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Mixed quantum-classical equilibrium in global flux surface hopping

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Global flux surface hopping (GFSH) generalizes fewest switches surface hopping (FSSH)—one of the most popular approaches to nonadiabatic molecular dynamics—for processes exhibiting superexchange. We show that GFSH satisfies detailed balance and leads to thermodynamic equilibrium with accuracy similar to FSSH. This feature is particularly important when studying electron-vibrational relaxation and phonon-assisted transport. By studying the dynamics in a three-level quantum system coupled to a classical atom in contact with a classical bath, we demonstrate that both FSSH and GFSH achieve the Boltzmann state populations. Thermal equilibrium is attained significantly faster with GFSH, since it accurately represents the superexchange process. GFSH converges closer to the Boltzmann averages than FSSH and exhibits significantly smaller statistical errors. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4922162]

I. INTRODUCTION

Physical processes on atomic and subatomic length scales are accurately described by quantum mechanics. Most systems of interest, however, are commonly composed of a large number of degrees of freedom, which are computationally expensive. Preserving all dominant quantum effects, while not compromising the underlying physics, becomes highly desirable. One of the most successful solutions is mixed quantum-classical dynamics, where highly quantum particles, i.e., subatomic particles, are reserved to a quantum mechanical description, while larger constituents, such as atoms, evolve classically. These guidelines change, however, depending on the nature of the study; for example, selected atomic motions describe tunneling and zero-point effects in proton transfer; thus, for such atoms, a quantum mechanical description would be more appropriate.

Having proved to be accurate in many applications, fewest switches surface hopping (FSSH) has retained its popularity within mixed quantum-classical dynamics. Electrons, for example, are treated quantum mechanically, to incorporate nonadiabatic transitions between states, while atoms evolve classically, on potential energy surfaces. For each atom, the particular surface, on which it evolves, depends on the active electronic state of its quantum subsystem. At each time step, the electron remains in its current state or switches to a state with positive population flux, ergo, the “fewest switches” criterion. Despite its success, FSSH has been subject to many setbacks, some of which have been resolved, i.e., phase correction and decoherence. In this manuscript, we highlight FSSH’s inability of realizing superexchange.

Superexchange is a class of dynamical processes where two electronic states are indirectly coupled by an intermediate state of higher energy. A typical example is singlet fission, where two singlet excitation converts to a triplet pair state by means of charge transfer states. Singlet fission is a spin-allowed process, which can potentially double the number of electron-hole pairs, and thus largely increases the efficiency of organic photovoltaics. To access an uncoupled state, a switch to the highest-energy state is required. When the energy needed to occupy an excited state is larger than the dispensable kinetic energy of the atom, the switch is not invoked. Such classically forbidden transitions are source of disagreement between FSSH and exact quantum results (obtained from wave propagation), where transmission (on the indirectly coupled excited state) was found to be strongly underestimated, in the region where atomic kinetic energy is less than the energy gap between the ground and intermediate, highest-energy states.

An alternative surface hopping strategy has been recently proposed called global flux surface hopping (GFSH), which is based on population flux flowing to and from all states. Its fundamental difference to FSSH is highlighted when states are not directly coupled. As opposed to FSSH, which requires direct coupling for single-hop transitions, GFSH does not. When tested against the superexchange mechanism, GFSH showed a dramatic qualitative improvement over FSSH. GFSH closely followed the exact results in the superexchange regime, while FSSH gave zero transmission.

Auger processes fall within the realm of superexchange since transitions into intermediate, higher-energy states are involved. Both surface hopping strategies have been applied to study the Auger mechanism in a quantum dot. The Auger process is a two-particle reaction, involving simultaneous electron and hole transitions. As a consequence of its ability to permit two-particle transfer in a single time step, GFSH gave a faster estimate of the Auger rate. FSSH was hindered by the relatively large energy barriers of the intermediate states, so classically forbidden transitions were frequently encountered, producing a slower, less accurate, estimate of the Auger rate.

