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Communication: Global flux surface hopping in Liouville space

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Recent years have witnessed substantial progress in the surface hopping (SH) formulation of non-adiabatic molecular dynamics. A generalization of the traditional fewest switches SH (FSSH) global flux SH (GFSH) utilizes the gross population flow between states to derive SH probabilities. The Liouville space formulation of FSSH puts state populations and coherences on equal footing, by shifting the hopping dynamics from Hilbert to Liouville space. Both ideas have shown superior results relative to the standard FSSH in Hilbert space, which has been the most popular approach over the past two and a half decades. By merging the two ideas, we develop GFSH in Liouville space. The new method is nearly as straightforward as the standard FSSH, and carries comparable computational expense. Tested with a representative super-exchange model, it gives the best performance among all existing techniques in the FSSH series. The obtained numerical results match almost perfectly the exact quantum mechanical solutions. Moreover, the results are nearly invariant under the choice of a basis state representation for SH, in contrast to the earlier techniques which exhibit notable basis set dependence. Unique to the developed approach, this property is particularly encouraging, because exact quantum dynamics is representation independent. GFSH in Liouville space significantly improves accuracy and applicability of SH for a broad range of chemical and physical processes. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4935971]

Numerous dynamical processes in physics, chemistry, biology, and material science involve multiple degrees of freedom, defying a fully quantum mechanical treatment. At the same time, a computationally efficient, fully classical description lacks the ability to characterize essential quantum effects. Mixed quantum-classical techniques become the only practical choice for simulating complex dynamics of electrons,1,13 excitons,8,6 and protons7,2 in large systems. Such dynamics are receiving intense attention, because they govern efficiencies of many modern devices, and since they are now accessible to experimental investigation, which requires detailed theoretical interpretation.

The mean-field Ehrenfest approach9 constitutes the most straightforward quantum-classical technique. It describes dynamics if the classical subsystem is weakly correlated with different quantum states.10 However, it excludes branching,11 which is essential for quantum wave-packets, and does not reproduce detailed balance required to achieve thermodynamic equilibrium.12 To overcome these deficiencies, the concept of surface hopping (SH) has been developed.13 Due to ease of implementation, together with high computational accuracy and efficiency, Tully’s fewest switches SH (FSSH)11 has been widely used for non-equilibrium simulations. FSSH is compatible with modern electronic structure methods and thus can explore complex dynamics at a first-principles level.14,15 Despite its great successes, traditional FSSH in Hilbert space has limitations in application to certain phenomena.15–17 Various modifications and corrections have been introduced, using FSSH as the initial platform. For instance, FSSH has been combined with classical molecular dynamics to build QM/MM-type techniques for large-scale simulations.18 Self-consistency checks have been added to solve the trivial crossing problem arising due to high density of states in aggregates and solids.19 Entanglement in an ensemble of trajectories has been considered with second quantization to account for nuclear tunneling effects.20 Most relevant for this work, FSSH transition probabilities have been generalized to cover the gross population flow between states, resulting in the global flux SH (GFSH) method.21 FSSH has been successfully re-formulated in Liouville space,22 providing an equal treatment of quantum populations and coherences, and generating novel insights into quantum dynamical pathways.

Both Hilbert space GFSH21 and Liouville space FSSH22 describe population transfer between indirectly coupled states. Such events are key to super-exchange and Auger-type processes. In particular, many-particle Auger-type energy exchange is ubiquitous in nanomaterials, due to a combination of significant Coulomb interaction and high state densities, giving rise to a spectrum of novel phenomena, including impact-ionization/multiple-exciton-generation23,24 and Auger-assisted electron transfer.25,26 The original FSSH only allows transition between directly coupled states, and blocks the pathways with high energy barriers.

In this work, we bridge the global flux generalization of FSSH and the FSSH formulation for Liouville space, and propose GFSH in Liouville space. We assess the performance using the representative super-exchange model21 in both diabatic and adiabatic representations. By comparing existing

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SH techniques in the series (Fig. 1(a)) with the new method and exact quantum mechanics, we demonstrate that Liouville space GFSH gives the best results. Perhaps most importantly, the developed method is nearly invariant with respect to the basis set representation, as required by quantum mechanics. In comparison, the earlier techniques exhibit strong basis dependence. Finally, the computational expense of Liouville space GFSH is comparable to that of the standard FSSH, and the implementation is nearly as straightforward. By combining GFSH and Liouville space, we have formulated what appears to be the most accurate SH method in the FSSH family, both improving accuracy and expanding applicability of SH towards various chemical and physical phenomena.

