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Nonadiabatic dynamics in open quantum-classical systems: Forward-backward trajectory solution

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A new approximate solution to the quantum-classical Liouville equation is derived starting from the formal solution of this equation in forward-backward form. The time evolution of a mixed quantum-classical system described by this equation is obtained in a coherent state basis using the mapping representation, which expresses N quantum degrees of freedom in a $2N$-dimensional phase space. The solution yields a simple dynamics in which a set of N coherent state coordinates evolves in forward and backward trajectories, while the bath coordinates evolve under the influence of the mean potential that depends on these forward and backward trajectories. It is shown that the solution satisfies the differential form of the quantum-classical Liouville equation exactly. Relations to other mixed quantum-classical and semi-classical schemes are discussed. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4736841]

I. INTRODUCTION

Nonadiabatic processes are at the core of many physical phenomena, including population transfer among electronic system states, quantum coherent evolution of a system interacting with environmental degrees of freedom, and electron and proton transfer reactions in condensed phase and biological systems, among others. In investigating such phenomena, one often focuses on certain quantum degrees of freedom whose dynamics is of primary interest. These may be the electronic degrees of freedom of a chromophore excited by a radiation to prepare the initial state of the system, the exciton states of a light harvesting system, or even the electron or proton degrees of freedom involved in the transfer of these particles. In such cases, we are led to consider how these quantum degrees of freedom interact with the environment in which they reside. Interactions with the environment can lead to the breakdown of the Born-Oppenheimer approximation and one must consider nonadiabatic dynamics in such open quantum systems.

A number of different approaches have been developed to describe nonadiabatic dynamics. These include mean-field and a variety of surface-hopping schemes,[1–7] methods based on semi-classical evaluations of path integral formulations of quantum mechanics,[8–20] and descriptions based on the quantum-classical Liouville equation.[21] An important ingredient in any approach dealing with nonadiabatic dynamics is the manner in which quantum coherence and decoherence are taken into account in the dynamics. The description of nonadiabatic dynamics necessarily entails dealing with coherence that is generated and destroyed as the system evolves while interacting with its environment. Many of the various nonadiabatic approaches that have been constructed deal with the issue of decoherence in various ways.[22–25]

Another characteristic of nonadiabatic schemes is the manner in which the environment is modeled. At the simplest level, the environment may be treated as a stochastic bath, which leads to reduced descriptions that do not explicitly include the environmental degrees of freedom in the evolution. Their effect only appears in certain parameters and terms that characterize the coupling to the environment. Schemes of this type include various quantum master equations[26] such as the Lindblad, Redfield, and Bloch equations.[27–29] Other methods explicitly account for the environmental degrees of freedom. It is challenging to treat large and complex systems fully quantum mechanically, although there are developments along these lines.[30–35] Some methods, for example, some path integral methods, begin with a full quantum treatment and then make semi-classical approximations to obtain tractable solutions.[17–20,36] Often the environment in which the quantum dynamics of interest occurs can be described by classical dynamics to a high degree of accuracy and this has spawned a number of mixed quantum-classical descriptions of nonadiabatic dynamics. Many surface-hopping schemes fall in this category as do some approximations to semi-classical path integral formulations and mean-field methods.[17,37,38] Here, we focus on descriptions based on the quantum-classical Liouville equation (QCLE).

The QCLE employs a partial Wigner representation of the environmental (bath) degrees of freedom and may be derived from full quantum dynamics by truncating the quantum evolution operator to first order in a small parameter related to the ratio of the characteristic masses of quantum and bath degrees of freedom.[39] It may also be derived from partially linearized path integral formulations,[40,41] indicating the close connection between these different starting points. This equation has been shown to provide an accurate description of nonadiabatic dynamics in many applications and to account for quantum decoherence.[21] A number of different methods, whose structure depends on the basis chosen to represent the quantum degrees of freedom, have been devised for its simulation.[42–48] Simulation methods that utilize an adiabatic basis can be cast into the form of surface-hopping

dynamics, but in a way that includes coherent evolution segments that account for the creation and destruction of coherence in a proper manner. More recently, as in some semi-classical approaches,[17] the mapping basis[49] was used to describe the quantum degrees of freedom in the QCLE in a continuous classical-like manner, leading to a trajectory description in the full system phase space.[50–52]

In this paper, we also utilize the mapping representation but instead of dealing directly with the solution of the QCLE using a Liouville propagator, we start with its solution in terms of forward-backward quantum-classical propagators constructed some time ago.[53] With this starting point and the introduction of a coherent state basis,[54,55] we are able to obtain a solution of the QCLE that involves the forward-backward trajectories of the coherent state variables, coupled to the evolution of the bath phase space variables. Formally, both forward and backward trajectories are propagated forward in time. The two sets of trajectories are distinguished and named by their association with the forward and backward quantum-classical propagators, respectively. This formulation leads to a simple set of equations of motion that describe the nonadiabatic dynamics of the system.

The outline of the paper is as follows: In Sec. II, we sketch the important features of the QCLE, its representation in the mapping basis, and formal solution in forward-backward form needed for our calculation. The forward-backward trajectory solution is constructed in Sec. III, which contains the most important results of the paper. A discussion of the results is presented in Sec. IV, while the Appendices give the additional technical details of the calculation.

II. QUANTUM-CLASSICAL LIOUVILLE EQUATION

We consider a quantum subsystem coupled to a bath. We assume that the dynamics of such a system is described by the quantum-classical Liouville equation.[39,42,46,56–60] For a quantum operator $\hat{B}_W(X)$, which depends on the classical phase space variables $X = (R, P) = (R_1, R_2, \ldots, R_{N_b}, P_1, P_2, \ldots, P_{N_b})$ of the bath, this evolution equation takes the form,

$$\frac{d}{dt}\hat{B}_W(X,t) = i\hat{\mathcal{L}}\hat{B}_W(X,t), \tag{1}$$

where the quantum-classical Liouville operator is

$$i\hat{\mathcal{L}}\cdot = \frac{i}{\hbar}[\hat{H}_W, \cdot] - \frac{1}{2}(\{\hat{H}_W, \cdot\} - \{\cdot, \hat{H}_W\}). \tag{2}$$

Here, the subscript W refers to a partial Wigner transform over the bath degrees of freedom (DOF), $\hat{H}_W(X)$ is the partial Wigner transform of the total Hamiltonian of the system, $[\cdot, \cdot]$ is the commutator and $\{\hat{A}_W, \hat{B}_W\} = \hat{A}_W(\overleftarrow{\frac{\partial}{\partial R}}\overrightarrow{\frac{\partial}{\partial P}} - \overleftarrow{\frac{\partial}{\partial P}}\overrightarrow{\frac{\partial}{\partial R}})\hat{B}_W = \frac{\partial \hat{A}_W}{\partial R}\frac{\partial \hat{B}_W}{\partial P} - \frac{\partial \hat{A}_W}{\partial P}\frac{\partial \hat{B}_W}{\partial R}$ is the Poisson bracket in the phase space X of the partially Wigner transformed $\hat{A}_W$ and $\hat{B}_W$ operators. The total Hamiltonian may be written as the sum of bath, subsystem, and coupling terms,

$$\hat{H}_W(X) = H_b(X) + \hat{h}_s + \hat{V}_c(R) \equiv H_b(X) + \hat{h}(R), \tag{3}$$

where $H_b(X) = P^2/2M + V_b(R)$ is the bath Hamiltonian with $V_b(R)$ the bath potential energy, $\hat{h}_s = \hat{p}^2/2m + \hat{V}_s$ is the subsystem Hamiltonian with $\hat{p}$ and $\hat{V}_s$ the subsystem momentum and potential energy operators, and $\hat{V}_c(R)$ is the coupling potential energy operator. The masses of the subsystem and bath particles are m and M, respectively. The evolution equation for the density matrix $\hat{\rho}_W(X,t)$ is analogous to Eq. (1) with a change in the sign of the evolution operator.

A. Formal solution

The QCLE may also be written in a form that is analogous to the quantum Liouville equation:[53]

$$\frac{d}{dt}\hat{B}_W(X,t) = \frac{i}{\hbar}\left(\overrightarrow{\mathcal{H}}_\Lambda\,\hat{B}_W - \hat{B}_W\,\overleftarrow{\mathcal{H}}_\Lambda\right), \tag{4}$$

where operators $\overrightarrow{\mathcal{H}}_\Lambda$ and $\overleftarrow{\mathcal{H}}_\Lambda$ are given by

$$\overrightarrow{\mathcal{H}}_\Lambda = \hat{H}_W\left(1 + \frac{\hbar\Lambda}{2i}\right), \quad \overleftarrow{\mathcal{H}}_\Lambda = \left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{H}_W, \tag{5}$$

with Λ the negative of the Poisson bracket operator, $\Lambda = \overleftarrow{\nabla}_P \cdot \overrightarrow{\nabla}_R - \overleftarrow{\nabla}_R \cdot \overrightarrow{\nabla}_P$.

The formal solution of the QCLE can be expressed in either of two forms as

$$\begin{aligned}\hat{B}_W(X,t) &= e^{i\hat{\mathcal{L}}t}\hat{B}_W(X) \\ &= \mathcal{S}\left(e^{i\overrightarrow{\mathcal{H}}_\Lambda t/\hbar}\hat{B}_W(X)e^{-i\overleftarrow{\mathcal{H}}_\Lambda t/\hbar}\right).\end{aligned} \tag{6}$$

The first equality follows from the formal solution of Eq. (1) while the second equality follows from Eq. (4). The $\mathcal{S}$ in this latter form simply specifies the order in which products of the left and right operators act in order to be identical with the first form involving the QCL operator. In particular, a general term $\mathcal{S}((\overrightarrow{\mathcal{H}}_\Lambda)^j\hat{B}_W(\overleftarrow{\mathcal{H}}_\Lambda)^k)$ in the expansion of the exponential operators is composed of $\frac{(j+k)!}{j!k!}$ separate terms each with a prefactor of $\frac{j!k!}{(j+k)!}$. Each of these separate terms corresponds to a specific order in which the $\overrightarrow{\mathcal{H}}_\Lambda$ and $\overleftarrow{\mathcal{H}}_\Lambda$ operators act on $\hat{B}_W$. This formal solution will be used in the calculations presented below.

B. Mapping representation

We will be concerned with the representation of the QCLE in the quantum subsystem basis and its equivalent representation in the mapping basis. The subsystem basis, $\{|\lambda\rangle;\ \lambda = 1, \ldots, N\}$, is defined by the eigenvalue problem $\hat{h}_s|\lambda\rangle = \epsilon_\lambda|\lambda\rangle$, and a matrix element of an operator $\hat{B}_W(X)$ is given by $B_W^{\lambda\lambda'}(X) = \langle\lambda|\hat{B}_W(X)|\lambda'\rangle$.