Internal consistency ensures that the fraction of trajectories on each potential energy surface is equivalent to the corresponding average probability determined by a coherent

Global flux surface hopping (GFSH) generalizes fewest switches surface hopping (FSSH)—one of the most popular approaches to nonadiabatic molecular dynamics—for processes exhibiting superexchange. We show that GFSH satisfies detailed balance and leads to thermodynamic equilibrium with accuracy similar to FSSH. This feature is particularly important when studying electron-vibrational relaxation and phonon-assisted transport. By studying the dynamics in a three-level quantum system coupled to a classical atom in contact with a classical bath, we demonstrate that both FSSH and GFSH achieve the Boltzmann state populations. Thermal equilibrium is attained significantly faster with GFSH, since it accurately represents the superexchange process. GFSH converges closer to the Boltzmann averages than FSSH and exhibits significantly smaller statistical errors. © 2015 AIP Publishing LLC.
propagation of quantum amplitudes. Both FSSH and GFSSH satisfy internal consistency.\footnote{10-12} This property is violated, however, when trivial crossings are encountered,\footnote{10-12} which occur when the energy gaps between potential energy surfaces are negligible. As a result, the finite time step cannot ensure an accurate evaluation of the surface hopping probabilities. A solution to this problem has been proposed, where probabilities are corrected by a self-consistency check.\footnote{11} GFSH automatically satisfies this criteria, so unlike FSSH, it needs no additional correction.\footnote{7}

Until now, it has not been shown whether GFSH satisfies detailed balance at thermal equilibrium. It is well known that when total quantum-classical energy conservation is not accounted for, a quantum system in contact with a classical bath does not attain the correct equilibrium behavior, but rather transitions between states occur with equal probability, i.e., a bath does not attain the correct equilibrium behavior, but rather that when total quantum-classical energy conservation is not satisfied this criteria, so unlike FSSH, it needs no additional correction.\footnote{7}

Moreover, the self-consistent field (Ehrenfest) method also fails at thermal equilibrium, strongly limiting its applicability. In fact, studies have shown that Ehrenfest deviates dramatically from Boltzmann when \( T \) is much smaller than the energy gap in a two-level system.\footnote{14} This is not the case for surface hopping, which does attain the Boltzmann populations,\footnote{14} thereby making it a more reliable method for mixed quantum-classical simulations at thermal equilibrium. GFSH is equivalent to FSSH for two-state systems, so it automatically attains the correct equilibrium behavior in this limit. In this study, using a three-level superexchange model, we test GFSH (and compare it to FSSH).

Furthermore, we compare relaxation rates due to an abrupt change in temperature using both methods. Relaxation dynamics have been a common interest within the last couple decades; an example is vibrational energy relaxation, where an excited vibrational mode releases excess energy to a bath of intermolecular and/or intramolecular accepting modes.\footnote{15} This phenomena has been studied in context of the hydrogen stretch in a moderately strong hydrogen-bonded complex dissolved in polar liquid.\footnote{15}

\section{Equations of Motion}

\subsection{Electronic dynamics}

Without loss of generality, we consider a quantized electron, coupled to its classically governed atom. The combined Hamiltonian is

\begin{equation}
H = \frac{p^2}{2m} + H_e (r, R),
\end{equation}

where \( r \) and \( R \) represent the electronic and atomic coordinates, respectively, and \( p \), the atomic momentum. The time-dependent Schrödinger equation is

\begin{equation}
i \hbar \frac{\partial \psi (r, R)}{\partial t} = H_e (r, R) \psi (r, R).
\end{equation}

The wavefunction \( \psi (r, R) \) can be expanded in terms of an orthonormal basis set \( \{ \phi_i (r, R) \} \),

\begin{equation}
\psi (r, R) = \sum_j c_j \phi_j (r, R),
\end{equation}

where \( c_j \) is the complex-valued amplitude associated to basis function \( \phi_j (r, R) \). Substituting Eq. (3) into Eq. (2), multiplying on the left by \( \phi_i (r, R) \), and integrating over all electronic coordinates gives

\begin{equation}
i \hbar \dot{c}_i = \sum_j c_j (V_{ij} - i \hbar \mathbf{R} \cdot \mathbf{d}_{ij}),
\end{equation}

