Analysis of the Trajectory Surface Hopping Method from the Markov State Model Perspective

Alexey V. Akimov¹, Dhara Trivedi², Linjun Wang¹, and Oleg V. Prezhdo¹*

¹Department of Chemistry, University of Southern California, Los Angeles, CA 90089, U.S.A.
²Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627, U.S.A.

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We analyze the applicability of the seminal fewest switches surface hopping (FSSH) method of Tully to modeling quantum transitions between electronic states that are not coupled directly, in the processes such as Auger recombination. We address the known deficiency of the method to describe such transitions by introducing an alternative definition for the surface hopping probabilities, as derived from the Markov state model perspective. We show that the resulting transition probabilities simplify to the quantum state populations derived from the time-dependent Schrödinger equation, reducing to the rapidly switching surface hopping approach of Tully and Preston. The resulting surface hopping scheme is simple and appeals to the fundamentals of quantum mechanics. The computational approach is similar to the FSSH method of Tully, yet it leads to a notably different performance. We demonstrate that the method is particularly accurate when applied to superf_exchange modeling. We further show improved accuracy of the method, when applied to one of the standard test problems. Finally, we adapt the derived scheme to atomistic simulation, combine it with the time-domain density functional theory, and show that it provides the Auger energy transfer significantly improving upon other considered techniques.

1. Introduction

Theory of molecular dynamics with quantum transitions is an actively developing field of computational chemistry.¹–¹⁴ The interest in this subject is constantly stimulated by the need for accurate and computationally tractable simulation methodologies for modeling processes involving coupled electron–nuclear dynamics in contemporary materials. In particular, such techniques are required for studying photo-induced charge transfer in photovoltaic and photocatalytic materials,¹⁵–²⁰ long-distance energy transfer in biological photosynthetic complexes, or photo- and electro-stimulated mechanical response in nanoscale systems.²¹–²⁶

A great body of methods for modeling molecular dynamics with quantum transitions has been developed over the last several decades. We refer the reader to specialized reviews discussing some of these methods.²²–²⁷ Among the variety of techniques, Tully’s fewest switches surface hopping (FSSH)¹⁹ remains one of the most utilized methods, due to its conceptual and practical simplicity, good accuracy, and high computational efficiency. The FSSH method is not a panacea, and there are examples where it breaks down. In particular, the superf_exchange problem requires a more advanced treatment.

The need for consideration of superf_exchange effects is motivated by applications by excitation, many-particle processes, such as Auger recombination and energy transfer,²⁹–³⁵ singlet fission³⁶–³⁹ or Raman scattering. The superf_exchange mechanism is also important for tunneling and conductivity in molecular electronics.⁴⁰–⁴⁴ In all these processes, transitions between excitonic states can involve more than one simultaneous single-particle transition. A direct consideration of the dynamics of such excitations is prohibited by the Slater rules, and only sequential mechanisms are viable.

The problem of superf_exchange arises when there is at least one pair of states that are not coupled to each other directly. The states can be either diabatic or adiabatic. The transition between these states is mediated by an intermediate high-lying state. The overall transition rates are strongly underestimated in FSSH theory because the transitions through such intermediate states are inhibited by the probabilities of overcoming the high-energy barrier. Simulations of non-adiabatic processes using FSSH are usually performed in the adiabatic basis, in which FSSH shows reasonable accuracy. However, the use of diabatic states (e.g., donor and acceptor states) may be advantageous, both in terms of computational efforts and for interpretation of the problem physics. Diabatic states are used regularly in phenomenological models of charge and energy transfer because they have well-defined physical meaning. Super_exchange effects are traditionally described in a diabatic representation. An adiabatic picture can lead to spurious effects arising from artificial delocalization of an adiabatic state between donor and acceptor sites that are very distant from each other. Finally, the adiabatic representation leads to numerical problems with calculation of non-adiabatic coupling.⁴⁵–⁴⁶ Under the conditions when diabatic states are strongly localized and many pairs of states are decoupled, the accuracy of the original FSSH method is often unacceptable when diabatic states are used, motivating development of the alternative formulations.²⁸,⁴⁷

Recently, the problem of superf_exchange has been addressed by Wang et al.²⁸ who proposed a global flux surface hopping (GFSH) algorithm. In it, hopping between a pair of states is determined by a relative change of state population during the infinitesimal time slice. The method avoids computing hopping probabilities based on one-particle properties (such as non-adiabatic couplings between one-particle states), thus solving the superf_exchange problem phenomenologically. In the alternative second-quantized surface hopping (SQUASH) approach,⁴⁷ the superf_exchange problem was solved by extending the quantum dynamics to the space of second-quantized states representing coupled trajectories. The method introduces many-particle states, allowing a single transition between a pair of states to capture a many-body transition.

