All-forward semiclassical simulations of nonlinear response functions

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We propose a quantum trajectory algorithm for computing nonlinear response functions of condensed phase molecular systems based on a time-ordered expansion of the density matrix. The nth-order response function is expressed as a sum of 2^n *impulsive response pathways* representing trajectories involving zero, one, and up to n interactions with short external pulses. These are evaluated using a forward propagation algorithm based upon a Liouville space extension of the Bohmian propagation method. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1756582]

I. INTRODUCTION

The development of fast algorithms that reduce the computational overhead required to find accurate numeric solutions of the time-dependent Schrödinger equation has been a long-standing goal in molecular dynamics simulations. Striking the right balance between accuracy and efficiency is important for polyatomic molecules and unavoidable for condensed phase matter, since exact direct integration is not possible. The many-body wave function (or density matrix) describing a complex molecular system contains much more information than necessary to calculate experimental observables; thus, many-body theory focuses on the direct calculation of the single-point and multipoint time correlation functions which carry the desired information.[1,2] These can describe, for example, the response of a material system to external fields. Schwinger[3] had formulated these calculations using closed time loops which represent the forward propagation of the ket and the backward propagation of the bra in a matrix element $\langle \psi(t)|A|\psi(t)\rangle$. Keldysh[4,5] had recast this picture within the perturbation theory for Green functions, which has now become a standard tool in many-body equilibrium and nonequilibrium diagrammatic techniques. The forward–backward propagation involved in the Schwinger–Keldysh loop is an extremely powerful formal device for carrying out computations.

Perhaps owing to the popularity and success of molecular dynamics methods in simulating the dynamics of large-scale molecular and condensed phase systems via classically evolving atomic trajectories, considerable research activity has been dedicated to the development and application of methodologies which strive to incorporate quantum interference effects into a trajectory based description of molecular systems.[6–21] The forward–backward formalism,[12,22–24] which combines semiclassical propagation with the Schwinger–Keldysh time loop, has been extensively and successfully applied to a broad range of physical problems (see Ref. 25 for a comprehensive review).

In this paper we develop an alternative semiclassical strategy for calculating nonlinear response functions for con-

densed phase systems. We work exclusively with time-ordered expressions for the response which require only forward propagation in Liouville space. We show that a more transparent physical insight may be obtained by working in real time and formulating the problem using the density matrix.[26–28] Consider a quantum material system, described by the Hamiltonian H, driven by an external field $E(t)$ that is coupled to a dynamical variable V via $H_{\text{int}} = -E(t)\cdot V$. The expectation value of V at time t may be computed in the interaction picture according to

$$\langle V(t)\rangle = \left\langle TV_+(t)\exp\left[\frac{i}{\hbar}\int_{-\infty}^{t}d\tau\, E(\tau)V_-(\tau)\right]\right\rangle, \quad (1)$$

where $\langle A\rangle \equiv \text{Tr}[A\rho_{\text{eq}}]$ denotes averaging with respect to the equilibrium density matrix ρ_{eq}. The $\pm$ subscripts denote superoperators defined by their action on an ordinary operator B:

$$V_+B \equiv (VB+BV)/2, \quad (2)$$

$$V_-B \equiv VB-BV. \quad (3)$$

$V_\pm(\tau)$ in Eq. (1) are Heisenberg picture superoperators given by

$$V_\pm(\tau) = \exp\left(\frac{i}{\hbar}H_-\tau\right)V_\pm \exp\left(-\frac{i}{\hbar}H_-\tau\right). \quad (4)$$

T is a positive time-ordering operator in Liouville space that rearranges all products of superoperators in order of decreasing time from left to right.[27,28]

Nonlinear response measurements are usually interpreted by expanding $\langle V(t)\rangle$ in powers of the incoming field. The nth-order contribution to Eq. (1) is given by

$$\langle V^{(n)}(\tau_{n+1})\rangle = \int_{-\infty}^{\tau_{n+1}}d\tau_n\int_{-\infty}^{\tau_n}d\tau_{n-1}\cdots\int_{-\infty}^{\tau_2}d\tau_1$$
$$\times E(\tau_n)\cdots E(\tau_1)S^{(n)}(\tau_{n+1},\ldots,\tau_1), \quad (5)$$

where the nth-order *nonlinear response function*

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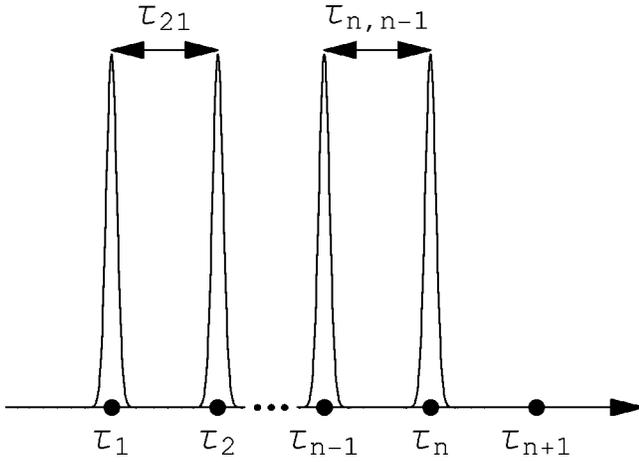
FIG. 1. Schematic diagram of pulse sequencing in a typical nonlinear experiment. Successive pulses arriving at times $\tau_1, \tau_2, \dots, \tau_{n-1}, \tau_n$ are separated by the time intervals $\tau_{21}, \dots, \tau_{n,n-1} \geq 0$.