where \( V_{ij} = \langle \phi_i (r, R) | H_e (r, R) | \phi_j (r, R) \rangle \) and \( \mathbf{d}_{ij} = \langle \phi_i (r, R) | \nabla_R | \phi_j (r, R) \rangle \). The latter is the nonadiabatic coupling vector. State probabilities \( c_i c_j^* \) are determined by integrating Eq. (4). Using Eq. (4),

\begin{equation}
i \hbar \dot{\rho}_{ij} = \sum_l \rho_{lj} (V_{il} - i \hbar \mathbf{R} \cdot \mathbf{d}_{il}) - \rho_{li} (V_{ij} - i \hbar \mathbf{R} \cdot \mathbf{d}_{ij}),
\end{equation}

where \( \rho_{ij} = c_i c_j^* \). Deriving Eq. (5) requires the use of

\begin{equation}
\dot{d}_{ij} = -d_{ji}
\end{equation}

and

\begin{equation}
d_{ii} = 0,
\end{equation}

which are simply consequences of the orthonormality of the basis set. From Eq. (5), the time-evolution of state probabilities directly follows:

\begin{equation}
\dot{\rho}_{ii} = \sum_{j \neq i} b_{ij},
\end{equation}

where \( b_{ij} = 2 \hbar^{-1} \text{Im} \left( \rho^*_{ij} V_{ij} \right) - 2 \text{Re} \left( \rho^*_{ij} \mathbf{R} \cdot \mathbf{d}_{ij} \right) \).

\subsection{Atomic dynamics}

As shown in Eq. (1), the electronic Hamiltonian \( H_e (r, R) \) acts as the potential energy of the atom. The atom evolves on the potential energy surface associated to the occupied state of its quantum subsystem. When the electron is in state \( i \), the atom is governed by

\begin{equation}
\dot{\mathbf{p}}_j = -\frac{\partial V_{ii}}{\partial R_j},
\end{equation}

where \( j \) is a cartesian coordinate. In the adiabatic representation, \( V_{ii} \) is the \( i \)th eigenvalue of \( H_e (r, R) \). The occupied state of the quantum subsystem at a consecutive time step is determined by the particular surface hopping algorithm used in the simulation. Equation (8) must be modified if the system was subjected to any additional atomic forces.

\section{Surface hopping}

\subsection{Fewest switches surface hopping}

At every time step, the probability of a transition from state \( i \) to \( j \) for \( i \neq j \) is calculated,

\begin{equation}
g_{ij} = \max \left( \frac{-\Delta t \, b_{ij}}{\rho_{ii}}, 0 \right),
\end{equation}

where \( -\Delta t \, b_{ij} \) is the flux of population, transferred from state \( i \) to \( j \) in time \( \Delta t \). A switch from state \( i \) to \( k \) is invoked when

\begin{equation}
\sum_{j=1}^{j=k-1} g_{ij} < \xi < \sum_{j=1}^{j=k} g_{ij},
\end{equation}

where \( \xi \) is the switch probability.
where \( \xi \) is a random number between 0 and 1. When \( \xi \geq \sum_i s_{ij} \), the electron remains in its current state.

If the electron transitions to a state of different energies, the atomic velocity is rescaled to conserve energy. Rescaling typically occurs in the direction of the nonadiabatic coupling vector.\(^3\)

\[
\dot{R}(t + \Delta t) = \dot{R}(t) - \gamma_{ij} \frac{d_{ij}}{m},
\]

(11)

where \( \gamma_{ij} \) is the scaling factor determined by energy conservation,

\[
\gamma_{ij} = \begin{cases} 
\gamma_{ij}^+ & \text{for } \dot{R} \cdot d_{ij} < 0 \\
\gamma_{ij}^- & \text{for } \dot{R} \cdot d_{ij} > 0'
\end{cases}
\]

(12a)

where

\[
\gamma_{ij}^\pm = \frac{m}{d_{ij}} \left( \dot{R} \cdot d_{ij} \pm \sqrt{(\dot{R} \cdot d_{ij})^2 - 2 \frac{d_{ij}^2}{m} \Delta \epsilon_{ij}} \right)
\]

(12b)

and

\[
\Delta \epsilon_{ij} = V_{jj}(\dot{R}) - V_{ii}(\dot{R}).
\]

(12c)

