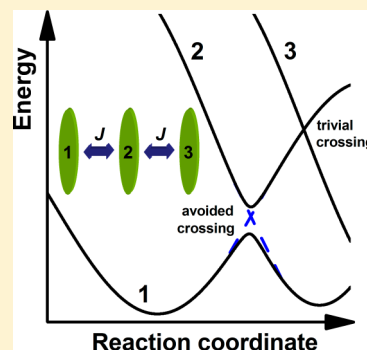


A Simple Solution to the Trivial Crossing Problem in Surface Hopping

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ABSTRACT: Surface hopping studies on supramolecular and nanoscale systems suffer severely from the trivial crossing problem, arising due to high density of adiabatic potential energy surfaces. We present a straightforward solution to the problem by introducing a self-consistency test to the well-known fewest switches surface hopping (FSSH) procedure. If the test is failed, the hopping probabilities are corrected with a simple procedure. The novel self-consistent fewest switches surface hopping (SC-FSSH) approach is applied to the Holstein Hamiltonian to study the time-dependence of the electron population. Already in the five-state system, SC-FSSH allows us to reduce the simulation time 10^4 -fold to achieve the FSSH accuracy. The reliable performance and simple formulation of SC-FSSH greatly expands the applicability range of the surface hopping method.



SECTION: Molecular Structure, Quantum Chemistry, and General Theory

Numerous dynamical processes in physics, chemistry, and biology, such as proton transfer,¹ vibrational energy relaxation,^{2–4} exciton dynamics,^{5–7} electron transfer,^{8–11} and charge transport,^{12,13} involve only a small portion of particles that should be dealt with quantum mechanically. The rest of the system can be treated simply, in a classical manner. Such a mixed quantum/classical dynamics idea has found growing interest in various applications.¹⁴ About 20 years ago, Tully's seminal work¹⁵ described the fewest switches surface hopping (FSSH) algorithm, which has become the most popular quantum/classical approach for condensed phase systems. Within the FSSH formalism, the classical particles evolve on a potential energy surface (PES) through Newtonian equations, the quantum parts are propagated according to the time-dependent Schrödinger equation, and nonadiabatic transitions between PESs occur stochastically. The FSSH algorithm has retained its popularity because of its simplicity and ease of implementation.^{16–18}

Despite its popularity and success, FSSH suffers from several shortcomings. One of them is the so-called trivial, or unavoided, crossing problem, which becomes increasingly critical in complex molecular systems.^{12,19–22} Due to the short-range of intermolecular interactions, the energy splitting between two PESs dominated by non-neighboring molecules is very small, leading to the trivial crossings (see Figure 1). In these cases, the nonadiabatic coupling shows a sharp peak that is strongly localized in time.²¹ The surface hopping probability grows to infinity at the exact crossing point and vanishes rapidly elsewhere. The consequence is that a surface hop always needs to happen at this point, hence the name “trivial crossing”. However, numerical simulations are carried out with a finite time step, making it impossible to account accurately for the trivial crossings. If a surface hop does not happen during a trivial crossing, an artificially long-ranged charge or energy transfer may occur, exemplifying the trivial crossing problem.

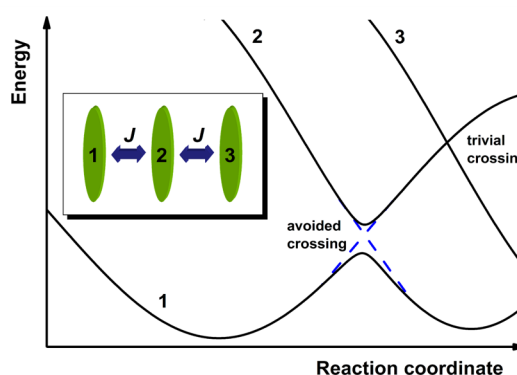


Figure 1. Schematic representation of the potential energy surfaces of a molecular trimer, where the first molecule is coupled with the second, and the second one interacts with the third. Avoided crossings happen between the two adiabatic states dominated by molecules 1 and 2, while trivial crossings are present between the two adiabatic states dominated by molecules 1 and 3.

