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ABSTRACT

Chemical relaxation phenomena, including photochemistry and electron transfer processes, form a vigorous area of research in which nonadiabatic dynamics plays a fundamental role. However, for electronic systems with spin degrees of freedom, there are few if any applicable and practical quasiclassical methods. Here, we show that for nonadiabatic dynamics with two electronic states and a complex-valued Hamiltonian that does not obey time-reversal symmetry (as relevant to many coupled nuclear-electronic-spin systems), the optimal semiclassical approach is to generalize Tully's surface hopping dynamics from coordinate space to phase space. In order to generate the relevant phase-space adiabatic surfaces, one isolates a proper set of diabats, applies a phase gauge transformation, and then diagonalizes the total Hamiltonian (which is now parameterized by both **R** and **P**). The resulting algorithm is simple and valid in both the adiabatic and nonadiabatic limits, incorporating all Berry curvature effects. Most importantly, the resulting algorithm allows for the study of semiclassical nonadiabatic dynamics in the presence of spin–orbit coupling and/or external magnetic fields. One expects many simulations to follow as far as modeling cutting-edge experiments with entangled nuclear, electronic, and spin degrees of freedom, e.g., experiments displaying chiral-induced spin selectivity.

I. INTRODUCTION

Coupled nuclear–electronic, nonadiabatic dynamics underlie critical aspects of many photochemical[1–5] and electron transfer processes.[6,7] The basic premise is that, when electronic transitions occur, energy must be provided or absorbed by the nuclei, and there are a host[3] of standard approaches for modeling such nonadiabatic energy conversion, including Ehrenfest dynamics,[8] quasi-classical mapping,[9–11] surface hopping,[12] multiple spawning,[13] and exact factorization.[14,15] Although not usually considered within the chemical physics community, nonadiabatic effects can also arise, which conserve energy within the context of molecular dynamics (i.e., nonadiabatic effects can arise, which bend nuclear trajectories without changing their kinetic energy). For instance, single surface on-diagonal Berry curvature effects can arise when there is an external magnetic field and the Hamiltonian is complex-valued.[16–20] In such a case, the nuclei experience a Lorentz-like force on their motion. In the adiabatic limit, this force is[17]

$$\mathbf{F}_n^B = i\hbar\dot{\mathbf{R}} \times (\nabla \times \mathbf{D}_{nn}^A), \tag{1}$$

where n is the adiabatic surface, $\dot{\mathbf{R}}$ is the nuclear velocity, and $\mathbf{D}_{nn}^A$ is the derivative coupling (also called Berry connection) on surface n. More generally, one can argue that nonadiabatic pseudo-magnetic field effects occur whenever there are degenerate or nearly degenerate electronic states coupled together, e.g., when one considers spin states coupled together with spin–orbit coupling (SOC).[21] These effects must be accounted for when modeling many cutting-edge spin-related chemical and physical reactions, including chiral induced spin selectivity (CISS)[22,23] or other magnetic chemical reactions.[24]

The simplest nonadiabatic model with spin–orbit coupling is an avoided crossing of two doublets. In a basis $\{|1\uparrow\rangle, |2\uparrow\rangle, |1\downarrow\rangle, |2\downarrow\rangle\}$ (1 and 2 labeling two diabatic states), the Hamiltonian reads[25,26]

$$H = \begin{bmatrix} E_1 & v + i\lambda_z & 0 & i\lambda_x + \lambda_y \\ v - i\lambda_z & E_2 & -i\lambda_x - \lambda_y & 0 \\ 0 & i\lambda_x - \lambda_y & E_1 & v - i\lambda_z \\ -i\lambda_x + \lambda_y & 0 & v + i\lambda_z & E_2 \end{bmatrix}, \tag{2}$$

where v is the diabatic coupling and $\lambda_x, \lambda_y, \lambda_z$ are the three SOC components. If one ignores λ_x and λ_y (the spin–flip terms), Hamiltonian (2) becomes a pair of 2×2 complex-valued blocks corresponding to spin up and down electrons. For molecular systems, the matrix elements are all functions of nuclear coordinates that give rise to complex-valued derivative couplings and the Berry curvature.