Equation (11) ensures \( \Delta \dot{R} \) is in the direction of \( d_{ij} \) or \(-d_{ij} \); the sign is determined by Eq. (12a). In simple terms, for \( \Delta \epsilon_{ij} < 0 \), \( \Delta \dot{R} \) is along the direction of nonadiabatic coupling that increases \( \dot{R} \), and vice versa for \( \Delta \epsilon_{ij} > 0 \). If \( \frac{1}{2} m \left( \frac{\dot{R} \cdot d_{ij}}{a_{ij}} \right)^2 < \Delta \epsilon_{ij} \), the quantity under the square root, in Eq. (12b), is negative and so the switch is not invoked and \( \dot{R} \) is unchanged. This is known as a classically forbidden transition. The process is repeated for as many time steps needed to fulfill the objective of the study.

B. Global flux surface hopping

At each time step, the change in state population is calculated,

\[
\Delta \rho_{ii} = \rho_{ii}(t + \Delta t) - \rho_{ii}(t).
\]

(13)

The states are then classified into one of two groups: one with reduced population (group A) and the other with increased population (group B). Only state transitions from group A to B are considered. The probability of a switch from state \( i \in A \) to \( j \in B \) is

\[
g_{ij} = \frac{\Delta \rho_{jj}}{\rho_{ii}} \frac{\Delta \rho_{ii}}{\sum_{k \in A} \Delta \rho_{kk}}.
\]

(14)

The probability increase of state \( j \), \( \Delta \rho_{jj} \), is attributed to the reduction of probability from all states in group A. To limit this quantity to the exiting states’ contribution, i.e., state \( i \), one multiplies by \( \frac{\Delta \rho_{ii}}{\sum_{k \in A} \Delta \rho_{kk}} \), which is the ratio of state \( i \)’s probability change to the total probability change in group A. Finally, Eq. (14) is normalized by the probability of the exiting state. For two-level systems, Eq. (14) reduces to the FSSH algorithm in Eq. (9). All subsequent steps in FSSH, i.e., random number generation and velocity rescaling, are then implemented for GFSH.

IV. MODEL

Numerical calculations are carried out, with an \( N \)-atom linear chain (shown in Fig. 1), governed classically via the nearest-neighbor, attractive Morse potential,\(^16\)

\[
V = \sum_{i=1}^{N} V_M(q_i - q_{i+1}),
\]

(15a)

where

\[
V_M(q) = V_0 (a^2 q^2 - a^3 q^3) + 0.58 a^4 q^4
\]

(15b)

and \( q_i \) is the position of the \( i \)th atom. The term \( q_{N+1} \) is held constant. A three-level superexchange model, \( V_{ij} \), is coupled to atom 1,

\[
H_1 = \frac{P^2}{2m} + V_M + V_{ij}.
\]

(16)

The electronic state amplitudes evolve according to Eq. (4), with constant state energies, i.e., \( V_{ii} \), and constant nonadiabatic coupling vectors, shown in Table I. Atom \( N \) is governed by the Langevin equation,

\[
P_N = -\frac{\partial V}{\partial q_N} - \gamma m q_N + F_R.
\]

(17)

where \( \gamma \) is the Langevin friction parameter and \( F_R \) is a Gaussian random force with mean zero and standard deviation \( \sqrt{2 \gamma m k_B T} \Delta t^{-1} \), with \( k_B \) being the Boltzmann constant. The integration time step, \( \Delta t \), is chosen to be 0.01 fs. All parameters regarding the linear chain are shown in Table I. The coefficients in Eq. (15b) represent those of an attractive Morse potential. The purpose of Langevin dynamics is to introduce a heat bath, from which the quantum subsystem can equilibrate to the Boltzmann state populations,

\[
\text{population}_i = \frac{\exp(-\epsilon_i/k_B T)}{\sum_i \exp(-\epsilon_i/k_B T)},
\]

(18)

where \( \epsilon_i \) is the energy of the \( i \)th state. States 1 and 3 are not coupled since \( V_{13} = V_{31} = 0 \) and \( d_{13} = d_{31} = 0 \). An intermediate hop to state 2 is required to connect states 1 and 3. GFSH, however, allows for direct transitions.