This is especially harmful when studying long-range dynamical processes, such as charge transport^{23,24} and exciton diffusion.^{6,7}

There are several strategies to solve the trivial crossing problem. The most straightforward way is to reduce the time step in order to make a more accurate description of the dynamics. This approach is computationally too expensive, and thus is restricted to very small systems. Alternatively, one may use interpolation approaches to achieve flexible descriptions of the PESs and their nonadiabatic couplings at a reduced expense.¹⁹ Still a very small time step is unavoidable. One can also attempt to detect trivial crossings based on certain rules, and make the necessary hops manually each time. Several

Received: January 5, 2014

Accepted: January 31, 2014

algorithms for detecting trivial crossings have been described in the literature, based on thresholds for energy gaps between states, nonadiabatic coupling terms,²⁰ and overlaps between adiabatic wave functions.²¹ However, a clean treatment remains hard, because there always exists a certain number of intermediate cases that are not easily distinguishable as trivial crossings or normal avoided crossings. Alternatively, one can utilize the fact that only nuclear vibrations that are spatially close to the electron are important for the electron dynamics, as proposed recently in the flexible surface hopping approach.¹² Here, a filter is used to determine which states are important for the dynamics, and this filter may change from system to system. There also exists the local diabaticization approach, which transforms the adiabatic states in a locally diabatic representation.²² In this approach, the electron wave function propagation has no explicit reference to the nonadiabatic couplings, and a larger time step can be used to reduce the computational cost. However, local diabaticization is not uniquely defined in general, and requires a rather complex calculation, such as Löwdin orthogonalization, every time step. Further, usually surface hopping in the adiabatic representation gives more accurate results than in a diabatic representation.^{25,26} In short, numerical simulation of electron dynamics in the presence of trivial crossings remains a big challenge.

In this Letter, we present a novel procedure to solve the trivial crossing problem. Normal FSSH calculations are performed in the adiabatic basis, while the electronic wave function is propagated in a basis that does not require the nonadiabatic coupling, e.g., a diabatic basis, a spatial grid, a plane-wave basis, etc. Thereby, the electronic dynamics is described accurately, while surface hopping is carried out in the preferred, adiabatic representation. Key to the method is the self-consistency test for the total surface hopping probability. Not utilized previously, the test is based on the standard FSSH equations and is used to correct the error in the surface hopping probability arising from the trivial crossings. The self-consistent fewest switches surface hopping (SC-FSSH) approach is applied to a Holstein Hamiltonian describing molecular aggregates consisting up to five molecules. To achieve comparable accuracy, SC-FSSH requires a 10 000 times smaller time than the standard FSSH! The reliable performance and simplicity of SC-FSSH provide overwhelming evidence of its great advantages for quantum-classical simulations.

The surface hopping method investigates the dynamics of a general system consisting of a quantum particle and a number of classical degrees of freedom. For the sake of clarity and without loss of generality, we focus our study on the electron–phonon interacting systems characterized by the Holstein model.²⁷ The total Hamiltonian can be written as a summation of the electronic part, H_e , and the nuclear part, H_n , as²⁸

$$H = H_e + H_n \quad (1)$$

$$H_e = \sum_i^{N-1} J(|i\rangle\langle i+1| + |i+1\rangle\langle i|) + \sum_i^N \alpha x_i |i\rangle\langle i| \quad (2)$$

$$H_n = \frac{1}{2} \sum_i (Kx_i^2 + mv_i^2) \quad (3)$$

Here, we investigate N molecules arranged in a one-dimensional stack with open boundary condition. Each molecule i has an associated diabatic electronic orbital $|i\rangle$ (e.g., the highest occupied molecular orbital for hole dynamics

and the lowest unoccupied molecular orbital for electron dynamics) and one vibrational mode (x_i , v_i , m , and K are the corresponding nuclear coordinate, velocity, effective mass and force constant). J is the intermolecular transfer integral, and α is the local electron–phonon coupling constant. The frequency of the harmonic vibration is $\omega = (K/m)^{1/2}$. From previous studies, we know that this kind of Hamiltonian gives an electronic reorganization energy of $\lambda = \alpha^2/K$.²⁸