In order to better understand how nonadiabatic dynamics, the Berry curvature, and the presence of spins does or does not affect chemical dynamics, especially in *ab initio* calculations of real systems, it is essential to have cheap, inexpensive semi-classical algorithms. A proper algorithm must capture both the magnitude of a momentum change upon hopping (in the spirit of Tully's trajectory surface hopping[12]) and the pseudo-magnetic Berry force that rotates momentum (in the spirit of Berry's half-classical dynamics[17]); to date, there is no well established, reliable protocol. Previous attempts to study the 2×2 complex-valued Hamiltonians by incorporating the Berry curvature effect with Tully's fewest switch surface hopping (FSSH) have had some success[21,27–29] but inevitably failed when the nonadiabatic effects became strong enough.[27,29]

With these failures in mind, below we show that the solution is to run semiclassical phase-space surface hopping (PSSH) calculations in the spirit of (but not equivalent to) Ref. 30. According to PSSH, trajectories move on phase-space adiabatic surfaces $E(\mathbf{R}, \mathbf{P})$ that are functions of both nuclear position and momentum. For a two-state problem, the PSSH approach effectively transforms a complex-valued Hamiltonian into a real-valued Hamiltonian while achieving an accuracy well beyond previously published algorithms.[27,29] Finally and equally importantly, a PSSH approach is applicable for modeling dynamics in a magnetic field or under illumination by circularly polarized light.[31]

II. THEORY

A. Construction of the phase-space Hamiltonian

Consider a general two-state nonadiabatic Hamiltonian,

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \hat{h}_{\mathrm{el}}(\hat{\mathbf{R}}, \hat{\mathbf{r}}), \tag{3}$$

where $\hat{\mathbf{P}}$ and $\hat{\mathbf{R}}$ are the nuclear momentum and position operators, respectively, and $\hat{\mathbf{r}}$ represents the electronic degrees of freedom. A common situation is an avoided crossing. The typical topology of an avoided crossing is shown in Fig. 1(a): the two diabats cross each other, and the adiabats are repelled by the diabatic couplings. For this paper, we will focus on a very simple avoided crossing. We assume that (1) the pair of states cross only once and (2) there is a pair of "proper diabats" that coincides with the adiabats asymptotically, as shown in Fig. 1(a). Based on these two assumptions, we can write the electronic Hamiltonian in the proper diabatic basis $|\chi_0\rangle$ and $|\chi_1\rangle$ in the vicinity of the crossing as

$$\hat{h}_{\mathrm{el}} = \begin{bmatrix} h_0(\hat{\mathbf{R}}) & V(\hat{\mathbf{R}})e^{i\phi(\hat{\mathbf{R}})} \\ V(\hat{\mathbf{R}})e^{-i\phi(\hat{\mathbf{R}})} & h_1(\hat{\mathbf{R}}) \end{bmatrix}, \tag{4}$$

where the proper diabatization requires $|V| \ll |h_0 - h_1|$ outside the crossing seam. Physically, this Hamiltonian can be mapped to a single 2×2 spin block in the doublet–doublet crossing Hamiltonian (2); by ignoring all spin-flips, we effectively choose a model that does not obey time reversal symmetry.

Within the usual Born–Oppenheimer picture, one rotates the Hamiltonian (3) to the adiabatic basis, where the nuclear motion is coupled to electronic amplitudes via the derivative coupling terms.[32]

