Fewest Switches Surface Hopping in Liouville Space

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ABSTRACT: The novel approach to nonadiabatic quantum dynamics greatly increases the accuracy of the most popular semiclassical technique while maintaining its simplicity and efficiency. Unlike the standard Tully surface hopping in Hilbert space, which deals with population flow, the new strategy in Liouville space puts population and coherence on equal footing. Dual avoided crossing and energy transfer models show that the accuracy is improved in both diabatic and adiabatic representations and that Liouville space simulation converges faster with the number of trajectories than Hilbert space simulation. The constructed master equation accurately captures superexchange, tunneling, and quantum interference. These effects are essential for charge, phonon and energy transport and scattering, exciton fission and fusion, quantum optics and computing, and many other areas of physics and chemistry.

Numerous processes of interest in modern physics, chemistry, and biology require consideration of quantum dynamics; however, a fully quantum description is generally forbidden due to computational cost. Frequently, only a small portion of particles under investigation, such as electrons and excitons, must be treated quantum mechanically, while the remaining degrees of freedom, typically nuclei, can be considered classically. Motivated by this fact, mixed quantum-classical methods have become the most popular choice for studying time-dependent phenomena including charge transport,1−5 photoinduced electron transfer,6 photochemistry,7 exciton relaxation,8 single fission,9 and bioluminescence.10 A series of quantum-classical techniques have been developed over the last few decades.11−15 Tully’s fewest switches surface hopping (FSSH)13 is the most popular option. FSSH is straightforward to implement, accurate, and efficient. It is also easily compatible with modern electronic structure methods. FSSH is widely adopted as the platform to introduce modifications as needed. It has been corrected for decoherence effects soon after its invention.16 More strategies to incorporate decoherence have been presented,17,18 although proper handling of decoherence in realistic systems is still not finally settled. A QM/MM-like flexible surface hopping has been proposed, grasping all charge transport regimes in organic crystals.19 Self-consistency checks20 have been recently added, solving the trivial crossing problem arising due to high state density in large systems. The fewest switches concept has been generalized to gross population flow between states.21 FSSH has been reformulated in the second quantization language to include entanglement within the trajectory ensemble.22

Standard FSSH is carried out in Hilbert space. Fifty years ago, Fano coined the concept of Liouville space, which is a direct product of two Hilbert spaces.23 This space has been extensively applied by Zwanzig24 and Redfield25 in the quantum theory of relaxation and by Mukamel in nonlinear optical spectroscopy.26 Quantum dynamics in Liouville space is described by a time-dependent density vector, which is formally equivalent to the time-dependent wave function in Hilbert space; however, the resulting dynamic pathways are completely different.27 In Hilbert space, surface hops happen between directly coupled states. Population transfer is expressed in a more elaborate way in Liouville space: Changes in quantum coherence depend on magnitudes of quantum populations and vice versa. Coherences play an extremely important role in quantum dynamics.28,29 Liouville space allows us to treat populations and coherences on equal footing, leading to dramatic, qualitative improvements in accuracy and allowing FSSH to treat many important phenomena.

Quantum-mechanical mapping between the Hilbert and Liouville spaces is known in quantum optics26 and computing.30 While such mapping is straightforward in pure quantum mechanics, it is neither obvious nor unique in a quantum-classical description. Quantum-classical theories raise multiple questions, such as the quantum backreaction,31−33 answers to which require extensive research and testing. Furthermore, quantum-classical theories are much more broadly applicable and carry significant impact in a wide spectrum of fields, including nanoscale, condensed phase, soft matter, and gas-phase systems in physics, chemistry, biology, materials, and related disciplines.