The wave function is generally expressed as a linear combination, $|\psi\rangle = \sum_i c_i |i\rangle$, of a set of orthogonal basis states, $\{|i\rangle\}$. All possible $|\psi\rangle$ span Hilbert space. The time evolution of the wave function follows the Schrödinger equation,

$$\frac{d}{dt} |\psi(t)\rangle = \frac{i}{\hbar} \hat{H} |\psi(t)\rangle,$$

where $\hat{H}$ is the Hamiltonian. Alternatively, a new basis set, $\{|ij\rangle\} \equiv |i\rangle|j\rangle$, can be constructed to generate Liouville space, which is simply a Cartesian product of the two corresponding Hilbert spaces. For any pure state $|\psi\rangle$, the density vector $|\rho\rangle \equiv |\psi\rangle\langle\psi|$ is a linear expansion of basis states in Liouville space, $|\rho\rangle = \sum_{ij} \rho_{ij} |ij\rangle$, and satisfies the Liouville equation,

$$\frac{d}{dt} |\rho(t)\rangle = \frac{i}{\hbar} L |\rho(t)\rangle,$$

where $L$ is the Liouville super-operator defined by $L_{ij,kl} = \hat{H}_{ij} \delta_{j,k} - \hat{H}_{kl} \delta_{i,k}$. Eq. (2) in Liouville space is formally analogous to Eq. (1) in Hilbert space, and thus most SH techniques normally implemented in Hilbert space can be naturally generalized to Liouville space.

To complete the Liouville space construction for SH, additional definitions are needed. Following the previous studies, we set the energy of each $|ij\rangle$ state as

$$E_{ij} = (V_i + V_j)/2,$$

where $V_i$ is the energy of state $|i\rangle$. Eq. (3) leads to $E_{ii} = V_{ii}$, agreeing with quantum mechanics. Furthermore, the trajectories obtained in Liouville space must be projected to Hilbert space for final analysis. Suppose the fraction of trajectories populating state $|ij\rangle$ is $f_{ij}$. The corresponding fraction of trajectories projected onto state $|i\rangle$, $F_i$, follows

$$F_i = \sum_j (f_{ij} \eta_{ij-i} + f_{ji} \eta_{ji-i}),$$

where

$$\eta_{ij-i} = \begin{cases} 0.5 & \text{when } E_k + E_j \geq \max \{V_i, V_j\} \\ 0 & \text{when } V_i > E_k + E_j \geq V_j \\ 1 & \text{when } V_j > E_k + E_j \geq V_i \end{cases}$$

and $\eta_{ji-i} = 1 - \eta_{ij-i}$, and $E_k$ is the classical kinetic energy. Eq. (5) accounts for energy conservation, and is consistent with the energy convention in Eq. (3). When decoherence occurs rapidly and is properly taken into account, $f_{ij}$ with $i \neq j$ decays to zero, and Eq. (4) reduces to $F_i = f_{ii}$.

Solving Eq. (1), we obtain $|\psi(t)\rangle$ and the population of each $|i\rangle$ state, $a_i(t) = |c_i(t)|^2$. In FSSH, the time derivative of the population is analytically expressed as a sum over contributions from different pathways,

$$\frac{da_i}{dt} = \sum_{j \neq i} b_{ij},$$

where $b_{ij} = 2\hbar^{-1} \text{Im} \left[ c_j^* c_i (H - i\hbar \mathbf{v} \cdot \mathbf{d}_{ij}) \right]$ with $(\mathbf{v} \cdot \mathbf{d}_{ij}) = (i \cdot d |j\rangle)/dt$ being the non-adiabatic coupling. For $i \neq j$, $H_{ij}$ is zero in the adiabatic representation, while $(\mathbf{v} \cdot \mathbf{d}_{ij})$ is zero in the diabatic representation. The FSSH probability of switching from state $|i\rangle$ to another state $|j\rangle$ is

$$g_{ij} = \frac{-\Delta b_{ij}}{a_i},$$

where $\Delta$ is the time interval.