Although the developed techniques provide notable improvement of the accuracy in modeling the superf_exchange problem, they have certain limitations. Specifically, the
GFSH approach relies on an ad hoc scheme for splitting total probability to leave a state into probabilities of doing this via different channels \( i \to j \). As it is pointed out by Wang et al.,\cite{Wang2015} there are, in principle, many possibilities of such splitting. Different splitting schemes define different hopping probabilities, which may affect the results of surface hopping simulations. Thus, the question of uniqueness, physical meaning and rigor of the definition of surface hopping probabilities remains open, presenting a conceptual challenge. On the other hand, SQUASH\cite{Zhou2014} introduces coupled trajectories that may exchange energy. The number of \( N \)-particle states describing \( N \) coupled trajectories increases the dimensionality of the problem very rapidly, making the computations costly. The method also relies on the conceptually challenging prescription of the energy exchange in this ensemble-based approach to quantum dynamics.

In a search for a conceptually simple and computationally tractable model that can capture superexchange effects, and that can be applied easily to atomistic simulations, we have revised Tully’s FSSH method. Specifically, we questioned the “fewest switches” aspect of the method. This approximation demands that only a single (quasi)particle hop can occur at a time. In other words, the dynamics is limited to the first-order excitations. The two-body and higher excitations are neglected by construction. In the present work we lift the “fewest switches” approximation and analyze the consequences this assumption has on quantum dynamics. In our approach the electronic transitions are not limited to the hopping out of an active state only, but a reverse process is also possible. As a result, we have considered the surface hopping method from the viewpoint of a Markov state model. For convenience, we call this approach a Markov state surface hopping (MSSH) method. The method differs from the FSSH only in the definition of the surface hopping probabilities. Despite the close similarity of the methods, their performance differs notably, as will be shown further.

The rationale for the present model is to go beyond the assumptions of the FSSH method. Namely, the cornerstone of the FSSH approach is the requirement to minimize the number of stochastic hops between electronic states. As a consequence of this requirement only a possibility of hopping out of state, not into the state, is considered at any given time of propagation. As a result, only one-particle transitions are possible. If one also allows a simultaneous influx into the present state from all other states, the multi-particle transitions can be captured. The model that permits such a multi-channel population transfer to occur at any given time, rather than sequentially, is essentially a Markov state model.

In Sect. 2, we present the conceptual basis and the derivation of the MSSH method. Further, we show that the approach reduces to the old, and somewhat abandoned, frequent switching surface hopping of Tully and Preston.\cite{Tully1980} In Sect. 3, we demonstrate that the MSSH method delivers an excellent agreement with the results of exact simulations when modeling superexchange in an abstract three-state model system. We then demonstrate the performance of MSSH in adiabatic representation as applied to the modified double avoided crossing (m-DAC) model of Tully.\cite{Tully1990} We show that MSSH does not reduce to the mean-field (MF) method and yields much better results, despite the strong resemblance with the MF method. Finally, we adapt the MSSH method to the classical path approximation (CPA), which neglects electron back-reaction on nuclei, and apply it to compute Auger-type energy transfer dynamics in atomistic quantum dots (QDs). We conclude that the method can be useful for a number of systems and processes, where the standard FSSH may have problems. We also discuss limitations of the proposed approach.

2. Theory

2.1 Analysis of the FSSH

One of the basic elements of Tully’s FSSH method is the definition of hopping probabilities. The method is derived from the following assumption of hopping out of a single state. Assume that the number of trajectories in the current state \( i \) at time \( t \) is \( N_i(t) \). If at the later time \( t + dt \) this number decreases to \( N_i(t + dt) \), with \( N_i(t + dt) < N_i(t) \), the probability to leave state \( i \) during the time interval \( [t, t + dt] \), \( P_i(t) dt \), is given by the relative change of population in that state:

\[
P_i(t) dt = \frac{N_i(t) - N_i(t + dt)}{N_i(t)}. \tag{1a}
\]

Requiring that the number of trajectories in a given state is proportional to the quantum populations, \( a_{ii} \), derived from the time-dependent Schrödinger equation (TD-SE) and expanding the properties at time \( t + dt \) in the Taylor series, one obtains:

\[
P_i(t) dt = \frac{N_i(t) - N_i(t + dt)}{N_i(t)} a_{ii}(t) = \frac{a_{ii}(t) - a_{ii}(t + dt)}{a_{ii}(t)} \approx -\frac{\partial a_{ii}(t)}{a_{ii}(t)}, \tag{1b}
\]

where the quantum populations are given by the diagonal elements of the density matrix. The latter is defined as

\[a_{ii}(t) = c_{i}^\dagger(t)c_i(t).\tag{2}\]

