Quantum-classical path integral. I. Classical memory and weak quantum nonlocality

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(Received 25 September 2012; accepted 31 October 2012; published online 4 December 2012)

We consider rigorous path integral descriptions of the dynamics of a quantum system coupled to a polyatomic environment, assuming that the latter is well approximated by classical trajectories. Earlier work has derived semiclassical or purely classical expressions for the influence functional from the environment, which should be sufficiently accurate for many situations, but the evaluation of quantum-(semi)classical path integral (QCPI) expressions has not been practical for large-scale simulation because the interaction with the environment introduces couplings nonlocal in time. In this work, we analyze the nature of the effects on a system from its environment in light of the observation [N. Makri, J. Chem. Phys. \textbf{109}, 2994 (1998)] that true nonlocality in the path integral is a strictly quantum mechanical phenomenon. If the environment is classical, the path integral becomes local and can be evaluated in a stepwise fashion along classical trajectories of the free solvent. This simple “classical path” limit of QCPI captures fully the decoherence of the system via a classical mechanism. Small corrections to the classical path QCPI approximation may be obtained via an inexpensive random hop QCPI model, which accounts for some “back reaction” effects. Exploiting the finite length of nonlocality, we argue that further inclusion of quantum decoherence is possible via an iterative evaluation of the path integral. Finally, we show that the sum of the quantum amplitude factors with respect to the system paths leads to a smooth integrand as a function of trajectory initial conditions, allowing the use of Monte Carlo methods for the multidimensional phase space integral.

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I. INTRODUCTION

As is well known, the difficulty of obtaining accurate solutions to the Schrödinger equation increases exponentially with the number of degrees of freedom. This situation necessitates the use of approximations for studying the real-time dynamics of large molecular systems or condensed phase processes. For many chemical or biological processes of interest, molecular dynamics methods, which are based on the classical equations of motion for the coordinates of the nuclei on a single Born-Oppenheimer potential energy surface, are adequate and practical for simulations with millions of atoms. On the other hand, nonadiabatic effects allowing electronic transitions are commonly encountered in chemical and biological processes. Such effects, along with zero-point energy and tunneling, require a quantum mechanical treatment.

Since a quantum mechanical description is often necessary only for a small number of degrees of freedom, mixed quantum-classical treatments are extremely appealing. However, the difference in the structure of quantum and classical theory makes it difficult to devise quantum-classical approximations that are consistent and accurate in a variety of situations. Perhaps the oldest quantum-classical approximation is the Ehrenfest model,\(^1\) which is also closely connected to time-dependent self-consistent field approximations.\(^2,3\) These methods integrate the trajectories for the nuclei under the influence of a force averaged with respect to the wavefunction of the quantum system. In the context of electronic transitions, the Ehrenfest model implies that the nuclear trajectory moves on the average Bohn-Oppenheimer potential, an assumption which can lead to unphysical results.\(^4\) Pechukas has described a semiclassical approximation in which the classical trajectory is determined along with the evolution of the quantum wavefunction between initial and final states in a self-consistent way.\(^5\) The procedure is rigorous and accurate, but the self-consistent determination of the trajectory is very demanding, making the method impractical for large-scale simulation.

Tully introduced in the 1970s the so-called surface hopping methods,\(^6\) in which trajectories can incur electronic transitions at random times specified by the magnitude of the nonadiabatic coupling strength. The surface hopping model corrects the most serious shortcomings of the Ehrenfest model, allowing for population branching.\(^7\) The surface hopping method, in particular its “fewest switches” version,\(^4\) also known as molecular dynamics with quantum transitions, has been applied to proton transfer processes,\(^8\) and its generalized multiconfigurational version has been used to simulate multiple proton transfer and proton-coupled electron transfer.\(^9\) Other surface hopping schemes that utilize the Pechukas force for short time intervals or a mean field force are also available and have been applied to condensed phase processes.\(^10,11\) Similar in spirit to surface hopping is the multiple spawning method, which calculates quantum mechanical transition amplitudes using local basis sets that surround classical trajectories.\(^12,13\) A different idea for treating nonadiabatic dynamics via classical trajectories was originally...
proposed by Meyer and Miller\textsuperscript{15} and further developed by Stock and Thoss.\textsuperscript{16} This involves mapping each electronic state on a pair of action-angle variables, thus replacing discrete states by continuous degrees of freedom which are directly amenable to standard classical or semiclassical trajectory treatments on a single potential surface, circumventing the need for hops between quantum states.\textsuperscript{17} Another approach involves solving the quantum-classical Liouville equation, which involves a first-order expansion in the ratio of masses corresponding to the quantum and classical particles.\textsuperscript{18,19} Bohm’s quantum trajectory formulation has also been exploited in the development of nonadiabatic dynamics approximations.\textsuperscript{20–22}

