

Phase-corrected surface hopping: Correcting the phase evolution of the electronic wavefunction

Neil Shenvi,^{1,a)} Joseph E. Subotnik,² and Weitao Yang¹¹*Department of Chemistry, Duke University, Durham, North Carolina 27708, USA*²*Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA*

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In this paper, we show that a remarkably simple correction can be made to the equation of motion which governs the evolution of the electronic wavefunction over some prescribed nuclear trajectory in the fewest-switches surface hopping algorithm. This corrected electronic equation of motion can then be used in conjunction with traditional or modified surface hopping methods to calculate nonadiabatic effects in large systems. Although the correction adds no computational cost to the algorithm, it leads to a dramatic improvement in scattering probabilities for all model problems studied thus far. We show that this correction can be applied to one of Tully's original one-dimensional model problems or to a more sophisticated two-dimensional example and yields substantially greater accuracy than the traditional approach. © 2011 American Institute of Physics. [doi:10.1063/1.3603447]

I. INTRODUCTION

Twenty years ago, the publication of John Tully's fewest-switches surface hopping (FSSH) algorithm prompted an increased interest in nonadiabatic methods.¹ The beauty of Tully's method was that it (1) ensured nuclei always propagated on an electronic adiabatic surface, (2) accurately predicted nonadiabatic hopping rates between electronic surfaces, and (3) ensured that system dynamics were self-consistent such that the total energy was conserved. The implementation of FSSH has been important for the investigation of many nonadiabatic physical processes^{2,3} such as scattering at metal surfaces,⁴ dynamics near conical intersections,⁵ proton transfer,⁶ and proton-coupled electron transfer.^{7,8}

Because of its popularity, there is a large body of research which has aimed to correct the known shortcomings of surface hopping, such as overcoherence.^{9–14} There are also a host of other trajectory-based mixed quantum-classical algorithms that have been introduced for use in large systems.^{9,15–19} For instance, several methods employ the quantum Liouville equation to propagate the nuclear density matrix over several coupled adiabatic surfaces.^{16,17} Multiple spawning methods, including the most recent adaptation in Ref. 19, propagate a swarm of Gaussian wavepackets on multiple adiabatic surfaces simultaneously.^{15,20,21} The semiclassical approach described in Ref. 18 propagates swarms of trajectories with a semiclassical phase which can constructively or destructively interfere to yield correct branching ratios. Among all of these different options, FSSH has retained its popularity because of its simplicity and ease of implementation. Within the FSSH formalism, the nuclei are treated as classical point particles which follow familiar Newtonian trajectories, the electrons are propagated quantum mechanically according to the time-dependent electronic Schrödinger equation (TDESE), and nonadiabatic transitions between surfaces occur

stochastically. Although more sophisticated methods may provide increased accuracy, it is difficult to find a method as straightforward to implement and as computationally efficient as FSSH.

In this paper, we will focus on the equation of motion which couples the quantum electronic dynamics to the classical nuclear dynamics. The necessity of some coupled electronic-nuclear equation of motion is not unique to FSSH but is required by any mixed quantum-classical algorithm. For instance, Ehrenfest dynamics and FSSH both use the same TDESE for the electronic wavefunction and differ only in how they propagate the nuclei and render the electronic and nuclear dynamics self-consistent. In both cases, if we assume that the nuclear dynamics are described by some classical trajectory $\mathbf{x}(t)$, then the electronic Hamiltonian $H(\mathbf{x}(t))$ can be viewed as an implicit function of time such that the dynamics of the electronic wavefunction $|\Psi(t)\rangle$ is specified by the TDESE (Ref. 1),

$$i\hbar d|\Psi(t)\rangle/dt = H(\mathbf{x}(t))|\Psi(t)\rangle. \quad (1)$$

Throughout this paper, we will assume that the electronic Hilbert space has dimension two; results can be easily generalized to larger electronic Hilbert spaces. In the case of a two-dimensional electronic Hilbert space, the traditional electronic Hamiltonian in the adiabatic electronic basis is given by

$$H = \begin{pmatrix} V_1(\mathbf{x}(t)) & -\frac{i\hbar}{m}\mathbf{p}(t) \cdot \mathbf{d}_{12}(\mathbf{x}(t)) \\ -\frac{i\hbar}{m}\mathbf{p}(t) \cdot \mathbf{d}_{21}(\mathbf{x}(t)) & V_2(\mathbf{x}(t)) \end{pmatrix}. \quad (2)$$

