A Phase-Space Semiclassical Approach for Modeling Nonadiabatic Nuclear Dynamics with Electronic Spin

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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 $\mathbf{R}$ and $\mathbf{P}$). 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 and electron transfer processes. The basic premise is that, when electronic transitions occur, energy must be provided or absorbed by the nuclei, and there are a host of standard approaches for modeling such nonadiabatic energy conversion, including Ehrenfest dynamics, quasi-classical mapping, and exact factorization. Although not usually considered within the chemical physics community, nonadiabatic effects can also arise that conserve energy within the context of molecular dynamics; i.e., nonadiabatic effects can arise that 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. In such a case, the nuclei experience a Lorentz-like force on their motion. In the adiabatic limit, this force is given by

$$F_n^A = i\hbar \mathbf{R} \times (\nabla \times \mathbf{D}_n^{A})$$

where $n$ is the adiabatic surface, $\mathbf{R}$ is the nuclear velocity and $\mathbf{D}_n^{A}$ 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. These effects must be accounted for when modeling many cutting-edge spin-related chemical and physical reactions, including chiral induced spin selectivity (CISS), or other magnetic chemical reactions.

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 being the two doublet labels), the Hamiltonian reads:

$$H = \begin{pmatrix}
E_1 & v + i\lambda_x & 0 & i\lambda_z + \lambda_y \\
v - i\lambda_z & E_2 & -i\lambda_z - \lambda_y & 0 \\
0 & i\lambda_z - \lambda_y & E_1 & v - i\lambda_z \\
-i\lambda_z + \lambda_y & 0 & v + i\lambda_z & E_2
\end{pmatrix}$$

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

In order to better understand how nonadiabatic dynamics, 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 semiclassical algorithms. A proper algorithm must capture both the magnitude of a momentum change upon hopping (in the spirit of Tully’s trajectory surface hopping) and the pseudo-magnetic Berry force that rotates momentum (in the spirit of Berry’s half-classical dynamics); to date, there is no well established, reliable protocol. Previous attempts to study the $2 \times 2$ complex-valued Hamiltonians by incorporating the Berry curvature effect with Tully’s fewest switch surface hopping (FSSH) have had some success, but inevitably failed when the nonadiabatic effects became strong enough.

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. Ac-
where we assign phases but out- 
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). (7) 

\hat{h}_\psi = \left[ \begin{array}{cc} h_0(\hat{R}) & V(\hat{R}) e^{i\phi(\hat{R})} \\ V(\hat{R}) e^{-i\phi(\hat{R})} & h_1(\hat{R}) \end{array} \right] 

(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 \times 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. However, here we will make a different choice: we will represent Hamiltonian (3) in a pseudo-diabatic basis \(|\chi_0\rangle, |\chi_1\rangle, e^{-i\phi} |\chi_1\rangle\) where we assign phases but no rotations to a set of diabats. The result is a pseudo Born-Oppenheimer Hamiltonian:

\begin{equation}
\hat{H}_{PD} = \left( \frac{\hat{P}^2}{2M} \right) + \left[ \begin{array}{cc} h_0(\hat{R}) & V(\hat{R}) \\ V(\hat{R}) & h_1(\hat{R}) \end{array} \right]
\end{equation}

(5)

where \(\hat{D} = -i\nabla \phi \langle |\chi_1\rangle \hat{D} \langle |\chi_1\rangle\) is the derivative coupling in this pseudo-diabatic basis. Note here that \(i\hat{D}, h_0, h_1, V\) 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 SM. 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):

\begin{equation}
H_{PD}(\mathbf{R}, \mathbf{P}) = \left( \frac{\mathbf{P}^2}{2M} \right) + \left[ \begin{array}{cc} h_0(\mathbf{R}) & V(\mathbf{R}) \\ V(\mathbf{R}) & h_1(\mathbf{R}) \end{array} \right]
\end{equation}

(6)

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

\begin{equation}
H_{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
\end{equation}

(7)

We will call the resulting eigenvalues and eigenvectors “phase-space diabats.”