<table>
<thead>
<tr>
<th>TABLE I. Simulation parameters.</th>
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<tbody>
<tr>
<td>Parameter</td>
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<tr>
<td>Quantum subsystem</td>
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<tr>
<td>( V_{11} )</td>
</tr>
<tr>
<td>( V_{22} )</td>
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<tr>
<td>( V_{33} )</td>
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<tr>
<td>( d_{12} )</td>
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<tr>
<td>( d_{13} )</td>
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<tr>
<td>( d_{23} )</td>
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<tr>
<td>Classical linear-chain</td>
</tr>
<tr>
<td>( N )</td>
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<tr>
<td>( m )</td>
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<tr>
<td>( V_0 )</td>
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<td>( a )</td>
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<td>( \gamma )</td>
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</table>
V. RESULTS AND DISCUSSION

A. Detailed balance

The fraction of trajectories on each state has been calculated at every time step, as the system approaches thermal equilibrium. All trajectories were 50 ps (5 × 10⁶ time steps) in length, with the quantum subsystem initially prepared in the ground state. To show detailed balance, the fraction of trajectories was averaged every 1 ps (10⁵ time steps). Averaged results are referred to as state populations. Differential equations were integrated using fourth-order Runge-Kutta (RK4). The stochastic Langevin equation of Eq. (17) was also solved at the RK4 level. A sample, at 500 K, of the time-dependent state populations is shown in Fig. 2.

All transitions within FSSH require an intermediate switch to the highest-energy state. A switch is prohibited when energy conservation is not satisfied. This is evidenced in multiple locations, shown in Fig. 2(a), where state 3 is overpopulated for relatively long time compared to the 1 ps sampling interval. As a result, detailed balance is not accurately attained. Fig. 2(c) shows the corresponding number of classically forbidden transitions, while occupying either state 1 or 3. There is a clear correlation between Figs. 2(a) and 2(c); as the population of state 1 or 3 increases, the number of forbidden transitions increases as well. The magnitude of the y-axis in Fig. 2(d) is two orders smaller than that shown in Fig. 2(c); so, even the slightest increase in forbidden transitions could affect detailed balance.

By equipartition, atomic kinetic energy has mean value \( k_\text{B}T/2 \) at thermal equilibrium. At 500 K, \( k_\text{B}T/2 \) is about 13 times smaller than the largest energy gap. Therefore, it is common for state 3 to be overpopulated, until enough dispensable kinetic energy allows for a transition to state 2. A similar situation arises when state 1 is occupied.

GFSH bypasses the intermediate, highest-energy state; hence, transitions are less restricted by energy conservation, particularly between states 1 and 3, as shown in Fig. 2(d). Unlike FSSH, which requires state 1 to access state 3 by way of state 2, GFSH allows for a direct transition, requiring
only \( V_{33} - V_{11} = 0.005 \text{ a.u.} \), as opposed to \( V_{22} - V_{11} = 0.01 \text{ a.u.} \). Moreover, transitions from state 3 to 1 are not restricted by energy conservation. In Fig. 2(b), state populations are steadily maintained after 30 ps and with less-apparent occurrences of overpopulating states 1 and 3. GFSH would perform even better than FSSH for smaller sampling intervals. Thus, for superexchange systems, GFSH is a more accurate description of not only thermal equilibrium but also physical processes that occur on short time scales (where both methods give significantly different results).

Detailed balance has been tested at multiple temperatures, the highest being 2000 K, which gives \( k_B T/2 \) about 3 times smaller than the largest energy gap. The difference in the number of classically forbidden transitions, between FSSH and GFSH, increases as temperature increases. At thermal equilibrium, kinetic energy is sampled from a Maxwell-Boltzmann distribution (for a one-dimensional particle), which is monotonically decreasing; therefore, the probability of \( 0.005 \text{ a.u.} < E < 0.01 \text{ a.u.} \) increases as \( k_B T/2 \) increases. This effect becomes less important towards detailed balance, however, since the number of implemented and forbidden transitions converge toward similar orders of magnitude.