$$S^{(n)}(\tau_{n+1}, \dots, \tau_1)$$

$$= \left(\frac{i}{\hbar}\right)^n \mathrm{Tr}[V_+(\tau_{n+1}) V_-(\tau_n) \cdots V_-(\tau_1) \rho_{\mathrm{eq}}] \tag{6}$$

represents the measurement of V at time τ_{n+1} following the interaction with n time-ordered short pulses centered at $\tau_1 \leq \cdots \leq \tau_n$. In Liouville space all superoperators in the response function are time ordered, leading naturally to semiclassical and path integral descriptions.

Each of the commutators $V_-(\tau)$ in Eq. (6) contributes two terms corresponding to its "left" and "right" actions. This leads a total of 2^n distinct n-point quantum correlation functions. Each of these terms constitutes a unique *Liouville space pathway* (LSP) that may be represented by a single double-sided Feynman diagram.[27] The subtle interference between the pathways determines the overall nth-order quantum response. An individual LSP does not have a well-defined classical limit. Only after they are combined according to Eq. (6), will the $\hbar^{-n}$ prefactor cancel and the classical limit be recovered.[28]

Equation (6) may be recast in the form

$$S^{(n)}(\tau_{n+1,n}, \dots, \tau_{21})$$

$$= \left(\frac{i}{\hbar}\right)^n \mathrm{Tr}[V_+ e^{-iH_-\tau_{n+1,n}/\hbar} V_- \cdots e^{-iH_-\tau_{21}/\hbar} V_- \rho_{\mathrm{eq}}], \tag{7}$$

where we have used Eq. (4) to expand the Heisenberg superoperators and $\tau_{ji} \equiv \tau_j - \tau_i \geq 0$ are the time intervals between successive pulses as illustrated in Fig. 1. Equation (7) implies that the quantum response is obtained by an alternating sequence of interactions V_- and wave packet propagations $\exp[(i/\hbar)H_-\tau]$ in Liouville space. Given the equilibrium density matrix, we obtain the perturbed state at time τ_1 by evaluating $\rho(\tau_1) = V_- \rho_{\mathrm{eq}} \equiv [V, \rho_{\mathrm{eq}}]$. The density matrix resulting from this first interaction is then propagated for a time τ_{21} and followed by a second interaction with the field V_-. This process is repeated n times. Finally, the response for a given set of time intervals is evaluated by operating with V_+ and taking the trace. The entire nonlinear response function is obtained by repeating this procedure for various values of the

time intervals $\tau_{j+1,j}$. This method can be implemented independently of how the density matrix is propagated in time and how the interactions with the field are carried out.[29] In the classical limit we replace each $(i/\hbar)V_-$ factor by a Poisson bracket. This results in expressions involving stability matrices representing the sensitivity of trajectories to small perturbations.[30–38] These matrices are hard to compute, making it difficult to develop tractable semiclassical approximations.

The present approach is based on computing the impulsive response to a sequence of very short pulses and avoiding the perturbation expansion in the field amplitude altogether. Computation of the resulting *impulsive response pathways* (IRPs) is more numerically stable than the LSPs. Rather than computing 2^n LSPs, we recast the response as a sum over 2^n IRPs, which are represented by perturbed quantum trajectories calculated using the derivative propagation method (DPM).[21,39,40] Unlike the LSPs, each IRP has a well-defined classical limit. Explicit calculation of stability matrices is avoided and the desired response functions are then obtained as specific combinations of the IRPs.

II. QUANTUM IMPULSIVE RESPONSE PATHWAYS

To define the impulsive response pathways, we assume that the field envelope $E(t)$ is a sum of n very short time-ordered pulses each with area ϵ_j:

$$E(t) = \sum_{j=1}^{n} \epsilon_j \delta(t - \tau_j), \tag{8}$$

with $\tau_1 \leq \cdots \leq \tau_n$. The response to these pulses is calculated exactly, via Eq. (1), rather than perturbatively via Eq. (5). The expectation value of V at time τ_{n+1}, $\langle V(\tau_{n+1}) \rangle$, is now parametrically dependent on the ordered sequence of interactions times $\tau_1, \dots, \tau_n$ and will be denoted as the nth-order *impulsive response pathway* $F^{(n)}(\tau_{n+1}, \dots, \tau_1)$. Substituting Eq. (8) into Eq. (1) yields

$$F^{(n)}(\tau_{n+1}, \dots, \tau_1)$$

$$\equiv \mathrm{Tr}\left[V_+(\tau_{n+1}) \exp\left(\frac{i}{\hbar} \epsilon_n V_-(\tau_n)\right) \cdots \right.$$

$$\left. \times \exp\left(\frac{i}{\hbar} \epsilon_1 V_-(\tau_1)\right) \rho_{\mathrm{eq}} \right]. \tag{9}$$