In some sense, this new basis mimics what Berry has labeled “superadiabats”, i.e. the basis recovered by first diagonalizing the electronic Hamiltonian \(h_\psi(\mathbf{R})\) and then second re-diagonalizing the sum of adiabatic electronic energies.
$E_A(R)$, the kinetic term and the relevant derivative couplings $D_A$:

$$H_{\text{super}}(R, P) = \frac{(P - i\hbar D_A(R))^2}{2M} + \begin{bmatrix} E_0^A(R) & 0 \\ 0 & E_1^A(R) \end{bmatrix}$$  \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). That being said, we must be clear that the basis set is identical to the usual position-space adiabats, while according to Shenvi’s approach, the tensor $D_A$ is not even 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\textsuperscript{[10]} 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 $c$ and an active phase-space adiabatic label $n$. Note that the phase-space momentum $P$ is different from the kinetic momentum $P_{\text{kinetic}} = MR$ in general, and should be transformed according to

$$P_n = P_{\text{kinetic}} + i\hbar \langle \psi_n | D | \psi_n \rangle$$  \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

$$\dot{R} = \nabla_P E_n$$
$$\dot{P} = -\nabla_R E_n$$

$$\dot{c}_j = -\frac{i}{\hbar} E_j c_j - d_{jk} P \cdot \dot{R} c_k - d_{jk} P \cdot \dot{P} c_k$$  \tag{12}

where $d_{jk} = \langle \psi_j | \nabla_R | \psi_k \rangle$ and $d_{jk} = \langle \psi_j | \nabla_P | \psi_k \rangle$ 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, Eq. (10) and (11) have been known as the eikonal method\textsuperscript{[39]} and have been applied previously in modeling certain flavors of semiclassical nonadiabatic dynamics.\textsuperscript{[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:\textsuperscript{[12, 30]}

$$g_{k \rightarrow j} = \frac{\rho_{kj} \Delta t}{\rho_{kk}}$$
$$= \frac{\Delta t}{\hbar} \text{Im} \left\{ \frac{c_j^*}{c_k} \left( -i \hbar \frac{d_{jk}^R \cdot \dot{R} - i \hbar \frac{d_{jk}^P \cdot \dot{P}}{P} \right) \right\}$$  \tag{13}

From the perspective of a Monte Carlo process, Eq. (13) is the hopping rate that is necessary to maintain consistency between $\rho_{ij}$ and the number of trajectories moving along surface $j$.\textsuperscript{[41, 42]}

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.\textsuperscript{[29]}, i.e. we collapse the amplitudes by setting $c_j \rightarrow \delta_{nj}$ if we find $(P \cdot d_{nj}^R)(P_{t=0} \cdot d_{nj}^R) < 0$. Here, $n$ is the active surface. We will say more about decoherence below in the discussion section.

### III. COMPUTATIONAL RESULTS

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

$$\hbar \omega(x, y) = A \begin{bmatrix} -\cos \theta & e^{iW y} \sin \theta \\ -e^{-iW y} \sin \theta & \cos \theta \end{bmatrix}$$  \tag{14}

where $\theta = \frac{\pi}{2} (\text{erf}(Bx) + 1)$, $A = 0.03$, $B = 3$ and $W = \pm 5$. All parameters above are in atomic units. The diabatic, (position-space) adiabatic surfaces and typical phase-space adiabatic surfaces are shown in Fig. 1b. 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:

$$\Psi_0(R) = e^{-(R-R_0)^2/\sigma^2 + i P_0 \cdot R} | \chi_{\text{init}} \rangle$$  \tag{15}

where $\sigma = 1$, $R_0 = (-3, -3)$, $P_0 = (P_{\text{init}}, P_{\text{init}})$, and $\chi_{\text{init}}$ 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 $\{\xi_0, \xi_1\}$ are chosen according to the initial diabat: If $\chi_{\text{init}} = \chi_0$, then $|\xi_0\rangle = |\chi_0\rangle$ and $|\xi_1\rangle = |\chi_1\rangle e^{-i W y}$, otherwise $|\xi_1\rangle = |\chi_1\rangle$ and $|\xi_0\rangle = |\chi_0\rangle e^{i W y}$. The exact quantum mechanics is performed using a split-operator method\textsuperscript{[43]} with a 768 $\times$ 768 grid.
inside a 48 × 48 box and a timestep of 0.05 au. For this problem, the phase-space adiabats and diabats are equivalent as $x \rightarrow \pm \infty$, 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 $|\xi_1\rangle = |\chi_1\rangle e^{-iW_y}$. In such a case, we would expect a $-\hbar W_y$ 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 $\tilde{P}_y = 0$ (according to Eq. (11)). For more discussions, see the SM.

The surface hopping simulations were performed with $10^4$ trajectories with a timestep of 0.05 au for each data point. The initial positions and momenta for surface hopping simulations are sampled according to the Wigner distribution of $\Psi_0(R)$. 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 $j$’s). 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 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 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. 1b. 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 SM.