The wavefunction coefficients, \( c_i(t) \), evolve according to the TD-SE:

\[
\hbar \frac{d}{dt} c_i = \sum_j H_{ij}c_j, \tag{3}
\]

where \( H_{ij} = V_{ij} - i\hbar d_{ij} \) is the effective vibronic Hamiltonian, \( d_{ij} \) are the non-adiabatic couplings. The latter are zero in the diabatic representation.

The assumption of hopping only out of the current state does not work when more than one particle or state are involved simultaneously (e.g., superexchange, Auger process, Raman scattering, two-photon transitions). One can construct a situation where the same probability to leave state \( i \) can be accommodated by simultaneous hops from and to this state \( i \). Thus, the factual population flux out of the present state may be larger (and compensated by the counter-flux from other states) than the one predicted by Eq. (1). This is the reason why FSSH does not work well for the processes involving multiple states, such as superexchange or Raman scattering.

2.2 Markov state surface hopping

To overcome the limitations of the FSSH method in regard to multi-photon processes, we formulate a Markov state surface hopping method. The method follows the overall
FSSH prescription, including hop rejection, velocity rescaling, propagation of nuclei and electronic amplitudes. The only distinction from the FSSH enters via the way the surface hopping probabilities are defined. To derive these rates, we follow the kinetic considerations discussed below. Consider the number of trajectories, \( N_i(t + dt) \), in state \( i \) at time \( t + dt \). It can be computed based on the numbers of trajectories, \( \{N_i(t)\} \), in all states at time \( t \), and the "rates" of transition between states \( i \) and \( j \), \( \{k_{j\rightarrow i}(t; t + dt)\} \):

\[
N_i(t + dt) = \sum_j k_{j\rightarrow i}(t; t + dt)N_j(t). \tag{4a}
\]

It can be seen from the dimensionality analysis that the "rates" should be interpreted as the fraction of trajectories transferred from the source to target states during a given time interval. Thus, it is more accurate to think of the "rates" as not local in time, unlike the quantities \( a_{ij}(t)/a_{ij}(t) \) used to define the hopping probabilities in FSSH. Instead, the "rates" carry integral information about the dynamics during for the time slice \([t, t + dt]\). This information may implicitly include many-particle transitions.

Normalization to the total number of trajectories transforms Eq. (4a) to the equation for quantum populations:

\[
a_i(t + dt) = \sum_j k_{j\rightarrow i}(t; t + dt)a_j(t). \tag{4b}
\]

and in the matrix form:

\[
a(t + dt) = K(t; t + dt)a(t). \tag{4c}
\]

Here, \( a(t) = (a_0(t) a_1(t) \cdots a_M(t))^\top \) is the population state-vector, \( M \) is the number of states, \( K(t; t + dt) \) is the matrix representation of the population transfer operator discussed above. Note that the element \((i,j)\) of the matrix defines the rate of the "reverse" transition, that is, the transition from the state \( j \) to the state \( i \):

\[
K_{ij} = k_{j\rightarrow i}. \tag{5}
\]

Now the question is how to define the population transfer operator such that the surface hopping populations are consistent with the populations obtained from the TD-SE, Eq. (3). Using vector algebra, one can see that the matrix \( K(t; t + dt) \) is an outer product of the source and target population state-vectors:

\[
K(t) = \frac{a(t + dt)d^\top(t)}{a(t)d(t)} = \frac{a(t + dt)d^\top(t)}{||a(t)||^2}. \tag{6}
\]

Note that all elements of the matrix \( K(t; t + dt) \) are non-negative, because all elements of the population vectors are non-negative. Thus, there is no additional complication associated with negative hopping probabilities, unlike in FSSH.

We are now in position to define the Markov state model. It is defined by the transition probability matrix, \( T \), the elements of which are related to the elements of the "rate" matrix \( K(t; t + dt) \) by the following equation:

\[
T_{i\rightarrow j} = \frac{k_{j\rightarrow i}}{\sum_k k_{k\rightarrow i}} = \frac{K_{ij}}{\sum_k K_{ki}}. \tag{7}
\]

The elements of the matrix \( K(t; t + dt) \) are non-negative, so are the elements of the matrix \( T \). Thus, the ad hoc schemes for setting negative transition probabilities to zero, used in other surface hopping algorithms, including FSSH and GFSSH, are not needed.