To connect $F^{(n)}$ with $S^{(n)}$ we make use of the identity

$$\frac{i}{\hbar} V_- = \lim_{\epsilon \to 0} \frac{1}{\epsilon} \left[\exp\left(\frac{i}{\hbar} \epsilon V_-\right) - 1 \right]. \tag{10}$$

Substituting Eq. (10) into Eq. (6), we obtain

$$S^{(n)}(\tau_{n+1}, \dots, \tau_1)$$

$$= \lim_{\epsilon_j \to 0} \mathrm{Tr}\left[V_+(\tau_{n+1}) \frac{1}{\epsilon_n} (e^{(i/\hbar)\epsilon_n V_-(\tau_n)} - 1) \cdots \right.$$

$$\left. \times \frac{1}{\epsilon_1} (e^{(i/\hbar)\epsilon_1 V_-(\tau_1)} - 1) \rho_{\mathrm{eq}} \right]. \tag{11}$$

Expanding Eq. (11) generates 2^n terms corresponding to the various impulsive response pathways $F^{(0)}\cdots F^{(n)}$. For example, the three lowest-order response functions are given by

$$S^{(1)}(\tau_2,\tau_1) = \frac{1}{\epsilon_2\epsilon_1}[F^{(1)}(\tau_2,\tau_1) - F^{(0)}(\tau_2)], \tag{12}$$

$$S^{(2)}(\tau_3,\tau_2,\tau_1) = \frac{1}{\epsilon_3\epsilon_2\epsilon_1}[F^{(2)}(\tau_3,\tau_2,\tau_1) - F^{(1)}(\tau_3,\tau_2) - F^{(1)}(\tau_3,\tau_1) + F^{(0)}(\tau_3)], \tag{13}$$

$$S^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1) = \frac{1}{\epsilon_4\epsilon_3\epsilon_2\epsilon_1}[F^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1) - F^{(2)}(\tau_4,\tau_3,\tau_2) - F^{(2)}(\tau_4,\tau_3,\tau_1) - F^{(2)}(\tau_4,\tau_2,\tau_1)$$
$$+ F^{(1)}(\tau_4,\tau_3) + F^{(1)}(\tau_4,\tau_2) + F^{(1)}(\tau_4,\tau_1) - F^{(0)}(\tau_4)], \tag{14}$$

and so forth.

Alternatively the impulsive response pathways serve as *generating functions* for the response functions, which can be obtained as their derivatives

$$S^{(n)}(\tau_{n+1},\ldots,\tau_1) = \frac{\partial^n}{\partial\epsilon_1\cdots\partial\epsilon_n}$$
$$\times F^{(n)}(\tau_{n+1},\ldots,\tau_1)\bigg|_{\epsilon_1=\cdots=\epsilon_n=0}. \tag{15}$$

Note that there is no simple one to one connection between the 2^n Liouville space paths with the 2^n impulsive response paths. In contrast to the LSPs, each IRP has a well-defined classical limit and can be represented by a distinct ensemble of all-forward propagating trajectories in Liouville space. This is best seen by recasting Eq. (9) in the form

$$F^{(n)}(\tau_{n+1},\ldots,\tau_1)$$
$$= \text{Tr}\left[V_+ \exp\left(-\frac{i}{\hbar}H_-\tau_{n+1,n}\right)\exp\left(\frac{i}{\hbar}\epsilon_n V_-\right)\cdots\right.$$
$$\left.\times\exp\left(-\frac{i}{\hbar}H_-\tau_{21}\right)\exp\left(\frac{i}{\hbar}\epsilon_1 V_-\right)\rho_{\text{eq}}\right]. \tag{16}$$

Each $F^{(n)}$ and its corresponding ensemble of trajectories is distinguished by the sequence of time-ordered impulsive but nonperturbative interactions with the external field. The zeroth-order impulsive response contains no impulsive interactions and is obtained by choosing the "one" part of Eq. (10) each time the interaction superoperator is applied in Eq. (11). Note that $F^{(0)} \equiv \text{Tr}[V_+(\tau)\rho_{\text{eq}}] = \langle V \rangle$ is independent of τ and this term is represented by an ensemble of freely evolving reference trajectories. The trajectories corresponding to higher-order $F^{(n)}$'s are constructed from these reference trajectories by making small perturbations at the appropriate times. To compute the nth-order response we launch multiple ensembles of trajectories consisting of the unperturbed one plus $2^n - 1$ weakly perturbed ones at various combinations of times. These trajectories interfere with one another in the sense that they make slightly different contributions to the response for a given sequence of interactions with the field.

