problem.[123]

Thus, one must ask: Is not Ehrenfest (rather than surface hopping) a better formalism for including Berry force? More specifically, one must ask: Is Berry force perhaps embedded in the zero point energy of the electronic degrees of freedom? Indeed, in unpublished results, we have shown that some elements of Berry force can be extracted from enhanced sampling of initial conditions; yet, as is always the case for the nonadiabatic problem, the devil is in the details and it is not yet known whether such an Ehrenfest-inspired approach can work in general. Thus, exploring Berry force with advanced nonadiabatic problems using Ehrenfest-like trajectories (e.g., SQC,[16] PLDM,[19,20] and forward-backward trajectories[125]) or trajectories that mix Ehrenfest with surface hopping[126] or spawning[127] dynamics represents another key path forward for future theoretical research.

C. The elephant in the room: Nuclear friction

Wavepacket dynamics in a few dimensions can be excellent for yielding intuition about isolated dynamics in the gas phase, but often these dynamics are not relevant in the condensed phase where friction drives the system to equilibrium and eliminates any initially prepared coherences between eigenstates. Moreover, according to Eq. (5) within a two state model, a Berry force is sometimes just an effective magnetic force, and magnetic field effects are usually small in the condensed phase. For instance, transition state theory

(TST) does not depend on the existence of a magnetic field;[41] any correction to TST based on a magnetic field would be a dynamical correction, e.g., Kramer's theory,[128,129] and these corrections tend to be modest. Note also that Fermi's golden rule (FGR) rate ($\Gamma = 2\pi|H|^2\rho$) is agnostic to the distinction between the Hamiltonian (H) and the conjugate of the Hamiltonian H^*; thus, at least with the FGR theory, the Berry force cannot affect a rate constant. Indeed, recent reviews of rate theories for ISC processes have not addressed Berry forces.[130–132] For all of these reasons, one must ask: In the condensed phase, will the dynamics described above (either ISC or more generally dynamics with degenerate states) survive in the condensed phase?

To that end, two points are worth noting. First, the Berry force acting on a nucleus can be much larger than a magnetic field acting on that same nucleus. To see this point, consider Eq. (5); the effective Berry magnetic field is proportional to the derivative coupling **d**, and so, for instance, the effective magnetic field will diverge near a conical intersection. In fact, we have recently shown that the magnetic field as caused by a conical intersection can be large enough to induce complete spin separation in the context of a vacuum calculation;[50] thus, one must wonder if such complete spin separation will have a significant signature in the condensed phase. One caveat is that unlike an external magnetic field, the Berry force is a built-in magnetic field whose direction rotates with the molecular frame, and thus, even though Berry forces might be extremely large, one can expect that experimentally confirming and isolating such Berry force effects will be difficult.

Second, it is also worth emphasizing that many molecular processes in the condensed phase do not proceed at equilibrium. For example, photochemical processes are driven dynamically for at least the first few hundred femtoseconds[133] after stimulation by a photon; the environment does not catch up or equilibrate in this time period. What is the effect of Berry force? As another example, when current runs through a molecule at finite voltage, that molecule will experience an explicitly nonequilibrium[134–136] environment, and there is no reason to believe that Berry forces (or any magnetic force) will be damped away. Note that in the context of the CISS experiments on DNA described above, spin-selectivity does increase as a function of voltage.[78] As discussed above, we believe this CISS effect may reflect underlying Berry forces.

Clearly, there are many open questions about the effect of Berry forces in the condensed phase, especially out of equilibrium, and these questions reflect the richness of this area of theoretical chemistry.

V. CONCLUSIONS

To date, there is no simple surface hopping algorithm for propagating noadiabatic dynamics in the presence of a complex-valued and/or degenerate electronic Hamiltonian, e.g., the Hamiltonian that describe spin dynamics. There is very little data so far regarding the performance of Ehrenfest-inspired algorithms or the exact factorization approaches[137,138] as far as treating Berry force. The lack of such an algorithm strongly limits our ability to develop intuition for such nonadiabatic transitions. Yet, given how many processes involve degenerate states (e.g., all ISC processes) and the fact that spin can be easily measured and spin-polarization seems to be emerging more often than not through CISS-like processes, finding improved computational nonadiabatic dynamics approaches would appear to be a top priority (or a "growth area") for young physical chemists. It is our hope that this Perspective will offer some light on and encourage new directions in this difficult but important new research direction.

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APPENDIX: THE CONNECTION BETWEEN A COMPLEX-VALUED HAMILTONIAN AND A DEGENERATE HAMILTONIAN

In Sec. II A above, we reviewed how standard FSSH fails for the case of a complex-valued two-state Hamiltonian. We argued that FSSH fails because (i) there is no well-defined derivative coupling direction for momentum rescaling and (ii) FSSH does not include a Berry force. More generally, however, one can argue that this failure can be traced to the failure of FSSH to treat degenerate problems.

To make such a connection, consider a two-state electronic problem with basis $|a\rangle, |b\rangle$ and a complex-valued electronic Hamiltonian, **A**. Let us now artificially introduce two more electronic states (which may be the time-reversed states $T|a\rangle, T|b\rangle$) that are completely uncoupled from the original two states such that the total Hamiltonian becomes

$$\mathbf{H} = \begin{pmatrix} \mathbf{A} & 0 \\ 0 & \mathbf{A}^* \end{pmatrix}. \tag{A1}$$

If one now changes basis with a transformation matrix

$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} \mathbf{I} & \mathbf{I} \\ i\mathbf{I} & -i\mathbf{I} \end{pmatrix}, \tag{A2}$$

the resulting Hamiltonian will be entirely real,

$$\tilde{\mathbf{H}} = \begin{pmatrix} \mathrm{Re}(\mathbf{A}) & -\mathrm{Im}(\mathbf{A}) \\ -\mathrm{Im}(\mathbf{A}) & \mathrm{Re}(\mathbf{A}) \end{pmatrix}. \tag{A3}$$

Clearly, if one could propagate the four state dynamics in $\tilde{\mathbf{H}}$, one could propagate the correct nonadiabatic dynamics in **A**. However, the matrices **H** and $\tilde{\mathbf{H}}$ are doubly degenerate. As a result, standard FSSH cannot successfully model the corresponding dynamics. Thus, the failure of surface hopping dynamics to treat complex-valued Hamiltonian can indeed be generalized to the failure of surface hopping to treat electronically degenerate Hamiltonians.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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