Finally, the expression Eq. (7) can be simplified using the definitions in Eqs. (5) and (6):

\[
T_{i\rightarrow j} = \frac{a_{ij}(t + dt)a_{ii}(t)}{\sum_k a_{ik}(t + dt)a_{kk}(t)} = \frac{a_{ij}(t + dt)a_{ii}(t)}{\sum_k a_{ik}(t + dt)a_{kk}(t)} = a_{ij}(t + dt). \tag{8}
\]

We now see that MSSH defines the surface hopping probabilities as the quantum populations of the target states at the next time step. The result is unexpectedly simple and reflects the well-known concept of quantum mechanics—that the quantum amplitudes \( a_{ij}(t) \) have the meaning of the probability to find the system in a given state \( i \) at time \( t \). Note that, in general, the probability to find the system in a specific state and the probability to hop to a given state from another arbitrary state are different quantities. For example, in both FSSH and GFSSH, the hopping probability depends on the current quantum state. In MSSH, the hopping probability depends only on the population of the final state. Moreover, this probability does not explicitly depend on non-adiabatic coupling between the source and target states. Thus, a transition is possible even when the non-adiabatic coupling between these states is zero. The transition is accommodated by the population flow via alternative channels, as implicitly encoded in the diagonal elements of the propagated density matrix, \( a(t + dt) \).

We note that the result, Eq. (8), was utilized in one of the first surface hopping algorithms by Tully and Preston. However, there are two main distinctions with our approach we would like to point out. First, at the technical level, the MSSH hopping probability is defined differently from the one used by Tully and Preston. In their formulation the surface hopping probabilities are defined as the TS-SE initial populations of the target states, \( T_{i\rightarrow j} = a_{ij}(t) \), while MSSH uses final populations of the target states \( T_{i\rightarrow j} = a_{ij}(t + dt) \). Second, the derivation of the Tully–Preston and MSSH methods are conceptually different. In our approach we start by explicitly requesting the higher-order effects to be included and employ the general Markov state model framework. The frequent switches surface hopping method of Tully and Preston relied on the intuitive probabilistic interpretation of quantum populations, without rigorous derivation.

3. Applications

In this section, we present the results of our calculations on model and atomistic systems. To demonstrate the capabilities of MSSH with regard to the superexchange, we apply the method to the three-state superexchange problem of Wang et al. Next, to show the performance of the method with the standard test models and to illustrate the advantages of
MSSH over the MF method, we apply MSSH to a modified double avoided crossing (m-DAC) problem.1,49) Finally, a CPA version of the MSSH algorithm is developed and applied to compute the timescales of Auger relaxation in a small QD.

3.1 A three-state superexchange problem

The model consists of three states, with the energy alignment and coupling shown schematically in Fig. 1(a). The direct coupling between states 1 and 2 is set to zero. The Hamiltonian is defined by the matrix elements in the diabatic representation (diabatic energy levels and diabatic couplings):

\[ E_1(x) = 0, \quad E_2(x) = 0.005, \quad E_3(x) = 0.01, \quad V_{12}(x) = V_{23}(x) = V_{13}(x) = V_{31}(x) = 0.001 \exp(-x^2/2), \quad V_{12}(x) = V_{23}(x) = 0.01 \exp(-x^2/2). \]

The simulations are performed in the diabatic representation. The atomic units of length and energy are used. The mass of the particle is set to 2000 a.u. The initial momenta and positions of the classical particle are set to the defined values for all trajectories, with no additional spread, to exclude any related effects. The initial position is set to \(-15\) a.u., so that trajectory starts far away from the strong coupling region. The initial momentum varies over the interval from 1 to 50 a.u. with the 0.25 step in scattering calculations, or is set to a specified value in the trajectory analysis calculations. The ensemble of 2500 trajectories is propagated, to generate statistically-meaningful and smooth distributions of electronic populations at all times. Equations of motion for the electronic and nuclear degrees of freedom are integrated using split-operator technique, which leads to stable and symplectic integration. The time-step is set to \(200/p\) a.u., where \(p\) is the initial momentum. Each trajectory is propagated for 2000 steps with properties of interest printed every 2 steps. The propagation of each individual trajectory is stopped whenever the trajectory leaves the interest interval defined as \([-15, 20]\). The exact solution is obtained via integration of the TD-SE on a grid numerically, as explained in the previous work.28)