III. SEMICLASSICAL SIMULATIONS OF THE IMPULSIVE RESPONSE

To implement a numerical propagation strategy for the IRPs that will scale favorably with the number of degrees of freedom we must consider the two primary operations in Eq. (16): the free propagation of the density matrix $\exp[-(i/\hbar)H_-\tau]$ and the interaction with the field $\exp[(i/\hbar)\epsilon V_-]$.

We consider the Hamiltonian

$$H(P,Q,t) = \frac{P^2}{2M} + U(Q) - V(Q)E(t), \tag{17}$$

where P and Q are the momentum and position operators for a particle with mass M evolving on a potential energy surface $U(Q)$. The operator $V(Q)$ determines the coupling to the driving field $E(t)$. In the absence of $E(t)$, the density matrix $\rho(Q_L,Q_R)$ evolves according to

$$i\hbar\partial_t\rho(Q_L,Q_R)$$
$$= \left(-\frac{P_L^2}{2M} + \frac{P_R^2}{2M} - U(Q_L) + U(Q_R)\right)\rho(Q_L,Q_R), \tag{18}$$

where Q_L ("left") and Q_R ("right") are the Liouville space coordinates associated with the ket and bra, respectively. Substituting the symmetric $Q = \frac{1}{2}(Q_L+Q_R)$ and antisymmetric $Q_- = Q_L - Q_R$ combinations of the left and right coordinates into Eq. (18), we obtain

$$i\hbar\partial_t\rho(Q,Q_-) = -\frac{\hbar^2}{M}\partial_{QQ_-}\rho(Q,Q_-)$$
$$+ U_-(Q,Q_-)\rho(Q,Q_-), \tag{19}$$

where $U_-(Q,Q_-)$ is defined by

$$U_-(Q,Q_-) = U(Q + \tfrac{1}{2}Q_-) - U(Q - \tfrac{1}{2}Q_-). \tag{20}$$

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We next perform a local cumulant expansion of the density matrix about a reference trajectory $\Gamma(t) \equiv (Q(t), Q_-(t))$. This procedure is based upon the de Broglie–Bohm interpretation of quantum mechanics,[41–44] the statistical reformulation of quantum dynamics in terms of the moments and cumulants of hydrodynamiclike distributions,[45–50] and the derivative propagation method.[21,39,40] We begin by writing the density matrix in a complex exponential form

$$\rho(Q, Q_-, t) = \exp\left(g(Q, Q_-, t) + \frac{i}{\hbar} A(Q, Q_-, t) \right), \quad (21)$$

where $g(Q, Q_-, t)$ and $A(Q, Q_-, t)$ are real-valued functions. Substituting Eq. (21) into Eq. (19) and separating the real and imaginary parts we obtain a pair of exact coupled partial differential equations for the evolution of g and A:

$$\partial_t g = -\frac{1}{M}(A^{(1,1)} + g^{(1,0)}A^{(0,1)} + A^{(1,0)}g^{(0,1)}), \quad (22)$$

$$\partial_t A = -U_- + \frac{\hbar^2}{M}(g^{(1,1)} + g^{(1,0)}g^{(0,1)}) - \frac{1}{M}A^{(1,0)}A^{(0,1)}, \quad (23)$$

where $f^{(m,n)} \equiv \partial_Q^m \partial_{Q_-}^n f(Q, Q_-, t)$ denotes partial derivatives of $f(Q, Q_-)$ with respect to Q and Q_-. We next expand g, A, and U_- in a Taylor series with respect to an arbitrarily chosen configuration space reference trajectory $\Gamma(t)$:

$$g(Q, Q_-, t) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{g_{m,n}(t)}{m! n!} [Q - Q(t)]^m \times [Q_- - Q_-(t)]^n, \quad (24)$$

$$A(Q, Q_-, t) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{A_{m,n}(t)}{m! n!} [Q - Q(t)]^m \times [Q_- - Q_-(t)]^n, \quad (25)$$

$$U_-(Q, Q_-) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{U_-^{(m,n)}(Q(t), Q_-(t))}{m! n!} \times [Q - Q(t)]^m [Q_- - Q_-(t)]^n, \quad (26)$$

where

$$f_{m,n}(t) \equiv f^{(m,n)}(Q(t), Q_-(t), t) \quad (27)$$

indicates that the function $f^{(m,n)}(Q, Q_-, t)$ is evaluated along the trajectory $\Gamma(t)$. Equation (21) together with Eqs. (24) and (25) constitutes a cumulant expansion of $\rho(Q, Q_-, t)$, where $g_{m,n}$ and $A_{m,n}$ are known as the (m,n)th cumulants of $\rho(Q, Q_-, t)$ about $\Gamma(t)$.