Here $V_j(\mathbf{x})$ is the energy of the j th adiabatic state $|j(\mathbf{x})\rangle$ at position \mathbf{x} , \mathbf{p} is the momentum of the particle, and \mathbf{d} is the nonadiabatic coupling matrix,

$$\mathbf{d}_{jk}(\mathbf{x}) = \langle j(\mathbf{x}) | \nabla | k(\mathbf{x}) \rangle. \quad (3)$$

These nonadiabatic coupling terms $\mathbf{d}_{jk}(\mathbf{x})$ arise because the electronic adiabatic states change in character as a function of the nuclear coordinate \mathbf{x} . The simplicity of Eqs. (1) and (2)

^{a)}Electronic mail: neil.shenvi@duke.edu.

is one factor in their widespread use as the basis for mixed quantum-classical algorithms. However, it is crucial to notice that Eq. (1) involves an inherent simplification which renders its results somewhat suspect.

To derive Eq. (1), it is assumed that the time evolution of the nuclei can be described by a single trajectory $\mathbf{x}(t)$. If this assumption is true then Eq. (1), which governs the evolution of the electronic wavefunction $|\Psi(t)\rangle$, immediately follows. Unfortunately, this assumption is generally false. In reality, the path taken by a wavepacket often depends strongly on which electronic component of the electronic wavepacket is being considered. For instance, let us consider a wavepacket moving on two constant adiabats separated in energy by ΔE . The component of the wavepacket on the lower surface will be moving at a significantly higher velocity than the component of the wavefunction on the upper surface. As a result, there is not a single path $\mathbf{x}(t)$ which captures the trajectory of the particle, but two different paths $\mathbf{x}_1(t)$ and $\mathbf{x}_2(t)$ which are taken by the two different components of the wavepacket. Only in the limit of extremely high momentum will the paths on the two different adiabats be roughly identical.

The FSSH formalism recognizes this fact when it labels each trajectory at every point in time with the particular surface on which it is propagating. Within the FSSH formalism, a surface label λ specifies which adiabatic surface is used to calculate the forces experienced by the nuclear degrees of freedom \mathbf{x} . So in addition to coherently propagating the electronic wavefunction $|\Psi(t)\rangle$ according to the TDESE in Eq. (1), FSSH also propagates the surface label λ which governs the evolution of the nuclear trajectory $\mathbf{x}(t)$. Because the particle hops stochastically between surfaces, FSSH must propagate an ensemble of independent trajectories to sample all possible hops between surfaces. Nonetheless, every individual trajectory is associated with one particular path $\mathbf{x}(t)$.

Another way to see the inconsistency of the traditional TDESE derivation is to consider the phase evolution of the components of the electronic wavefunction $|\Psi(t)\rangle$. The traditional TDESE derivation implies that the momentum of the nuclei $\mathbf{p}(t)$ and the phase of the electronic wavefunction $|\Psi(t)\rangle$ are distinct entities; the momenta of the nuclei have no direct bearing on the phase of the electronic wavefunction. However, a fully quantum treatment would make use of a single combined nuclear-electronic wavefunction $|\Psi(\mathbf{x}, t)\rangle$. In this case, the momentum of the particle on some particular adiabatic surface i would be exactly specified by the phase oscillation of the combined nuclear-electronic wavefunction on the i th adiabat, $\Psi_i(\mathbf{x})$. So while the traditional TDESE formalism treats nuclear momentum as independent of the electronic wavefunction phase, in reality they are intimately related.

Although the TDESE may be inconsistent, it is not immediately clear whether there is any alternative or whether the inconsistency makes any practical difference. In this paper, however, we will show that a very simple correction can be made to Eq. (1) which leads to substantial improvement in the agreement between the exact and FSSH results. Most importantly, the phase correction we suggest carries with it *no extra computational cost*. It consists of merely modifying the on-diagonal elements of the electronic Hamiltonian in Eq. (2) without altering any of the other machinery of sur-

face hopping. Consequently, we are not introducing a new surface hopping algorithm. Rather, we are making a small but significant correction to the existing FSSH algorithm. Our phase-corrected FSSH algorithm will fill precisely the same niche that traditional FSSH fills, providing a simple, mixed quantum-classical algorithm based on Newtonian trajectories and hops between surfaces. The only difference is that our phase-corrected version of FSSH appears to provide significantly improved accuracy over traditional FSSH with no additional computational cost.

Our paper is organized as follows: Sec. II gives a brief derivation of our phase correction which shows that our phase-corrected equation of motion can be justified by appealing to the behavior of Gaussian wavepackets. Section III applies our phase-corrected version of FSSH and the traditional version to two model problems and shows that our phase correction substantially improves both the quantitative and qualitative accuracy of the results. Finally, conclusions are presented in Sec. IV.