The results obtained with the MSSH method coincide with the exact solution to a great degree of accuracy, Fig. 1. On the contrary, FSSH reproduces only the high-energy results. However, the high incident momentum region is essentially classical, with negligible quantum effects. In this region, any semiclassical theory, including mean-field, as well as classical propagation would give the same accuracy as the fully quantum description. Thus, we judge the quality of the MSSH based on its capability to capture low-energy effects. The main difference between MSSH and FSSH is observed in this region of the initial momentum. For the initial momentum in the range of 4–6 a.u. FSSH simply does not allow a transition to state 2. The transition would require overcoming a high-energy barrier to the intermediate state 3. This cannot be accomplished when the nuclear kinetic energy is low. In contrast, MSSH makes the surface hopping decision solely on the basis of the TD-SE-derived populations. The hop rejection criterion based on the energy conservation is verified after each attempted transition, similar to FSSH. However, the transition is no longer mediated by the high-lying state 3 and can proceed directly.

Fig. 1. (Color online) A three-state superexchange model. Schematic representation of the model Hamiltonian (a). Probabilities of transmission on (b) first, (c) second, and (d) third states. Performance of the MSSH method is compared with the results of FSSH and exact quantum simulations.
Therefore, one observes a notable population transfer to state 2 in the intermediate energy region.

The transmission on state 3 as a function of the initial incident momentum [Fig. 1(d)] shows a slight deviation of the MSSH curve with respect to the exact results. The deviation is larger in the region of low initial momenta. The high-energy results are very close to the exact and FSSH data. The total transmission probability on state 3 is very small, an order of magnitude smaller than the transmission on state 2. Thus, the better agreement between the FSSH and exact data compared to the MSSH performance is not indicative of the overall superiority of FSSH over MSSH. It can be attributed to technical sides, such as choice of initial conditions, statistical properties of the trajectory ensemble, etc. One can observe a small, but systematic tendency of the MSSH to overestimate transition probabilities slightly. Still, MSSH provides qualitative and quantitative improvement over FSSH for a number of systems, including the present superexchange model.

We also illustrate the distinctions between the two methods by considering the evolution of the initial state population and active state index (denoted istate) for a typical trajectory (Fig. 2). We compute the ensemble-averaged populations of two types—those that come from the fully coherent TD-SE (denoted SE) and those computed via the surface hopping algorithms (denoted SH). These populations are computed along the particular trajectory shown in figures. The main assumption used to derive the surface hopping probabilities (both FSSH and MSSH) states that the SH populations must reach the SE populations, in the limit of sufficiently large number of trajectories. There can be two sources of deviation of SH populations from the corresponding SE values: a) due to the wavepacket branching; b) due to intrinsic properties of the TSH algorithm. The branching affects the results in the following way. In Figs. 2 and 4, we plot SH and SE along a single trajectory, but other trajectories may take alternative paths, resulting in distinction of the SH and SE populations computed along the path chosen for plotting. The trajectory branching is absent in the superexchange model, because the potential energy surfaces are flat and the diabatic basis is used. Thus, the results in Fig. 2 reflect only the intrinsic properties of the TSH algorithm. Hence all trajectories will take the same path. Although the evolution of populations implied their dependence on time, we plot the populations as the function of positions, to facilitate the analysis with the model Hamiltonian in mind. In particular, the position \( x = 0 \) correspond to the maximum of the off-diagonal (coupling) Hamiltonian matrix element.

First, we analyze the behavior of the populations in the low incident momentum region (\( p = 5 \) a.u.)—Figs. 2(a) and 2(b). One can clearly observe that the SH populations computed with FSSH do not follow the corresponding SE populations. The active state remains unchanged. In other words, no population transfer to other states occurs, as we have observed in Fig. 1. On the contrary, the SH populations computed with MSSH follow the corresponding SE values.

Fig. 2. (Color online) Evolution of the ensemble-averaged TD-SE populations (SE) and TSH-based populations (SH) computed with FSSH (a, c) and MSSH (b, d) methods. The active state (istate) evolution for a representative individual trajectory is shown by dotted line. The evolutions for two initial momenta are shown: \( p = 5 \) a.u. (a, b) and \( p = 10 \) a.u. (c, d).
One can also observe multiple switches of the active state (dotted line). This behavior is consistent with non-negligible population transfer probabilities observed at this value of incident momentum.