In this work, we describe a rigorous, yet practical path integral approach to quantum-classical dynamics. Starting from the full path integral formulation of the density matrix and taking the $\hbar \to 0$ limit with respect to the “heavy” particles (e.g., the nuclei in the case of nonadiabatic dynamics, or just the heavier atoms in the case of proton transfer), which are referred to as the “bath” or “solvent”, restricts the path sum to classical trajectories for these particles, maintaining the full quantum path sum for the “light” particles (e.g., the electronic degrees of freedom or the hydrogen atoms). It is clear that such quantum-classical path integral (QCPI) treatments are theoretically sound and should provide a faithful description of the dynamics, while the classical trajectory treatment of the majority of degrees of freedom is appealing for application to condensed phase systems or large biomolecules. Yet, evaluation of real-time path integral expressions is an extremely difficult task, requiring computational resources that scale exponentially with propagation time. Thus, the major challenge is how to evaluate the QCPI expression without making additional severe approximations.

In this work and also in the companion paper\textsuperscript{23} we address this challenge. We point out that the quantum path summed expression is a smooth function of the initial coordinates of those degrees of freedom treated via classical mechanics, allowing efficient evaluation of the phase space integral by Monte Carlo methods.\textsuperscript{24} Further, we argue that the classical or near-classical character of these degrees of freedom offers an advantageous starting point that captures the bulk of the effects on the quantum system from the bath, including the partial destruction of coherence; this is so because time nonlocality is a strictly quantum mechanical phenomenon and plays a minor role in the classical limit. In the companion paper,\textsuperscript{23} we present efficient discretized QCPI expressions and develop a systematic methodology for including this residual quantum nonlocality (which is associated with quantum decoherence) that should converge with modest computational effort in many situations of interest. The QCPI approach is quite general and can be used to propagate the density matrix or to evaluate time correlation functions at zero or finite temperature, and is easy to combine with standard molecular dynamics software. In addition, it may be used in conjunction with purely classical or upgraded semiclassical versions of the bath dynamics.

In Sec. II, we discuss quantum-semiclassical and quantum-classical path integral expressions and examine the behavior of the integrand as a function of initial trajectory coordinates. The features of the quantum-classical path sum are analyzed in Sec. III, where we point out that bath-induced memory vanishes in the classical limit (which corresponds to the classical path approximation), and that time nonlocality plays a minor role under near-classical or weak-coupling conditions. These ideas are illustrated with numerical examples in Sec. IV. Finally, a summary and outlook are given in Sec. V.

II. QUANTUM-SEMICLASSICAL AND QUANTUM-CLASSICAL PATH INTEGRAL

The degrees of freedom of the quantum mechanical system are described by the coordinate $x$, while $x$, $p$ describe collectively the coordinates and momenta of the bath particle(s) with mass $m_b$, which are to be treated via classical trajectories. The Hamiltonian has the form

$$\hat{H} = H_0(\delta, \dot{\rho}_s) + T_b(\dot{\rho}_s) + V(\delta, \dot{\delta}) \equiv H_0(\delta, \dot{\rho}_s) + H_b(\delta, \dot{\delta}, \dot{\rho}_s),$$

where $H_b$ describes the quantum particle, $T_b$ is the kinetic energy of the classical degrees of freedom, and $V$ is the interaction potential. We focus on the reduced density matrix of the quantum subsystem at the time $t$,