Substituting Eqs. (24)–(26) into Eqs. (22) and (23) and collecting powers of $[Q - Q^{\alpha}(t)]^m [Q_- - Q^{\alpha}(t)]^n$ we obtain an infinite hierarchy of coupled ordinary differential equations

$$\dot{g}_{m,n} = -\frac{1}{M} A_{m+1,n+1} - \frac{1}{M} \sum_{i=0}^{m} \sum_{j=0}^{n} \binom{m}{i}\binom{n}{j}$$
$$\times (g_{i+1,j}A_{m-i,n-j+1} + A_{i+1,j}g_{m-i,n-j+1})$$
$$+ \dot{Q}(t)g_{m+1,n} + \dot{Q}_-(t)g_{m,n+1}, \quad (28)$$

$$\dot{A}_{m,n} = -U_-^{(m,n)}(Q(t), Q_-(t)) + \frac{\hbar^2}{M}\left(g_{m+1,n+1} \right.$$
$$\left. + \sum_{i=0}^{m} \sum_{j=0}^{n} \binom{m}{i}\binom{n}{j} g_{i+1,j}g_{m-i,n-j+1} \right)$$
$$- \frac{1}{M} \sum_{i=0}^{m} \sum_{j=0}^{n} \binom{m}{i}\binom{n}{j} A_{i+1,j}A_{m-1,n-j+1}$$
$$+ \dot{Q}(t)A_{m+1,n} + \dot{Q}_-(t)A_{m,n+1}. \quad (29)$$

Each cumulant is clearly coupled to both higher- and lower-order cumulants. Neglecting terms greater than second order in the expansion leads to a system of 14 coupled differential equations [six equations of each g, six for A, and two unspecified equations for $\Gamma(t)$] to evaluate the density matrix along a single trajectory at a later point in time. For a Gaussian wave packet evolving on a quadratic potential this truncation is exact. For anharmonic problems, however, there will be unavoidable truncation errors. We note that this does not imply that the global density matrix is Gaussian—rather, only that the local structure of the density matrix in the neighborhood of an individual trajectory is Gaussian.

A successful implementation of this procedure depends on the truncation of the hierarchy, which, in turn, requires a judicious choice of the reference trajectory $\Gamma(t)$. In Liouville space, the velocity components of a Bohmian quantum trajectory are given by

$$\dot{Q} = A_{0,1}/M, \quad (30)$$

$$\dot{Q}_- = A_{1,0}/M. \quad (31)$$

From a hydrodynamic viewpoint, Eqs. (30) and (31) correspond to the equations of motion for a fluid element that evolves with the flow of the probability current density—i.e., the Lagrangian representation—as described in Appendix A. This choice simplifies the equations of motion somewhat by canceling two terms coming from the double summations in both Eqs. (28) and (29).

In addition to free propagation of the density matrix, evaluation of the IRPs requires computation of the interactions with the field. Within the present representation, Eq. (21), we need to calculate effect of the interaction operator $\exp(i\epsilon V_-/\hbar)$ on g and A:

$$e^{i\epsilon V_-/\hbar} e^{g + iA/\hbar} = e^{q' + iA'/\hbar}. \quad (32)$$

Since V depends only depends on the coordinates (and not the momenta), the $g_{m,n}$'s are unaffected by the transformation and we obtain

$$g'_{m,n} = g_{m,n}, \quad (33)$$

$$A'_{m,n} = A_{m,n} + \epsilon \sum_{k=(n-1)/2}^{\infty} \frac{V^{(m+2k+1)}(Q(t))}{2^{2k}(2k+1-n)!}$$
$$\times Q_-(t)^{2k+1-n}. \tag{34}$$

There are many possible choices for representing Liouville space wave packets. One strategy is to construct an ensemble of reference trajectories $\{\Gamma^\alpha(t)\}$. Each member of the ensemble is distinguished by its initial conditions and its own set of cumulants $g^\alpha_{m,n}$ and $A^\alpha_{m,n}$. For example, the total density matrix of the system may be represented as a pointwise sum over the ensemble of reference trajectories:

$$\rho(Q, Q_-, t) = \sum_\alpha \exp\left(g^\alpha_{0,0}(t) + \frac{i}{\hbar} A^\alpha_{0,0}(t)\right)$$
$$\times \delta(Q - Q^\alpha(t)) \delta(Q_- - Q^\alpha(t)). \tag{35}$$

In this representation we only keep the zeroth-order cumulants along many trajectories to represent the total density matrix. Rather than using high-order cumulants, we add many pointwise trajectories where the coefficients $g^\alpha_{0,0}(t)$ and $A^\alpha_{0,0}(t)$ carry information about the vicinity of each trajectory.