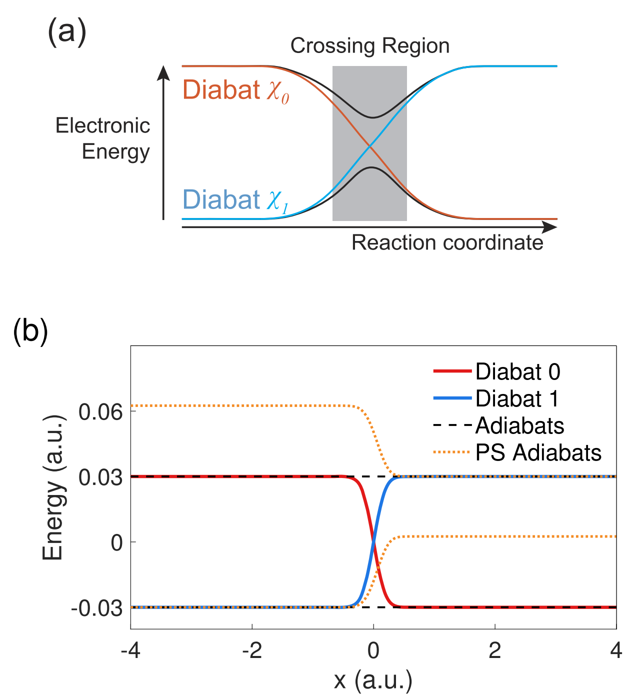

FIG. 1. (a) A schematic depiction of a curve crossing, where χ_0 and χ_1 are two proper diabats. (b) The diabatic and (position-space) adiabatic surfaces of our test model [see Eq. (14)] as well as typical phase-space adiabatic surfaces (shifted by $-P^2/2M$) as functions of nuclear coordinate x. Note that the position-space adiabats are flat, while the phase-space adiabats have a barrier, a distinct signature of complex-valued Hamiltonians. The parameters used to plot the phase-space adiabats are $W = -5$, $P_y = 8$, and $\chi_{\mathrm{init}} = \chi_0$.

However, here we will make a different choice: we will represent Hamiltonian (3) in a pseudo-diabatic basis $|\xi_0\rangle = |\chi_0\rangle, |\xi_1\rangle = e^{-i\phi}|\chi_1\rangle$ where we assign phases but not rotations to a set of diabats. The result is a pseudo Born–Oppenheimer Hamiltonian,

$$\hat{H}_{\rm PD} = \frac{(\hat{\mathbf{P}} - i\hbar\hat{\mathbf{D}})^2}{2M} + \begin{bmatrix} h_0(\hat{\mathbf{R}}) & V(\hat{\mathbf{R}}) \\ V(\hat{\mathbf{R}}) & h_1(\hat{\mathbf{R}}) \end{bmatrix}, \tag{5}$$

where $\hat{\mathbf{D}} = -i\nabla\phi|\xi_1\rangle\langle\xi_1|$ is the derivative coupling in this pseudo-diabatic basis. Note here that $i\hat{\mathbf{D}}$, h_0, h_1, and V are all real-valued; by performing a pseudo-diabatic transformation, we have turned the complex-valued Hamiltonian (3) into a real-valued Hamiltonian (5), which will enable us to use simple (or simpler) semiclassical approaches for modeling. For a deeper discussion of the choice pseudo-diabats in the two-state system, see the supplementary material. Note also that, while this choice of phase is straightforward for the two-state case, such a phase convention is impractical for a general multistate dense Hamiltonian; future work will necessarily need to address the case of many states all crossing together.

To implement semiclassical (surface-hopping) dynamics, we first replace the nuclear operators in Hamiltonian (5) by their classical counterparts (in the spirit of a Wigner transformation[33,34]),

$$H_{\rm PD}(\mathbf{R},\mathbf{P}) = \frac{(\mathbf{P} - i\hbar\mathbf{D}(\mathbf{R}))^2}{2M} + \begin{bmatrix} h_0(\mathbf{R}) & V(\mathbf{R}) \\ V(\mathbf{R}) & h_1(\mathbf{R}) \end{bmatrix}. \tag{6}$$

Second, after diagonalizing Hamiltonian (6), we arrive at a basis depending on both position $\mathbf{R}$ and momentum $\mathbf{P}$,

$$H_{\rm PD}(\mathbf{R},\mathbf{P})|\psi_j(\mathbf{R},\mathbf{P})\rangle = E_j(\mathbf{R},\mathbf{P})|\psi_j(\mathbf{R},\mathbf{P})\rangle. \tag{7}$$

We will call the resulting eigenvalues and eigenvectors "phase-space adiabats."

In some sense, this new basis mimics what Berry has labeled "superadiabats,"[35,36] i.e., the basis recovered by first diagonalizing the electronic Hamiltonian $h_{\rm el}(\mathbf{R})$ and then second re-diagonalizing the sum of adiabatic electronic energies $E_A(\mathbf{R})$, the kinetic term and the relevant derivative couplings $\mathbf{D}_A$,[30,35–37]

$$H_{\rm super}(\mathbf{R},\mathbf{P}) = \frac{(\mathbf{P} - i\hbar\mathbf{D}_A(\mathbf{R}))^2}{2M} + \begin{bmatrix} E_0^A(\mathbf{R}) & 0 \\ 0 & E_1^A(\mathbf{R}) \end{bmatrix}. \tag{8}$$