II. DERIVATION

To derive our phase correction, we imagine two Gaussian wavepackets $g_1(\mathbf{x})$ and $g_2(\mathbf{x})$ which are placed on the electronic adiabats $|1\rangle$ and $|2\rangle$ such that the total nuclear-electronic wavefunction is given by

$$|\Psi(\mathbf{x})\rangle = c_1 |g_1(\mathbf{x}); 1\rangle + c_2 |g_2(\mathbf{x}); 2\rangle, \quad (4)$$

where

$$g_j(\mathbf{x}) = \exp(-(\mathbf{x} - \mathbf{x}_j)A(\mathbf{x} - \mathbf{x}_j) + i\mathbf{k}_j \cdot (\mathbf{x} - \mathbf{x}_j) + i\gamma_j). \quad (5)$$

Our first assumption is that at time $t = 0$, both Gaussians start at the same position $\mathbf{x}_1 = \mathbf{x}_2$ with the same phase $\gamma_1 = \gamma_2$ but with different momenta $\mathbf{k}_1 \neq \mathbf{k}_2$. Our second assumption is that we are operating in a region with no nonadiabatic coupling, i.e., $\mathbf{d} = 0$, so that the wavepackets evolve independently. We now consider the time evolution of such a wavepacket. To obtain equations of motion for this Gaussian wavepacket, we follow Heller's pioneering work in Ref. 22 in which he expands the potential $V(\mathbf{x})$ in a Taylor series about the center of the Gaussian wavepacket \mathbf{x}_j , keeping terms up to second-order. Ignoring the dynamics of the width matrix A and expanding in time, we find that the Gaussian positions, momenta, and phases evolve as²²

$$\mathbf{x}_j(t) = \mathbf{x}_j(0) + \frac{\hbar}{m} \mathbf{k}_j t, \quad (6)$$

$$\hbar \mathbf{k}_j(t) = \hbar \mathbf{k}_j(0) + \mathbf{F}_j t, \quad (7)$$

$$\gamma_j(t) = \gamma_j(0) + \left(\frac{\hbar}{m} k_j(0)^2 - \frac{1}{\hbar} E \right) t, \quad (8)$$

where $E = \hbar^2 k_1^2/2m + V_1 = \hbar^2 k_2^2/2m + V_2$ is the total energy of the particle (which is a conserved quantity), $\mathbf{F}_j(\mathbf{x})$ is the adiabatic force on a particle on surface j at position \mathbf{x} ,

$$\mathbf{F}_j(\mathbf{x}) = -\nabla V_j(\mathbf{x}), \quad (9)$$

and where we have assumed that the nonadiabatic coupling $\mathbf{d}(\mathbf{x})$ is zero. These equations of motion give us exact expressions for the short-time dynamics of the Gaussian wavepackets on the different surfaces in the absence of nonadiabatic coupling.

Given these equations of motion, we must decide how to calculate the relative phase that accumulates between the two components of the electronic wavefunction. To do so, we imagine that a given trajectory is “moving on” the lower adiabatic surface (i.e., $\lambda = 1$) according to some surface hopping protocol such that our position and momentum are specified by $\mathbf{x}_1(t)$ and $\mathbf{p}_1(t) = \hbar\mathbf{k}_1(t)$. We then consider what the relative phase of the second Gaussian $g_2(\mathbf{x})$ will be *at the center of the Gaussian wavepacket* \mathbf{x}_1 as a function of time. In other words, we consider the phase of the function $g_2(\mathbf{x} = \mathbf{x}_1(t))$ relative to the phase of the function $g_1(\mathbf{x} = \mathbf{x}_1(t))$. If we plug Eqs. (6)–(8) into our definition for the Gaussian wavepackets in Eq. (5), we obtain

$$\begin{aligned} g_1(\mathbf{x}) &= \exp\left(-(\mathbf{x} - (\mathbf{x}_1(0) + \hbar\mathbf{k}_1 t/m))A(\mathbf{x} - (\mathbf{x}_1(0) + \hbar\mathbf{k}_1 t/m))\right. \\ &\quad + i(\mathbf{k}_1(0) + \mathbf{F}_1 t/\hbar) \cdot (\mathbf{x} - (\mathbf{x}_1(0) + \hbar\mathbf{k}_1 t/m)) \\ &\quad \left. + i\left(\gamma_1(0) + \left(\frac{\hbar}{m}k_1^2 - \frac{1}{\hbar}E\right)t\right)\right), \end{aligned} \quad (10)$$

$$\begin{aligned} g_2(\mathbf{x}) &= \exp\left(-(\mathbf{x} - (\mathbf{x}_2(0) + \hbar\mathbf{k}_2 t/m))A(\mathbf{x} - (\mathbf{x}_2(0) + \hbar\mathbf{k}_2 t/m))\right. \\ &\quad + i(\mathbf{k}_2(0) + \mathbf{F}_2 t/\hbar) \cdot (\mathbf{x} - (\mathbf{x}_2(0) + \hbar\mathbf{k}_2 t/m)) \\ &\quad \left. + i\left(\gamma_2(0) + \left(\frac{\hbar}{m}k_2^2 - \frac{1}{\hbar}E\right)t\right)\right). \end{aligned} \quad (11)$$