Second, we extend the above analysis to the larger incident momentum value \( p = 10 \) a.u. As it follows from Fig. 1, there are no important superexchange effects in this region of kinetic energies: both FSSH and MSSH perform well. This conclusion is indeed supported by the time evolution of populations shown in Figs. 2(c) and 2(d). In both cases, the SH populations coincide with the corresponding SE counterparts. There is no surface hop for the trajectory depicted in Fig. 2(c), but it occurs for other trajectories in the ensemble. Surface hops are still more frequent in the MSSH algorithm, but are less frequent than for \( p = 5 \) a.u. momentum.

The recently developed GFSH method\(^{28}\) is also capable of handling the superexchange problem. However, some disagreement between the GFSH and exact results remains. MSSH shows much closer agreement with the exact results.

### 3.2 Modified double avoided crossing problem

A double avoided crossing (DAC) model was originally proposed by Tully.\(^{1}\) The model is formulated in terms of matrix elements of the diabatic Hamiltonian as \( E_1(x) = 0, E_2(x) = -A \exp(-B x^2) + E_0, V_{12}(x) = V_{21}(x) = C \exp(-D x^2) \), with the parameters chosen to be \( A = 0.10, B = 0.28, E_0 = 0.05, C = 0.015 \), and \( D = 0.06 \). We have employed a modified version of this problem in one of our previous studies.\(^{49}\) Our modification sets the parameter \( B = 0.028 \), increasing the separation between the avoided crossing regions and allowing stronger interference patterns to develop. The simulations are performed in the adiabatic representation, as in the original work.\(^{1}\) The adiabatic potential energy profiles are shown in Fig. 3(a).

The scattering probabilities computed with MSSH and FSSH are compared with the reference exact results in Figs. 3(b) and 3(c). The exact numerical solution was reported in the earlier work.\(^{49}\) In general, the qualitative behavior of the MSSH solution agrees with both FSSH and exact results. Notably, the MSSH solution is closer to the fully quantum result than FSSH, as demonstrated by the good agreement of the peak positions in Fig. 3(b). The position of the MSSH peaks is in the middle between the positions of the FSSH and exact peaks, leaning toward the exact solution. This effect is especially pronounced for the low incident momentum region. As we noted earlier, the quantum effects become less important at higher energies. As a consequence, all methods produce similar results in this limit.

By construction, the MSSH method is based on frequent surface hops. As discussed by Tully,\(^{1}\) such frequent hops make the MSSH method similar to the MF/Ehrenfest approach. The similarity originates from the observation that the effective potential energy surface on which a system evolves in SH with frequent hops is, on average, close to the wavefunction-weighted potential energy surface used in the MF dynamics. The similarity of the frequent switches surface hopping with the MF theory was one of the reasons why the approach was abandoned, and why the FSSH method gained...
more popularity. In this work we demonstrate that this conclusion is not always true. Quite the opposite, the MSSH method performs much better than the MF technique. To demonstrate this result, we utilize the modified DAC (m-DAC) model defined above.

The scattering probabilities for the m-DAC model problem computed with the MSSH and MF methods are shown in Fig. 3(c). The exact solution is also shown as a reference. The transition probabilities computed with MSSH and MF are very close to each other when the initial momentum is sufficiently high (e.g., $>20$ a.u.). This agreement can be attributed to the almost classical regime of the dynamics. As the nuclear kinetic energy decreases, quantum effects become dominating. In the intermediate energy region ($15 < p < 20$ a.u.) the positions of the peaks obtained with the MSSH method shift toward the peaks of the exact solution, away from those of the MF curve.

The most notable difference between the results obtained with the MSSH and MF theories is observed in the region of low initial momenta ($<15$ a.u.). The MF solution shows unphysical large-amplitude fluctuations of transition probabilities on states 1 and 2. The MSSH solution converges toward the probabilities of 1.0 and 0.0, respectively, in agreement with the fully quantum solution.

Analogously to the superexchange problem, we analyze the evolution of the populations generated by the FSSH and MSSH methods applied to the m-DAC problem (Fig. 4). The parameters of simulations are same as for the superexchange problem, except that we choose different incident momenta for trajectory analysis. Namely, we analyze trajectories with initial $p = 10$ a.u. [Figs. 4(a) and 4(b)] and $p = 25$ a.u. [Figs. 4(c) and 4(d)]. In case when the initial momentum is small, the FSSH results show the trajectories turning twice—approximately at the points of strong nonadiabatic coupling, $x = \pm 5$ a.u. The turning of the trajectory is the reason why Fig. 4(a) shows a multi-valued function. For larger initial momentum we do not observe spatial oscillations—the trajectory simply passes through the regions of strong coupling, without reflecting.