Interestingly, Shenvi proposed phase-space surface-hopping dynamics more than ten years ago (for real-valued Hamiltonians) and the idea has some clear benefits (and a few problems).[30,38] That being said, we must be clear that the present basis $\{|\psi\rangle\}$ defined in Eq. (7) is not exactly the same as the superadiabatic basis: In Shenvi's approach, the superadiabats are obtained from diagonalizing the Born–Oppenheimer adiabatic Hamiltonian (which includes derivative couplings) in Eq. (8), while in our present approach the phase-space adiabats are obtained from diagonalizing the pseudo-diabatic Hamiltonian (6). In fact, for a real-valued Hamiltonian where $\phi \equiv 0$, our pseudo-diabatic basis will always give $\mathbf{D} \equiv 0$ and the basis set $\{|\psi\rangle\}$ is identical to the usual position-space adiabats, while according to Shenvi's approach, the tensor $\mathbf{D}_A$ is not zero—even for real-valued Hamiltonians. Thus, though certainly related, for clarity, one should not confuse the concept of a superadiabat and the concept of a phase-space adiabat; one must also distinguish between Shenvi's adiabatic PSSH algorithm and the present pseudo-diabatic PSSH algorithm. More discussion can be found below.

B. Phase-space surface hopping

Following Shenvi[30] in spirit, we now propose to propagate the semiclassical dynamics by moving nuclei along phase-space eigenvalues and then allowing for surface hops. At the beginning of the simulation, we initialize a swarm of trajectories, each associated with an electronic amplitude vector $\mathbf{c}$ and an active phase-space adiabatic label n. Note that the phase-space momentum $\mathbf{P}$ is different from the kinetic momentum $\mathbf{P}_{\rm kinetic} = M\dot{\mathbf{R}}$, in general, and should be transformed according to

$$\mathbf{P}_n = \mathbf{P}_{\rm kinetic} + i\hbar\langle\psi_n|\mathbf{D}|\psi_n\rangle \tag{9}$$

before the simulation begins.

At each time step of the simulation, we construct Hamiltonian (6) and diagonalize it according to Eq. (7) for each trajectory. The trajectory's equation of motion is then given by

$$\dot{\mathbf{R}} = \nabla_P E_n, \tag{10}$$

$$\dot{\mathbf{P}} = -\nabla_R E_n, \tag{11}$$

$$\dot{c}_j = -\frac{i}{\hbar}E_j c_j - \mathbf{d}_{jk}^R\cdot\dot{\mathbf{R}}c_k - \mathbf{d}_{jk}^P\cdot\dot{\mathbf{P}}c_k, \tag{12}$$

where $\mathbf{d}_{jk}^R = \langle\psi_j|\nabla_R\psi_k\rangle$ and $\mathbf{d}_{jk}^P = \langle\psi_j|\nabla_P\psi_k\rangle$ are the phase-space analogs of the derivative couplings. Note that the dynamics above conserve the energy of the relevant phase-space adiabat, i.e., $dE_n/dt = 0$ along any given trajectory. Historically, Eqs. (10) and (11) have been known as the eikonal method[39] and have been applied previously in modeling certain flavors of semiclassical nonadiabatic dynamics.[37,40]

Similar to FSSH, within PSSH, trajectories are allowed to change their active phase-space adiabatic label or "hop" between phase-space adiabats at each step. The hopping probability from surface k to j is computed according to Tully's method,[12,30]

$$\begin{aligned} g_{k\to j} &= \frac{\dot{\rho}_{jj}\Delta t}{\rho_{kk}} \\ &= \frac{2\Delta t}{\hbar}\mathrm{Im}\left\{\frac{c_j^*}{c_k^*}\left(-i\hbar\mathbf{d}_{jk}^R\cdot\dot{\mathbf{R}} - i\hbar\mathbf{d}_{jk}^P\cdot\dot{\mathbf{P}}\right)\right\}. \end{aligned} \tag{13}$$

From the perspective of a Monte Carlo process, Eq. (13) is the hopping rate that is necessary to maintain consistency between ρ_{jj} and the number of trajectories moving along surface j.[41,42] Whenever a hop from $j\to k$ succeeds, we rescale the momentum along the direction of $\mathbf{d}_{jk}^R$ (which is real-valued by construction) to conserve energy. If such momentum cannot be found, the hop is frustrated and the trajectory keeps moving along the original surface. Note that, as with the usual FSSH algorithm, frustrated hops are necessary to maintain detailed balance.