Using Eqs. (10) and (11) and assuming that at $t = 0$, $x_1(0) = x_2(0)$ and $\gamma_1(0) = \gamma_2(0)$, we find that to first order in t the relative phase is

$$\begin{aligned} g_1(\mathbf{x}_1(t))/g_2(\mathbf{x}_1(t)) &= \exp(i(\hbar\mathbf{k}_1 \cdot (\mathbf{k}_1 - \mathbf{k}_2)/m)t) \\ &= \exp(i(\mathbf{p}_1 \cdot (\mathbf{p}_1 - \mathbf{p}_2)/m)t/\hbar). \end{aligned} \quad (12)$$

If we are propagating a single trajectory on surface 1, then the time-dependent phase difference between state 1 and 2 at position $\mathbf{x}_1(t)$ is given by $\exp(it\hbar\mathbf{k}_1 \cdot (\mathbf{k}_1 - \mathbf{k}_2)/m)$. One simple way to achieve this phase difference is to propagate the electronic wavefunction in the adiabatic basis with the Hamiltonian,

$$H = \begin{pmatrix} -\mathbf{p}_1(t) \cdot \mathbf{p}_1(t)/m & -i\frac{\hbar}{m}\mathbf{p}_1(t) \cdot \mathbf{d}_{12}(\mathbf{x}(t)) \\ -i\frac{\hbar}{m}\mathbf{p}_1(t) \cdot \mathbf{d}_{21}(\mathbf{x}(t)) & -\mathbf{p}_1(t) \cdot \mathbf{p}_2(t)/m. \end{pmatrix}. \quad (13)$$

Assuming, as before, that we are moving in a region without nonadiabatic coupling ($\mathbf{d} = 0$), this Hamiltonian causes the two electronic components to oscillate with the desired relative phase (see Eq. (12)). Notice that Eq. (13) is not symmetric with respect to indices 1 and 2 because the particle is assumed

to be moving on the lower adiabatic surface (i.e., $\lambda = 1$). If the particle is moving instead on the upper adiabatic surface ($\lambda = 2$), then the TDESE is given by the Hamiltonian,

$$H = \begin{pmatrix} -\mathbf{p}_1(t) \cdot \mathbf{p}_2(t)/m & -i\frac{\hbar}{m}\mathbf{p}_2(t) \cdot \mathbf{d}_{12}(\mathbf{x}(t)) \\ -i\frac{\hbar}{m}\mathbf{p}_2(t) \cdot \mathbf{d}_{21}(\mathbf{x}(t)) & -\mathbf{p}_2(t) \cdot \mathbf{p}_2(t)/m. \end{pmatrix}. \quad (14)$$

Although $\mathbf{x}_1(t)$ and $\hbar\mathbf{k}_1(t) = \mathbf{p}_1(t)$ are well-defined for a classical particle moving on surface 1, the value of $\mathbf{k}_2(t)$, which corresponds to the wavevector of the Gaussian wavepacket on surface 2, is not well-defined. At some past time, the two Gaussian wavepackets may have had identical positions and parallel momenta. But in the exact calculation, a Gaussian wavepacket on adiabat 2 will experience different forces than the wavepacket on the adiabat 1. Hence $\mathbf{k}_2(t)$ will depend in a highly nontrivial way on the particle’s past history. To avoid this problem, consider the relation,

$$\mathbf{k}_1(t) \cdot \mathbf{k}_2(t) = k_1(t)k_2(t) \cos(\theta(t)), \quad (15)$$

where $k_1(t)$ and $k_2(t)$ are the magnitudes of the wavevectors and $\theta(t)$ is the angle between the two vectors. Although the exact value of $\theta(t)$ will be very complicated, we will assume that $\theta = 0$ such that the two momenta are always parallel. This is clearly a major assumption, whose validity will depend greatly on the particular system in question. But if we are willing to make this assumption, then the magnitude of k_2 can be immediately calculated simply based on energy conservation,

$$\hbar^2 k_1^2/2m + V_1(\mathbf{x}_1) = \hbar^2 k_2^2/2m + V_2(\mathbf{x}_1), \quad (16)$$

and the Hamiltonian in Eq. (13) is well-specified.