This letter reports a novel method for description of quantum dynamics. For the first time, the most practical

Received: July 14, 2015
Accepted: September 8, 2015
Published: September 8, 2015
The time-dependent wave function, \( \psi(t) \), is expressed as a linear combination of a set of orthogonal basis states in Hilbert space, \( \{ i \} \)

\[
\psi(t) = \sum_i c_i(t) i
\]

Its time evolution follows the Schrödinger equation

\[
\frac{d\psi(t)}{dt} = \frac{1}{i\hbar} [\hat{H}, \psi(t)]
\]

where \( \hat{H} \) is the system Hamiltonian. Alternatively, one can describe the quantum system using the density operator, \( \rho \). For a pure state, it reads

\[
\dot{\rho}(t) = \psi(t)\psi(t)\dagger
\]

The dynamics follow the Liouville equation

\[
\frac{d\rho(t)}{dt} = \frac{1}{i\hbar} [\hat{H}, \rho]
\]

Consider a two-level system as an illustration. The Hamiltonian is written as

\[
\hat{H} = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}
\]

Equation 4 becomes

\[
\frac{d}{dt} \begin{pmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{pmatrix} = \frac{1}{i\hbar} \begin{pmatrix} -V_{22}\rho_{12} + V_{12}\rho_{21} & V_{12}\rho_{21} - (V_{11} - V_{22}) & V_{22}\rho_{12} & 0 \\ V_{22}\rho_{12} & -V_{22}\rho_{12} + V_{12}\rho_{21} & V_{12}\rho_{21} & 0 \\ V_{11} - V_{22} & V_{12} & -V_{12} & 0 \\ V_{11} - V_{22} & V_{12} & -V_{12} & 0 \end{pmatrix} \begin{pmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{pmatrix}
\]

and can be re-formatted as

\[
\frac{d}{dt} \begin{pmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{pmatrix} = \frac{1}{i\hbar} \begin{pmatrix} 0 & -V_{21} & V_{12} & 0 \\ -V_{12} & V_{11} - V_{22} & 0 & V_{12} \\ 0 & V_{22} - V_{11} - V_{21} & 0 & V_{22} \\ 0 & V_{21} - V_{12} & 0 & 0 \end{pmatrix} \begin{pmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{pmatrix}
\]

If we define

\[
|\rho\rangle = \sum_i \rho_{ij} |ij\rangle
\]

where \( |ij\rangle \equiv |i\rangle \langle j| \), eq 7 can be further simplified as

\[
\frac{d}{dt} |\rho\rangle = \frac{1}{i\hbar} \hat{L}|\rho\rangle
\]

Here the superoperator \( \hat{L} \) connects all elements of \( |\rho\rangle \).

Tully’s FSSH is carried out in Hilbert space. The time derivative of the population of state \( |i\rangle \), \( \rho_{ii} \), is expressed as

\[
\frac{d\rho_{ii}}{dt} = \sum_{j\neq i} b_{ij}
\]

where

\[
b_{ij} = 2\hbar^{-1} \text{Im}(\rho_{ij}^* H_{ij})
\]

In FSSH, the switching probability from state \( i \) to another state \( j \) within a time interval \( \Delta t \) is

\[
g_{ij} = -\Delta t b_{ij} / \rho_{ii}
\]

Drawing upon the similarity between the Hilbert and Liouville formulations, eqs 1 and 2 and 8 and 9, we define the population of state \( |ij\rangle \) in Liouville space as \( \rho_{ij} \equiv |ij\rangle \langle ij| \). \( \text{Tr}^2 \rho = 1 \) always holds for pure states, and hence \( \sum_i \rho_{ii} = 1 \). \( \{ ij \} \) forms a complete, orthonormal basis for a quantum system in Liouville space, similar to \( \{ i \} \) in Hilbert space. Analogously, we obtain

\[
\frac{d\rho_{ij}}{dt} = \sum_{k \neq i, l \neq j} b_{ijkl}
\]

where

\[
b_{ijkl} = 2\hbar^{-1}[\delta_{il}\text{Im}(\rho_{ij}^* H_{kl}) + \delta_{ik}\text{Im}(\rho_{ij}^* H_{kl})]
\]

Similar to eq 12, the surface hopping probability in Liouville space is given by

\[
g_{ijkl} = -\Delta t b_{ijkl} / \rho_{ij}
\]