The $|\lambda\rangle$ eigenfunctions of an N-state quantum subsystem can be replaced with the eigenfunctions of N fictitious harmonic oscillators,[17,49] $|m_\lambda\rangle$, having occupation numbers, which are limited to 0 or 1: $|\lambda\rangle \to |m_\lambda\rangle = |0_1, \ldots, 1_\lambda, \ldots 0_N\rangle$. Creation and annihilation operators on these states, $\hat{a}_\lambda^\dagger$ and $\hat{a}_\lambda$, respectively, are defined as

$$\hat{a}_\lambda^\dagger = \frac{1}{\sqrt{2\hbar}}(\hat{q}_\lambda - i\,\hat{p}_\lambda), \quad \hat{a}_\lambda = \frac{1}{\sqrt{2\hbar}}(\hat{q}_\lambda + i\,\hat{p}_\lambda), \tag{7}$$

and satisfy the commutation relation $[\hat{a}_\lambda, \hat{a}_{\lambda'}^\dagger] = \delta_{\lambda,\lambda'}$. The actions of these operators on the single-excitation

mapping states are $\hat{a}_\lambda^\dagger|0\rangle = |m_\lambda\rangle$ and $\hat{a}_\lambda|m_\lambda\rangle = |0\rangle$, where $|0\rangle = |0_1 \ldots 0_N\rangle$ is the ground state of the mapping basis.

We may then define the mapping versions of operators, $\hat{B}_m(X)$, given by

$$\hat{B}_m(X) = B_W^{\lambda\lambda'}(X)\hat{a}_\lambda^\dagger \hat{a}_{\lambda'}, \tag{8}$$

so that a matrix element of $\hat{B}_W$ in the subsystem basis is equal to the matrix element of the corresponding mapping operator in the mapping single-excitation basis: $B_W^{\lambda\lambda'}(X) = \langle\lambda|\hat{B}_W(X)|\lambda'\rangle = \langle m_\lambda|\hat{B}_m(X)|m_{\lambda'}\rangle$. (The Einstein summation convention will be used throughout although sometimes sums will be explicitly written if there is the possibility of confusion.) In particular, the mapping Hamiltonian operator is

$$\hat{H}_m = H_b(X) + h^{\lambda\lambda'}(R)\hat{a}_\lambda^\dagger \hat{a}_{\lambda'} \equiv H_b(X) + \hat{h}_m, \tag{9}$$

where we applied the mapping transformation only on the part of the Hamiltonian that involves the subsystem DOF in Eq. (9). The pure bath term, $\hat{H}_b(X)$ in Eq. (3), acts as an identity operator in the subsystem basis and is mapped onto the identity operator of the mapping space.

The QCLE (4) may now be written in terms of mapping operators as

$$\frac{d}{dt}\hat{B}_m(X,t) = \frac{i}{\hbar}\big(\overrightarrow{\mathcal{H}}_\Lambda^m \hat{B}_m - \hat{B}_m \overleftarrow{\mathcal{H}}_\Lambda^m\big), \tag{10}$$

where $\overrightarrow{\mathcal{H}}_\Lambda^m$ is given by $\overrightarrow{\mathcal{H}}_\Lambda^m = \hat{H}_m(1 + \hbar\Lambda/2i)$, with an analogous definition for $\overleftarrow{\mathcal{H}}_\Lambda^m$. One may verify that the mapping space matrix elements of this equation are identical to the subsystem matrix elements of Eq. (4). Consequently, the formal solution of this equation is similar to that in Eq. (6) and is given by

$$\hat{B}_m(X,t) = \mathcal{S}\big(e^{i\overrightarrow{\mathcal{H}}_\Lambda^m t/\hbar}\hat{B}_m(X)e^{-i\overleftarrow{\mathcal{H}}_\Lambda^m t/\hbar}\big). \tag{11}$$

This equation will form the starting point for the explicit solution of the QCLE in terms of forward-backward trajectories.

III. FORWARD-BACKWARD TRAJECTORY SOLUTION

In this section, we derive a new approximate solution to the QCLE for an operator $\hat{B}_W(X,t)$ in the subsystem basis. This new solution is based on Eq. (6), which shows that the time evolution of $\hat{B}_W(X,t)$ can be formally expressed in the mixed quantum-classical analogue of the forward-backward form for a quantum operator in the Heisenberg picture. We then apply the mapping transformation and introduce sets of forward and backward coherent state variables to compute the matrix elements of the the mixed quantum-classical propagators in terms of classical-like trajectories. Throughout the derivation presented in the current section, we often rely on standard approximations such as Trotter decomposition, which is bounded by $\mathcal{O}(\tau^2)$, where τ is an infinitesimal time slice that we use to break up the propagators as explained in the next paragraph. In addition, we will invoke an approximation, Eq. (35), on the inner products between coherent state variables introduced in adjacent time steps. This last approximation is essential as it allows the trajectory segments in adjacent time slices to be pieced together and form a smooth trajectory in the phase space. Further discussion on the implications of making such an approximation is elaborated in Sec. III C.

The formal solution of the QCLE can be written in terms of a sequence of M short-time propagators acting on the initial value of the operator:

$$\hat{B}_W(X,t) = e^{i\hat{\mathcal{L}}\Delta t_1}e^{i\hat{\mathcal{L}}\Delta t_2}\ldots e^{i\hat{\mathcal{L}}\Delta t_M}\hat{B}_W(X), \tag{12}$$

where $\Delta t_j = t_j - t_{j-1} = \tau$ for all j with $t_0 = 0$ and $t_M = t$. (When information about a specific time step is needed, we use the Δt_j notation, otherwise the common value τ will be used.) In the above equation, the chronological order[45] of the time steps goes from left to right. This ordering convention is chosen such that the propagator $e^{i\hat{\mathcal{L}}\Delta t_j}$ at time j updates all the propagators at later times before it acts on the operator $\hat{B}_W$. This prescription allows us to parametrize the Liouville operators, $\hat{\mathcal{L}}(X_t)$, with the trajectories of bath coordinates, $X_t \equiv X(t)$.

Consequently, in view of Eq. (11), the formal solution applies in each time segment so that $\hat{B}_W(X,t)$ may also be written as

$$\begin{aligned}\hat{B}_m(X,t) = \mathcal{S}\big(e^{i\Delta t_1\overrightarrow{\mathcal{H}}_\Lambda^m/\hbar}\mathcal{S}\big(e^{i\Delta t_2\overrightarrow{\mathcal{H}}_\Lambda^m/\hbar}\ldots \\ \times \mathcal{S}\big(e^{i\Delta t_M\overrightarrow{\mathcal{H}}_\Lambda^m/\hbar}\hat{B}_m(X)e^{-i\Delta t_M\overleftarrow{\mathcal{H}}_\Lambda^m/\hbar}\big) \\ \times \ldots e^{-i\Delta t_2\overleftarrow{\mathcal{H}}_\Lambda^m/\hbar}\big)e^{-i\Delta t_1\overleftarrow{\mathcal{H}}_\Lambda^m/\hbar}\big),\end{aligned} \tag{13}$$

where there are M concatenated $\mathcal{S}(\cdots)$ brackets.

A. Representation in coherent states

In order to proceed with the evaluation, we must consider the computation of the forward and backward propagators in this expression. To order τ^2, we have

$$e^{i\tau\overrightarrow{\mathcal{H}}_\Lambda^m/\hbar} = e^{\hat{H}_m\Lambda\tau/2}e^{i\hat{H}_m\tau/\hbar} + \mathcal{O}(\tau^2). \tag{14}$$

Also, to order τ^2, we may write the first exponential operator as

$$\begin{aligned}e^{\hat{H}_m\Lambda\tau/2} &= 1 + \frac{\tau}{2}\hat{H}_m\Lambda + \ldots, \\ &= 1 + \frac{\tau}{2}H_b(X)\Lambda + \frac{\tau}{2}h^{\lambda\lambda'}\hat{a}_\lambda^\dagger\hat{a}_{\lambda'}\Lambda + \ldots, \\ &= 1 + \frac{\tau}{2}H_b(X)\Lambda + \frac{\tau}{2}(h^{\lambda\lambda'}\hat{a}_{\lambda'}\hat{a}_\lambda^\dagger - \mathrm{Tr}_s\, h)\Lambda + \ldots,\end{aligned} \tag{15}$$

where we have reversed the normal-ordered product of annihilation and creation operators into an anti-normal order form using their commutation relation. The by-product of reversing the ordering of creation and annihilation operators is the emergence of a trace term in the last line of this equation. Since the trace term is independent of the quantum state, it may be combined with the bath potential, $V_0(R) = V_b(R) - \mathrm{Tr}_s\, h(R)$, to give $H_0(X) = P^2/2M + V_0(R)$ so that we have the simpler form of Eq. (15),

$$e^{\hat{H}_m\Lambda\tau/2} = 1 + \frac{\tau}{2}H_0(X)\Lambda + \frac{\tau}{2}h^{\lambda\lambda'}\hat{a}_{\lambda'}\hat{a}_\lambda^\dagger\Lambda + \mathcal{O}(\tau^2). \tag{16}$$

In this form, the propagator can be expressed conveniently in coherent states.[54]

We define the coherent states $|z\rangle$ in the mapping space,

$$\hat{a}_\lambda |z\rangle = z_\lambda |z\rangle, \quad \langle z| \hat{a}_\lambda^\dagger = z_\lambda^* \langle z|, \tag{17}$$

where $|z\rangle$ is a coherent state with N degrees of freedom and the eigenvalue is $z_\lambda = (q_\lambda + ip_\lambda)/\sqrt{2\hbar}$. The variables $q = (q_1, \ldots, q_N)$ and $p = (p_1, \ldots, p_N)$ are the mean coordinates and momenta of the harmonic oscillators in the state $|z\rangle$, respectively; i.e., we have $\langle z|\hat{q}_\lambda|z\rangle = q_\lambda$ and $\langle z|\hat{p}_\lambda|z\rangle = p_\lambda$.

The coherent states form an overcomplete basis; thus, we have to specify the inner product between any pair of coherent states and the resolution of identity.[54] The inner product is

$$\begin{aligned}\langle z|\, z'\rangle &= e^{-\frac{1}{2}(|z|^2+|z'|^2)+z^*\cdot z'}, \\ &= e^{-\frac{1}{2}(|z-z'|^2)-i\Im(z\cdot z'^*)}.\end{aligned} \tag{18}$$

The norm of the inner product measures how far away the two coherent states $|z\rangle$ and $|z'\rangle$ are in the phase space of coherent state variables. The resolution of the identity is

$$1 = \int \frac{d^2z}{\pi^N} |z\rangle \langle z|, \tag{19}$$

where $d^2z = d(\Re(z))d(\Im(z)) = dqdp/(2\hbar)^N$.