In summary, the numerical procedure for calculating the nth-order nonlinear response function is as follows: We construct an n-dimensional grid of points in the time interval domain $\tau_{21} \geq 0, ..., \tau_{n+1,n} \geq 0$. The dimensions and resolution of this grid are determined by the details of the experiment to be simulated. For a given set of time intervals the nonlinear response is calculated as a sum of 2^n impulsive response pathways. Each IRP is computed by taking the trace of a unique nonequilibrium density matrix represented over an ensemble of reference trajectories. This density matrix is generated by acting on ρ_{eq} with a specific sequence of interaction and propagation operations according to the methods described in this section. Repeating these steps for various choices of the time intervals, finally, generates the nth-order response function.

IV. SEMICLASSICAL PROPAGATION COUPLED TO A CLASSICAL BATH

The formalism of Sec. III can be extended to condensed phases, where the system of interest is coupled to a classical bath. The all-forward propagation is particularly transparent for describing dephasing processes induced by a bath.

The total Hamiltonian for a quantum degree of freedom (the system S) coupled to many classical molecular variables (the bath B) is given by

$$H_T(P, Q, \mathbf{p}, \mathbf{q}, t) = H(P, Q) + \sum_j^n \frac{p_j^2}{2m_j} + U_B(\mathbf{q}) + U_{SB}(Q, \mathbf{q}), \tag{36}$$

where $H(P, Q)$ is given by Eq. (17). The bath is composed of n classical particles with masses $\{m_1, ..., m_n\}$, positions $\mathbf{q} = \{q_1, ..., q_n\}$, and momenta $\mathbf{p} = \{p_1, ..., p_n\}$ that interact with one another through the multidimensional potential energy surface $U_B(\mathbf{q})$. The interaction potential $U_{SB}(Q, \mathbf{q})$ couples the system and bath. We assume that the field interacts only with the system $V = V(Q)$.

We invoke the time-dependent Hartree approximation by assuming that the total many-body density matrix Φ for the mixed system is factorizable into $n+1$ single-particle density matrices:

$$\Phi(Q_L, Q_R, \mathbf{q}_L, \mathbf{q}_R, t) = \rho(Q_L, Q_R, t) \prod_{j=1}^n \rho_j(q_{jL}, q_{jR}, t), \tag{37}$$

where q_{jL} and q_{jR} are the Liouville space coordinates associated with the single-particle density matrix ρ_j of the jth bath particle. Using symmetric and antisymmetric combinations of "left" and "right" bath coordinates, we can define the classical single-particle density matrices in terms of classical trajectories in phase space:

$$\phi_j(q_j, p_j, t) = \int_{-\infty}^{\infty} \rho_j(q_j, q_{j-}, t) e^{ip_j q_{j-}/\hbar}$$
$$= \delta(q_j - q_j(t)) \delta(p_j - p_j(t)). \tag{38}$$

The bath trajectories are given by Hamilton's equations

$$\dot{q}_j(t) = \partial_{p_j} H = p_j/m_j, \tag{39}$$

$$\dot{p}_j(t) = -\partial_{q_j} H = -\partial_{q_j} U_B - \partial_{q_j} \langle U_{SB} \rangle, \tag{40}$$

and are parametrically dependent on the system's coordinates through the expectation value $\langle U_{SB}(Q, \mathbf{q}) \rangle = \text{Tr}[U_{SB\rho}]$. In the absence of the driving field $E(t)$, ρ evolves according to

$$i\hbar \partial_t \rho = -\frac{\hbar^2}{M} \partial_{QQ_-} \rho + U_- \rho + U_{SB-} \rho, \tag{41}$$

where U_{SB-} is defined by

$$U_{SB-}(Q, Q_-, \mathbf{q}) = U_{SB}(Q + \tfrac{1}{2}Q_-, \mathbf{q}) - U_{SB}(Q - \tfrac{1}{2}Q_-, \mathbf{q}). \tag{42}$$

Following the procedure outlined in Sec. III, we can rewrite Eq. (41) as an infinite hierarchy of coupled differential equations:

$$\dot{g}^S_{m,n} = \dot{g}_{m,n}, \tag{43}$$

$$\dot{A}^S_{m,n} = \dot{A}_{m,n} - U^{(m,n)}_{SB-}(Q(t), Q_-(t), \mathbf{q}), \tag{44}$$

where $\dot{g}_{m,n}$ and $\dot{A}_{m,n}$, given by Eqs. (28) and (29), now depend parametrically on $\mathbf{q}$. The velocity components of the trajectory are

$$\dot{Q} = A^S_{0,1}/M, \tag{45}$$

$$\dot{Q}_- = A^S_{1,0}/M. \tag{46}$$

The final semiclassical equations of motion for a system coupled to a classical bath are given by Eqs. (43)–(46) together with Eqs. (39) and (40). In this approach we have explicitly included the bath degrees of freedom into the equations of motion.

Alternatively, one can adopt a reduced description to the system–bath dynamics by appealing to reduced equations of

motion where the bath degrees of freedom have been eliminated. In Appendix B we derive the cumulant expansion for a reduced density matrix described by the Caldeira–Leggett master equation.