Equations 11 and 14 are derived for time-independent basis in the diabatic representation. In general, one needs to replace \( \hat{H} \) with \( \hat{H} - i\hbar \nu \cdot d \), where \( \nu \cdot d \) is the nonadiabatic coupling

\[
(\nu \cdot d)_j = \langle i | i \frac{d}{dt} |j\rangle
\]

When a surface hop is assigned, velocities need to be adjusted to conserve the total quantum-classical energy. In the adiabatic representation of Hilbert space FSSH, velocity rescaling is normally performed in the direction of the nonadiabatic coupling vector. If a surface hop happens from \( |ij\rangle \) to \( |kl\rangle \) in Liouville space, one projects \( d_d \) onto \( d_j \) to define the scaling direction. The situation is less clear in the diabatic representation because the nonadiabatic coupling is zero in this case. In principle, one needs to find the direction along which the surface hopping probabilities based on eqs 12 and 15 are maximized. Velocity rescaling is straightforward for 1D models because there is only one classical degree of freedom. Quantum-classical energy conservation achieved by velocity rescaling is critical to achieve the detailed balance between transitions up and down in energy and the quantum-classical equilibrium in the long time limit. For multidimensional realistic systems, one can adopt the classical path approximation, and replace velocity rescaling by multiplying the surface hopping probabilities upward in energy with the Boltzmann factor. Valid in the case of rapid redistribution of energy within the classical subsystem, compared with the
transition time, the Boltzmann approximation achieves the detailed balance.

Several additional definitions are needed. First, we define the energy for each \(|ij\rangle\rangle\) state, \(E_{ij}\). If \(i = j\), \(E_{ij}\) equals the energy of the \(i\)th state in Hilbert space, \(V''_{ii}\). When \(i \neq j\), we follow the analysis of refs 36 and 37 and adopt \(E_{ij} = (V''_{ii} + V''_{jj})/2\). In principle, only Hilbert states have well-defined energies. If a coherence state is regarded as a superposition of two Hilbert states, its energy should be an average over both states, perhaps weighted by the corresponding amplitudes. Placing the energy of the Liouville space coherence state in the middle of the two corresponding Hilbert states is an approximate yet rational way to mimic the role of coherence in quantum dynamics. (See the numerical demonstrations later.) The same convention has been adopted in the previous works.\(^{36,37}\) Second, the fraction of trajectories populating coherence states in Liouville space, that is, \(|ij\rangle\rangle\) with \(i \neq j\), needs to be converted back to Hilbert space populations for data analysis. Energy conservation is essential. When the total energy, that is, classical kinetic energy \((E_{k})\) plus \(E_{ij}\), is more than both \(V''_{ii}\) and \(V''_{jj}\) (half of the trajectories on \(|ij\rangle\rangle\) contribute to \(|i\rangle\) and the other half contribute to \(|j\rangle\)), to be consistent with the energy convention. If the total energy is larger than \(V''_{ii}\) but smaller than \(V''_{jj}\) (the trajectories on \(|ij\rangle\rangle\) fully contribute to \(|i\rangle\) in Hilbert space or vice versa. When decoherence occurs rapidly and is properly considered,\(^{16,18,38,41}\) no additional treatment is needed.

The internal consistency,\(^{15}\) which ensures that the fraction of trajectories on each potential energy surface is equivalent to the corresponding quantum probability, is a key characteristic of the standard Hilbert space FSSH. Because the Liouville space FSSH is formally similar, the fraction of trajectories on state \(|ij\rangle\rangle\), \(P_{ij}\), also equals to the corresponding population, \(P_{ij}\). In the absence of hop rejection,\(^{13}\) the fraction of trajectories on state \(i\), \(P_{i}\), can be obtained through

\[
P_{i} = P_{ii} + \sum_{j \neq i} \left( P_{ij} + P_{ji} \right) / 2
\]

which equals \(\Sigma_{j} P_{ij} = \Sigma_{j} P_{ji} = \Sigma_{j} \rho_{ij} \rho_{ji} = \Sigma_{j} \rho_{ij} \rho_{ji} = \rho_{i}\) considering \(P_{0j} = P_{ji}\). Hence, Liouville space FSSH holds the same level of internal consistency as Hilbert space FSSH. Note that rigorous internal consistency cannot be realized when running each trajectory independently.