$$\rho_{\text{red}}(s^\pm_1; t) = \int dx f(s^+_1 x_1) e^{-i\hat{H}_t/\hbar} \rho(0) e^{i\hat{H}_t/\hbar} |s^-_1 x_1\rangle \langle s^-_1 x_1|$$

$$= \int dx \int dx_0^\pm \int dx_0^- |s^+_1 x_1\rangle \langle s^+_1 x_1| e^{-i\hat{H}_t/\hbar} |s^-_0 x_0^+\rangle \langle s^-_0 x_0^+| e^{i\hat{H}_t/\hbar} |s^-_0 x_0^-\rangle \langle s^-_0 x_0^-|. \quad (2.2)$$

Using the path integral\textsuperscript{25,26} representation of the forward and backward propagators, the reduced density matrix becomes

$$\rho_{\text{red}}(s^\pm_1; t) = \int Ds^\pm e^{i\Phi(s^\pm)}/h F[s^\pm] e^{-i\Phi(s^-)/h}, \quad (2.3)$$

where $Ds^\pm$ denotes a functional integral (i.e., sum with appropriate prefactors) with respect to all forward and backward system paths $s^\pm$ with final values $s^\pm_1$, $\Phi_0$ is the action integral for the bare system, and

$$F[s^\pm] = \text{Tr}_b \left( \hat{U}_b[s^\pm] \hat{\rho}(0) \hat{U}_b^{-1}[s^-] \right) \quad (2.4)$$

is the influence functional\textsuperscript{27} from the bath. In Eq. (2.4) $U_b[s^\pm]$ is the time evolution operator for the time-dependent bath Hamiltonian $H_b$ along the system path $s^\pm$. Equations (2.3) and (2.4) are exact. Applying the semiclassical approximation in the Herman-Kluk coherent state representation,\textsuperscript{28} Makri and Thompson have obtained the following forward-backward semiclassical dynamics (FBSD) approximation to the influence functional:\textsuperscript{29,30}

$$F_{\text{FBSD}}[s^\pm] = \int dx_0 \int dp_0 D_{\text{FBSD}}(x_0, p_0; [s^\pm]) e^{i\Phi^\text{FBSD}_b(x_0, p_0; [s^\pm])/h}. \quad (2.5)$$

Here, $|x_0 p_0\rangle$ are coherent states, whose wavefunctions are

$$|x| x_0 p_0\rangle = \frac{(2\gamma)^{\frac{1}{4}}}{\pi^{\frac{1}{4}}} e^{-\gamma(x-x_0)^2 + \frac{i}{\hbar}p_0(x-x_0)} \quad (2.6)$$

and $\Phi^\text{FBSD}_b$ is the net action along a classical trajectory originating at $x_0$, $p_0$, integrated first forward in time under
the time-dependent bath Hamiltonian $H_b(s^+(t'))$ and subsequently backward in time under $H_b(s^-(t'))$. The weight of each trajectory is specified by the function

$$D_{\text{FBSD}}(x_0, p_0; \{s^\pm\}) = (2\pi\hbar)^{-1} C(x_0, p_0)(s^+_0 x_0 p_0 | \bar{\rho}(0)| s^-_0 x_1 p_1). \quad (2.7)$$

Here, $x_f$, $p_f$ are the final phase space coordinates of the forward-backward trajectory, and the derivatives of these coordinates with respect to the initial ones determine the prefactor $C(x_0, p_0)$. The FBSD expression (2.5) is the rigorous stationary phase limit of the influence functional and produces the exact Feynman-Vernon result if the classical particle trajectory is described by a quadratic Hamiltonian linearly coupled to the quantum system. Unlike semiclassical expressions for the time evolution of a wavefunction, the partial cancellation of the forward and backward actions in Eq. (2.5) tempers naturally the oscillatory character of the integrand, allowing efficient evaluation of the integral by Monte Carlo methods.