![FIG. 2: State-to-state transmitted and reflected probabilities according to an exact wavepacket simulation, pseudo-diabatic PSSH and FSSH for our test system (Eq. (14)). We have tested four conditions: $W = 5$ and initial diabat $\chi_{\text{init}} = 0$ (subfig (a),(c),(l),(m)), $W = -5, \chi_{\text{init}} = 0$ (subfig (b),(f),(j),(n)), $W = 5, \chi_{\text{init}} = 1$ (subfig (c),(g),(k),(o)) and $W = -5, \chi_{\text{init}} = 1$ (subfig (d),(h),(j),(p)). Note that reflections are prevalent at 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. Parameters are: $A = 0.03, B = 3, M = 1000$.](image-url)
vature effects. And yet, interestingly, the entire concept of Berry force has been replaced: we no longer apply a pseudomagnetic field to motion along an adiabat, but rather use the relevant Hamiltonian dynamics as applicable to a magnetic field. Thus, one must assume 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 has worked investigate many different FSSH algorithms (incorporating Berry curvature effects) within a host of two-dimensional models Ref. 29. We found that for many problems, if one chooses the right rescaling approach, FSSH can yield good results; however, the final algorithm always felt overly complicated. By contrast, the present PSSH algorithm is simple to understand and to 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 SM. 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 SM. 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 towards 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)). How should we select such an optimal basis in practice? For an idealized, well-defined avoided crossing problem as in Fig. 1a, 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, 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. 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, if one were to make such an attempt, one would necessarily need to choose a gauge for the diabats (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.

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 – whereas, in the context of real-valued Hamiltonians, decoherence arises only after wavepackets leave the vicinity of a crossing. With 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. 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 electronic Hamiltonian. For example, consider the following diabatic electronic Hamiltonian:

\[
\hat{h}_\text{el} = \begin{bmatrix}
1 & V_1 e^{i\phi_1} & V_2 e^{i\phi_2} \\
V_1 e^{-i\phi_1} & h_2 & V_3 e^{i\phi_3} \\
V_2 e^{-i\phi_2} & V_3 e^{-i\phi_3} & h_3
\end{bmatrix}
\]

If \(\phi_1, \phi_2, \phi_3\) are not related to each other, there is no choice of simple pseudo-diabats for making \(\hat{h}_\text{el}\) 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.

Fourth and finally, it is known that the surface hopping algorithm can be derived roughly from the mixed quantum-classical Liouville equation (QCLE) if one makes some very strong approximations – e.g. the single-trajectory approximation, etc. In this paper, upon hopping we have followed...
standard procedure 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 upon hopping. 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.

V. CONCLUSION

In summary, we have proposed a pseudo-diabatic phase-space surface hopping (PSSH) 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 and chiral induced spin separated dynamics.

SUPPLEMENTARY MATERIAL

See 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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citation text

34. Note that the Wigner transform of an operator product (e.g., $\hat{P} \cdot \hat{D}$) can be expanded as the product of Wigner transformed operators plus higher order terms in $\hbar$. Since in Eq. (5) we find that there is already a factor of $\hbar$ multiplying $\hat{D}$, if we ignore higher order terms when we calculate $\langle \hat{P} \cdot \hat{D} \rangle_{\text{wigner}}$, we effectively ignore residual terms on the order of $\hbar^2$. This approximation is in agreement with the treatment in Ref. 33, and indeed, here we have made such an approximation in Eq. (6).
44. In a future publication, we will address what are the results if we choose a different pseudo-diabatic basis.
We will address the performance of Shenvi’s adiabatic phase-space surface hopping algorithm in a future publication.

In principle, one can anticipate another obstacle when applying Shenvi’s algorithm to nonadiabatic dynamics with spin-orbit coupling: namely, the presence of degenerate states which makes it impossible to isolate unique adiabatic states. Nevertheless, in the future, it will be essential to benchmarks the Shenvi algorithm for complex-valued Hamiltonians.


For our current model Hamiltonian (14), one can justify using momentum rescaling alone (without position rescaling) to maintain energy conservation because \( \mathbf{P} \cdot \mathbf{d}E_j/\mathbf{d}t = -\nabla R E_j \cdot \langle \psi_j | \nabla P \psi_k \rangle = 0 \) (assuming the trajectory is on surface \( j \)). After all, \( E_j, |\psi_j\rangle \), and \( |\psi_k\rangle \) are all functions of only \( x \) and \( P_y \) (see the Supplementary Info for the derivation). That being said, this approach may not be robust for a more general case.


Diabatic Reaction Coordinate

Electronic Energy

Crossing Region

Diabat $\chi_0$

Diabat $\chi_1$