First, we examine Tully’s dual avoided crossing model,\(^{15}\) which is defined in the diabatic representation: \(V_{11}(x) = 0\), \(V_{22}(x) = -0.1 e^{-0.28 x^2} + 0.05\), \(V_{12}(x) = V_{21}(x) = 0.015 e^{-0.06 x^2}\) (see Figure 1A). The mass of the \(x\) degree of freedom, \(m_{x}\), is 2000 au, which is close to the mass of a hydrogen atom. Initially, a Gaussian wave packet is prepared on the negative \(x\) side of state 1, and the corresponding width is set to be \(20/k_{x}\) with \(k_{x}\) being the initial momentum. This model exhibits two avoided crossings, where the quantum interference causes Stueckelberg oscillations in the transmission probabilities.\(^{15}\)

For such a two-level system, there are two basis states and only one channel of population transfer in Hilbert space. The evolution of the wave function is represented by a single-sided Feynman diagram\(^{27}\) (see Figure 2). In contrast, there exist four basis states and population transfer channels in Liouville space. The wave function propagation is expressed by a double sided Feynman diagram. Because (1) the coherence states \(|12\rangle\rangle\) and

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**Figure 1.** Dual avoided crossing model. (A) Diabatic potential energies and interstate couplings. (B) Reflection on the lower state. Transmission on (C) the lower state and (D) the upper state. The energy of the coherence state \(|12\rangle\rangle\) is shown as a dashed blue line in panel A. Open circles are exact quantum mechanical results. Red (blue) lines are FSSH results in Hilbert (Liouville) space with diabatic representation, and purple (green) lines are Hilbert (Liouville) space FSSH results with adiabatic representation. The vertical orange dashed lines in panels B–D express the critical kinetic energy, which is equal to \(V_{22} - V_{11}\) at \(V_{11} \gg S\). \(E = k_{x}^{2}/2m\) is the initial kinetic energy.

DOI: 10.1021/acs.jpcl.5b01502

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$15$, coherence states play an important role in the Liouville
points.

coherence states become energetically allowed in Liouville
$1$→$2$ forbidden in the Hilbert space FSSH due to
violation of energy conservation. The situation changes
significantly if $(V_{22} - V_{11})/2 \leq E_{k}$. Surface hops to the
coherence states become energetically allowed in Liouville
space.

It is well known$^{13,42,43}$ that Hilbert space FSSH in the
adiabatic representation gives unrealistically large reflection
on the lower state for energy lower than $V_{22} - V_{11}$ (i.e., $\log(E) \leq
-3$; see Figure 1B). Such inaccuracy is strongly related to
quantum interference. Simply switching to Liouville space results
in a much better agreement with the exact solution. As
expected, no transmission on the upper state is observed when
$\log(E) < -3$ (see Figure 1D) because energy conservation
cannot be fulfilled. FSSH reproduces quantum interference and
the peak positions. At high energies, the Liouville space transmission is almost identical to the Hilbert space results. At
low energies, the Liouville space FSSH improves upon the
Hilbert space FSSH in both diabatic and adiabatic representations. In Figure 1C, the peak intensity in the former case is enhanced, while the peak has been shifted to the right position in the latter case, getting closer to the quantum standard in both cases. Figure 1B shows an artificially high peak for the Hilbert adiabatic representation, overestimating the exact answer 10-fold. By switching to Liouville space, while remaining in the adiabatic representation, one reduces the peak intensity to within 50% of the exact answer, thus achieving more than
10-fold improvement in accuracy. This model shows that the
Liouville space FSSH achieves higher accuracy than the
standard Hilbert space FSSH, while maintaining simplicity
and reliability.

It is worth noting that the interference effect may play an
even more important role in other systems, and several novel
surface hopping methods have shown significant improvement
in this case.$^{32-46}$ Liouville space representation can be combined with these methods, for instance, phase-corrected
surface hopping$^{32,43}$ to improve the performance further.