Finally, to capture the decoherence of a reflected wavepacket, we further employ the most naive decoherence algorithm possible, similar to what was published in Ref. 29, i.e., we collapse the amplitudes by setting $c_j \to \delta_{nj}$ if we find $(\mathbf{P}\cdot\mathbf{d}^R_{nj})(\mathbf{P}_{t=0}\cdot\mathbf{d}^R_{nj}) < 0$. Here, n is the active surface. We will say more about decoherence in Sec. IV.

III. COMPUTATIONAL RESULTS

To test the performance of our algorithm, we study the simplest (standard) two-state $\{|\chi_0\rangle, |\chi_1\rangle\}$ electronic Hamiltonian associated with two nuclear degrees of freedom, x and y,

$$h_{\mathrm{el}}(x,y) = A\begin{bmatrix} -\cos\theta & e^{iWy}\sin\theta \\ e^{-iWy}\sin\theta & \cos\theta \end{bmatrix}, \tag{14}$$

where $\theta = \frac{\pi}{2}(\mathrm{erf}(Bx)+1)$, $A = 0.03$, $B = 3$, and $W = \pm 5$. All the above-mentioned parameters are in atomic units. The diabatic and (position-space) adiabatic surfaces as well as typical phase-space adiabatic surfaces are shown in Fig. 1(b). Note that the position-space adiabats are completely flat, but the phase-space adiabats are typically not. The initial wavefunction is chosen as a Gaussian,

$$\Psi_0(\mathbf{R}) = e^{-(\mathbf{R}-\mathbf{R}_0)^2/\sigma^2 + i\mathbf{P}_0\cdot\mathbf{R}}|\chi_{\mathrm{init}}\rangle, \tag{15}$$

where $\sigma = 1$, $\mathbf{R}_0 = (-3,-3)$, $\mathbf{P}_0 = (P_{\mathrm{init}}, P_{\mathrm{init}})$, and χ_{init} is either the diabat 0 or 1. To make sure that the kinetic momentum is equal to the phase-space momentum at $t = 0$, in our calculation, the pseudo-diabats $\{|\xi_0\rangle, |\xi_1\rangle\}$ are chosen according to the initial diabat: If $\chi_{\mathrm{init}} = \chi_0$, then $|\xi_0\rangle = |\chi_0\rangle$ and $|\xi_1\rangle = |\chi_1\rangle e^{-iWy}$; otherwise, $|\xi_1\rangle = |\chi_1\rangle$ and $|\xi_0\rangle = |\chi_0\rangle e^{iWy}$. The exact quantum mechanics is performed using a split-operator method[43] with a 768×768 grid inside a 48×48 box and a timestep of 0.05 a.u. For this problem, the phase-space adiabats and diabats are equivalent as $x \to \pm\infty$, and, therefore, we can expect the outgoing wavepackets to have an asymptotic momentum shift depending on the initial and the final pseudo-diabatic states. For example, suppose a wavepacket is incoming along $|\chi_0\rangle$, and without loss of generality, we choose $|\xi_0\rangle = |\chi_0\rangle$ and $|\xi_1\rangle = |\chi_1\rangle e^{-iWy}$. In such a case, we would expect a $-\hbar W\hat{y}$ kinetic momentum shift for the wavepacket that ends up on the $|\chi_1\rangle$ surface, given the definition in Eq. (9) and the fact that $\dot{P}_y = 0$ [according to Eq. (11)]; for more discussion, see the supplementary material.