Diagonalizing the electronic Hamiltonian given in eq 2, i.e., $H_e|\phi_i\rangle = E_i|\phi_i\rangle$, one obtains all PES, $\{E_i\}$, and the adiabatic states in terms of the original diabatic orbitals $\{|\phi_i\rangle = \sum_j p_{ji}|j\rangle\}$. We can express the electronic wave function by a linear combination of these adiabatic states, $|\Phi\rangle = \sum_i c_i |\phi_i\rangle$. According to the Schrödinger equation, we obtain^{12,29}

$$\dot{c}_i = \frac{1}{i\hbar} c_i E_i - \sum_{j \neq i} c_j \sum_k^N v_k d_{ij}^k \quad (4)$$

where $d_{ij}^k = \langle \phi_i | d\phi_j / dx_k \rangle$ are nonadiabatic couplings. The nuclei evolve on an active PES a , and the corresponding equation of motion reads

$$m\ddot{x}_i = -Kx_i - dE_a/dx_i \quad (5)$$

According to the Hellmann–Feynman theorem, we obtain^{12,30}

$$d_{ij}^k = \frac{\alpha p_{ki} p_{kj}}{E_j - E_i} \quad (6)$$

$$dE_a/dx_i = \alpha p_{ia}^2 \quad (7)$$

Following Tully's standard fewest switches algorithm, the switching probability from the active surface a to another surface i is

$$g_i = dt \cdot \frac{2\text{Re}[c_a^* c_i] \sum_k v_k d_{ai}^k}{c_a^* c_a} \quad (8)$$

where dt is the time step for electron dynamics.

From eq 6, we find that the nonadiabatic coupling depends inversely on the energy differences between two adiabatic surfaces. When we encounter a trivial crossing, the energy difference changes rapidly and approaches zero. Since numerical calculations are performed with a finite time step, a huge error can arise in the two places that depend on the nonadiabatic coupling, namely, the electronic dynamics in eq 4 and the surface hopping probabilities in eq 8.

In principal, the electronic wave function can be propagated in any basis. Instead of the adiabatic basis we can use, for instance, the diabatic basis to define the Holstein Hamiltonian. Time-domain *ab initio* calculations can be performed on a spatial grid^{31–33} or in a plane-wave basis. Expanded in the diabatic basis, the wave function reads, $|\Phi\rangle = \sum_i c'_i |i\rangle$, and the Schrödinger equation becomes²⁸

$$\dot{c}'_i = \frac{\alpha}{i\hbar} x_i c'_i + \frac{J}{i\hbar} (c'_{i-1} + c'_{i+1}) \quad (9)$$

The coefficients of the electronic wave function in the diabatic and adiabatic bases are linked through the relation

$$c_i = \sum_j^N p_{ji} c'_j \quad (10)$$

Therefore, one can do the electronic dynamics accurately in diabatic basis with eq 9, and convert the electronic coefficients

to the adiabatic basis through eq 10. This approach does not suffer from the trivial crossing difficulty since the nonadiabatic couplings are not involved in the electronic dynamics.

FSSH gives more accurate results in the adiabatic rather than diabatic representation.²⁵ Diabatic representation can lead to inaccuracies in the limit of weak nonadiabatic coupling,²⁶ for instance, misrepresenting the coherent transport regime in organic electronics.¹² From eq 8, we can prove that the sum of the surface hopping probabilities from the active adiabatic state a to all other adiabatic states i is

$$\sum_i^N g_i = dt \cdot \frac{-d(c_a^* c_a)/dt}{c_a^* c_a} \quad (11)$$

When we implement a finite time step, eq 11 goes to

$$\sum_i^N g_i = \frac{c_a^*(t)c_a(t) - c_a^*(t+dt)c_a(t+dt)}{c_a^*(t)c_a(t)} \quad (12)$$

Equations 11 and 12 give the total surface hopping probability for the time step dt . Since we can obtain accurately the electronic wave function coefficients in the adiabatic basis with eqs 9 and 10, we can use eq 11 or 12 to compute the correct total surface hopping probability. By comparing the result of eq 11 or 12, based purely on the wave function evolution, with the sum of the standard FSSH probabilities, eq 8, dependent on the nonadiabatic coupling, we perform a self-consistency test of FSSH. A test failure indicates that a trivial crossing problem is encountered.

From eq 6, we know that the surface hopping probabilities are strongly influenced by the energy difference between the two adiabatic states. If we calculate the energy differences between the active adiabatic state a and all other adiabatic states, and find the adiabatic state j that gives the smallest energy difference, we identify the source of the trivial crossing problem. Then, we can correct the error by computing the surface hopping probability corresponding to the trivial crossing, g_j , using

$$g_j = \sum_i^N g_i - \sum_{i \neq j}^N g_i \quad (13)$$

Here, the first term on the right side, $\sum_i^N g_i$, is the exact total surface hopping probability obtained from eq 12. All g_i in the second term, $\sum_{i \neq j}^N g_i$, are calculated from eqs 6 and 8. This simple step removes the overwhelming majority of the errors arising from trivial crossings. It does not fully account for situations in which multiple trivial crossings occur within the same time steps. However, such situations are rare, and can be resolved by reducing the time step further. As demonstrated with the examples below, SC-FSSH gives enormous computational advantages. For the three-state example, it allows us to use a 200-fold larger time step than the standard FSSH. For the five-state example, the advantage is 10 000-fold!