In the FSSH case [Figs. 4(a) and 4(c)], one can also observe two surface hops ($0 \to 1$) and ($1 \to 0$) per the representative trajectory. The hops occur around the crossing points, as expected. In the MSSH case, multiple transitions between the two states are observed for the representative trajectory. At low incident momentum of classical particle, $p = 10$ a.u., both FSSH and MSSH methods show progressively diverging SH and SE populations. This divergence is facilitated by strong nonadiabatic coupling regions. As we have mentioned in the previous section, the difference in SH and SE population may arise because of the wavepacket branching. In other words, the agreement between the SH and SE populations characterizes how typical the chosen trajectory is for the computed ensemble. For instance, one can see a good degree of agreement of the SE and SH FSSH-based populations in the region $[-15, -5]$ [Fig. 4(a)]. This means that almost all trajectories pass this region with similar populations of electronic states. In the MSSH case, the trajectories pass a bigger common interval $[-15, 5]$ [Fig. 4(b)].
The time evolution of the energy levels of the Cd$_{33}$Se$_{33}$ QD is illustrated in Fig. 5(a). The Cd$_{33}$Se$_{33}$ QD is a "magic"-size cluster with a diameter of 1.3 nm. It has been shown experimentally to be very stable, making it an excellent model for the electronic structure studies of CdSe QDs. We firstly run quantum-mechanical molecular dynamics (MD) using the Vienna Ab initio Simulation Package (VASP) followed by nonadiabatic molecular dynamics (NA-MD) simulations performed using the PYthon eXtension for Ab Initio Dynamics (PYXAID).

The QD structure is initially optimized using the conjugate-gradient algorithm until the force convergence threshold of 0.001 eV/Å is reached. Subsequently, the system is thermalized by running a 10 ps ab initio MD simulation in the canonical ensemble. The collisional thermostat as implemented in the VASP program maintains the average temperature. The velocities are rescaled every 4 fs to match the target phonon temperature of 300 K.

The thermalized structures are utilized as input for the NA-MD calculations. Starting from these structures, 10 ps MD trajectories are computed in the microcanonical ensemble. All MD calculations utilize the velocity Verlet algorithm with the time step of 1 fs to propagate nuclear coordinates. The Kohn–Sham energies and orbitals computed at each time-step are utilized to obtain the NA couplings and information is stored and used to perform the NA-MD simulations with the help of the PYXAID package. The CPA is applied to all three semiclassical methods — MSSH, FSSH, and GFSH — to achieve considerable computational savings.

All quantum calculations employ density functional theory (DFT) with the PBE exchange–correlation functional as implemented in the VASP program. To accelerate calculations and to account for the effects of core electrons, the projector-augmented-wave (PAW) pseudopotentials for Cd and Se are employed. Valence electrons are described using plane waves with the energy cutoff of 280 eV. To avoid interaction of the QD with its image, a sufficient vacuum is added around the QD, resulting in a 25 × 25 × 25 Å simulation box. Only the gamma-point of the Brillouin zone is used.
The Auger relaxation process, where an electron in the initially prepared 1P\textsubscript{e} state relaxes down to the 1S\textsubscript{e} state by exchanging energy with the hole, is used for integration because this is a process: the electron in the initially prepared 1P\textsubscript{e} state relaxes down to the 1S\textsubscript{e} state by exchanging energy with the hole; (b) Time evolution of the electron population in the 1S\textsubscript{e} state computed with the FSSH, GFSH, and MSSH methods.

is used for integration because this is a finite system. Further computational details can be found in the work of Trivedi et al.,\textsuperscript{63} in which the Auger process was studied using the GFSH approach.\textsuperscript{28}

The electronic energy levels of the CdSe QD are shown in Fig. 5(b). The asymmetry of the density of states (DOS) favors the Auger relaxation channel. That is the photoexcited electron overcomes the larger energy barrier between the 1P\textsubscript{e} and 1S\textsubscript{e} states by transferring its energy to the hole, as shown schematically in Fig. 6(a). In turn, the hole rapidly transfers its energy to phonons, by relaxing down the manifold of dense energy levels, Figs. 5(b) and 6(a). The calculated mean energy gap between the 1P\textsubscript{e} and 1S\textsubscript{e} states of the electron is 0.4 eV. It agrees reasonably well with the experimental observations of 0.1–0.3 eV for CdSe QDs.\textsuperscript{50} The slightly larger value arises because the investigated QD is smaller than experimental QDs. Smaller size emphasizes the quantum confinement (particle-in-a-box) effect that increases the energy level separation. Because of the large gaps between one-electron orbital energies, the many-electron states involved in the Auger energy transfer are separated by the gaps of comparable magnitude.\textsuperscript{63} Thus, the conditions favoring the emergence of superexchange are met most of the time, and it is expected that MSSH can work well.