Given these properties of the coherent states, we may insert the resolution of the identity in the bath Hamiltonian terms and between the $\hat{a}_{\lambda'}$ and $\hat{a}_\lambda^\dagger$ operators in Eq. (16) to obtain

$$\begin{aligned}e^{\frac{\tau}{2}\hat{H}_m\Lambda} &= \left(1 + \frac{\tau}{2}H_0(X)\Lambda\right)\int \frac{d^2z}{\pi^N}|z\rangle\langle z| \\ &\quad + \frac{\tau}{2}\int \frac{d^2z}{\pi^N} h^{\lambda\lambda'}\hat{a}_{\lambda'}|z\rangle\langle z|\hat{a}_\lambda^\dagger\Lambda + \mathcal{O}(\tau^2), \\ &= \int \frac{d^2z}{\pi^N}|z\rangle\left(1 + \frac{\tau}{2}(H_0(X) + h^{\lambda\lambda'}z_\lambda^* z_{\lambda'})\Lambda\right. \\ &\quad \left. + \mathcal{O}(\tau^2)\right)\langle z|, \\ &= \int \frac{d^2z}{\pi^N}|z\rangle\, e^{\frac{\tau}{2}H_{cl}(X,z)\Lambda}\langle z| + \mathcal{O}(\tau^2).\end{aligned} \tag{20}$$

In this calculation, we used Eq. (17) to eliminate the annihilation and creation operators in Eq. (20). Note that $h^{\lambda\lambda'}z_\lambda^* z_{\lambda'} = \frac{1}{2\hbar}h^{\lambda\lambda'}(q_{\lambda'}q_\lambda + p_\lambda p_{\lambda'})$ since $h^{\lambda\lambda'}$ is symmetric. In the last line of Eq. (20), we defined the "classical" Hamiltonian

$$\begin{aligned}H_{cl}(X,z) &= H_0(X) + h^{\lambda\lambda'}z_\lambda^* z_{\lambda'} \equiv H_0(X) + h_{cl}(R,z), \\ &= \frac{P^2}{2M} + h_{s,cl}(z) + V_{cl}(R,z),\end{aligned} \tag{21}$$

where $V_{cl}(R,z) = V_0(R) + V_c^{\lambda\lambda'}(R)z_\lambda^* z_{\lambda'}$.

The operator $H_{cl}(X,z)\Lambda$ acts on all bath phase space variables to its right. Therefore, it is convenient to introduce a notation that makes this action evident. More specifically, we let

$$H_{cl}(X,z)\Lambda = \frac{\partial H_{cl}}{\partial P}\cdot\frac{\vec{\partial}}{\partial R} - \frac{\partial H_{cl}}{\partial R}\cdot\frac{\vec{\partial}}{\partial P} \equiv i\,\vec{\mathcal{L}}\,(X,z), \tag{22}$$

so that

$$e^{\frac{\tau}{2}\hat{H}_m\Lambda} = \int \frac{d^2z}{\pi^N}|z\rangle\, e^{i\vec{\mathcal{L}}(X,z)\tau/2}\langle z| + \mathcal{O}(\tau^2). \tag{23}$$

Similarly, we can define

$$\Lambda H_{cl}(X,z) = \frac{\overleftarrow{\partial}}{\partial P}\cdot\frac{\partial H_{cl}}{\partial R} - \frac{\overleftarrow{\partial}}{\partial R}\cdot\frac{\partial H_{cl}}{\partial P} \equiv -i\,\overleftarrow{\mathcal{L}}\,(X,z), \tag{24}$$

and

$$e^{-\frac{\tau}{2}\Lambda\hat{H}_m} = \int \frac{d^2z}{\pi^N}|z\rangle\, e^{i\overleftarrow{\mathcal{L}}(X,z)\tau/2}\langle z| + \mathcal{O}(\tau^2). \tag{25}$$

The other quantity that will enter in the evaluation of the time evolution is the action of the exponential operator $e^{i\hat{H}_m(X)\tau/\hbar}$ on a coherent state. In Appendices A and B, we show that

$$\begin{aligned}e^{-i\hat{H}_m(X)\tau/\hbar}|z\rangle &= e^{-iH_b(X)\tau/\hbar}e^{-i\hat{h}_m(R)\tau/\hbar}|z\rangle, \\ &= e^{-iH_b(X)\tau/\hbar}|z(\tau)\rangle,\end{aligned} \tag{26}$$

with $z(\tau)$ determined from the solution of the evolution equation,

$$\frac{dz_\lambda}{dt} = -\frac{i}{\hbar}\frac{\partial h_{cl}}{\partial z_\lambda^*}. \tag{27}$$

B. Time evolution of an operator

These results may now be used to compute the value of the matrix elements of an operator $\hat{B}_W(X,t)$ in the subsystem basis: $B_W^{\lambda\lambda'}(X,t) = \langle m_\lambda|\hat{B}_m(X,t)|m_{\lambda'}\rangle$. We have

$$\begin{aligned}B_W^{\lambda\lambda'}(X,t) = \sum_{\mu\mu'}\int\prod_{i=1}^{M}\frac{d^2z_i}{\pi^N}\frac{d^2z_i'}{\pi^N} \\ \times \langle m_\lambda|z_1\rangle\,\mathcal{S}(e^{i\vec{\mathcal{L}}(X,z_1)\frac{\Delta t_1}{2}}\langle z_1|\,e^{i\hat{H}_m\frac{\Delta t_1}{\hbar}}|z_2\rangle \\ \times \mathcal{S}(e^{i\vec{\mathcal{L}}(X,z_2)\frac{\Delta t_2}{2}}\langle z_2|\,e^{i\hat{H}_m\frac{\Delta t_2}{\hbar}}\ldots|z_M\rangle \\ \times \mathcal{S}(e^{i\vec{\mathcal{L}}(X,z_M)\frac{\Delta t_M}{2}}\langle z_M|\,e^{i\hat{H}_m\frac{\Delta t_M}{\hbar}}|m_\mu\rangle \\ \times B_W^{\mu\mu'}(X)\langle m_{\mu'}|e^{-i\hat{H}_m\frac{\Delta t_M}{\hbar}}|z_M'\rangle e^{i\overleftarrow{\mathcal{L}}(X,z_M')\frac{\Delta t_M}{2}}) \\ \times \langle z_M'|\ldots e^{-i\hat{H}_m\frac{\Delta t_2}{\hbar}}|z_2'\rangle e^{i\overleftarrow{\mathcal{L}}(X,z_2')\frac{\Delta t_2}{2}}) \\ \times \langle z_2'|e^{-i\hat{H}_m\frac{\Delta t_1}{\hbar}}|z_1'\rangle e^{i\overleftarrow{\mathcal{L}}(X,z_1')\frac{\Delta t_1}{2}})\langle z_1'|m_{\lambda'}\rangle.\end{aligned} \tag{28}$$

We may now make use of the definition of the $\mathcal{S}$ operator to rewrite the actions of the right and left operators acting on the bath coordinates of an arbitrary operator $\hat{A}_W(X)$ in terms of a single effective operator $\mathcal{L}_e(X,z,z')$ that depends on the coherent state variables z and z' associated with the forward and backward propagators, respectively. In Appendix C, we show that

$$\begin{aligned}\mathcal{S}(e^{i\vec{\mathcal{L}}(X,z)\frac{\tau}{2}}\hat{A}_W(X)e^{i\overleftarrow{\mathcal{L}}(X,z')\frac{\tau}{2}}) \\ = e^{i\mathcal{L}_e(X,z,z')\tau}\hat{A}_W(X) \equiv \hat{A}_W(X_\tau).\end{aligned} \tag{29}$$

The explicit form of $i\mathcal{L}_e(X, z, z')$ is

$$i\mathcal{L}_e(X, z, z') = \frac{P}{M}\cdot\frac{\partial}{\partial R} - \frac{\partial V_e(X, z, z')}{\partial R}\cdot\frac{\partial}{\partial P}, \qquad (30)$$

where $V_e(X, z, z') = (V_{cl}(R, z) + V_{cl}(R, z'))/2$. From Eqs. (29) and (30), we can see that the time evolution of the bath coordinates under the effective Liouville operator is given by the solutions of the equations

$$\frac{dR}{dt} = \frac{P}{M}, \qquad \frac{dP}{dt} = -\frac{\partial V_e(X, z, z')}{\partial R}. \qquad (31)$$

These results may be used in the expression for $B_W^{\lambda\lambda'}(X, t)$ in Eq. (28) to give

$$\begin{aligned} B_W^{\lambda\lambda'}(X, t) = \sum_{\mu\mu'}\int\prod_{i=1}^{M}\frac{d^2z_i}{\pi^N}\frac{d^2z_i'}{\pi^N}\langle m_\lambda|z_1\rangle\langle z_1'|m_{\lambda'}\rangle \\ \times e^{i\mathcal{L}_e(X,z_1,z_1')\frac{\Delta t_1}{2}}(\langle z_1|e^{i\hat{H}_m\frac{\Delta t_1}{\hbar}}|z_2\rangle \\ \times e^{i\mathcal{L}_e(X,z_2,z_2')\frac{\Delta t_2}{2}}(\langle z_2|e^{i\hat{H}_m\frac{\Delta t_2}{\hbar}}\ldots|z_M\rangle \\ \times e^{i\mathcal{L}_e(X,z_M,z_M')\frac{\Delta t_M}{2}}(\langle z_M|e^{i\hat{H}_m\frac{\Delta t_M}{\hbar}}|m_\mu\rangle \\ \times B_W^{\mu\mu'}(X)\langle m_{\mu'}|e^{-i\hat{H}_m\frac{\Delta t_M}{\hbar}}|z_M'\rangle) \\ \times\langle z_M'|\ldots e^{-i\hat{H}_m\frac{\Delta t_2}{\hbar}}|z_2'\rangle)\langle z_2'|e^{-i\hat{H}_m\frac{\Delta t_1}{\hbar}}|z_1'\rangle). \end{aligned} \qquad (32)$$

This expression is evaluated sequentially, from smallest to largest times, by taking the bath phase space propagators in expressions such as $e^{i\mathcal{L}_e(X,z_i,z_i')\frac{\Delta t_i}{2}}(\cdots)$ to act on all quantities in the parentheses, including other propagators at later times and the matrix elements $B_W^{\mu\mu'}(X)$. For example, the action of the first effective bath operator updates the bath phase space coordinates from $X = X_{t_0}$ to X_{t_1}. Thus,

$$\begin{aligned} B_W^{\lambda\lambda'}(X, t) = \sum_{\mu\mu'}\int\prod_{i=1}^{M}\frac{d^2z_i}{\pi^N}\frac{d^2z_i'}{\pi^N}\langle m_\lambda|z_1\rangle\langle z_1'|m_{\lambda'}\rangle \\ \times(\langle z_1|e^{i\hat{H}_m(X_{t_1})\frac{\Delta t_1}{\hbar}}|z_2\rangle \\ \times\ldots B_W^{\mu\mu'}(X_{t_1})\ldots\langle z_2'|e^{-i\hat{H}_m(X_{t_1})\frac{\Delta t_1}{\hbar}}|z_1'\rangle). \end{aligned} \qquad (33)$$