One important question to ask is what happens when the upper adiabatic surface is energetically inaccessible. In other words, what happens if the solutions to Eq. (16) require k_2 to be imaginary? In this case, we will simply set $k_2 = 0$. The real test of this approximation will come when we apply the phase-corrected FSSH algorithm to scattering problems below the threshold of the upper state where the upper surface can be populated only transiently.

At this point, we can compare the phase-corrected Hamiltonian in Eq. (13) to the electronic Hamiltonian derived from the traditional TDESE in Eq. (2) for a particle moving on surface 1. The two Hamiltonians are identical except for the values of the on-diagonal terms. Note that, because we are propagating along surface $\lambda = 1$, then $\mathbf{p} = \mathbf{p}_1$ if we compare Eq. (2) to Eq. (13). We now claim that the corrected Hamiltonian in Eq. (13) reduces to the traditional Hamiltonian *in the limit of high momentum*, which is precisely the regime in which both components of the wavepacket will follow identical, straight-line trajectories $\mathbf{x}(t)$. To see this correspondence, we expand the Hamiltonian in Eq. (13) in the limit where $\hbar^2 k_1^2 \gg 2m(V_2(\mathbf{x}_1) - V_1(\mathbf{x}_1))$. Using Eq. (16), we find that the diagonal elements of the electronic Hamiltonian in Eq. (13) are

$$H_{11}(\mathbf{x}) = -\frac{\hbar^2 k_1^2}{m}, \quad (17)$$

$$\begin{aligned}
H_{22}(\mathbf{x}) &= -\frac{\hbar^2}{m} k_1 k_2 \\
&= -\frac{\hbar^2}{m} k_1 \sqrt{k_1^2 - 2m(V_2(\mathbf{x}_1) - V_1(\mathbf{x}_1))/\hbar^2} \\
&= -\frac{\hbar^2 k_1^2}{m} + (V_2(\mathbf{x}_1) - V_1(\mathbf{x}_1)) + \dots \quad (18)
\end{aligned}$$

Consequently, up to some constant factor times the identity matrix, the electronic Hamiltonian in Eq. (13) simplifies exactly to the Hamiltonian in Eq. (2) in the high-momentum limit. To put it another way, the traditional TDESE uses an electronic Hamiltonian which is actually the high-momentum limit of our more general phase-corrected electronic Hamiltonian in Eq. (13). This correspondence gives us confidence that our corrected electronic Hamiltonian is physically reasonable.

To summarize, we outline our phase-corrected version of the surface hopping algorithm below. Note that our phase-corrected version affects only a single step in the traditional FSSH algorithm (Step 3), where it uses the phase-corrected equation of motion given by Eq. (13) (or Eq. (14)) rather than Eq. (2).

A. Summary of the phase-corrected FSSH algorithm

1. Set the initial conditions of the simulation. The initial surface λ is set to i and the electronic wavefunction $|\psi\rangle = |i\rangle$.
2. Propagate the position, \mathbf{x} , and momentum, \mathbf{p} , of the nuclei according to Newton's equations of motion.
3. Integrate the electronic wavefunction according to the time-dependent Schrödinger equation using the electronic Hamiltonian at \mathbf{x} ,

$$d|\psi\rangle/dt = -\frac{i}{\hbar} H(\mathbf{x})|\psi\rangle. \quad (19)$$

While the traditional FSSH algorithm uses the Hamiltonian in Eq. (2) to propagate Eq. (19), the phase-corrected Hamiltonian will depend on which surface the particle is propagating on. If the particle is propagating on adiabatic surface $\lambda = 1$, then we use the phase-corrected Hamiltonian in Eq. (13) and obtain \mathbf{k}_2 from energy conservation with the parallel momentum assumption $\theta = 0$. If the particle is propagating on adiabatic surface $\lambda = 2$, then we use the phase-corrected Hamiltonian in Eq. (14) and obtain \mathbf{k}_1 from energy conservation with the parallel momentum assumption $\theta = 0$. If surface 2 is energetically inaccessible, then we set $\mathbf{k}_2 = 0$.