Recently, FSSH in Hilbert space has been successfully generalized to Liouville space. From Eq. (2), we obtain $|\rho(t)\rangle$ and the population on each $|ij\rangle$ state, $p_{ij}(t) = |\rho_{ij}(t)|^2$. The corresponding time derivative is analogously expressed as

$$\frac{dp_{ij}}{dt} = \sum_{k \neq i} \tilde{q}_{ij,ik},$$

where $\tilde{q}_{ij,kl} = 2\hbar^{-1} \text{Im} \left[ \tilde{p}_{ik}^* \rho_{kl} (H - i\hbar \mathbf{v} \cdot \mathbf{d}_{ij}) \delta_{jk} + 2\hbar^{-1} \text{Im} \left[ \tilde{p}_{ik}^* \rho_{ik}^* (H - i\hbar \mathbf{v} \cdot \mathbf{d}_{ik}) \delta_{ij} \right] \right]$. Similar to Eq. (7), the transition probability for the $|ij\rangle \rightarrow |kl\rangle$ pathway reads

$$g_{ij,kl} = \frac{-\Delta \tilde{q}_{ij,kl}}{p_{ij}}.$$
examine the population change of all states during a time interval \([t, t + \Delta t]\),

\[
\Delta a_i = a_i(t + \Delta t) - a_i(t),
\]

and classify the states into two subgroups: one with reduced \(a_i\) (group A), and the other with increased \(a_i\) (group B). Since the total population is conserved, transitions are assumed to occur strictly from group A to B. For \(i \in A\) and \(j \in B\), the SH probability is

\[
g_{ij} = \frac{\Delta a_j}{a_j} \frac{\Delta a_i}{\sum_{k \in A} \Delta a_k},
\]

where \(\Delta a_j/a_j\) is the total transition probability of accessing state \(|j\rangle\) during the time interval, and \(\Delta a_i/\sum_{k \in A} \Delta a_k\) weighs the contribution of the departure state \(|i\rangle\) among all states in group A. It has been shown that GFSH satisfies detailed balance and leads to thermal equilibrium.\(^{38}\)

GFSH can be easily implemented in Liouville space. During a time \(\Delta t\), the population changes are

\[
\Delta p_{ij} = p_{ij}(t + \Delta t) - p_{ij}(t).
\]

The identity, \(\sum_{j} p_{ij} = 1\), always holds true for pure states.\(^{22}\)

The Liouville states can be analogously classified: group A with negative \(\Delta p_{ij}\), and group B with positive \(\Delta p_{ij}\). The transition probability from \(|ij\rangle\) in group A to \(|kl\rangle\) in group B is

\[
g_{ij,kl} = \frac{\Delta p_{il}}{p_{ij}} \frac{\Delta p_{jk}}{\sum_{mn \in A} \Delta p_{mn}}.
\]

By design, all other pathways are blocked.

We now have a series of four SH techniques in our tool box: Hilbert space FSSH, Liouville space FSSH, Hilbert space GFSH, and Liouville space GFSH (Fig. 1(a)). They can be implemented in either the diabatic or adiabatic representation. To assess their performance, a recently proposed super-exchange model is adopted (Fig. 1(b)).

The diabatic state energies and interstate couplings in atomic units are\(^{21}\) \(V_{11}(x) = 0, V_{22}(x) = 0.01, V_{33}(x) = 0.005, V_{12}(x) = V_{21}(x) = 0.001e^{-x^2/2}, V_{23}(x) = V_{32}(x) = 0.01e^{-x^2/2}\), and \(V_{13}(x) = V_{31}(x) = 0\) (Fig. 2(a)). States 1 and 3 are coupled indirectly through the intermediate state 2 with higher energy. The adiabatic potential energy surfaces are eigenvalues of the diabatic Hamiltonian (Fig. 2(b)). The mass of the \(x\) degree of freedom, \(m\), is 2000 a.u. Initially, the system is prepared on the negative \(x\) side of the first diabatic surface, and the momentum, \(k\), is sampled from a Gaussian distribution with a standard deviation of \(k/20\).