The coherent state matrix elements can now be evaluated using Eq. (26) to give

$$\begin{aligned} B_W^{\lambda\lambda'}(X, t) = \sum_{\mu\mu'}\int\prod_{i=1}^{M}\frac{d^2z_i}{\pi^N}\frac{d^2z_i'}{\pi^N}\langle m_\lambda|z_1\rangle\langle z_1'|m_{\lambda'}\rangle \\ \times(e^{iH_b(X_{t_1})\Delta t_1/\hbar}\langle z_1(t_1)|z_2\rangle e^{i\mathcal{L}_e(X_{t_1},z_2,z_2')\frac{\Delta t_2}{2}}(\langle z_2|\ldots \\ \times B_W^{\mu\mu'}(X_{t_1})\ldots|z_2'\rangle)e^{-iH_b(X_{t_1})\Delta t_1/\hbar}\langle z_2'|z_1'(t_1)\rangle\rangle), \\ = \sum_{\mu\mu'}\int\prod_{i=1}^{M}\frac{d^2z_i}{\pi^N}\frac{d^2z_i'}{\pi^N}\langle m_\lambda|z_1\rangle\langle z_1'|m_{\lambda'}\rangle \\ \times(\langle z_1(t_1)|z_2\rangle e^{i\mathcal{L}_e(X_{t_1},z_2,z_2')\frac{\Delta t_2}{2}}(\langle z_2|\ldots \\ \times B_W^{\mu\mu'}(X_{t_1})\ldots|z_2'\rangle)\langle z_2'|z_1'(t_1)\rangle\rangle). \end{aligned} \qquad (34)$$

In writing the last equality, we canceled the phase factors involving $H_b(X_{t_1})$.

At this point, we can see how a description involving continuous trajectories may be constructed. The classical bath propagator for the next time step from t_1 to t_2, $e^{i\mathcal{L}_e(X_{t_1},z_2,z_2')\frac{\Delta t_2}{2}}$, involves the coherent state phase space variables z_2 and z_2', which may take any values from the set of coherent state values. The coherent states involved in the matrix elements $\langle z_1(t_1)|z_2\rangle$ and $\langle z_2'|z_1'(t_1)\rangle$ are not orthogonal since the coherent states are overcomplete. However, in view of Eq. (18), we see that the overlap between two coherent states decays rapidly if their phase space coordinates differ significantly. Consequently, we assume that

$$\begin{aligned} \langle z_1(t_1)|z_2\rangle &\approx \pi^N\delta(z_2 - z_1(t_1)), \\ \langle z_2'|z_1'(t_1)\rangle &\approx \pi^N\delta(z_2' - z_1'(t_1)). \end{aligned} \qquad (35)$$

Under this approximation, we integrate over z_2 and z_2' and obtain

$$\begin{aligned} B_W^{\lambda\lambda'}(X, t) = \sum_{\mu\mu'}\int\frac{d^2z_1}{\pi^N}\frac{d^2z_1'}{\pi^N}\langle m_\lambda|z_1\rangle\langle z_1'|m_{\lambda'}\rangle \\ \times\int\prod_{i=3}^{M}\frac{d^2z_i}{\pi^N}\frac{d^2z_i'}{\pi^N}(e^{i\mathcal{L}_e(X_{t_1},z_1(t_1),z_1'(t_1))\frac{\Delta t_2}{2}} \\ \times(\langle z_1(t_1)|\ldots B_W^{\mu\mu'}(X_{t_1})\ldots|z_1'(t_1)\rangle)). \end{aligned} \qquad (36)$$

All coherent state and bath phase space variables have now been updated to time t_1 and process can now be repeated for all M time steps, starting with the application of the effective bath evolution operator for the time step Δt_2. The result of this process is the simple expression

$$\begin{aligned} B_W^{\lambda\lambda'}(X, t) = \sum_{\mu\mu'}\int\frac{d^2z_1}{\pi^N}\frac{d^2z_1'}{\pi^N}\langle m_\lambda|z_1\rangle\langle z_1'|m_{\lambda'}\rangle \\ \times\left(\langle z_1(t)|\,m_\mu\rangle B_W^{\mu\mu'}(X_t)\langle m_{\mu'}\,|z_1'(t)\rangle\right). \end{aligned} \qquad (37)$$

The matrix elements between coherent states and the single-excitation mapping states may be evaluated explicitly to give

$$\langle m_\lambda\,|z\rangle = z_\lambda e^{-|z|^2/2}. \qquad (38)$$

Writing this expression in terms of the $x = (q, p)$ variables, and using the fact that $\sum_\nu(q_\nu^2 + p_\nu^2)$ is conserved under coherent state dynamics, we obtain

$$\begin{aligned} B_W^{\lambda\lambda'}(X, t) = \sum_{\mu\mu'}\int dx dx'\phi(x)\phi(x') \\ \times\frac{1}{2\hbar}(q_\lambda + ip_\lambda)(q_{\lambda'}' - ip_{\lambda'}')B_W^{\mu\mu'}(X_t) \\ \times\frac{1}{2\hbar}(q_\mu(t) - ip_\mu(t))(q_{\mu'}'(t) + ip_{\mu'}'(t)), \end{aligned} \qquad (39)$$

where $\phi(x) = (2\pi\hbar)^{-N}e^{-\sum_\nu(q_\nu^2+p_\nu^2)/2\hbar}$ is the normalized Gaussian distribution function and we have removed the subscript 1 from the dummy coherent state variables. The coupled

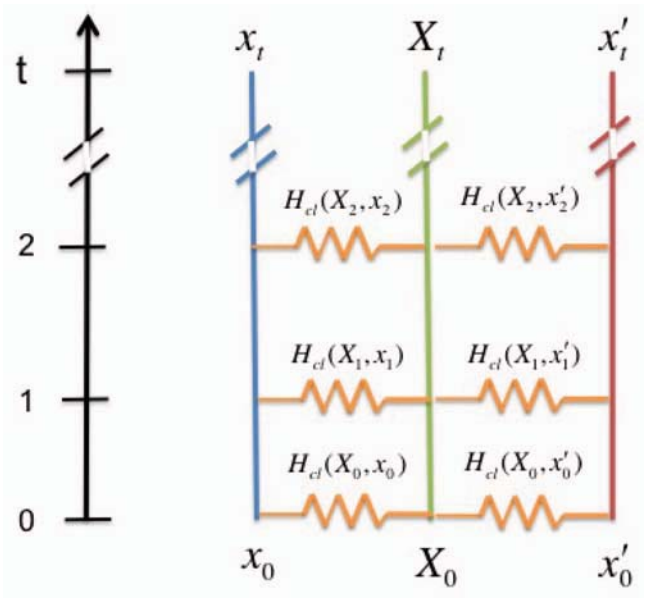

FIG. 1. Schematic diagram of the time evolution of the bath coordinates $X = (R, P)$ (the green line), the forward coherent state coordinates $x = (q, p)$ (the blue line), and the backward coherent state coordinates $x' = (q', p')$ (the red line). The vertical axis denotes the time. At each time step i, the classical Hamiltonians $H_{cl}(X_i, x_i)$ and $H_{cl}(X_i, x'_i)$ are parametrized with the updated coordinates. The wiggly, orange lines represent the direct coupling between the evolutions of different sets of phase space coordinates under the influence of the classical Hamiltonians. As shown, the two sets of coherent state variables are only coupled via the bath coordinates.

equations of motion governing this evolution are

$$\frac{dq_\mu}{dt} = \frac{\partial H_{cl}(R,P,q,p)}{\partial p_\mu}, \quad \frac{dp_\mu}{dt} = -\frac{\partial H_{cl}(R,P,q,p)}{\partial q_\mu},$$
$$\frac{dq'_\mu}{dt} = \frac{\partial H_{cl}(R,P,q',p')}{\partial p'_\mu}, \quad \frac{dp'_\mu}{dt} = -\frac{\partial H_{cl}(R,P,q',p')}{\partial q'_\mu},$$
$$\frac{dR}{dt} = \frac{P}{M}, \qquad \frac{dP}{dt} = -\frac{\partial H_e(R,P,q,p,q',p')}{\partial R}, \tag{40}$$

where

$$H_e(R,P,q,p,q',p') = \frac{1}{2}(H_{cl}(R,P,q,p) + H_{cl}(R,P,q',p')). \tag{41}$$

Equation (39) and the associated non-Hamiltonian evolution equations (40) are the results we set out to derive.[61] They constitute a simple algorithm for obtaining a solution to the QCLE. Figure 1 presents a schematic picture that depicts the dynamics of coordinates prescribed by the evolution equations (40). As noted earlier, although both forward and backward trajectories are propagated forward in time, the two sets of trajectories arise from the forward and backward quantum-classical propagators, respectively.

Earlier, it was shown that the solution to the QCLE in the mapping basis can be given in terms of an ensemble of entangled trajectories.[52] The solution in Eq. (40) is consistent with this interpretation in that the forward and backward trajectories of the coherent state variables are linked by the evolution of the bath variables. A more detailed link between these two different approaches to the QCLE in the mapping basis is a topic that merits further study.

C. Back to differential form

In this section, we discuss how the forward-backward solution satisfies the differential form of the QCLE but the approximation in Eq. (35) eventually leads to an accumulation of global errors. In particular, we construct a finite-difference expression for the time evolution of $B_W^{\lambda\lambda'}(X,t)$ using the forward-backward solution in Eq. (39) and show that the QCLE is obtained in the limit $\tau \to 0$. We first write the matrix element for $\langle\lambda|\hat{B}_W(X,t+\tau)|\lambda'\rangle$ using Eq. (37),

$$B_W^{\lambda,\lambda'}(X,t+\tau) = \sum_{\mu\mu'}\int d^2z(t)d^2z'(t)\phi(z)\phi(z') \times z_\lambda(t)z'^*_{\lambda'}(t)z^*_\mu(t+\tau)z'_{\mu'}(t+\tau) \times \left(e^{i\mathcal{L}_e\tau}B_W^{\mu\mu'}(X,t)\right), \tag{42}$$

where $\phi(z) = \pi^{-N}e^{-|z|^2/2}$. We then expand to first order in τ to obtain

$$B_W^{\lambda,\lambda'}(X,t+\tau) \approx \sum_{\mu\mu'}\int d^2z(t)d^2z'(t)\phi(z)\phi(z') \times z_\lambda(t)z'^*_{\lambda'}(t)\Big[z^*_\mu(t)z'_{\mu'}(t)B_W^{\mu\mu'}(X,t) + \tau\left(z^*_\mu(t)\frac{\partial z'_{\mu'}}{\partial t} + z'_{\mu'}(t)\frac{\partial z^*_\mu}{\partial t}\right)B_W^{\mu\mu'}(X,t) + \tau z^*_\mu(t)z'_{\mu'}(t)i\mathcal{L}_eB_W^{\mu\mu'}(X,t)\Big] + \mathcal{O}(\tau^2). \tag{43}$$

The integrals over $z(t)$ and $z'(t)$ may be performed and, after rearranging terms and taking the limit $\tau \to 0$, the result is (some details are given in Appendix D),

$$\lim_{\tau\to 0}\frac{B_W^{\lambda\lambda'}(t+\tau) - B_W^{\lambda\lambda'}(t)}{\tau} = \frac{d}{dt}B_W^{\lambda\lambda'}(t), = \langle\lambda|\frac{i}{\hbar}[\hat{H}_W,\hat{B}_W]|\lambda'\rangle - \frac{1}{2}(\langle\lambda|\{\hat{H}_W,\hat{B}_W\} - \{\hat{B}_W,\hat{H}_W\}|\lambda'\rangle), \tag{44}$$

which is the QCLE.