4. Perform surface hopping. Calculate the quantities

$$\dot{a}_{jj} = \sum_{l \neq j} b_{jl}, \quad (20)$$

$$b_{ji} = \frac{2}{\hbar} \text{Im} a_{ji}^* H_{ji} - 2 \text{Re} a_{ji}^* \dot{\mathbf{x}} \cdot \mathbf{d}_{ji}. \quad (21)$$

The rate of surface hopping from state i to state j is then given by b_{ji}/a_{ii} . Given a random number $\zeta = [0, 1]$, then a hop is made if $\Delta t b_{ji}/a_{ii} > \zeta$ and if the hop is not energetically forbidden. If a hop occurs, then respawn

the trajectory on surface j with the momentum rescaled in the direction \hat{d}_{ji} .

5. Return to Step 2 and repeat until the trajectory $x(t)$ leaves the region of interest.

III. NUMERICS

To test our phase-corrected electronic Hamiltonian, we applied it to two model problems, the first of which was originally constructed by Tully and has been used in the literature to test new surface hopping algorithms. The second model is a non-separable two-dimensional problem in which a second nuclear coordinate is involved in a non-trivial way. It must be emphasized that the cost of our phase-corrected algorithm is identical to that of the original FSSH algorithm. The only alteration we make to the FSSH algorithm is to replace the on-diagonal components of the electronic Hamiltonian in Eq. (2) with those from Eq. (13). To state it even more plainly, our phase correction requires the alteration of only four lines of FORTRAN code. The correction we have derived can be readily applied to any algorithm which makes use of the traditional TDESE, simply by substituting the phase-corrected Hamiltonian in Eq. (13) for the traditional Hamiltonian in Eq. (2).

A. Dual avoided crossing model

Our first model was originally constructed by Tully in Ref. 1. The 2×2 diabatic Hamiltonian matrix is given by the matrix elements,

$$V_{11}(x) = 0, \quad (22)$$

$$V_{22}(x) = -A \exp(-Bx^2) + E_0, \quad (23)$$

$$V_{12}(x) = V_{21}(x) = C \exp(-Dx^2), \quad (24)$$

with $A = 0.10$, $B = 0.28$, $E_0 = 0.05$, $C = 0.015$, and $D = 0.06$. Figure 1 shows the resulting adiabatic curves and nonadiabatic coupling. In this model, there are two distinct regions of nonadiabatic coupling, one at $x = -1.5$ and the other at $x = 1.5$. Consequently, the phase difference that accumulates between the two components of the electronic wavefunction will play an important role in determining the final scattering probability on the upper or lower state. The exact result was calculated using a grid-based matrix inversion method and was then convoluted with a Gaussian envelope function to capture the smoothing effects of a wavepacket.¹⁴

The results shown in Fig. 2 demonstrate that our phase-corrected algorithm yields a dramatic improvement in the final scattering probabilities. As noted by Tully, traditional FSSH shows significant deviations from the exact answer at low energies. To quote him at length, Tully writes that "At low energies the trajectory and quantal oscillations become out of phase... The discrepancy is particularly significant at energies below 0.05 [i.e., $k < 14.1$].... it is certainly encouraging that (FSSH) can reproduce the quantum interference effects so well at high energy, but the low energy discrepancy is disappointing".¹ In contrast, the phase-corrected version of

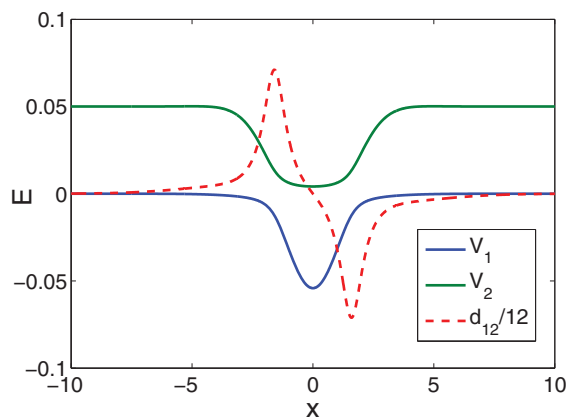


FIG. 1. The adiabatic potential energy curves $V_1(x)$ and $V_2(x)$ for Model 1 as a function of x . Also shown is the nonadiabatic coupling function $d_{12}(x)$, divided by a factor of 12 for the sake of visibility. In this problem, there are two regions of nonadiabatic coupling centered on the curve crossings at $x = -1.5$ and $x = 1.5$.