We start with a smaller molecular aggregate consisting of only three molecules, where the first molecule and the third molecule are not directly coupled according to the tight-binding Hamiltonian given by eq 2. This is the smallest system to have trivial crossings because directly coupled molecules induce merely avoided crossings (see Figure 1). The chosen parameters are $J = 0.01$ eV, $\hbar\omega = 0.01$ eV, $\lambda = 0.1$ eV, $m = 100$ amu, $T = 300$ K, and $dt = 0.1$ fs, which are typical for charge transport in molecular solids.¹² Note that the choices of these

parameters do not influence the conclusions made in the present study. Initially, the nuclear coordinates and velocities uniformly follow Boltzmann distributions with variances $k_B T/K$ and $k_B T/m$, respectively.^{28,34,35} The evolution of the electron wave function and nuclear coordinates are performed through the standard fourth-order Runge–Kutta algorithm.³⁶ This technique enables very accurate description of electron and nuclear dynamics, and the surface hopping probabilities in eq 8.

Initially, the electron wave function is placed on the first molecule, and the active state for surface hopping is chosen as the adiabatic state with the largest contribution from the first molecule. This defines state a in eqs 11 and 12 for the total surface hopping probability. A typical example of the potential energy surfaces is shown in Figure 2A. There we can easily find

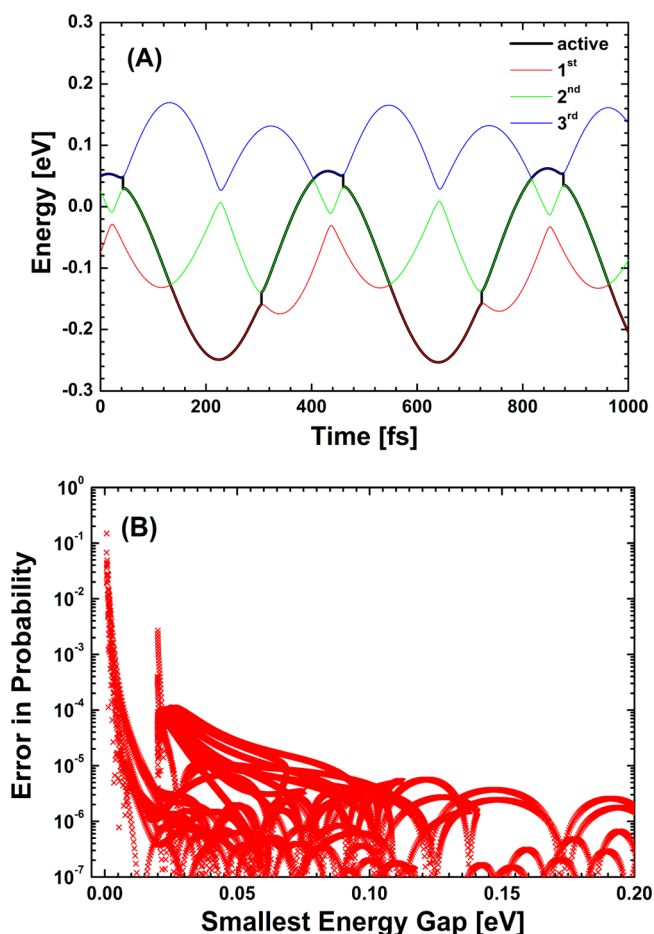


Figure 2. (A) Time dependence of the potential energy surfaces for the specified active state and the three adiabatic states of a molecular trimer. (B) Error of the total surface hopping probability obtained from eq 8 in comparison with eq 12 as a function of the smallest energy gap between the active state and other adiabatic states. The parameters are $J = 0.01$ eV, $\hbar\omega = 0.01$ eV, $\lambda = 0.1$ eV, $m = 100$ amu, $T = 300$ K, and $dt = 0.1$ fs.