If the forward and backward trajectories do not differ significantly (e.g., for small coupling and/or short times), the final phase space coordinates $x_f$, $p_f$ of the trajectory will be close to the initial values $x_0$, $p_0$ and the forward and backward actions will not differ substantially. Under these conditions one may proceed as in the derivation of the FBSD approximation for time correlation functions to obtain a quasiclassical approximation to Eq. (2.5), in which the forward and backward trajectories are replaced by a single trajectory that experiences the average of the forces along the forward and backward system paths,

$$F_{\text{coh}}^{\text{class}}[s^\pm] \approx \int dx_0 \int dp_0 D_{\text{coh}}(x_0, p_0; s^\pm) e^{i\Phi_{\text{class}}(x_0, p_0; s^\pm)/\hbar}, \quad (2.8)$$

where

$$D_{\text{coh}}(x_0, p_0; s^\pm) = (2\pi\hbar)^{-1}(s^+_0 x_0 p_0 | \bar{\rho}(0)| s^-_0 x_0 p_0) \quad (2.9)$$

and the action $\Phi_{\text{class}}$ is the difference of the action integrals along the classical trajectory experiencing the force exerted by the quantum particle traversing its forward and backward paths. This expression provides an excellent approximation to the influence functional from a high-temperature bath. Equation (2.9) is similar to the quasiclassical influence functional of Shi and Geva,\textsuperscript{13}

$$F_{\text{Wigner}}[s^\pm] = \int dx_0 \int dp_0 D_{\text{Wigner}}(x_0, p_0; s^\pm) e^{i\Phi_{\text{class}}(x_0, p_0; s^\pm)/\hbar}, \quad (2.10)$$

which employs the Wigner transform\textsuperscript{34} of the initial density

$$D_{\text{Wigner}}(x_0, p_0; s^\pm) = (2\pi\hbar)^{-1} \int d\Delta x_0 (s^+_0 x_0^+ | \bar{\rho}(0)| s^-_0 x_0^-) e^{-ip_0\Delta x_0/\hbar}, \quad$$

$$\Delta x_0 = x_0^+ - x_0^- \quad (2.11)$$

The relation between Eqs. (2.9) and (2.11) is established by recognizing the coherent state density in Eq. (2.9) as an expansion of the Wigner function.\textsuperscript{35,36} Equation (2.10) is the influence functional equivalent of the linearized path integral approximation\textsuperscript{37,38} for time correlation functions, which provides an alternative derivation of the linearized semiclassical (LS) initial value representation result obtained earlier by Wang, Sun, and Miller.\textsuperscript{39} We also note that the combination of a path integral description of the system with a linearized approximation to the influence functional is particularly valuable in spirit to the (double) semiclassical-classical treatment of Sun and Miller,\textsuperscript{40} which can account for phase interference in the quantum system, while retaining a simpler classical description of the bath. A similar double semiclassical/FBSD approximation has also been described.\textsuperscript{41}

Alternatively, a classical approximation may be obtained by using the high-temperature Trotter approximation to the density operator in the coordinate representation and substituting the coordinate (van Vleck\textsuperscript{42}) semiclassical representation of the forward and backward propagators in Eq. (2.4). Linearizing about the difference coordinates of the density matrix element, evaluating the resulting Gaussian integral with respect to the difference coordinate and changing integration variables to obtain an initial value representation leads to the following approximation to the influence functional:

$$F_{\text{Boltzmann}}^{\text{class}}[s^\pm] = \int dx_0 \int dp_0 D_{\text{Boltzmann}}^{\text{class}}(x_0, p_0; s^\pm) e^{i\Phi_{\text{class}}(x_0, p_0; s^\pm)/\hbar}, \quad (2.12)$$

where

$$D_{\text{Boltzmann}}^{\text{class}}(x_0, p_0; s^\pm) = (2\pi\hbar)^{-1} Z_{\text{cl}}^{-1} e^{-\beta p_0^2/2m - \beta V(x_0, x_0)} \quad (2.13)$$

is recognized as the classical Boltzmann factor.