The QCLE in the subsystem basis is a first order differential equation with respect to time; therefore, it only describes how the matrix elements of $\hat{B}_W(X,t)$ at the beginning and the end of a time step are related. That our solution is found to satisfy the QCLE is consistent with the fact that all approximations used to derive the evolution in a single time step are exact to $\mathcal{O}(\tau^2)$. However, in order to connect the trajectories of coherent state phase variables from adjacent time steps, we made the approximation, $\langle z_i(\tau)|z_{i+1}\rangle \approx \pi^N\delta(z_{i+1} - z_i(\tau))$. whether the proposed solution satisfies the QCLE or not. To understand the effects of this approximation, we consider how our solution would be modified if the approximation were not made. One way to re-formulate the solution is to insert a set of single-excitation mapping states between

every inner product of coherent states, i.e., $\langle z_i(\tau)|z_{i+1}\rangle = \sum_{\mu_i}\langle z_i(\tau)|m_{\mu_i}\rangle\langle m_{\mu_i}|z_{i+1}\rangle$. Once the mapping states are inserted, one loses the continuous trajectory picture in the coherent state phase space but one can formally integrate out the z_i and z_i' variables in sequential (or chronological) order. This sequence of formal integrations is equivalent to the evaluations of the matrix elements of $\hat{B}_W(X,t)$ at every time step. Computationally, this is a very demanding task because one needs to sample, propagate, and integrate out coherent state trajectories at every time step. However, this prescription (a continuous evolution of matrix elements) coincides exactly with the dynamics one would expect from the QCLE in the subsystem basis.

At this point, it is obvious that the coherent-state orthogonality approximation replaces the continuous evolution of the matrix elements, $B_W^{\lambda\lambda'}(X,t)$, with continuous trajectories, $z(t)$ and $z'(t)$. Instead of taking $B_W^{\mu\mu'}(X,t-\tau)$ as the starting point to compute $B_W^{\lambda\lambda'}(X,t)$ at the next time step, the orthogonality approximation actually takes the operator $|z(t-\tau)\rangle\langle z(0)|\hat{B}_m(X,0)|z'(0)\rangle\langle z'(t-\tau)|$ as the starting point and further propagates trajectories from the previous time step to obtain $|z(t)\rangle\langle z(0)|\hat{B}_m(X,0)|z'(0)\rangle\langle z'(t)|$. Although the orthogonality approximation inevitably yields nonlocal errors, it does provide a computationally efficient way to simulate the dynamics. Other semi-classical approaches for solving the system-bath dynamics indicate that this is a sensible approximation to make. For instance, if we do not use the orthogonality approximation then we can write our solution in the form of a standard coherent state path integral. Application of the stationary phase approximation will yield the same set of equations of motion for the coherent state phase variables. Similar coherent state dynamics was obtained in the context of a different semi-classical framework.[20]

Finally, we comment on the fact that the semiclassical analysis yields exact quantum mechanical solution for quadratic Hamiltonians. This is certainly true when the system is isolated from the bath. The same also holds true for our solution; if there are no bath terms then there is no need to make the orthogonality approximation. However, when a bath is present, the semi-classical analysis is equivalent to implicitly making the orthogonality approximation, which becomes exact in the limit $\hbar \to 0$ in view of Eq. (18). The potential source of errors, which arises from the system-bath interactions, can easily be overlooked because it is eliminated as soon as semi-classical conditions are imposed.

IV. DISCUSSION

The results derived above provide a simple simulation algorithm for the dynamics described by the QCLE. Most often it is the average value of an operator (or correlation function) that is of interest. The average value of a quantum operator $\hat{B}_W(X,t)$ is given by

$$\begin{aligned}\overline{B(t)} &= \int dX\ \mathrm{Tr}\,(\hat{B}_W(X)\hat{\rho}_W(X,t)),\\ &= \int dX\ B_W^{\lambda\lambda'}(X,t)\rho_W^{\lambda'\lambda}(X),\\ &= \sum_{\substack{\mu,\mu'\\ \lambda,\lambda'}}\int dX dx dx'\ \frac{1}{2\hbar}(q_\mu(t)+ip_\mu(t))\\ &\quad\times(q'_{\mu'}(t)-ip'_{\mu'}(t))B_W^{\mu\mu'}(X_t)\\ &\quad\times\frac{1}{2\hbar}(q_\lambda-ip_\lambda)(q'_{\lambda'}+ip'_{\lambda'})\rho_W^{\lambda\lambda'}(X)\phi(x)\phi(x'),\end{aligned} \tag{45}$$

where the trace is taken in the quantum subsystem space. In the above equation, the average value may be computed by sampling over the coherent state variable functions $\phi(x)$ and $\phi(x')$ and the given initial density matrix element $\rho_W^{\lambda'\lambda}(X)$ for the bath coordinates.

Our solution for $B_W^{\lambda\lambda'}(X,t)$ has a number of elements in common with other approaches that have been devised to simulate nonadiabatic dynamics and it is instructive to make comparisons with methods that have been constructed in a similar spirit.

A. Comparison with partially linearized path integral methods

First, we draw comparisons between two mixed quantum-classical formalisms: the QCLE and partially linearized path integral methods. The formal equivalence between the two formalisms was established in a general setting[41] when the subsystem DOF were expressed as quantum operators. Therefore, the close resemblance between our solution and that of Huo and Coker[20] is expected, since they are approximate solutions to the QCLE and a particular form of the partially linearized path integral, respectively. However, in view of the derivation of our solution presented above, the result in Ref. 20 is not an exact solution of the QCLE. In our formalism, H_{cl} defined in Eq. (21) contains $V_0(R) = V_b(R) - \mathrm{Tr}_s\hat{h}$ instead of simply the bath potential $V_b(R)$. Recall that the trace term arose from the commutation relation for the annihilation and creation operators and the need to use an anti-normal order for the product of these operators to evaluate the short-time propagator. If this trace term is absent, one can show that the solution does not satisfy the differential form of the QCLE.

The system Hamiltonian, $\hat{H}_W(X) = H_b(X) + \hat{h}(R)$, can be written in an equivalent form $\hat{H}_W(X) = H_b(X) + (Tr_s\hat{h}(R))/N + \hat{\bar{h}}(R)$, where $\hat{\bar{h}}(R)$ is traceless. Since this is an identity, the QCLE is independent of the choice of the form, which is used in this equation. Our solution is also independent of the way the Hamiltonian is written, although the equations of motion take a somewhat different form. If the Hamiltonian with the trace removed is used in the derivation, the evolution equations have the same structure as is in Eq. (40) but $H_{cl}(X,z)$ in Eq. (21) is replaced by $H_{cl}(X,z) = H_0(X) + \bar{h}^{\lambda\lambda'}z_\lambda^* z_{\lambda'}$ with $H_0(X) \to H_b(X) + (Tr_s\hat{h}(R))/N$ (Ref. 62). When the calculation given in Sec. III C is repeated with this form of the Hamiltonian, the QCLE is again obtained, confirming that the different but equivalent forms of the Hamiltonian yield the same evolution.

However, this is not the case when other approximate theories are considered. In particular, it was shown[52] that the choice of Hamiltonian form is crucial in the Poisson Bracket Mapping Equation (PBME) approximation to the QCLE (discussed below). When the traceless form is used, dynamical instabilities that arise in the course of the evolution can be tamed, while if the original form of the Hamiltonian is used, the instabilities can lead to difficulties.

The form of the Hamiltonian also affects the nature of the dynamics in the semi-classical approach used in Ref. 20. While the evolution equations in this approach differ from those in Eq. (40), the equivalence is restored between the two solutions if the traceless form of the Hamiltonian is used. The reason that the partially linearized path integral solution depends sensitively on the form of the Hamiltonian is due to the semi-classical approach used to solve the dynamics. According to the semi-classical calculation, the dynamics of the bath momenta are governed by the force, $-\frac{1}{2}(\partial \tilde{H}_{cl}(X,z)/\partial R + \partial \tilde{H}_{cl}(X,z')/\partial R)$, where $\tilde{H}_{cl}(X,z) = H_b(X) + h_{cl}(R,z)$. The Hamiltonian $\tilde{H}_{cl}(X,z)$ misses the term $-Tr_s\hat{h}(R)$ in $H_{cl}(X,z)$ in Eq. (21) in the current formulation. This extra term is required to restore the equivalence between the solution using the original Hamiltonian and that using the traceless form of the Hamiltonian.

B. Comparison with Poisson bracket mapping equation

Next, we compare the current solution to the PBME approximation to the quantum-classical Liouville equation,[50–52] which is obtained from the mapping form of the QCLE by dropping an excess coupling term.[51] In the case of an isolated subsystem, one can perform a change of variables $\bar{z} = (z + z')/2$ and $\Delta z = z - z'$ and show that both the mean, $\bar{z}$, and the difference, Δz, variables follow exactly the same Hamiltonian dynamics, as described in Eq. (27) with no R dependence. This implies that if $\bar{z}(0) = \Delta z(0)$ then $\bar{z} = \Delta z(t)$ for all t. Since the computation of the time evolution of an operator in the subsystem basis requires integration over the entire coherent state phase space, as prescribed in Eq. (39), Δz becomes a redundant variable. A direct comparison between the two methods can be made if one either integrates out Δz, or replaces the integral of Δz by the integral of $\bar{z}$ as follows:

$$\int \frac{d^2\bar{z}}{\pi^N} e^{-2|\bar{z}|^2} \bar{z}_\lambda \bar{z}_\mu(t) \int \frac{d^2\Delta z}{\pi^N} e^{-\frac{1}{2}|\Delta z|^2} \Delta z_{\mu'}(t) \Delta z_{\lambda'} = 2^N \int \frac{d^2\bar{z}}{\pi^N} e^{-2|\bar{z}|^2} \left(\bar{z}_\lambda \bar{z}^*_\mu(t) \bar{z}_{\mu'}(t) \bar{z}^*_{\lambda'} - \bar{z}_\lambda \bar{z}^*_{\lambda'} \delta_{\mu,\mu'} + \frac{1}{4}\delta_{\lambda,\lambda'}\delta_{\mu,\mu'} \right). \quad (46)$$

The above identity can be easily proved in a basis that diagonalizes the Hamiltonian, followed by the transformation of the resulting identity back to the original basis, in the same spirit as the computation of the exact coherent state dynamics in Appendix A.