the two kinds of crossings: avoided crossings due to the interaction between the first and second molecules, and trivial crossings between the adiabatic states dominated by the first and third molecules. The energy splitting of the avoided crossings is about 0.02 eV, i.e., 2 times the intermolecular transfer integral. Comparatively, the energy splitting of the trivial crossing is nearly 2 orders of magnitude smaller, only 0.0007 eV, giving rise to the trivial crossing problem. Note that

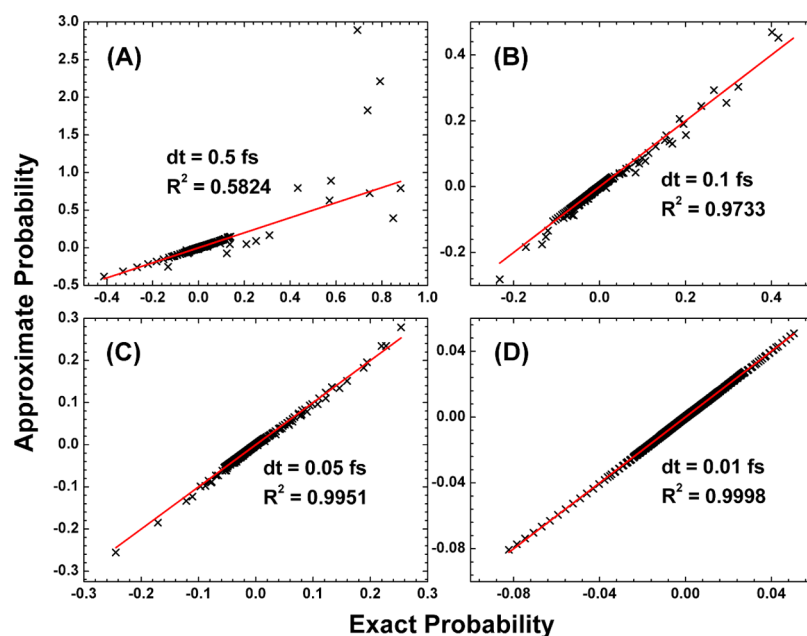


Figure 3. Approximate total surface hopping probability from eq 8 in comparison with the exact surface hopping probability from eq 12 obtained using different time steps. The parameters are the same as in Figure 2. Negative values are set equal to 0 in the FSSH calculation.¹⁵