Equations (2.8)–(2.13) are quantum-classical expressions which may be used as a warrant for the particular situation of interest. For example, the Boltzmann-weighted density of Eq. (2.13), which provides the simplest form for sampling the phase space of the bath, is sufficiently accurate at high temperature. The use of this classical weight in the path integral expression is analogous to a single-bead treatment of the heavier atoms in equilibrium path integral calculations, where only the coordinates of light particles are quantized in terms of multiple path integral beads. The two quasiclassical expressions allow full quantization of the density, accounting for zero point energy effects that may be important for light atoms and/or at low temperatures. Of these, the coherent state expression is easier to quantize using an imaginary time path integral method with multiple beads.\textsuperscript{43} The Wigner-weighted expression produces the exact influence functional at any temperature for a harmonic bath, but the Wigner transform is considerably harder to evaluate accurately in the case of an anharmonic many-particle Hamiltonian. (However, we note that some accurate and practical procedures for this task have recently become available.\textsuperscript{44,45}) The main difference between these quantum-classical approximations and the quantum-semiclassical FBSD expression is that the semiclassical influence functional, Eq. (2.5), involves trajectories that experience the actual force exerted by the
system in its instantaneous quantum state, while the classical expressions employ the average of the forces in the two quantum states on the forward and backward paths. Thus, the quantum-semiclassical treatment should be more accurate in general, but its computational cost is somewhat higher.

Since integration of the classical equations of motion is much more efficient than full solution of the Schrödinger equation, the quantum-(semi)classical approximations to the path integral expression are very attractive for simulating the quantum-classical time-dependent self-consistent field (QCT) (or Monte Carlo) methods, which are subject to time-dependent forces specific to the particular combination of Newtonian trajectory of the bath, which is subject to time-dependent bath phase space density). The quantum influence function is well approximated by classical mechanics. Unlike widely employed quantum-classical wavefunction methods, where the force experienced by the classical trajectory is averaged with respect to the wavefunction of the quantum particle, the quantum-(semi)classical path integral expressions (QCPI) allow a faithful description of the dynamics. For example, it is known that some versions of mean-field-type (also referred to as quantum-classical time-dependent self-consistent field) methods fail to account for the dynamics of linearly coupled harmonic oscillators or wavepacket splitting and tunneling, and that the analogous Ehrenfest model fails to predict correct branching ratios in avoided crossing models. By contrast, Eqs. (2.5) and (2.10) (and also Eqs. (2.8) and (2.12) at high temperature) produce the exact value of the reduced density matrix if the classical particles are described by a quadratic Hamiltonian linearly coupled to the system. With these considerations in mind we now turn to the evaluation of the reduced density matrix using a quantum-(semi)classical path integral approximation.

Employing the standard discretization of the path integral based on the Hamiltonian partitioning suggested by Eq. (2.1) with a time step \( \Delta t = t/N \), in conjunction with the influence functional approximations, leads to quantum-semiclassical or quantum-classical path integral expressions of the form

\[
\bar{\rho}(s_N^\pm, N \Delta t) = (2\pi \hbar)^{-1} \int ds_N^0 \int ds_1^\pm \cdots \int ds_{N-1}^\pm \int dx_0 \times \frac{dp_0(s_0^\pm \exp[-i\hat{H}_0\Delta t/k]|s_1^+ \cdots |s_{N-1}^\pm \exp[-i\hat{H}_0\Delta t/k]|s_N^0)}{D(s_0^\pm, p_0^\pm, s_1^\pm, \ldots, s_N^\pm)}/\hbar. \tag{2.14}
\]

(Note that in the case of the FBSD influence functional, the density function depends on the final trajectory values as well, but as discussed in Ref. 29, it can be separated into a part that depends only on initial conditions and another part that can be combined with the other integrand factors. For simplicity, we do not indicate that partitioning explicitly in Eq. (2.14).) These expressions involve a sum with respect to all discretized system paths and a phase obtained from the Newtonian trajectory of the bath, which is subject to time-dependent forces specific to the particular combination of forward-backward system paths.