After properly removing Δz, one can show that Eq. (39) reduces to

$$B^{\lambda\lambda'}_W(X,t) = \sum_{\mu,\mu'} \int dx \left(\bar{z}_\lambda \bar{z}^*_{\lambda'} \bar{z}^*_\mu(t) \bar{z}_{\mu'}(t) - \frac{1}{4}\bar{z}_\lambda \bar{z}^*_{\lambda'} \delta_{\mu,\mu'} - \frac{1}{2}\bar{z}_\mu(t)\bar{z}^*_{\mu'}(t)\delta_{\lambda,\lambda'} + \frac{1}{8}\delta_{\lambda,\lambda'}\delta_{\mu,\mu'} \right) 4\phi(x) B^{\mu\mu'}_W(X_t),$$
$$= \sum_{\mu,\mu'} \int dx\, g_{\lambda,\lambda'}(x) B^{\mu\mu'}_W(X_t) c_{\mu\mu'}(x(t)), \quad (47)$$

where $x = (q = \sqrt{2\hbar}\Re\bar{z},\ p = \sqrt{2\hbar}\Im\bar{z})$ and the functions[52] $g_{\lambda\lambda'}(x) \equiv (|m_\lambda\rangle\langle m_{\lambda'}|)_W$ and $c_{\mu\mu'}(x) \equiv (\hat{a}^\dagger_\lambda \hat{a}_{\lambda'})_W$ represent the Wigner transformation $(.)_W$ of the outer product of states and a pair of annihilation and creation operators, respectively. The last expression in Eq. (47) is exactly the evolution of $B^{\lambda\lambda'}_W(X,t)$ in the PBME method. Furthermore, the Wigner transformation variables, x, in the PBME method follow the same Hamiltonian dynamics derived above for the mean coordinates of the coherent state variables. Despite the very different starting points of the two solutions, this comparison reveals the close relation between the dynamics of Wigner transformed coordinates and the mean coordinates in the coherent state phase space. Although, this close relation can only be made obvious after the effects of difference variables are properly taken into account of and removed (either explicitly integrated out, or replaced using Eq. (46)). Essentially, the dynamical information encoded in the coherent states variables of $2N$ harmonic oscillators can be merged and be encoded in N Wigner transformed coordinates.

We next comment on the comparison to the PBME method in the presence of a bath. One may linearize the bath potential $V_e(X,z,z') \approx (V_{cl}(R,\bar{z}) + \frac{\partial V_{cl}}{\partial \bar{z}}\Delta z + V_{cl}(R,\bar{z}) - \frac{\partial V_{cl}}{\partial \bar{z}}\Delta z)/2 = V_{cl}(R,\bar{z})$ such that the dynamics of the bath variables only depends on the mean coordinates $\bar{z}$. The bath potential linearization allows one to properly remove the difference variables and encode the approximate dynamics in N harmonic oscillators. Repeating the same calculations and using the coherent-state orthogonality approximation, one can show that Eq. (47) still holds in the general mixed quantum-classical setting.

C. Comparison with semi-classical schemes

Finally, we compare our results to some semi-classical schemes. The mapping representation consolidates the way subsystem dynamics is handled in the QCLE and in some semi-classical schemes. For instance, in the case of a linearized bath potential, the Hamiltonian dynamics prescribed by our solution is also identical to that in the semi-classical path integral approach of Stock and Thoss[13,17] as well as the linearized semi-classical initial value representation (LSC-IVR) of Miller.[8,15,63] Furthermore, the full version of the current solution also handles the subsystem dynamics in ways similar to the forward-backward semi-classical initial value representation (FB-IVR) approaches[14,64,65] that uses the Herman-Kluk propagator. One difference is that the

forward and backward trajectories are not linked in the present solution.

Finally, we observe that the classical-like system-bath dynamics prescribed in our solution could be similar to that of a mixed semi-classical scheme[66] in which the bath DOF and subsystem DOF are treated with LSC-IVR and the FB-IVR, respectively. Further investigations into the subtle connections between our solution of the QCLE and other semi-classical schemes might inspire further developments in nonadiabatic quantum dynamics.

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APPENDIX A: EXACT EVOLUTION OF COHERENT STATES

We restrict this analysis to real-valued, symmetric, quadratic Hamiltonian operators, $\hat{h}_m$, which are the only type of Hamiltonian encountered in the mapping formalism. It is always possible to diagonalize such a Hamiltonian matrix, to obtain

$$\begin{aligned}\hat{h}_m &= \sum_{\lambda,\lambda'} h^{\lambda\lambda'}\hat{a}^\dagger_\lambda \hat{a}_{\lambda'} = \sum_{\lambda,\lambda'}\sum_{\mu} M_{\lambda\mu}h^d_\mu M^T_{\mu\lambda'}\hat{a}^\dagger_\lambda\hat{a}_{\lambda'},\\ &= \sum_\mu h^d_\mu \left(\sum_\lambda \hat{a}^\dagger_\lambda M_{\lambda\mu}\right)\left(\sum_{\lambda'} M^T_{\mu\lambda}\hat{a}_{\lambda'}\right),\\ &= \sum_\mu h^d_\mu \hat{b}^\dagger_\mu \hat{b}_\mu \equiv \hat{h}^d_m, \end{aligned} \tag{A1}$$

where the operators $\hat{b}^\dagger_\mu$ and $\hat{b}_\mu$ are defined in the second line of the equation. We use the superscript d to emphasize that the Hamiltonian is now put in the diagonal form with respect to operators $\hat{b}_\mu$ and $\hat{b}^\dagger_\mu$. Since the Hamiltonian is real and symmetric, the matrix M is an orthogonal matrix.

With respect to the new operators $\hat{b}_\mu$ and $\hat{b}^\dagger_\mu$, we define the coherent state $|y\rangle$ by

$$\hat{b}_\mu |y\rangle = y_\mu |y\rangle, \quad \langle y|\hat{b}^\dagger_\mu = \langle y| y^*_\mu, \tag{A2}$$

where $y_\mu = \frac{1}{\sqrt{2\hbar}}\left(\tilde{q}_\mu + i\tilde{p}_\mu\right)$.

Consider the time evolution of the coherent state $|y\rangle$ with N degrees of freedom,

$$\begin{aligned} e^{-\frac{i}{\hbar}\hat{h}^d_m t}|y\rangle &= e^{-\frac{i}{\hbar}\hat{h}^d_m t}\otimes_{\nu=1}^N \left\{e^{-|y_\nu|^2}\sum_{m=0}^\infty \frac{y^m_\nu}{\sqrt{m!}}|m\rangle_\nu\right\},\\ &= \otimes_{\nu=1}^N \left\{e^{-|y_\nu|^2}\sum_{m=0}^\infty \frac{(y_\nu e^{-\frac{i}{\hbar}h^d_\nu t})^m}{\sqrt{m!}}|m\rangle_\nu\right\},\\ &= |y(t)\rangle, \end{aligned} \tag{A3}$$

where $y_\nu(t) = y_\nu(0)e^{-\frac{ih^d_\nu}{\hbar}t}$. In this calculation, we used the expansion of a coherent state in terms of a complete set of harmonic oscillator states:

$$|y_\nu\rangle = e^{-|y_\nu|^2}\sum_{m=0}^\infty \frac{y^m_\nu}{\sqrt{m!}}|m\rangle_\nu. \tag{A4}$$

Equation (A3) implies the equation of motion,

$$\frac{dy_\nu}{dt} = -\frac{i}{\hbar}h^d_\nu y_\nu(t) = -\frac{i}{\hbar}\frac{\partial \tilde{h}^d_{cl}}{\partial y^*_\nu}, \tag{A5}$$

where $\tilde{h}^d_{cl} = \sum_\mu h^d_\mu y^*_\mu y_\mu$. If we substitute in the variables $\tilde{q}$ and $\tilde{p}$ into the equation of motion for y then we get the usual Hamilton's equation for $\tilde{q}$ and $\tilde{p}$.

Next, we prove that Hamilton's equation is invariant under the linear transformation, $y_\mu = \sum_\lambda M^T_{\mu\lambda}z_\lambda$, and $y^*_\mu = \sum_\lambda z^*_\lambda M_{\lambda\mu}$. This proceeds as follows:

$$\begin{aligned}\frac{dz_\lambda}{dt} &= \sum_\mu M_{\lambda\mu}\frac{dy_\mu}{dt} = -\frac{i}{\hbar}\sum_\mu M_{\lambda\mu}\frac{\partial\tilde{h}^d_{cl}}{\partial y^*_\mu},\\ &= -\frac{i}{\hbar}\sum_\mu M_{\lambda\mu}h^d_\mu y_\mu = -\frac{i}{\hbar}\sum_{\mu,\lambda'} M_{\lambda,\mu}h^d_\mu M^T_{\mu\lambda'}z_{\lambda'},\\ &= -\frac{i}{\hbar}\sum_{\lambda'} h^{\lambda\lambda'}z_{\lambda'} = -\frac{i}{\hbar}\frac{\partial h_{cl}}{\partial z^*_\lambda}. \end{aligned} \tag{A6}$$

APPENDIX B: MATRIX ELEMENTS OF THE UNITARY EVOLUTION OPERATOR IN THE SINGLE EXCITATION SUBSPACE

In this Appendix, we evaluate matrix elements of the form $\langle m_\lambda|e^{-\frac{it}{\hbar}\hat{h}_m}|m_{\lambda'}\rangle$, where $\hat{h}_m$ is still the real-valued and symmetric Hamiltonian considered in Appendix A. We evaluate this matrix element in two ways: directly and also in terms of matrix elements $\langle\tilde{m}_\lambda|e^{-\frac{i}{\hbar}\hat{h}^d_m t}|\tilde{m}_{\lambda'}\rangle$ via a linear transformation. The state $|\tilde{m}_\lambda\rangle = |0_1\ldots 1_{\tilde{\lambda}}\ldots 0_N\rangle$ is an N-harmonic-oscillator state with a single excitation on the λth oscillator, $h^d_\lambda \hat{b}^\dagger_\lambda\hat{b}_\lambda$.