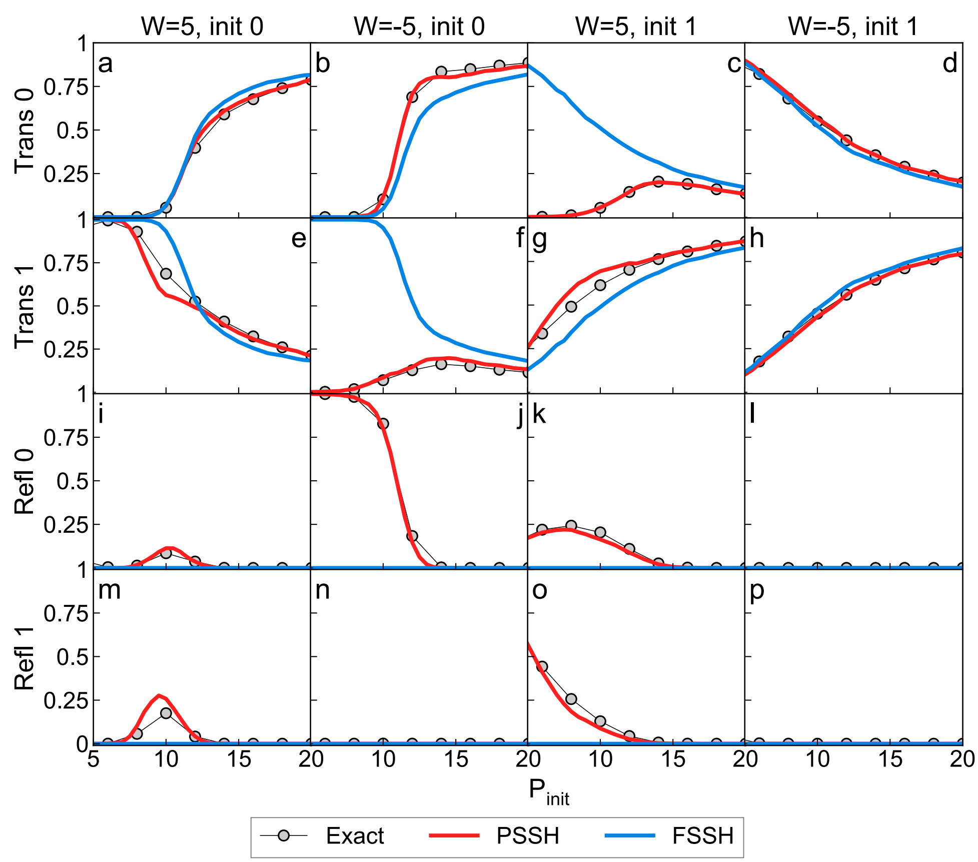

FIG. 2. State-to-state transmitted and reflected probabilities according to an exact wavepacket simulation and pseudo-diabatic PSSH and FSSH approaches for our test system [Eq. (14)]. We have tested four conditions: $W = 5$ and initial diabat $\chi_{\mathrm{init}} = 0$ [(a), (e), (i), and (m)]; $W = -5, \chi_{\mathrm{init}} = 0$ [(b), (f), (j), and (n)]; $W = 5, \chi_{\mathrm{init}} = 1$ [(c), (g), (k), and (o)]; and $W = -5, \chi_{\mathrm{init}} = 1$ [(d), (h), (l), and (p)]. Note that reflections are prevalent at a low incoming momentum, which is a signature of Berry curvature effects. The pseudo-diabatic PSSH results agree reasonably well with the exact simulations, while FSSH results deviate significantly for reflection. The parameters are $A = 0.03, B = 3$, and $M = 1000$.

The surface hopping simulations were performed with 10^4 trajectories with a timestep of 0.05 a.u. for each data point. The initial positions and momenta for surface hopping simulations are sampled according to the Wigner distribution of $\Psi_0(\mathbf{R})$. At each point in time, the phases of the phase-space adiabatic basis can be trivially chosen according to the "parallel transport" condition [i.e., $\langle \phi_j(t)|\phi_j(t+dt)\rangle \approx 1$ for all js]. Since the diabats and phase-space adiabats are equivalent outside the crossing, the diabatic population can be computed by counting trajectories on each phase-space surface adiabat.