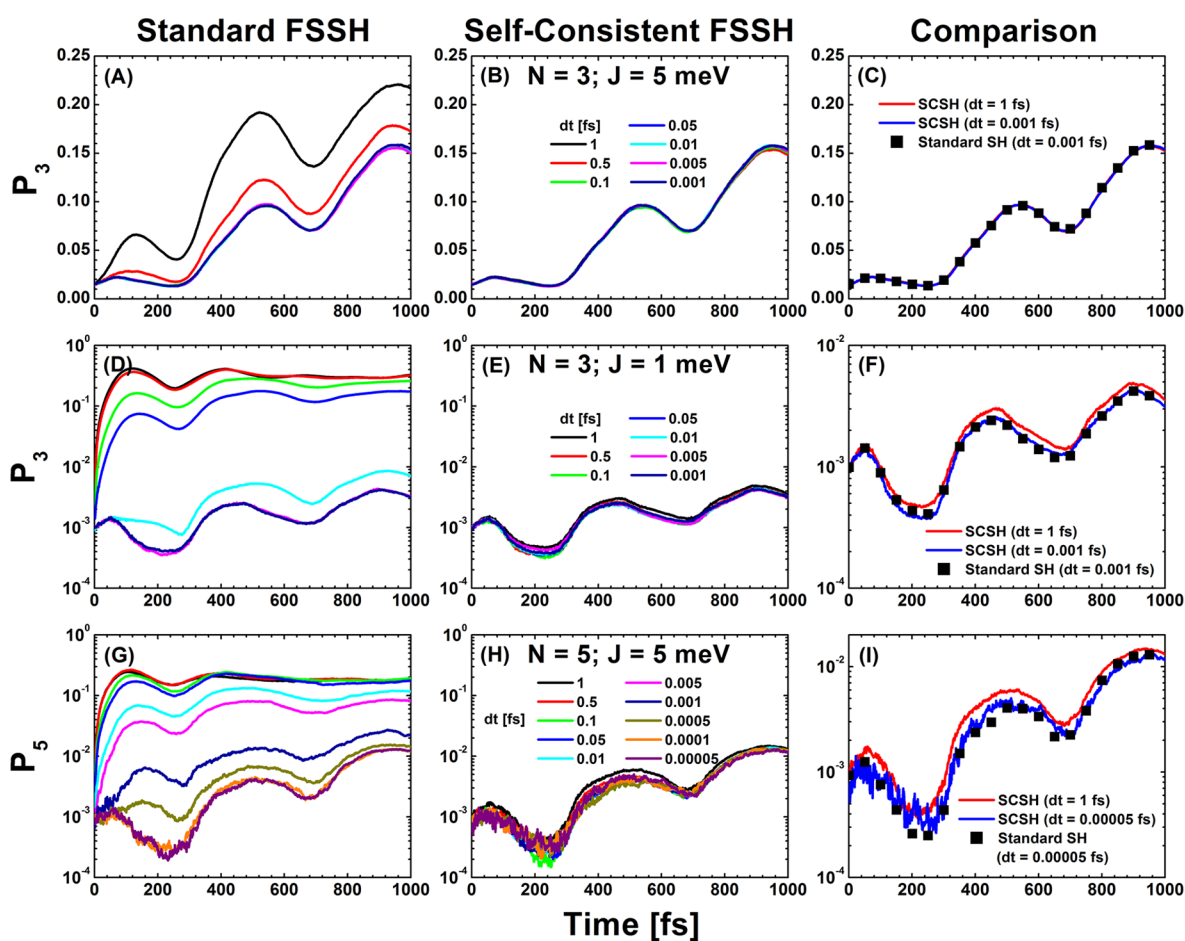


Figure 4. Time dependence of the population on the third molecule in a trimer (top 2 rows) and the fifth molecule in the pentamer (bottom row), obtained using FSSH (left column) and SC-FSSH (middle column). The right column compares the FSSH and SC-FSSH results. The parameters are the same as in Figure 2, except for the transfer integrals, J , which are indicated in the figure. In order to achieve the same accuracy, standard FSSH requires a 200-fold smaller time step for the trimer and a 10 000-fold smaller time step for the pentamer than SC-FSSH.

the energy splitting for the trivial crossings is small, but far from zero.

In Figure 2B, we show the deviation of the total surface hopping probability calculated using eq 8 from the exact total probability obtained with eq 12. We can find that there is a strong correlation between the error of the surface hopping probability and the lowest energy difference between the active state and other adiabatic states. Namely, the smaller the energy splitting, the larger the error in the surface hopping probability calculated by normal surface hopping algorithm. This finding agrees with our previous interpretations, and provides solid roots for adjusting the surface hopping probability with the lowest energy splitting using eq 13.

In order to achieve an accurate description of the electron dynamics by the standard FSSH using the adiabatic basis only, one needs to reduce the time step. In Figure 3, we show the accuracy of the calculated total surface hopping probabilities using different time steps in eq 8. For large time intervals, e.g., $dt = 0.5$ fs, huge errors are found when the exact total probability is large, greater than 0.4. This happens in regions close to trivial crossings, where the energy difference in the denominator of eq 8 is very small. With the reduction of the time interval, the correlation coefficient, R^2 , approaches unity, implying that the error is decreasing. An accurate description of the trivial crossings needs a time step of 0.01 fs or smaller, with the adopted parameters. Considering the fact that electron dynamics generally proceeds with a time step of about 0.1 fs, trivial crossings cannot be accurately treated in the normal surface hopping calculations. Reducing the time step greatly increases the computational cost.

The performance of the SC-FSSH scheme can be tested by tracking the time dependence of the electronic populations using the standard FSSH with a very small time step as a reference. In Figure 4A, we show the evolution of the population on the third molecule for different time steps. As before, the electron is on the first molecule initially. We can see that $dt = 0.1$ fs is already sufficiently small for the standard FSSH to accurately describe the dynamics in the molecular trimer with the transfer integral of 5 meV. The SC-FSSH results are shown in Figure 4B. We can find that SC-FSSH gives accurate time dependence of the population even with the time step as large as 1 fs (see Figure 4C). This clearly proves the correctness of the proposed modifications to the standard surface hopping.