We move further to the more complex three-level super-
exchange model$^{11}$ defined in atomic units as $V_{11}(x) = 0$, $V_{22}(x) = 0.01$, $V_{33}(x) = 0.005$, $V_{12}(x) = V_{23}(x) = 0.001e^{-x^2}/2$, $V_{35}(x) = V_{32}(x) = 0.01e^{-x^2}/2$, and $V_{13}(x) = V_{31}(x) = 0$. As illustrated in
Figure 3A, diabatic states 1 and 3 are coupled indirectly through
the intermediate state 2 with a higher energy. The other
parameters are chosen to be the same as those in the dual
avoided crossing model previously discussed.

We start the dynamics from state 1. When $V_{22} - V_{11} > E_{k}$, a certain amount of population can flow from state 1
to state 3 because they are indirectly coupled, representing the
superexchange mechanism of population transfer; however, the
hop $1 \rightarrow 2$ is forbidden in the Hilbert space FSSH due to
violation of energy conservation, and thus there is no net
population flux from state 1 to state 3. The superexchange
dynamics is totally misrepresented. The situation is completely
different in Liouville space, which allows additional population
transfer channels (See Figure 4). Coherence states act as
bridges connecting states $(111)$ and $(333)$ with smaller energy
barriers. A typical example is highlighted in Figure 4, where the
channel $(111) \rightarrow (221)) \rightarrow (331)) \rightarrow (321)) \rightarrow (333))$ involves a global energy barrier of $(V_{22} + V_{33})/2 - V_{11} = 0.0075$ au
instead of 0.01 au in Hilbert space. Furthermore, trajectories
occupying coherence states also contribute to the final
population of state 3. For instance, the channel $(111) \rightarrow
(211) \rightarrow (311))$ has an overall energy barrier of only $(V_{22} - V_{11})/2 = 0.005$ au and thus plays an even more important role in the
superexchange dynamics.

Figure 3B–D compare transmissions on different states obtained with Hilbert and Liouville spaces. The superexchange
model can be analyzed in detail by dividing all investigated
momenta into three regimes. In the first regime, $E_{k}$ is less than
$V_{33} - V_{11}$. Both methods agree perfectly with the quantum
standard.$^{21}$ There, the particle remains on state 1 after crossing
the interaction zone. In the second regime, $V_{22} - V_{11} > E_{k} > V_{33} - V_{11}$. The exact solution shows significant transmission on state 3, illustrating superexchange. The transmission is blocked in the Hilbert space FSSH because the transition probability directly from state 1 and state 3 is zero, and the indirect, superexchange pathway is classically disallowed. In contrast, the Liouville space FSSH has multiple surface hopping channels to state 3 and can reproduce nearly all of the transmission. (See Figure 3D.) In the adiabatic representation, the results of
Hilbert space FSSH are already quite close to the exact
solution. Nevertheless, Liouville space FSSH still shows
improvement, indicating that surface hopping in Liouville
space is generally superior to the standard strategy in Hilbert
space. In the third regime, where $E_{k} > V_{33} - V_{11}$, both methods give similar results again. Now, all channels are energetically
enabled. The Liouville space FSSH also gives a better
description for the “M-shaped” transmission on state 2. (See
Figure 3C.) This model demonstrated that the new method

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<th>Basis States</th>
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Figure 2. Comparison of Hilbert and Liouville spaces for a two-level system. Basis states and surface-hopping channels are shown in the upper two panels. A representative surface hopping channel is highlighted with dark circles. It is chosen for a detailed investigation of the energy landscape and further analysis. The lower two panels demonstrate the energy landscape and Feynman diagrams. The wavy arrows depict interaction with the classical particles at specific time points.

DOI: 10.1021/acs.jpclett.5b01502

J. Phys. Chem. Lett. 2015, 6, 3827−3833

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provides a dramatic, qualitative improvement over the standard technique for superexchange and tunneling, common in quantum electronics, charge and energy transfer, Auger phenomena, photochemistry, and related fields.