FSSH is able to predict correctly both the position and amplitude of the Stuckelberg oscillations in the transmission probabilities even at low energies. Stuckelberg oscillations arise when there are two or more regions of nonadiabatic coupling. Because trajectories acquire a relative phase difference on the upper and lower adiabatic surfaces between the nonadiabatic coupling regions, they can recombine either in-phase or out-of-phase at the second avoided crossing.²³ Therefore, the fact that our method quantitatively captures these Stuckelberg oscillations shows that we are correctly calculating the relative phase acquired by the trajectories on different surfaces. Even when the momentum is below the upper adiabatic threshold ($k < 14.1$), the phase-corrected version still gives answers

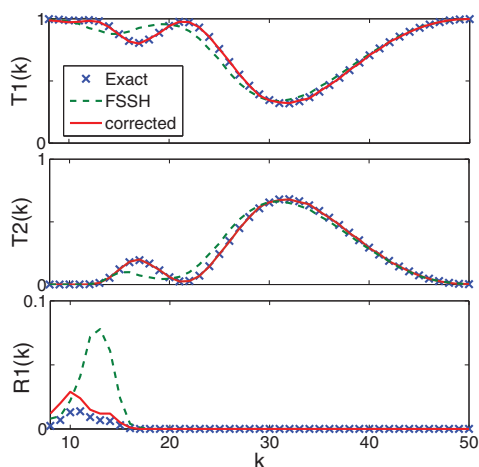


FIG. 2. The scattering probabilities $P(k)$ for transmission/reflection (T/R) on surface 1 or 2 as a function of incoming momentum k for Model 1 (see Eqs. (22)–(24)). The blue crosses are the exact quantum result, the dashed green lines are the traditional FSSH result, and the solid red lines are the phase-corrected version of FSSH. Here, the phase-corrected results are clearly and substantially more accurate than the traditional results. Below threshold ($k < 14.1$) the phase-correction results in the correct qualitative scattering behavior and a significant quantitative improvement where FSSH fails. Above threshold, phase-corrected FSSH also outperforms traditional FSSH, especially in the low energy region $k < 20$.

which are quantitatively and qualitatively more accurate than the traditional method. This result validates our methodology of setting $k_2 = 0$ when adiabatic states are energetically inaccessible (i.e., when $k < 14.1$). As expected, the traditional and phase-corrected versions yield similar answers in the high momentum limit. Altogether, these results are extremely encouraging.

B. Non-separable 2D model: Breakdown of the parallel momentum assumption

Second, we applied our phase-corrected FSSH algorithm to a non-separable two-dimensional potential. Although our algorithm was highly successful for the first model, one might suspect that its success was due to the validity of our approximation of Eq. (15) in one dimension. In one dimension, we are guaranteed that the two momenta \mathbf{k}_1 and \mathbf{k}_2 are parallel because all motion is confined to a line. The same approximation is true in quasi-1D problems where additional degrees of freedom are essentially spectators. To test the validity of our approximation, we needed to construct a 2D model in which the parallel momentum approximation was explicitly violated. For this reason, we constructed a non-separable 2D problem whose diabatic potentials were given by

$$V_{11}(x, y) = -E_0, \quad (25)$$

$$V_{22}(x, y) = -A \exp(-B(0.75(x+y)^2 + 0.25(x-y)^2)), \quad (26)$$

$$V_{12}(x, y) = C \exp(-D(0.25(x+y)^2 + 0.75(x-y)^2)), \quad (27)$$

$$V_{21}(x, y) = V_{12}(x, y), \quad (28)$$

with $A = 0.15$, $B = 0.14$, $C = 0.015$, $D = 0.06$, and $E_0 = 0.05$. Figure 3 shows a 2D plot of the adiabatic states which are coupled by the nonadiabatic coupling $d_{12}(x, y)$ (not shown). Note that in this non-separable 2D model, trajectories will experience very different forces depending on whether they are propagating on surface 1 or surface 2. As a result, our assumption that the two momenta \mathbf{k}_1 and \mathbf{k}_2 will be exactly parallel (i.e., $\theta = 0$ in Eq. (15)) is no longer true. Thus, this second model provides an important test for the accuracy of our method when the parallel momentum approximation breaks down.

In this 2D case, the exact solution was obtained using wavepacket propagation with the split-operator Fourier transform (SOFT) technique and a time step of $dt = 0.5$.²⁴ The initial wavepacket was started at $\mathbf{x} = (-8, 0)$ with initial momentum in the $+x$ direction and widths of $\sigma_x = 1$, $\sigma_y = 1$. For this model, we did not simulate scattering below threshold because of the numerical difficulty associated with simulating extremely long-lived resonance states using SOFT calculations. We could, of course, perform FSSH calculations in this regime, but we would not have exact answers against which to compare. Figure 4 shows the results of our simulations. It is clear from this figure that the phase-corrected version of the FSSH algorithm again significantly outperforms the