We further investigate systems with smaller transfer integrals. As shown in Figure 4D, the standard surface hopping approach with the 0.1 fs time step gives huge errors when the transfer integral is reduced to 1 meV. A time step as small as 0.005 fs is necessary to obtain the converged result. In comparison, SC-FSSH shows very accurate and stable performance over the whole range of the time steps (see Figure 4E). Especially, the 1 fs time step gives only a very slight error relative to the results obtained using $dt = 0.001$ fs (see Figure 4F).

Real molecular aggregates normally involve more molecules. In order to check the influence of the number of molecules on the SC-FSSH performance, we considered a molecular stack with five molecules. The intermolecular coupling is set to 5 meV, as in the top row of panels in Figure 4. From Figure 4G corresponding to the standard FSSH, we can find that the time step of 0.1 fs, which gives accurate results for the trimer in Figure 4A, no longer works for the stack of five molecules. Remarkably, with addition of only two extra molecules, we need reduce the time step of the standard FSSH by a factor of 1000,

to 0.0001 fs, in order to get the converged result. One explanation is that a larger number of trivial crossings exist in larger systems. More importantly, the coupling between the initially occupied site and the site on the other end of the aggregate gets weaker with extra molecules in between. Thereby, the energy splitting of the trivial crossings involving the first and last sites decreases, and an accurate description requires a much smaller time step. Considering the fact that the number of molecules in many processes, such as charge transport and exciton diffusion, is on the order of a hundred or more, the straightforward FSSH approach with small time becomes impractical. On the other hand, the time step required for the SC-FSSH method is independent of the number of molecules in the aggregate. As shown in Figure 4I, the 1 fs step is already sufficient to give a good description of the dynamics in the five-site system. The value is the same as in the three-site cases shown in Figures 4C and 4F.

In the discussion above, small molecular systems ($N = 3$ and 5) are used as examples to investigate the trivial crossing problem. In order to have a global view into the extent of trivial crossings within supramolecular systems, we further perform thousands of realizations on molecular aggregates with different size up to $N = 50$. For each realization, we prepare random nuclear conformations, and calculate the minimum energy differences between all adiabatic states. The distribution of such minimum energy splitting is shown in Figure 5. We can find that the peak of the distribution is continuously shifted to

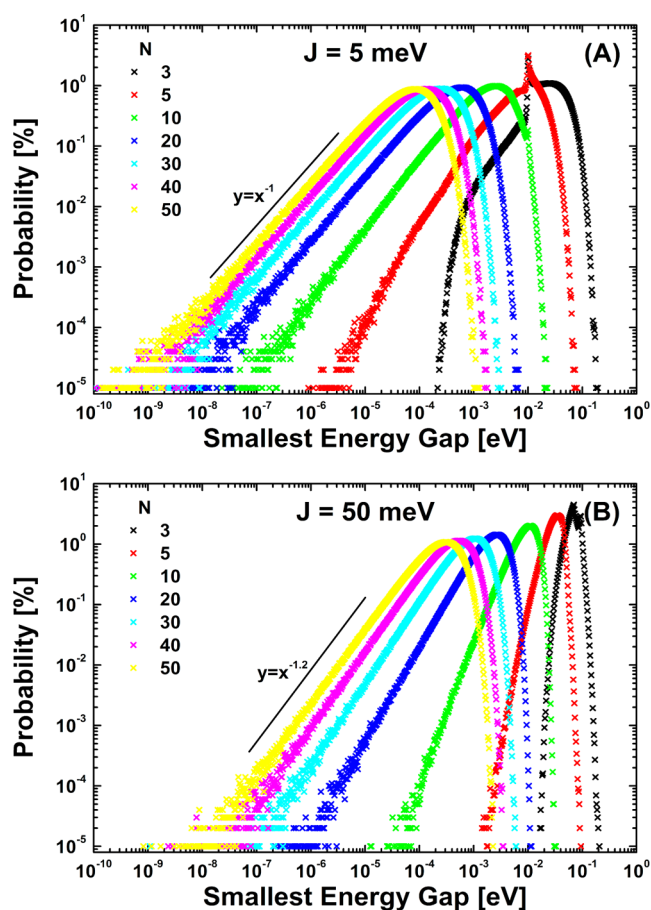


Figure 5. Distribution of the minimum energy splitting between all adiabatic states for systems with different size. The transfer integral is set to be (A) 5 meV and (B) 50 meV.

smaller energies with increase of the system size. Additionally, the probability follows an exponential decay at the smaller energy side of the peak. This means that there is a finite probability to have very small energy differences between adiabatic states in large systems. Although the probability appears quite small, a single improper treatment of such strong trivial crossings will have artificial electron jumps between molecules that are extremely far away from each other, inducing enormous errors. Systems with larger transfer integrals exhibit faster decay of the probabilities with decreasing energy splitting. Although the error from trivial crossings in these cases tends to be smaller, the intrinsic trivial crossing problem remains the same. For very large molecular systems, such as organic solids, almost all of the crossings are trivial crossings. It is impossible to perform standard FSSH calculations in these cases. In comparison, the SC-FSSH method developed in this study provides a simple, clean and reliable approach for mixed quantum/classical dynamics in the presence of trivial crossings.