V. DISCUSSION

When a measurement of a dynamical variable V is repeatedly performed on a system we obtain a joint probability distribution of the outcomes. The response function carries information that depends on delicate interferences among events that occur at the various points in time and may not be calculated from the joint probability of the $n+1$ measurements of V (Refs. 28 and 51). Quantum mechanically this interference may be understood in terms of either a sum over 2^n Liouville space pathways or 2^n impulsive response pathways. Even though we perform some operation on the system at $n+1$ points in time, n interactions with the field plus the time of observation, only the last interaction corresponds to an actual measurement. In the other times we merely perturb the system; therefore, the pathways interfere with one another. Individual LSPs do not have a classical limit; however, individual IRP do: classically, they represent impulsively perturbed trajectories.

Correlation functions are equilibrium objects and can be computed using sums over unperturbed trajectories. Classical response functions can, thus, be obtained either as equilibrium averages in terms of stability matrices or recast in terms of 2^n closely lying IRP trajectories that are perturbed at various points in time. In the equilibrium method one can evaluate the response function for all time arguments by propagating a single ensemble of unperturbed trajectories. The computational cost is that one must also propagate up to n stability matrices. For anharmonic systems the elements of the stability matrix can diverge exponentially.[31,32] In the impulsive simulation method the interference between perturbed trajectories is evaluated explicitly, so that one never has to compute the stability matrix; however, a new set of trajectories must be computed for each choice of time intervals $\tau_{21},\ldots,\tau_{n+1,n}$.

There are many different semiclassical propagation schemes and simulation of the IRP is not limited to the Bohmian trajectories [Eqs. (30) and (31)] discussed in this paper. Other possibilities are stationary trajectories (the Eulerian representation) $\{\dot{Q},\dot{Q}_-\}=0$ or even classical trajectories $\{\dot{Q},\dot{Q}_-\}=\{-U^{(1)}/M,0\}$. Equations (28)–(31) are our final closed equations for the density matrix propagation. Consider an ensemble constructed from the classical trajectories of the system—that is, the equilibrium trajectories $Q_{\mathrm{eq}}(t)$. Ordinarily, we could calculate the response function by computing the appropriate stability matrices and average over the ensemble of trajectories. Instead, we can treat the classical trajectory as an input to the derivative propagation method by letting $Q(t)=Q_{\mathrm{eq}}(t)$ and $Q_-(t)=0$. Thus we expand the density matrix about the classical trajectories evolving in Q, but stationary in Q_-. We can then evaluate the density matrix along these trajectories in a way similar to the method described in Sec. II.

The cumulant expansion has some limitations. It was argued by Bittner[40] that truncating the derivative hierarchy in the expansion of g and A is tantamount to including artificial dissipation in the system. This leads to a loss of coherence between different trajectories and is not expected to be successful for nondissipative systems. However, when there is dissipation due to the coupling of the bath (see Sec. IV and Appendix B) one can justify truncating the hierarchy at some low order depending on the strength of the dissipation.

ACKNOWLEDGMENT

APPENDIX A: LAGRANGIAN VELOCITY COMPONENTS IN LIOUVILLE SPACE

In this appendix we identify the velocity components of a Bohmian quantum trajectory in Liouville space. In Hilbert space, we can write the wave function as

$$\psi(Q,t)=\exp[C(Q,t)+iS(Q,t)/\hbar]. \tag{A1}$$

The local conservation of probability $\rho=\psi\psi^*$ is expressed through the continuity equation

$$\partial_t\rho+\nabla\cdot J=0, \tag{A2}$$

where J is the probability current density. For a wave function satisfying the time-dependent Schrödinger equation, this current is defined by

$$J=\frac{\hbar}{2mi}(\psi^*\nabla\psi-\psi\nabla\psi^*). \tag{A3}$$

Substituting Eq. (A1) into Eq. (A3), it is easy to show that $J=\rho\nabla S/m$. By analogy with fluid mechanics we can identify a velocity field $v=\nabla S/m$ for a quantum probability fluid using the definition $J=\rho v$. For a pure state $\rho(Q_L,Q_R)=\psi(Q_L)\psi^*(Q_R)$ the functions g and A are given in terms of C and S according to

$$g(Q_L,Q_R,t)=C(Q_L,t)+C(Q_R,t), \tag{A4}$$

$$A(Q_L,Q_R,t)=S(Q_L,t)-S(Q_R,t). \tag{A5}$$

In Liouville space we keep track of both forward and backward evolving current density. Thus the velocity field is given by

$$v(Q_L,Q_R)=\frac{1}{m}\{\nabla_L S(Q_L),-\nabla_R S(Q_R)\}. \tag{A6}$$

Transforming to the symmetric and antisymmetric coordinate frame, we obtain

$$v(Q,Q_-)=\frac{1}{m}\{\nabla_+ A(Q,Q_-),\nabla_- A(Q,Q_-)\}. \tag{A7}$$

Equation (A7) is the multidimensional analog of Eqs. (30) and (31).