In Fig. 3, each state population was averaged over the last 20 ps, to neglect any dependence on initial conditions.\(^2\)\(^2\)\(^1\)\(^2\)\(^1\)\(^2\)\(^3\)\(^0\)\(^0\)\(^5\)\(^0\)\(^1\) \( 300 \) trajectories were generated for each temperature. Data were recorded every 1 ps, and \( N = 6000 \) data points were used to obtain the averages, i.e., 20 data points per each of the 300 trajectories. The variance in the mean \( \mu \) is \( \sigma_\mu^2 = \sigma^2/N \), where \( \sigma^2 \) is the variance in the sample.\(^2\)\(^2\)\(^1\)\(^2\)\(^1\)\(^2\)\(^3\)\(^0\)\(^0\)\(^5\)\(^0\)\(^1\) Due to the large sample size, these errors are insignificant. Nonetheless, GFSH shows less variance and better convergence than FSSH.

Figs. 3(a)–3(c) show GFSH agreeing more with Boltzmann overall. This is particularly true for low temperatures, where paths to states 2 and 3 are more restricted by energy conservation. Fig. 3(d) shows the number of data points, \( N_{\text{GFSH}} \), required by GFSH to match the statistical accuracy of FSSH achieved with \( N_{\text{FSSH}} = 6000 \) points. \( N_{\text{GFSH}} \) was chosen based on the criterion, \( \sigma_{\text{GFSH}}^2/N_{\text{GFSH}} = \sigma_{\text{FSSH}}^2/N_{\text{FSSH}} \). For states 1 and 3 involved in superexchange, the statistical error in GFSH is consistently smaller than in FSSH. The errors of state 2 are similar; a consequence of the fact that state 2 is unaffects by classically forbidden transitions. Overall, GFSH attains the same statistical accuracy as FSSH with fewer trajectories.

Although the discrepancy is small, surface hopping does not exactly match Boltzmann. States 2 and 3 are consistently overpopulated, while state 1 is underpopulated. This effect was previously studied for a two-state system, where the ratio of attempted upward and downward transitions, \( k_{\alpha\beta}/k_{\beta\alpha} \), was found to be greater than 1, and the fraction of accepted upward transitions was less than the Boltzmann factor, \( \exp(-\Delta/k_B T) \), where \( \Delta = \epsilon_\beta - \epsilon_\alpha > 0 \).\(^2\)\(^3\) Detailed balance is defined as the product of \( k_{\alpha\beta}/k_{\beta\alpha} \) and the fraction of upward transitions; therefore, unless the amount overestimated by \( k_{\alpha\beta}/k_{\beta\alpha} \) exactly cancels the amount underestimated by \( \exp(-\Delta/k_B T) \), results would not yield Boltzmann. Analytic expressions argue that the correct equilibrium behavior is attained in specific regions: small adiabatic splitting and/or strong nonadiabatic coupling.\(^2\)\(^3\) Numerical results show that when the (magnitude of) nonadiabatic coupling \( d_{\alpha\beta} \) was increased from 6.5 Å to 104 Å, the ratio of the excited and ground state populations more closely resembled \( \exp(-\Delta/k_B T) \).\(^1\)\(^4\)\(^2\)\(^3\) It is expected that the same holds true for GFSH. Even outside these limits, FSSH (and GFSH) is likely to introduce relatively small deviations, while still reproducing the expected exponential decay of the excited state.

![Equilibrated population of states (a) 1, (b) 2, and (c) 3, at various temperatures, where each data point is an average of the last 20 ps of a 300-trajectory ensemble. Dashed black lines in (a)–(c) are Boltzmann populations given by Eq. (18). Figure (d) shows the required-number of GFSH data points to match the statistical accuracy of FSSH, where \( N_{\text{FSSH}} = 6000 \).](image-url)
populations as the temperature of the system is reduced, as shown in Figs. 3(b) and 3(c).

B. Equilibration rate

Detailed balance is a static assessment of the two surface hopping methods. In this section, their differences are highlighted from a dynamical perspective, by comparing rate of equilibration. The temperature was initially set to 1700 K and as before, the quantum subsystem was fully prepared in the ground state. After equilibrium, at approximately 20 ps, the temperature was abruptly changed to 600 K. A total of 600 trajectories were used, each 50 ps in length, and the sampling interval was set to 0.05 ps.