A few final notes are in order. Only one surface hopping probability is corrected within the SC-FSSH approach. Generally, the number of trivial crossings increases linearly with the system size. To avoid having multiple trivial crossings within one time step, one needs to reduce the time step when dealing with systems composed of large numbers of molecules. Fortunately, due to the linear scaling of the number of trivial crossings with the system size, the time step needed for accurate SC-FSSH calculations will remain sufficiently large. For example, when using the same set of parameters as for pentamers in Figure 4, we can reduce the time step to 0.1 fs to get comparable results for molecular aggregates with $N = 50$. The time step should also be chosen in line with the frequency of the major nuclear vibrations and the magnitude of state energy differences. In practical calculations, test calculations for short simulation time using different time steps are needed. Note that the present SC-FSSH can be potentially combined with the flexible surface hopping idea¹² to further reduce the computational cost. Therein, the time step can be larger, since the system for surface hopping is smaller.

At every time step, we calculate the energy differences between the active state and all other states. We find the state that gives the lowest energy difference, and introduce the correction to the FSSH transition probability to this state. This state is not necessarily experiencing a trivial crossing; however, it has the highest likelihood to give a probability error. The state energetically closest to the active state can be encountering an avoided crossing, or no crossing at all. In these cases, the correction to the surface hopping probability is generally negligible.

The present and similar studies based on model Hamiltonians use a diabatic representation,^{12,13,28,29,34,35} where application of SC-FSSH is straightforward. If the Hamiltonian is given in the adiabatic basis, one can employ a local diabatic representation.²² Yarkony,³⁷ Baer,³⁸ Cave, and Newton³⁹ have done extensive work on diabaticization for a different purpose. The SC-FSSH approach can also be applied within any representation in which the wave function can be propagated accurately without the use of the nonadiabatic coupling. This can be achieved in ab initio simulations using the “diabatic” atomic orbital representation, a plane-wave basis, or a spatial grid.^{31–33} Thus, SC-FSSH can be combined with the time-dependent density functional theory, which has a wide range of applications.^{40–44}

The trivial crossing problem stems from the specific fewest switches hopping algorithm, explicitly involving the non-adiabatic coupling.¹⁵ To sample the hops, the original surface hopping method⁴⁵ used the standard quantum-mechanical probabilities given by the squares of the wave function coefficients. The trivial crossing problem does not arise in this case. As explained by ref 15, surface hopping based on the quantum probabilities errs in condensed phase. Bittner and Rossky⁴⁶ showed that condensed phase quantum/classical calculations require a decoherence correction. Prezhdo's formulation of the decoherence effects⁴⁷ restored the use of quantum probabilities to achieve hops in condensed phase systems, leading to decoherence induced surface hopping.⁴⁸ Decoherence-based approaches^{47–50} do not suffer from the trivial crossing problem, but require a model for the coherence time.

In summary, we have proposed a simple correction to the standard FSSH algorithm. The resulting SC-FSSH approach solves the electron dynamics avoiding nonadiabatic coupling, while performing FSSH in the preferred, adiabatic basis. The trivial crossing problem of the adiabatic FSSH is corrected using a self-consistency check, based on the accurate solution of the Schrödinger equation. Through several representative studies on the Holstein Hamiltonian, we have proved that SC-FSSH can resolve the trivial crossing problem in complex materials with high accuracy and reliability. A time step as large as 1 fs allows SC-FSSH achieve the converged result, while the standard FSSH requires time steps that are many orders of magnitude smaller. The advantages of SC-FSSH become more significant for systems with weaker interactions and larger size. Because supramolecular systems suffer strongly from the trivial crossing problem, the SC-FSSH approach greatly broadens FSSH applicability.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the U.S. National Science Foundation, Grant No. CHE-1300118.

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