APPENDIX B: SEMICLASSICAL DYNAMICS USING THE CALDEIRA–LEGGETT MASTER EQUATION

Consider a model system described by a tagged degree of freedom Q, linearly coupled to a bath of harmonic oscillators. The total Hamiltonian for this system is given by

$$H(Q,P,\mathbf{q},\mathbf{p},t) = \frac{P^2}{2M} + U(Q) - V(P,Q)E(Q,t)$$
$$+ \sum_j^n \frac{p_j^2}{2m_j} + \frac{m_j \omega_j^2}{2}\left(q_j - \frac{c_j}{m_j \omega_j^2}Q\right)^2. \quad (B1)$$

Because the bath degrees of freedom $\mathbf{q}$ are not explicitly coupled to the field, we can eliminate them from our description by taking a partial trace of the many-body density matrix. The Caldeira–Leggett master equation (the coordinate space equivalent of the quantum Fokker–Planck equation) provides a convenient description for the reduced dynamics of the system.[52] At high temperatures, the time evolution of the reduced density matrix $\rho = \rho(Q,Q_-)$, in the absence of $E(t)$, is determined by the master equation

$$i\hbar\,\partial_t\rho = -\frac{\hbar^2}{M}\partial_{QQ_-}\rho + U_-\rho - 2i\hbar\,\gamma Q_-\partial_{Q_-}\rho$$
$$-\frac{2i\gamma MkT}{\hbar}Q_-^2\rho. \quad (B2)$$

The first and second terms in Eq. (B2) constitute the Liouville superoperator for the tagged oscillator in the absence of the bath. The third and fourth terms correspond to frictional relaxation and phase relaxation (decoherence), respectively. The frictional relaxation rate γ is determined by the strength of the interaction with the bath and sets the time scale for energy exchange between the tagged oscillator and heat bath. The fourth term influences only the off-diagonal elements of the density matrix (i.e., $Q_- \neq 0$) which become exponentially damped at a rate $\propto 2\gamma MkTQ_-^2/\hbar^2$.

In the Caldeira–Leggett model the interaction coupling strength is, by construction, assumed to be weak and only strictly valid for the long-time behavior of the tagged oscillator in the high-temperature limit (e.g., if Ω is the highest frequency in the bath, then the model is applicable for time scales $\tau \gg \Omega^{-1}$ and thermal energies $kT \gg \hbar\Omega$). Other models[53–55] have been constructed that are less restrictive than the Caldeira–Leggett master equation; however, the resulting master equations contain time-dependent dissipative coefficients which complicate numerical integration. For the present study, it suffices to use Eq. (B2). In what follows we shall briefly review the reformulation of the Caldeira–Leggett equation in terms of an infinite hierarchy of dissipative equations motion for the cumulants of the reduced density matrix.

Substituting Eq. (21) into Eq. (B2) and separating the real and imaginary components, we obtain

$$\partial_t g^{\mathrm{CL}}(Q,Q_-,t) = \partial_t g(Q,Q_-,t) - 2\gamma Q_- g^{(0,1)}(Q,Q_-,t)$$
$$-\frac{2\gamma MkT}{\hbar^2}Q_-^2, \quad (B3)$$

$$\partial_t A^{\mathrm{CL}}(Q,Q_-,t) = \partial_t A(Q,Q_-,t) - 2\gamma Q_- A^{(0,1)}(Q,Q_-,t). \quad (B4)$$

Substituting Eqs. (24)–(26) into the Eqs. (B3) and (B4), we obtain

$$\dot{g}_{m,n}^{\mathrm{CL}}(t) = \dot{g}_{m,n}(t) - 2\gamma n g_{m,n}(t) + Q_-(t) g_{m,n+1}(t) \quad (B5)$$

$$-\frac{2\gamma MkT}{\hbar^2}\delta_{m,0}(Q_-(t)^2\delta_{n,0} + 2Q_-(t)\delta_{n,1} + 2\delta_{n,2}), \quad (B6)$$

$$\dot{A}_{m,n}^{\mathrm{CL}}(t) = \dot{A}_{m,n}(t) - 2\gamma n A_{m,n}(t) - 2\gamma Q_-(t)A_{m,n+1}(t). \quad (B7)$$

In the Lagrangian reference frame, the velocity components of the trajectory are given by

$$\dot{Q}(t) = A_{0,1}/M, \quad (B8)$$

$$\dot{Q}_-(t) = A_{1,0}/M + 2\gamma q_- . \quad (B9)$$

For dissipative systems we expect that the relaxation terms involving γ will counter the effects of the truncation error, thus effectively closing the hierarchy of equations of motion. We note that Trahan and Wyatt[39] have very recently extended the DPM to solve the quantum Fokker–Planck equation using quantum trajectories in phase space.

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