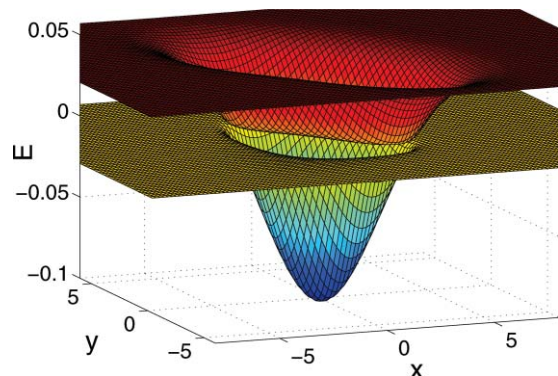


FIG. 3. The adiabatic potential energy curves $V_1(x, y)$ and $V_2(x, y)$ for Model 2 as a function of x and y . This two-dimensional potential is highly non-separable and thus serves as an important test-case for the phase-corrected version of FSSH.

traditional version of the FSSH algorithm. The traditional version of FSSH gives oscillatory transmission results which are almost perfectly out of phase with the exact results. In contrast, our phase-corrected version of FSSH yields almost quantitative accuracy for a wide range of initial momenta. This performance is particularly important since the assumption of parallel momenta is not valid for this model. Despite the breakdown of this assumption, our method still performs extremely well and yields a significant improvement over the traditional version of the FSSH algorithm.

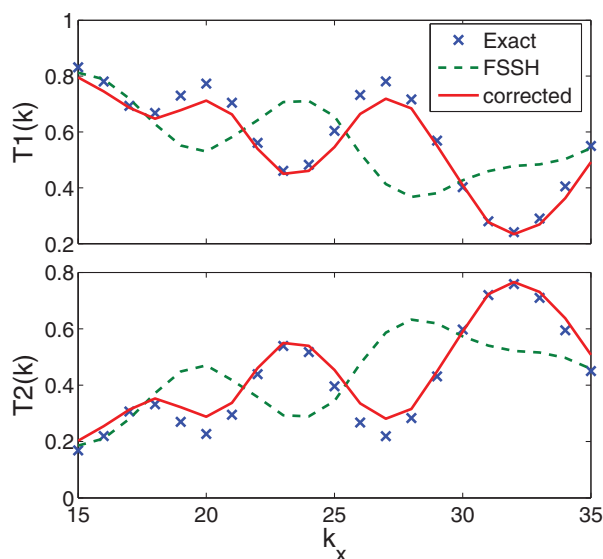


FIG. 4. The scattering probabilities $P(k)$ for transmission/reflection (T/R) on surface 1 or 2 as a function of the incoming momentum in the x -direction $\mathbf{k} = (k_x, 0)$ for the non-separable 2D problem in Model 2 (see Eqs. (25)–(28)). The blue crosses are the exact quantum result, the dashed green lines are the traditional FSSH result, and the solid red lines are the phase-corrected version of FSSH. Although the phase-corrected algorithm is slightly overdamped relative to the exact result, it nonetheless captures the Stueckelberg oscillations very accurately. In contrast, the traditional FSSH algorithm leads the Stueckelberg oscillations to be almost perfectly out of phase with the exact result, nearing agreement only in the high-energy, high-momentum limit.

IV. CONCLUSIONS

In conclusion, we have shown that a simple and easily-implemented correction to the electronic equations of motion can significantly improve algorithmic accuracy. More generally, the correction we have derived can be readily applied to any algorithm which makes use of the traditional TDESE, simply by substituting the phase-corrected Hamiltonian in Eq. (13) for the traditional Hamiltonian in Eq. (2). The correction was derived from the dynamics of Gaussian wavepackets and has been applied to two model problems. In both cases, the phase-corrected version of the algorithm yielded qualitative and quantitative improvements over the traditional version of the algorithm.

This result opens up numerous avenues for future work. First, because our algorithm provides a simple correction to the electronic equations of motion, it could be applied with very little effort to any of the myriad variations of FSSH which have been proposed over the last few decades. Second, our assumption that the two momenta \mathbf{k}_1 and \mathbf{k}_2 are always parallel such that $\theta = 0$ is not rigorously justified. It would be extremely helpful to derive a more rigorous justification for this assumption or to derive a better approximation. Finally, setting $k_2 = 0$ when the excited adiabat is energetically inaccessible was also a successful, but not rigorously justified, approximation. One intriguing possibility is to allow k_2 to become imaginary such that the wavefunction on energetically excited states could actually decay. Such an approach might provide a new route for taking into account decoherence. Regardless of which possibilities prove to be successful, the phase correction derived in this paper should have important implications for existing surface hopping methodologies and applications. In theory, our method could be used in the hundreds of applications to which FSSH has already been applied to yield more accurate results with no more computational cost than the traditional FSSH algorithm itself.

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