In Fig. 2, we compare the transmitted and reflected populations on the different surfaces according to exact wavepacket simulations, Tully's FSSH approach,[12] and our current pseudo-diabatic PSSH simulations. We find that in many systems, a considerable fraction of the population will be reflected when the momentum is relatively low (e.g., $P_{\text{init}} < 12$). If one assumes that trajectories follow position-space adiabatic surfaces, such reflection must be a characteristic of a Berry curvature effect; after all, the adiabatic forces here are completely flat. From the phase-space point of view, however, the reflection clearly arises from the barrier present in the phase-space adiabatic surfaces; see Fig. 1(b). Moreover, according to Fig. 2, when $W = 5$ and one begins on the upper diabat, the reflected population is distributed over both diabats 0 and 1, indicating that there can be no clean separation of nonadiabatic dynamics into energy conserving and energy non-conserving effects. While the pseudo-diabatic PSSH approach can capture most of the exact results qualitatively (and often quantitatively), Tully's FSSH algorithm has large errors. For more benchmarking results and a further discussion of the phase-space adiabatic surfaces, see the supplementary material.

IV. DISCUSSION AND PERSPECTIVE

The present results with pseudo-diabatic PSSH have demonstrated a surprising degree of accuracy by successfully incorporating both nonadiabatic effects and Berry curvature effects. However, interestingly, the entire concept of Berry force has been replaced: we no longer apply a pseudo-magnetic field to motion along an adiabat, but rather use the relevant Hamiltonian dynamics as applicable to a magnetic field. Thus, one must presume that the present approach would be optimal for running surface hopping in an external magnetic field as well. By using phase-space adiabatic surface hopping, it would appear that one can capture very new physics (all while reducing to normal FSSH when a 2×2 Hamiltonian is real-valued). In this same spirit, other semiclassical approaches, e.g., multiple spawning, might also benefit by employing a pseudo-diabatic representation and running along phase-space adiabats whenever one encounters complex-valued Hamiltonians. More generally, we are confident that the pseudo-diabatic PSSH algorithm proposed here (or some version thereof) is the optimal framework for semiclassical simulation of large, complicated nonadiabatic systems where electronic spin effects are important.

Now, in making the claim above, our confidence is based on several factors. First, over the past few years, our research group investigated many different FSSH algorithms (incorporating Berry curvature effects) within a host of two-dimensional models.[29] We found that for many problems, if one chooses the right rescaling approach, FSSH can yield good results; however, the final algorithm[29] always felt overly complicated. By contrast, the present PSSH algorithm is simple to understand and implement. Second, the algorithm in Ref. 29 fails when the diabatic coupling is very small; in such a case, the Berry force is not important and should not play a role in FSSH; the present PSSH algorithm does not fail in this limit; see Fig. S4 in the supplementary material. Third, the algorithm in Ref. 29 also fails when W gets large (even though one might presume that the Berry force grows larger and larger). This failure is completely corrected by the present PSSH approach; see Fig. S5 in the supplementary material. In short, the PSSH *ansatz* appears to be the optimal approach moving forward; in the future, it might be best to refer not to Berry forces *per se* but rather to nonadiabatic dynamics in phase space.

Looking forward, our initial success here would appear to be only the first step in a long road toward running on-the-fly nonadiabatic dynamics with nuclei, electrons, and spin. There are many obstacles that must be addressed and/or overcome. Here, we will list a few (though the list is not exhaustive). First, the success of our algorithm relies on the premise that there is an intrinsic diabatic basis to dress [as in Eq. (4)].[44] How should we select such an optimal basis in practice? For an idealized, well-defined avoided crossing problem as in Fig. 1(a), one can guess the correct proper diabats almost intuitively. However, for systems with a complicated topology, e.g., a conical intersection or a crossing between a singlet and a set of triplets,[45] picking the correct diabats would appear much more difficult. Semiclassical dynamics can be very sensitive to the choice of a diabatic basis, and a systematic understanding of the impact of diabatization (as well as practical algorithms for choosing diabats) is essential.

At this point, it is worthwhile to compare and contrast our approach with Shenvi's adiabatic PSSH algorithm.[30] As mentioned above, formally, the two algorithms have the same equation of motion, but they correspond to different definitions of the phase-space adiabats. This difference in definition arises because the two algorithms were designed for distinct goals: in his construction of PSSH, Shenvi's goal was to minimize the number of hops within a surface hopping framework; within our PSSH address, our goal was to address the possibility of degenerate electronic states (as present, e.g., with spin degrees of freedom). While Shenvi's algorithm has so far not been applied previously to complex-valued Hamiltonians,[46] if one were to make such an attempt, one would necessarily need to choose a gauge for the adiabats (before diagonalizing into a superadiabatic basis). In other words, our present need for a good diabatic basis would correspond to the need for a good gauge within Shenvi's adiabatic PSSH algorithm. There is no free lunch, but future work will need to run many simulations to make sure we find the most stable approximations.[47]