The least-squares method was used to fit the data to an exponential function of the form,

$$A + B \exp(-kt),$$

where $A$ is the final state population, $A + B$ is the initial population, and $k$ is the equilibration rate. The constants $A$ and $B$ were fixed to the populations given by Eq. (18); thus, the only variable in the fit is $k$, in order to draw a comparison from the rate of equilibration only, as opposed to also determining whether or not the subsystem reaches the Boltzmann populations, which has been studied in Subsection V A. Results are shown in Fig. 4. The $x$-axis is offset to start at the time at which temperature was changed to 600 K.

Not surprisingly, GFSH equilibrates faster than FSSH. This again is due to the unsurpassable energy barriers encountered by FSSH. GFSH is more free to transition, especially between states 1 and 3. Fig. 4 shows GFSH more consistent with the Boltzmann populations, while FSSH experiences multiple “oscillations,” similar to those observed in Fig. 2(a). We emphasize that increasing the number of trajectories does not eliminate this inconsistency. The fluctuation shown in Fig. 4(b), however, is likely to diminish with a larger number of trajectories. The difference in equilibration between both methods continues to diverge as temperature is reduced.

Equilibration obtained by GFSH is not only faster but also more accurate than FSSH. Irrespective of the model, Boltzmann must be reproduced. GFSH agrees more with these populations overall, indicating that the path taken to reach thermal equilibrium is better explained by GFSH. The significance of this can be illustrated in the context of charge mobility. For a one-dimensional lattice with static disorders and only nearest-neighbor electronic coupling, charge transport occurs with many superexchange-like transitions. GFSH would give a faster rate of population transfer than FSSH, thereby producing greater charge mobility. These studies are currently underway.

VI. CONCLUDING REMARKS

We showed that GFSH attains the Boltzmann populations at thermal equilibrium. The calculations were performed in the adiabatic basis. The energies, of the three-level superexchange model, and nonadiabatic couplings were chosen to be independent of the classical coordinate, signifying a model with weak electron-phonon coupling.

Unlike FSSH, GFSH allows for direct transitions between any two states. It more accurately attains the correct equilibrium behavior, and with less error, especially for when the number of implemented transitions is less than the number of classically forbidden transitions. In general, GFSH consistently gives better results at temperatures where $k_B T/2$ is less than the largest energy gap. Access to the excited states is more restricted by FSSH, since larger amounts of dispensable energy is required.

GFSH exhibits a larger number of transitions than FSSH, making population flux more dynamical. It therefore reaches thermal equilibrium faster. GFSH is particularly useful in describing non-equilibrium, superexchange processes, which widely occur in physical, chemical, and biological contexts. The distinction between both methods diminishes as temperature increases.

It would be valuable to study models that further accentuate the differences between both methods. For instance, one can increase the energy of the intermediate state, $V_{22}$, while making $V_{11}$ and $V_{33}$ nearly degenerate. In this case, the transitions between states 1 and 3 would be greatly affected by energy conservation within FSSH, which may result in inaccurate equilibrium behavior.

To recapitulate, the novel GFSH method satisfies detailed balance and leads to thermal equilibrium. GFSH has advantages over FSSH in describing the superexchange mechanism.
It reduces to FSSH in the two-state limit.\textsuperscript{7} Available evidence indicates that GFSH can fully replace FSSH, especially for studies at thermal equilibrium. Investigations are underway to determine the effect of incorporating decoherence. A common approach that utilizes “a stochastic wave function collapse” is augmented-FSSH.\textsuperscript{6} It would be beneficial to test this method within the GFSH framework to determine its degree of applicability and performance. Decoherence is important in explaining relatively slow transitions between states with significant energy gaps.\textsuperscript{24}

**ACKNOWLEDGMENTS**

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


\textsuperscript{16}P. M. Morse, Phys. Rev. \textbf{34}, 57 (1929).


\textsuperscript{20}Initial conditions of the linear chain were sampled from probability distributions using the Hamiltonian of a quantized one-dimensional harmonic oscillator.\textsuperscript{21} It is worth mentioning, however, that initial conditions generally have no impact on the properties of equilibrium discussed in this study.