First, we prove that $|m_\lambda\rangle = \sum_\mu M^T_{\mu\lambda}|\tilde{m}_\mu\rangle$. This is straightforward since $|m_\lambda\rangle = \hat{a}^\dagger_\lambda|0\rangle$ and $|\tilde{m}_\mu\rangle = \hat{b}^\dagger_\mu|0\rangle$, where $|0\rangle$ is the common ground state. Therefore, the two states are related by the orthogonal matrix M, which was used to establish the linear transformation between $\hat{a}^\dagger_\lambda$ and $\hat{b}^\dagger_\mu$. The evaluation proceeds as follows:

$$\begin{aligned}&\langle m_{\lambda'}|\, e^{-\frac{it}{\hbar}\hat{h}_m}\,|m_\lambda\rangle\\ &= \langle\tilde{m}_{\mu'}|M_{\lambda'\mu'}e^{-\frac{it}{\hbar}\hat{h}^d_m}M^T_{\mu\lambda}|\tilde{m}_\mu\rangle,\\ &= \int\frac{d\tilde{x}}{(2\pi\hbar)^N}M_{\lambda'\mu'}M^T_{\mu\lambda}\langle\tilde{m}_{\mu'}|e^{-\frac{it}{\hbar}\hat{h}^d_m}|y\rangle\langle y|\tilde{m}_\mu\rangle,\\ &= \int\frac{d\tilde{x}}{(2\pi\hbar)^N}M_{\lambda'\mu'}M^T_{\mu\lambda}\langle\tilde{m}_{\mu'}|y(t)\rangle\langle y|\tilde{m}_\mu\rangle,\\ &= \int\frac{d\tilde{x}}{(2\pi\hbar)^N}M_{\lambda\mu}M^T_{\mu'\lambda'}y_{\mu'}(t)y^*_\mu e^{-\frac{1}{2}|y(t)|^2}e^{-\frac{1}{2}|y|^2},\\ &= \int\frac{d\tilde{x}}{(2\pi\hbar)^N}z_{\lambda'}(t)z^*_\lambda e^{-|z|^2} = \int\frac{dx}{(2\pi\hbar)^N}z_{\lambda'}(t)z^*_\lambda e^{-|z|^2}, \end{aligned} \tag{B1}$$

where $d\tilde{x} = d\tilde{q}d\tilde{p}$ and $dx = dqdp$. To obtain the above result, we used the relation $z_\mu = M^T_{\nu\mu} y_\nu = M_{\mu\nu} y_\nu$ to re-express the y variables in terms of z variables and employed the volume element transformation, $d\tilde{x} = dx|\det[\partial y_\alpha/\partial z_\beta]| = dx|\det M| = dx$, since $|\det M| = 1$. Since the $y(t)$ variables satisfy Hamilton's equations, $|y(t)|^2 = |y|^2$. Finally, we note that $|y|^2 = \sum_\lambda y^*_\lambda y_\lambda = \sum_{\lambda,\mu,\mu'} M^T_{\mu'\lambda} M_{\lambda\mu} z^*_{\mu'} z_\mu = \sum_\mu z^*_\mu z_\mu = |z|^2$, completing the results needed to obtain Eq. (B1).

Next, we compute $e^{-\frac{it}{\hbar}\hat{h}_m}|z\rangle$ directly, where $|z\rangle$ is defined by $\hat{a}_\lambda|z\rangle = z_\lambda|z\rangle$. To carry out this calculation, we reconsider Eq. (B1),

$$\begin{aligned}\langle m_{\lambda'}| e^{-\frac{i}{\hbar}\hat{h}_m t}|m_\lambda\rangle &= \int \frac{dx}{(2\pi\hbar)^N} \langle m_{\lambda'}| e^{-\frac{i}{\hbar}\hat{h}_m t}|z\rangle \langle z|m_\lambda\rangle, \\ &= \int \frac{dx}{(2\pi\hbar)^N} \langle m_{\lambda'}| e^{-\frac{i}{\hbar}\hat{h}_m t}|z\rangle z^*_\lambda e^{-\frac{1}{2}|z|^2}.\end{aligned} \tag{B2}$$

Comparing the last lines of Eqs. (B1) and (B2), we see that $\langle m_{\lambda'}|e^{-\frac{i}{\hbar}\hat{h}_m t}|z\rangle = z_{\lambda'}(t)e^{-\frac{1}{2}|z(t)|^2} = \langle m_{\lambda'}|z(t)\rangle$. Since the identities hold for all possible $\langle m_{\lambda'}|$ and $|z\rangle$, we can identify $e^{-\frac{i}{\hbar}\hat{h}_m t}|z\rangle = |z(t)\rangle$.

APPENDIX C: EFFECTIVE LIOUVILLE OPERATOR

Below, we prove the identity in Eq. (29) that relates the forward and backward bath propagators to the effective Liouville operator:

$$\begin{aligned}&\mathcal{S}(e^{i\overrightarrow{\mathcal{L}}(X,x)\frac{\tau}{2}}\hat{A}_W(X)e^{i\overleftarrow{\mathcal{L}}(X,x')\frac{\tau}{2}}) \\ &= \sum_{j=0}^{\infty}\sum_{k=0}^{j}\frac{(i\tau/2)^j}{(j-k)!k!}S((\overrightarrow{\mathcal{L}})^k\hat{A}_W(\overleftarrow{\mathcal{L}'})^{j-k}), \\ &= \sum_{j=0}^{\infty}\frac{(i\tau/2)^j}{j!}\sum_{k=0}^{j}\binom{j}{k}S((\overrightarrow{\mathcal{L}})^k\hat{A}_W(\overleftarrow{\mathcal{L}'})^{j-k}), \\ &= \sum_{j=0}^{\infty}\frac{(i\tau/2)^j}{j!}\sum_{k=0}^{j}\sum_{\{p\}}\overrightarrow{\mathcal{L}}^{(p_1)}\overrightarrow{\mathcal{L}}^{(p_2)}\ldots\overrightarrow{\mathcal{L}'}^{(p_j)}\hat{A}_W, \\ &= \sum_{j=0}^{\infty}\frac{(i\tau)^j}{j!}\left(\frac{1}{2}(\overrightarrow{\mathcal{L}}+\overrightarrow{\mathcal{L}'})\right)^j\hat{A}_W(X), \\ &= e^{i\mathcal{L}_e(X,x,x')\tau}\hat{A}_W.\end{aligned} \tag{C1}$$

In these expressions, we used the shorthand notations, $\overrightarrow{\mathcal{L}} = \overrightarrow{\mathcal{L}}(X,x)$ and $\overleftarrow{\mathcal{L}'} = \overleftarrow{\mathcal{L}}(X,x')$, and the definition of $\mathcal{S}$ in going from the third to fourth lines. The sum on $\{p\}$ denotes a sum over all permutations.

APPENDIX D: DIFFERENTIAL FORM

The term zeroth order in τ in Eq. (43) is easily computed by performing the integrals over $z(t)$ and $z'(t)$ and the result is simply $B^{\mu\mu'}_W(X,t)$. The first term of order τ, which we call I_1, involves time derivatives coherent state variables. Using the equations of motion for the coherent state variables and performing the integrals, we find

$$\begin{aligned}I_1 &= \frac{i}{\hbar}\langle\lambda|[\hat{h}, \hat{B}_W(X,t)]|\lambda'\rangle, \\ &= \frac{i}{\hbar}\langle\lambda|[\hat{H}_W, \hat{B}_W(X,t)]|\lambda'\rangle,\end{aligned} \tag{D1}$$

which is the first term in the QCL operator in Eq. (2).

Next, we consider the first-order term involving the evolution of the spatial coordinates of the bath as given by the effective Liouville operator. Inserting its definition in Eq. (30), $i\mathcal{L}_e(X,z,z') = \frac{P}{M}\cdot\frac{\partial}{\partial R} - \frac{\partial V_e(X,z,z')}{\partial R}\cdot\frac{\partial}{\partial P}$, the evaluation of the term involving $\frac{\partial B^{\mu\mu'}_W}{\partial R}\cdot\frac{P}{M}$ is straightforward since it does not contain the coherent state variables. Performing the integrals over these variables yields $I_2 = \frac{\partial B^{\lambda\lambda'}_W}{\partial R}\cdot\frac{P}{M}$. The remaining terms require more attention since they involve the force acting on the bath variables, which depends on the effective potential where $V_e(X,z,z') = (V_{cl}(R,z) + V_{cl}(R,z'))/2$. Denoting this contribution I_3, we have

$$\begin{aligned}I_3 &= -\sum_{\mu\mu'}\int d^2z(t)d^2z'(t)\phi(z)\phi(z') \\ &\quad\times z_\lambda(t)z'^*_{\lambda'}(t)z^*_\mu(t)z'_{\mu'}(t)\frac{\partial B^{\mu\mu'}_W}{\partial P}\cdot\frac{\partial H_e(R,z,z')}{\partial R} \\ &= -\sum_{\mu\mu'}\int d^2z(t)d^2z'(t)\phi(z)\phi(z') \\ &\quad\times z_\lambda(t)z'^*_{\lambda'}(t)z^*_\mu(t)z'_{\mu'}(t)\frac{\partial B^{\mu\mu'}_W}{\partial P}\cdot \\ &\quad\times\left[\frac{\partial V_0(R)}{\partial R} + \frac{1}{2}\frac{\partial V_{cl}(R,z)}{\partial R} + \frac{1}{2}\frac{\partial V_{cl}(R,z')}{\partial R}\right] \\ &= -\frac{\partial B^{\lambda\lambda'}_W}{\partial P}\frac{\partial V_0(R)}{\partial R} + I_{3_1} + I_{3_2}.\end{aligned} \tag{D2}$$

The I_{3_1} integral may be evaluated as follows:

$$\begin{aligned}I_{3_1} &= -\frac{1}{2}\sum_{\mu\mu'}\int d^2z(t)d^2z'(t)\phi(z)\phi(z') \\ &\quad\times z_\lambda(t)z'^*_{\lambda'}(t)z^*_\mu(t)z'_{\mu'}(t)\frac{\partial B^{\mu\mu'}_W}{\partial P}\frac{\partial V_{cl}(R,z)}{\partial R} \\ &= -\frac{1}{4\hbar}\sum_{\mu\alpha\alpha'}\int d^2z(t)\phi(z)z_\lambda(t)z^*_\mu(t), \\ &\quad\times\frac{\partial B^{\mu\lambda'}_W}{\partial P}\cdot\frac{\partial V^{\alpha\alpha'}_c(R,z)}{\partial R}z_\alpha(t)z^*_{\alpha'}(t) \\ &= -\frac{1}{4\hbar}\sum_{\mu\alpha\alpha'}\int d^2z(t)\phi(z)\frac{\partial B^{\mu\lambda'}_W}{\partial P}\cdot\frac{\partial V^{\alpha\alpha'}_c(R,z)}{\partial R} \\ &\quad\times[|z_\lambda(t)|^2|z_\alpha(t)|^2\delta_{\alpha\alpha'}\delta_{\mu\lambda}(1-\delta_{\alpha\lambda}) \\ &\quad+|z_\lambda(t)|^2|z_\mu(t)|^2\delta_{\alpha\lambda}\delta_{\alpha'\mu}(1-\delta_{\alpha\alpha'}) \\ &\quad+|z_\lambda(t)|^4\delta_{\alpha\alpha'}\delta_{\alpha\lambda}\delta_{\mu\lambda}].\end{aligned}$$

Performing the z integrals, we find

$$I_{3_1} = -\frac{1}{2}\left(\sum_{\alpha\neq\lambda}\frac{\partial V_c^{\alpha\alpha}}{\partial R}\frac{\partial B_W^{\lambda\lambda'}}{\partial P} + \sum_{\mu\neq\lambda}\frac{\partial V_c^{\lambda\mu}}{\partial R}\frac{\partial B_W^{\mu\lambda'}}{\partial P} + 2\frac{\partial V_c^{\lambda\lambda}}{\partial R}\frac{\partial B_W^{\lambda\lambda'}}{\partial P}\right)$$
$$= -\frac{1}{2}\langle\lambda|\left(\frac{\partial \hat{V}_c}{\partial R}\frac{\partial \hat{B}_W}{\partial P} + \frac{\partial \mathrm{Tr}_s \hat{V}_c}{\partial R}\frac{\partial \hat{B}_W}{\partial P}\right)|\lambda'\rangle$$
$$= -\frac{1}{2}\langle\lambda|\left(\frac{\partial \hat{h}}{\partial R}\frac{\partial \hat{B}_W}{\partial P} + \frac{\partial \mathrm{Tr}_s \hat{h}}{\partial R}\frac{\partial \hat{B}_W}{\partial P}\right)|\lambda'\rangle. \quad \text{(D3)}$$

In writing the last line of this equation, we used the fact that the subsystem Hamiltonian is independent of R so $\hat{V}_c$ can be replaced by $\hat{h}$.