The computational difficulty of evaluating the path integral is that the number of discretized system paths grows exponentially with the number of time steps, while the nonlocality of the influence functional prevents a simple step-by-step evaluation of the multidimensional integral. As a consequence, the required number of integrand evaluations quickly becomes prohibitively large, while Monte Carlo evaluation of the multidimensional integral with respect to the auxiliary path integral variables encounters extreme difficulties due to phase cancellation. An alternative approach has been developed by our group. The basic idea is to exploit the decoherence properties of polyatomic (harmonic or nonlinear) environments to convert the multidimensional path integral into a series of low-dimensional integrals which involve relatively short path segments that span the bath-induced nonlocality, allowing an iterative propagation of the reduced density matrix. In the case where the environment is quadratic (or may be mapped on an effective harmonic bath), iterative path integral-influence functional methods are both easy to implement and efficient. In cases of long bath-induced memory, filtering techniques and a recent path integral renormalization procedure offer substantial computational savings.

Switching the order of the integration variables and assuming for convenience of notation that the initial density factorizes, such that

\[
D(s_0^\pm, p_0^\pm, s_N^0) = \rho_{\text{red}}(s_0^\pm, 0)P(x_0, p_0). \tag{2.15}
\]

Equation (2.14) may be rewritten in the following form:

\[
\rho_{\text{red}}(s_N^\pm, N \Delta t) = \int dx_0 \int dp_0 \frac{P(x_0, p_0)Q(x_0, p_0; s_N^\pm)}{\rho_{\text{red}}(s_0^\pm, 0)}. \tag{2.16}
\]

(The factorized assumption is not essential and can be removed by moving the integration with respect to \( s_N^\pm \) that appears in Eqs. (2.16) and (2.17).) According to Eq. (2.16), the initial density is propagated via multiplication with the “quantum influence function” \( Q \), which contains all dynamical effects due to the interaction of the bath with the quantum system (which are responsible for the time evolution of the bath phase space density). The quantum influence function is given by the expression

\[
Q(x_0, p_0; s_N^\pm) = \int ds_0^\pm \int ds_{N-1}^\pm \int dx_N^0 \int dp_0 \frac{\exp[-i\hat{H}_0\Delta t/k]|s_N^\pm \cdots |s_1^+ \cdots |s_0^\pm)}{D_0(x_0, p_0; s_0^\pm)/\hbar}. \tag{2.17}
\]

This expression contains quantum amplitude factors for the system and phase factors for the interaction between quantum and classical particles, summed with respect to all paths of the quantum system.

III. CLASSICAL MEMORY, QUANTUM NONLOCALITY, AND NEAR-CLASSICAL CONDITIONS

Assuming the quantum influence function can be evaluated numerically, integration with respect to the phase space coordinates of the classical particles must be performed by Metropolis Monte Carlo methods. Because the phase of the FBSD or classical influence functional expression involves
the net forward-backward action, which tends to be small due to cancellation.29, 30 the integrand is not a highly oscillatory function of the phase space variables \( x_0, p_0 \). In addition, summation over the system paths smoothes this phase further, making the Monte Carlo evaluation of the integral in Eq. (2.16) very even practical even with hundreds of bath particles. (We revisit this point near the end of this section.) Thus, the main computational challenge is the evaluation of the quantum influence function, Eq. (2.17).

In the absence of interaction with the classical particles and with a factorized initial condition, Eq. (2.17) reduces to the discretized path integral for the quantum system. Because each variable \( s_{k}^{\pm} \) is coupled only to those with adjacent indices (i.e., to \( s_{k\pm 1}^{\pm} \)) in this case, one may evaluate the path sum iteratively (after discretizing the system coordinate) by performing a series of matrix-vector multiplications,

\[
\rho_{\text{red}}(s_{k+1}^{\pm}; (k + 1)\Delta t) = \int ds_k^{\pm} (s_k^{+1}|e^{-i\hat{H}_0\Delta t/\hbar}|s_k^{+}) \rho_{\text{red}}(s_k^{\pm}; k\Delta t)(s_k^{+} e^{i\hat{H}_0\Delta t/\hbar}|s_{k+1}^{\pm}).
\]