To study the Auger relaxation dynamics, we compute the population of the 1S\textsubscript{e} state, into which the photogenerated electron relaxes due to Auger-type energy exchange with the hole [Fig. 6(a)]. To obtain reliable statistics, we average the results over 500 stochastic realizations of the surface hopping algorithms and over 30 starting geometries. The starting geometries are selected randomly from the initially computed MD trajectory. The computed averaged population of the 1S\textsubscript{e} state is presented in Fig. 6(b), along with the fitted exponential curves. The fits are used to extract the timescale for the electron relaxation.

The standard FSSH\textsuperscript{11} and the recently developed GFSH\textsuperscript{28} methods are used as references to understand the performance of the MSSH method reported in this work. MSSH exhibits significantly faster dynamics than the other two surface hopping techniques. The 0.7 ps time scale given by the MSSH is an order of magnitude smaller than the 8.2 ps time scale obtained through FSSH. The two-photon photoemission\textsuperscript{50} and transient absorption spectroscopy\textsuperscript{51,52} measurements have shown sub-picosecond timescales for the electron relaxation from 1P\textsubscript{e} to 1S\textsubscript{e}. In particular, the work of Sippel et al.\textsuperscript{50} reports the 0.22 ps relaxation timescale. The MSSH timescale agrees much better with the experiment than the FSSH and GFSH data. GFSH produces Auger dynamics that is faster than the one obtained in the FSSH method. Still, the GFSH dynamics is too slow compared with MSSH and the experiments. The MSSH approach provides the best description of the Auger-type process, involving a simultaneous transition of two particles.

4. Conclusions

We have presented the analysis of the trajectory surface hopping algorithms from the Markov state model perspective. Using the Markov state model we designed the MSSH method for accounting for many-particle transitions and higher-order effects in semiclassical nonadiabatic dynamics. One of such effects is superexchange, which is commonly considered to constitute one of the key charge and energy transfer mechanisms, and which arises when a diabatic basis is used in simulations.

We show that the general MSSH approach reduces to the frequent switches surface hopping method of Tully and Preston, but it is derived from different perspectives and may be generalized beyond the Tully–Preston version. Unlike Tully and Preston, who used the interpretation of the quantum mechanical probabilities to define surface hopping probabilities, our theoretical analysis is based on a general master equation approach. In our construction, we explicitly require the many-particle quantum transitions to be feasible—the point which is missing in the frequent switching surface hopping scheme. Although the original Tully–Preston approach was considered inferior to the FSSH formulation, and was eventually abandoned, it can address the conceptual shortcoming of the standard first-order FSSH technique, namely its inability to account properly for superexchange-type processes. This problem is also resolved with the presented MSSH model.

We demonstrate with two model systems (superexchange and double avoided crossing) that the approach leads to a good agreement with the exact quantum solutions. When the MSSH algorithm is applied to model Auger relaxation dynamics in a CdSe QD, it produces results that are in good agreement with available experimental measurements. On the contrary, the dynamics generated with FSSH and GFSH is characterized by too slow relaxation time scales. Given the conceptual and computational simplicity, the MSSH method and its CPA-based modification can be regarded as useful.
practical approaches for modeling photoinduced nonadiabatic dynamics in systems with non-negligible role of multi-particle transitions and high order effects. Our analysis shows that the applicability and accuracy of the investigated MSSH approach may depend on the system of interest. The deficiencies can be attributed to the problems common for many methods in the family of the TSH algorithms, including the lack of quantum nuclear effects, as well as decoherence, tunneling and zero-point energy. Our analysis also indicates that there is room for further improvement of the present methodology, for instance, by inclusion of non-Markovian and quantum nuclear effects.

To recapitulate, our analysis and numerical simulations suggest that the simple hopping algorithm based on the quantum state populations used as the surface hopping probabilities is suitable for modeling processes that involve higher-order scattering (many-particle transitions). In contrast, the definition used in the popular FSSH theory, captures only first-order effects (one-particle transitions). At the same time, MSSH has its own limitations. In particular, it may tend to overestimate electronic transition rates when applied to certain problems. Further studies are required to investigate such limitations in detail. Our present work suggests that the capabilities of the simple scheme based on the standard quantum probabilities should be re-evaluated in view of its unexpectedly encouraging accuracy with superexchange processes. We hope that the MSSH model can be used as a framework for constructing more elaborate and accurate non-Markovian models of quantum-classical dynamics.

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