Similarly, the I_{3_2} integral can be evaluated to give,

$$I_{3_2} = -\frac{1}{2}\langle\lambda|\left(\frac{\partial \hat{B}_W}{\partial P}\frac{\partial \hat{h}}{\partial R} + \frac{\partial \hat{B}_W}{\partial P}\frac{\partial \mathrm{Tr}_s \hat{h}}{\partial R}\right)|\lambda'\rangle. \quad \text{(D4)}$$

Recall that $V_0(R) = V_b(R) - \mathrm{Tr}_s\hat{h}$ so that $\frac{\partial B_W^{\lambda\lambda'}}{\partial P}\frac{\partial V_0(R)}{\partial R} = \frac{\partial B_W^{\lambda\lambda'}}{\partial P}\frac{\partial V_b(R)}{\partial R} - \frac{\partial B_W^{\lambda\lambda'}}{\partial P}\frac{\partial \mathrm{Tr}_s\hat{h}}{\partial R}$. Given these results, the entire I_3 integral is

$$I_3 = -\frac{1}{2}(\langle\lambda|\{\hat{H}_W, \hat{B}_W\} - \{\hat{B}_W, \hat{H}_W\}|\lambda'\rangle), \quad \text{(D5)}$$

where the $\mathrm{Tr}_s\hat{h}$ terms arising from the V_0, I_{3_1}, and I_{3_2} canceled.

[1] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
[2] J. C. Tully, in *Modern Methods for Multidimensional Dynamics Computations in Chemistry*, edited by D. L. Thompson (World Scientific, New York, 1998), p. 34.
[3] F. Webster, E. T. Wang, P. J. Rossky, and R. A. Friesner, J. Chem. Phys. **100**, 4835 (1994).
[4] O. V. Prezhdo, J. Chem. Phys. **111**, 8366 (1999).
[5] A. W. Jasper, C. Zhu, S. Nangia, and D. G. Truhlar, Faraday Discuss. **127**, 1 (2004).
[6] M. J. Bedard-Hearn, R. E. Larsen, and B. J. Schwartz, J. Chem. Phys. **123**, 234106 (2005).
[7] S. A. Fischer, C. T. Chapman, and X. Li, J. Chem. Phys. **135**, 144102 (2011).
[8] W. H. Miller and C. W. McCurdy, J. Chem. Phys. **69**, 5163 (1978).
[9] H. D. Meyer and W. H. Miller, J. Chem. Phys. **70**, 3214 (1979).
[10] X. Sun, H. B. Wang, and W. H. Miller, J. Chem. Phys. **109**, 7064 (1998).
[11] G. Stock and M. Thoss, Phys. Rev. Lett. **78**, 578 (1997).
[12] U. Müller and G. Stock, J. Chem. Phys. **108**, 7516 (1998).
[13] M. Thoss and G. Stock, Phys. Rev. A **59**, 64 (1999).
[14] K. Thompson and N. Makri, J. Chem. Phys. **110**, 1343 (1999).
[15] W. H. Miller, J. Phys. Chem. A **105**, 2942 (2001).
[16] M. Thoss and H. B. Wang, Annu. Rev. Phys. Chem. **55**, 299 (2004).
[17] G. Stock and M. Thoss, Adv. Chem. Phys. **131**, 243 (2005).
[18] S. Bonella and D. F. Coker, J. Chem. Phys. **122**, 194102 (2005).
[19] E. Dunkel, S. Bonella, and D. F. Coker, J. Chem. Phys. **129**, 114106 (2008).
[20] P. Huo and D. F. Coker, J. Chem. Phys. **135**, 201101 (2011).
[21] For a review with references see, [R. Kapral, Ann. Rev. Phys. Chem. **57**, 129 (2006)].
[22] S. Hammes-Schiffer and J. C. Tully, J. Chem. Phys. **101**, 4657 (1994).
[23] E. R. Bittner and P. J. Rossky, J. Chem. Phys. **103**, 8130 (1995).
[24] J. E. Subotnik and N. Shenvi, J. Chem. Phys. **134**, 024105 (2011).
[25] N. Shenvi, J. E. Subotnik, and W. Yang, J. Chem. Phys. **134**, 144102 (2011).
[26] *Quantum Dissipative Systems*, edited by U. Weiss (World Scientific, Singapore, 1999).
[27] G. Lindblad, Commun. Math. Phys. **48**, 119 (1976).
[28] A. Redfield, in *Advances in Magnetic Resonance*, edited by J. Waugh (Academic, New York, 1965), Vol. 1.
[29] *Density Matrix Theory and Applications*, edited by K. Blum (Plenum, New York, 1981).
[30] H.-D. Meyer, U. Manthe, and L. Cederbaum, Chem. Phys. Lett. **165**, 73 (1990).
[31] M. Beck, A. Jckle, G. Worth, and H.-D. Meyer, Phys. Rep. **324**, 1 (2000).
[32] M. Marques and E. Gross, Annu. Rev. Phys. Chem. **55**, 427 (2004).
[33] O. E. Alon, A. I. Streltsov, and L. S. Cederbaum, J. Chem. Phys. **127**, 154103 (2007).
[34] H. Wang and M. Thoss, J. Chem. Phys. **131**, 024114 (2009).
[35] M. Casida and M. Huix-Rotllant, Annu. Rev. Phys. Chem. **63**, 287 (2012).
[36] E. Bukhman and N. Makri, J. Phys. Chem. A **113**, 7183 (2009).
[37] J. C. Tully, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998).
[38] M. F. Herman, Annu. Rev. Phys. Chem. **45**, 83 (1994).
[39] R. Kapral and G. Ciccotti, J. Chem. Phys. **110**, 8919 (1999).
[40] Q. Shi and E. Geva, J. Chem. Phys. **121**, 3393 (2004).
[41] S. Bonella, G. Ciccotti, and R. Kapral, Chem. Phys. Lett. **484**, 399 (2010).
[42] C. C. Martens and J. Y. Fang, J. Chem. Phys. **106**, 4918 (1996).
[43] A. Donoso and C. C. Martens, J. Phys. Chem. A **102**, 4291 (1998).
[44] D. MacKernan, R. Kapral, and G. Ciccotti, J. Phys.: Condens. Matter **14**, 9069 (2002).
[45] D. MacKernan, G. Ciccotti, and R. Kapral, J. Phys. Chem. B **112**, 424 (2008).
[46] I. Horenko, C. Salzmann, B. Schmidt, and C. Schutte, J. Chem. Phys. **117**, 11075 (2002).
[47] C. Wan and J. Schofield, J. Chem. Phys. **113**, 7047 (2000).
[48] C. Wan and J. Schofield, J. Chem. Phys. **116**, 494 (2002).
[49] J. Schwinger, in *Quantum Theory of Angular Momentum*, edited by L. C. Biedenharn and H. V. Dam (Academic, New York, 1965), p. 229.
[50] H. Kim, A. Nassimi, and R. Kapral, J. Chem. Phys. **129**, 084102 (2008).
[51] A. Nassimi, S. Bonella, and R. Kapral, J. Chem. Phys. **133**, 134115 (2010).
[52] A. Kelly, R. van Zon, J. M. Schofield, and R. Kapral, J. Chem. Phys. **136**, 084101 (2012).
[53] S. Nielsen, R. Kapral, and G. Ciccotti, J. Chem. Phys. **115**, 5805 (2001).
[54] R. Glauber, Phys. Rev. **131**, 2766 (1963).
[55] In the present formulation, since we are interested in constructing an algorithm for the evolution of the QCLE in the subsystem basis and its mapping onto the harmonic oscillator single-excitation subspace, the coherent states are introduced in the mapping-transformed space. An interesting alternative approach is to introduce the coherent states directly in the subsystem space and bypass the mapping transformation. This approach, however, requires one to work with a microscopic model in which the Hamiltonian is conveniently represented in the second quantized form with the help of fermionic or bosonic creation and annihilation operators. We shall not pursue this alternative further here.
[56] I. V. Aleksandrov, Z. Naturforsch. **36**, 902 (1981).
[57] V. I. Gerasimenko, Theor. Math. Phys. **50**, 77 (1982).
[58] W. Boucher and J. Traschen, Phys. Rev. D **37**, 3522 (1988).
[59] W. Y. Zhang and R. Balescu, J. Plasma Phys. **40**, 199 (1988).
[60] Y. Tanimura and S. Mukamel, J. Chem. Phys. **101**, 3049 (1994).
[61] Although Eqs. (40) are not in Hamiltonian form, through a simple noncanonical transformation where the coherent state variables are scaled by a constant factor, they may be cast into Hamiltonian form.
[62] The use of the traceless form of the Hamiltonian from the outset simplifies the calculation. In particular, when the anti-normal form of the annihilation and creation operator product is introduced to evaluate the propagator, the trace term does not appear and the structure of the equations is simpler. We have chosen to carry out the derivation with the usual form of the Hamiltonian to stress that the final results are independent of how one chooses to write the Hamiltonian.
[63] N. Ananth, C. Venkataraman, and W. H. Miller, J. Chem. Phys. **127**, 084114 (2007).
[64] X. Sun and W. H. Miller, J. Chem. Phys. **110**, 6635 (1999).
[65] M. Thoss, H. B. Wang, and W. H. Miller, J. Chem. Phys. **114**, 9220 (2001).
[66] X. Sun and W. H. Miller, J. Chem. Phys. **106**, 916 (1997).