(3.1)

The absence of nonlocal couplings from the path integral expression for the bare system, which allows the iterative decomposition of Eq. (3.1), can be traced to the underlying time-dependent Schrödinger equation, which is local in time. The same locality exists in the presence of system-bath coupling if one works with the full Schrödinger equation for the system and bath, i.e., one may still evaluate the full (quantum mechanical) path integral via an iterative procedure for the wavefunction or density matrix of the composite system described by \( s \) and \( x \). On the other hand, a partial integration with respect to either of these degrees of freedom, which leads to influence functional descriptions27 (for example, Eq. (2.3)), destroys the local character of the dynamics, introducing distant couplings of the path integral variables which are commonly referred to as “memory.”

It is easy to see that a classical trajectory approximation to the bath dynamics, even if one works in the full space of system and bath coordinates, also introduces nonlocal effects. This is so because a classical trajectory depends on the coordinates of each forward-backward system path at all time points. If the quantum system is described by a grid of \( M \) coordinate values, there will be a total of \((M^2)^N\) trajectories emanating from a single initial phase space point upon propagation by \( N \) path integral time steps. (Note, of course, that the number of distinct force values due to the system coordinate may be somewhat smaller than \( M^2 \) in special cases because of symmetry, implying that a fraction of these trajectories may be identical. Still, the number of trajectories increases exponentially with the number of path integral steps.) This trajectory proliferation is the quantum-classical manifestation of time nonlocality. Below we explore the significance of this nonlocality in various regimes, in the interest of devising efficient strategies for evaluating the quantum influence function and the reduced density matrix of the quantum system.

It is useful to begin by understanding the connection between the apparent nonlocality of the classical trajectories in the quantum influence function and the memory/nonlocality in its integrated form, the influence functional. To this end, we consider the case where the classical particle experiences a harmonic potential and is linearly coupled to the quantum system, i.e.,

\[ V(s, x) = \frac{1}{2} m_b \omega^2 x^2 - c s x. \]

(3.2)

Its trajectory in the classical treatments (which involve the average of the forces along the forward and backward system paths) is given by the expression

\[ x(t) = \frac{p_0}{m_0\omega} \sin \omega t + \frac{c}{2 m_b \omega} \int_0^t dt' [s^+(t') + s^-(t')] \sin \omega(t - t'). \]

(3.3)

i.e., the trajectory depends on the entire history of the system path. This is the source of memory in the classical generalized Langevin equation.60 The relevant action integral is

\[ \Phi^\text{class}_b = \frac{c}{m_0} \int_0^t dt' [s^+(t') - s^-(t')] x(t'). \]

(3.4)

Substituting the trajectory expression in Eq. (3.4), the action becomes

\[ \Phi^\text{class}_b = c x_0 \int_0^t dt' [s^+(t') - s^-(t')] \cos \omega t' + \frac{p_0}{m_0\omega} \int_0^t dt' [s^+(t') - s^-(t')] \sin \omega t' + \frac{c^2}{2 m_b \omega} \int_0^t dt' \int_0^t dt'' [s^+(t') - s^-(t')] [s^+(t'')] + s^-(t'') \sin \omega(t' - t'')]. \]

(3.5)

Assuming a factorized initial condition with the bath at thermal equilibrium

\[ \rho(0) = \rho_{\text{red}}(0) Z_b^{-1} e^{-\beta \hat{H}_0}, \]

(3.6)

where \( \rho_{\text{red}}(0) \) is the initial density operator of the quantum system, \( \hat{H}_0 \) is the classical harmonic oscillator Hamiltonian, and \( Z_b \) is its partition function, the Wigner transform of the initial density has the form

\[ W(x_0, p_0; s^\pm) = (s_0^+ | \rho_{\text{red}}(0) | s_0^-)(\hbar \pi)^{-1} \left( \coth \left( \frac{\hbar \omega}{2} \right) \right) \times e^{-\frac{1}{2} e^{-\hbar \omega \beta} (m_0 \omega^2 / \hbar + p^2 / m_0 \omega)} . \]