One significant characteristic of the adopted model is the super-exchange mechanism of population transfer, which can be traced via the transmission on state 3. In Fig. 3, we compare results obtained from the quantum mechanical standard\(^{21}\) to the four SH methods shown in Fig. 1(a). We divide the investigated momenta into three regimes based on the magnitude of \(E_k = k^2/2m\): \(E_k < V_{33} - V_{11}\) (regime I), \(V_{33} - V_{11} < E_k < V_{22} - V_{11}\) (regime II), and \(E_k > V_{22} - V_{11}\) (regime III). All methods give no transmission on state 3 in regime I due to violation of energy conservation, agreeing exactly with the quantum standard. In contrast, all surface hops are allowed in regime III, in which \(E_k\) surpasses the largest energy barrier. Hence, all methods give similar results again.

The most remarkable differences occur in regime II in the diabatic representation (Fig. 3(a)). \(E_k\) therein is enough to activate surface hops from state 1 to state 3, but cannot grant access to state 2. As a result, the transmission on state 3 can only be achieved through super-exchange, bypassing the energy barrier of state 2. This is not possible with the traditional FSSH in Hilbert space, where the direct pathway ([1] \(\rightarrow\) [3]) is forbidden due to zero diabatic coupling, and the indirect pathway ([1] \(\rightarrow\) [2] \(\rightarrow\) [3]) is also blocked on account of energy conservation. The situation completely changes for Hilbert space GFSH, where the direct pathway is turned on following the gross population flux.\(^{21}\) The super-exchange transmission peak is reproduced, and about 80% of the exact intensity is captured. In Liouville space, there exist substantial pathways with coherence states as intermediates,\(^{22}\) e.g., \(|11\rangle\rightarrow|12\rangle \rightarrow |13\rangle \rightarrow |23\rangle \rightarrow |33\rangle\), which possess lower energy barriers than the Hilbert space channel, \(|1\rangle \rightarrow |2\rangle \rightarrow |3\rangle\) (Fig. 1(b)). The transmission through Liouville space FSSH is enhanced to about 90% in regime II. Since on the one hand, GFSH is superior to FSSH in Hilbert space, and on the other hand, FSSH works better in Liouville space than in Hilbert space, it is natural to explore whether the combination of GFSH and Liouville space will perform even better. This is true for super-exchange (Fig. 3(a)), where

![FIG. 2. Potential energy surfaces and interstate couplings of the super-exchange model in (a) diabatic and (b) adiabatic representations.](image-url)
FIG. 3. Transmission on the third state of the super-exchange model obtained from exact quantum dynamics, FSSH in Hilbert and Liouville space, and GFSSH in Hilbert and Liouville space in (a) diabatic and (b) adiabatic representations. The dashed arrows indicate the direction of observed improvement in performance. The transmission details are highlighted in the insets. The two short-dashed lines express the critical momenta that give kinetic energy equal to the energy gaps, $V_{33} - V_{11}$ and $V_{22} - V_{11}$, respectively. All investigated initial momenta are thus divided into the three regimes, I, II, and III. Liouville space GFSSH (green line) agrees almost perfectly with the exact solution (black circles) in both representations, while traditional Hilbert space FSSH (red line) is least accurate, especially in the diabatic basis. Moreover, the results of Liouville space GFSSH are nearly invariant with the basis choice, while the other approaches exhibit strong basis set dependence in the super-exchange regime II.

Liouville space GFSSH yields almost identical results to the exact solutions over the whole range of momenta. This is the best SH result so far for the adopted super-exchange model.

The diabatic studies lead to a strong and clear conclusion: GFSSH and Liouville space are superior to FSSH and Hilbert space, respectively. Thus, the investigated series of SH methods can be categorized and ranked based on performance (Fig. 1(a)). In order of decreasing accuracy, the methods are Liouville space GFSSH, Liouville space FSSH, Hilbert space GFSSH, and Hilbert space FSSH. Besides the super-exchange regime II, this trend also holds for regime III (inset in Fig. 3(a)).