Finally, we investigate convergence of the surface hopping results. As shown in Figure 5, the standard deviation of
quantum transmission in both dual avoided crossing and superexchange models decays rapidly as a function of the number of trajectories. One thousand trajectories are required to achieve a 99% accuracy (standard deviation around 0.01). In both cases, Liouville space FSSH requires fewer trajectories than Hilbert space FSSH to achieve the same statistical convergence. Considering the fact that Liouville and Hilbert space FSSH need similar efforts to obtain the surface hopping probabilities, one concludes that Liouville space FSSH is statistically more accurate.

The quantum-classical Liouville equation (QCLE) method of Martens and Kapral and Cicotti related closely to quantum-classical Lie brackets starts with the full quantum Liouville equation and takes the semiclassical limit through a partial Wigner transform over the nuclear degrees of freedom. The resulting equations of motion account for the time evolution of the coupled electronic and nuclear subsystems. QCLE can be simulated by an ensemble of trajectories undergoing momentum jumps. Recently, Subotnik et al. demonstrated that Tully’s FSSH algorithm approximately obeys QCLE, provided that several conditions are satisfied. In particular, Hilbert space FSSH can be viewed as a method for approximate propagation of quantum populations while neglecting the evolution of coherences. Liouville space FSSH is more closely related to QCLE. By treating populations and coherences on equal footing while maintaining FSSH simplicity and independent trajectory approximation, the new approach bridges the QCLE and FSSH worlds and achieves a good balance between accuracy and efficiency.

Frustrated hops, which violate the quantum-classical energy conservation, require special consideration. On the one hand, they provide a mechanism to achieve detailed balance between transitions upward and downward in energy, leading to thermodynamic equilibrium. On the other hand, they violate internal consistency between the quantum mechanical and statistical surface hopping probabilities and prevent superexchange processes. The superexchange problem has been recently addressed by global flux surface hopping, which redefines probability flux and introduces more reliable surface hopping probabilities, and second-quantized surface hopping, which uses an ensemble of correlated trajectories. Liouville space FSSH introduces coherence states into the surface hopping framework and could be combined with these methods to enhance the performance further.

Quantum decoherence effects can be very important and have been taken into account previously. The present technique treats the population and coherence terms on equal footing, potentially allowing for a more straightforward description and interpretation of decoherence. Providing a novel foundation for surface hopping, the developed approach can be combined with these methods to enhance the performance further.

The concept of surface hopping cannot be applied directly to a continuous spectrum of states. In such cases, one can either discretize the states or resort to other approaches developed for Hilbert space, such as combined mean-field/surface hopping, quantum trajectory mean-field approach for nonadiabatic molecular dynamics, and Bohmian quantum-classical dynamics. Similar ideas can be applied to surface hopping in Liouville space.

In conclusion, by drawing an analogy between the Hilbert and Liouville representations of quantum mechanics, we have proposed a new family of semiclassical techniques for nonadiabatic quantum dynamics. The novel Liouville space version maintains all advantages of the standard, Hilbert space formulation, including internal consistency, ease of implementation, and low computational cost. Liouville space results converge faster with the number of FSSH trajectories than Hilbert space data. By treating populations and coherences on equal footing, the method allows us to gain a comprehensive understanding of complex nonequilibrium quantum-mechanical processes. While the standard Tully’s FSSH technique exhibits qualitative problems in dealing with superexchange and tunneling, the developed method provides a satisfactory description of these phenomena. The reported advance opens up a new direction in semiclassical treatment of nonadiabatic dynamics and enables one to treat efficiently a broad spectrum of phenomena that are of great importance in multiple areas of physics and chemistry, including charge and energy transport, electron–phonon scattering, multiple exciton generation and annihilation, nonlinear optics, and quantum computing.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by U.S. National Science Foundation, grant CHE-1300118.

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DOI: 10.1021/acs.jpclett.5b01502
J. Phys. Chem. Lett. 2015, 6, 3827−3833