Second, the question of decoherence must be addressed and benchmarked. Within standard FSSH, decoherence appears to be very complicated for complex electronic Hamiltonians. After all, different Berry forces would appear to lead to wave packet separation in the vicinity of an avoided crossing[29]—whereas, in the context of real-valued Hamiltonians, decoherence arises only *after* wavepackets leave the vicinity of a crossing.[48–51] Within PSSH, however, it would appear that this distinction is removed and decoherence again is simple—wavepackets separate only after the packets leave the crossing region now as driven by a difference in adiabatic *phase-space eigenforces*. This hypothesis must be checked in the future.

In the future, we will also need to address the question of velocity reversal, which is known to be important for many simulations with frustrated hops;[48,52,53] see Fig. S3 in the supplementary material for some preliminary data. Thus far, our test cases indicate that momentum reversal and decoherence problems must be treated correctly for more complicated systems, e.g., systems with a bounded potential energy surface; see Fig. S3 in the supplementary material for some preliminary data about decoherence and momentum reversal.

Third, for systems with more than two states and couplings between each pair of diabats, the construction of pseudo-diabats may be impossible if we insist on (i) a one-to-one mapping between pseudo-diabats to diabats and (ii) a strictly real-valued the electronic Hamiltonian. For example, consider the following diabatic electronic Hamiltonian:

$$h_{\text{el}} = \begin{bmatrix} h_1 & V_1 e^{i\phi_1} & V_2 e^{i\phi_2} \\ V_1 e^{-i\phi_1} & h_2 & V_3 e^{i\phi_3} \\ V_2 e^{-i\phi_2} & V_3 e^{-i\phi_3} & h_3 \end{bmatrix}. \tag{16}$$

If $\phi_1, \phi_2,$ and ϕ_3 are not related to each other, there is no choice of simple pseudo-diabats for making h_{el} real-valued. In such a case, one will either need to accept a complex-valued pseudo-diabatic Hamiltonian or apply a more general "pre-conditioning" diabatization. Future research is clearly required on this front.

Finally, it is known that the surface hopping algorithm can be derived roughly from the mixed quantum-classical Liouville equation (QCLE)[33,54,55] if one makes some very strong approximations—e.g., the single-trajectory approximation, etc. In this paper, upon hopping, we have followed the standard procedure[12,33] and conserved energy by rescaling momentum. Nevertheless, according to Eq. (13), one might presume that the more rigorous framework is to rescale both position and momentum[56] upon hopping.[57] In the future, one will necessarily need to investigate the formal foundations of phase-space surface hopping (starting with the QCLE) and systematically analyze the rescaling approach. Ideally, one would also like to connect with multicomponent WKB theories as well.[58,59]

V. CONCLUSION

In summary, we have proposed a pseudo-diabatic phase-space surface hopping (PSSH) algorithm for propagating nonadiabatic dynamics for complex-valued avoided crossing problems. The approach is simple and intuitive, captures all Berry curvature effects (without directly applying a pseudo-magnetic field), and should be applicable for a wide-range of systems with coupled nuclear, electronic, and spin degrees of freedom. In short, by performing a basis transformation and generalizing Tully's algorithm to phase-space to treat complex-valued systems, we find results that far exceed what is possible from any existing standard (surface hopping/mean-field) semiclassical approach. Looking forward, we are very hopeful that this algorithm can be applied to larger, *ab initio* systems with spin-related phenomena, including chemical reactions displaying magnetic field effects[24] and chiral induced spin separated dynamics.[22]

SUPPLEMENTARY MATERIAL

See the supplementary material for a discussion about the choice of pseudo-diabats, an analysis of the phase-space adiabatic surfaces, and a benchmark of different surface hopping schemes.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yanze Wu: Data curation (lead); Investigation (lead); Writing – original draft (lead). **Xuezhi Bian:** Investigation (supporting). **Jonathan I. Rawlinson:** Conceptualization (supporting). **Robert G. Littlejohn:** Conceptualization (supporting). **Joseph E. Subotnik:** Supervision (lead); Writing – review and editing (lead).

DATA AVAILABILITY

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

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