Unlike the diabatic representation, where transmission on state 3 is generally underestimated and differs significantly from one SH strategy to another, the results in the adiabatic representation vary less, slightly overestimating the quantum standard (Fig. 3(b)). This is not surprising since super-exchange is no longer important for the adopted model in the adiabatic representation, where all surfaces are coupled through non-adiabatic couplings. Single-hop transitions from state 1 to state 3 can occur, and are well-characterized by all SH strategies, although small differences do exist. Using the transmission peak as an example (inset of Fig. 3(b)), Hilbert space FSSH gives the highest transmission, while Liouville space GFSSH gives the lowest, agreeing best with the exact solution. Although the performance ordering of Liouville space FSSH and Hilbert space GFSSH is switched, they still show intermediate performances, similar to the observations in the diabatic representation (Fig. 3(a)). Most importantly, the fundamental trend is held; that is, GFSSH performs better than FSSH, and Liouville space surpasses Hilbert space, suggesting that such findings may be true in general. Further studies on different models to solidify this conclusion are currently underway. Note that the adopted superexchange model mimics many important phenomena in nanoscience, e.g., Auger relaxation and Auger-assisted electron transfer.

FIG. 4. Transmission on the second state of the super-exchange model obtained from exact quantum dynamics, FSSH in Hilbert and Liouville space, and GFSSH in Hilbert and Liouville space. Results obtained in the (a) diabatic and (b) adiabatic representations are shown. The intensities of the two transmission peaks are indicated as $T_1$ and $T_2$. Their ratios obtained from all methods are given by insets. Liouville space GFSSH (green lines) gives similar results in both representations, and matches best with the exact solution (black open circles).
relaxation in quantum dots. The improved performance of Liouville space GFSH should allow us to treat similar phenomena with greater accuracy, and thus deserves further investigation.

The transmission on state 2 is also of special interest. It is more than one order of magnitude smaller than the transmission on state 3 (compare Fig. 3 with Fig. 4). Moreover, its momentum dependence is “M-shaped,” exhibiting two maxima. Both characteristics can be used to better assess the different SH strategies. The Hilbert space transmissions are underestimated for $k < 9$ a.u. in the diabatic representation and overestimated in the adiabatic representation (Fig. 4). In contrast, the Liouville space data are less representation-dependent, but an overall overestimation at low $k$ is observed. Quantitative assessments can be carried out by comparing the ratio of the two transmission peaks, $T_2/T_1$. Among all investigated methods, the ratio obtained by Liouville space GFSH (1.15 in the diabatic representation and 1.12 in the adiabatic representation) is closest to the exact value of 1.18. Liouville space FSSH performs slightly worse. In contrast, Hilbert space GFSH and GFSH give too high $T_2$ relative to $T_1$.

Since the performance of the standard Hilbert space FSSH is strongly representation-dependent, the similar transmission results in the diabatic and adiabatic representations for both state 3 (Fig. 3) and state 2 (Fig. 4) make Liouville space GFSH an important breakthrough toward designing representation-independent SH, which is still an open problem in the field. Note that both exact quantum dynamics and semi-classical Ehrenfest are completely independent of representation. And an Ehrenfest variant with decoherence, the decay-of-mixing method, also achieves a weak sensitivity to the choice of representation.

In summary, we have proposed a novel GFSH method in Liouville space for mixed quantum-classical simulations of non-adiabatic dynamics. We carefully examined its performance with a super-exchange model, in comparison to the quantum standard and three other methods in the same series, including Hilbert space FSSH, Hilbert space GFSH, and Liouville space FSSH. We have shown a clear trend in the performance. Namely, GFSH works better than FSSH, while Liouville space is superior to Hilbert space. By bridging both worlds, GFSH in Liouville space has the best performance for the adopted model from all aspects. Furthermore, we have found that it is largely invariant under choice of representation, paving a novel way for developing representation-independent SH methods. The developed technique maintains the simplicity and efficiency of FSSH, while improving the accuracy and expanding the applicability. Therefore, GFSH in Liouville space should be extremely useful for studying complex non-adiabatic dynamics in large systems, including, for instance, Auger-type many-particle phenomena that are common in nanomaterials.

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