(3.7)

It is straightforward to perform the Gaussian integral with respect to the phase space variables. The double time integral term in the action does not depend on the integration variables, so it remains in the result as a multiplicative factor. The terms that depend on the initial position and momentum of the bath give

\[ \exp \left[ -\frac{c^2}{4 m_b \omega \hbar} \coth \left( \frac{\hbar \omega}{2} \right) \left( \int_0^t dt' \Delta s(t') \cos \omega t' \right)^2 \right] \]

(3.8)

\[ + \left[ \int_0^t dt' \Delta s(t') \sin \omega t' \right]^2, \]

where

\[ \Delta s(t') = s^+(t') - s^-(t'). \]

(3.9)
Rewriting each quadratic term as a double integral and taking advantage of the form of the integrand to modify the upper limit of the inner integration variable, Eq. (3.8) becomes

\[
\exp \left[ -\frac{c^2}{2m\Phi_1}\coth \left( \frac{\hbar \omega}{2} \right) \int_0^t dt' \int_0^{t'} dt'' \Delta s(t') \Delta s(t'') \right] \times \left( \cos \omega t' \cos \omega t'' + \sin \omega t' \sin \omega t'' \right).
\] (3.10)

Recognizing the last factor as the cosine of the difference argument and combining Eq. (3.10) with the coordinate-free treatment of the quantum field as a classical oscillating dipole, one may separate the action into similar terms

\[
F_{\text{Wigner}}^{\text{class}} = \exp \left[ -\frac{1}{\hbar} \int_0^t dt' \int_0^{t'} dt'' \left[ s^+(t') - s^-(t') \right] \times \left[ \alpha(t' - t'')s^+(t'') - \alpha(t' - t'')s^-(t'') \right] \right],
\] (3.11)

where

\[
\alpha(t' - t'') = \frac{c^2}{2m\Phi_1} \left( \coth \left( \frac{\hbar \omega}{2} \right) \cos \omega(t' - t'') - i \sin \omega(t' - t'') \right).
\] (3.12)

Equation (3.11) is recognized as the standard Feynman-Vernon influence functional from a monochromatic harmonic bath. The extent of nonlocality is determined by the range of the kernel \(\alpha\), which is infinite in the case of a single harmonic oscillator because of the purely oscillating form of Eq. (3.12).

Even though both terms in Eq. (3.12) appear nonlocal in time, the memory associated with the real part of the influence functional is not present in its equivalent form, Eq. (3.8). Makri pointed out this fact in earlier work, noting that the nonlocality of the real part of the influence functional is of a classical origin and is removable through the introduction of auxiliary variables (which may be chosen as the bath trajectory coordinates). Since the real part dominates in the classical limit, one sees that the influence functional memory does not prevent a simple iterative evaluation of the path integral under near-classical conditions. The purely quantum mechanical imaginary part of the influence functional does not arise from memory-free classical driving and thus is truly nonlocal in this regard. In the classical limit, where the system coordinate is also treated via classical mechanics, the path integral-influence functional expression becomes the generalized Langevin equation, whose memory is removable via mapping to harmonic oscillator driving terms. In this case, complete removal of bath-induced memory is possible because of the local nature of the system classical trajectory. Under non-classical conditions, when the imaginary part contributes significantly to the influence functional, the time non-locality may be finite only by virtue of the self-decoherence properties of the bath, which in turn are determined by its frequency composition.

The real part of the influence functional originates from the coupling-independent part of the bath trajectory, which corresponds to the homogeneous solution of Hamilton’s differential equations in the case of a harmonic oscillator. In the absence of the inhomogeneous part, the trajectories are independent of the system path and are given by

\[
x_{\text{free}}(t) = x_0 \cos \omega t + \frac{p_0}{m\omega} \sin \omega t.
\] (3.13)

Thus, all trajectories arising from a given initial condition are identical if \(c = 0\), i.e., there is a single trajectory from each phase space point.

The behavior described above is not restricted to harmonic potentials. In the general case of a nonlinear bath, the unperturbed (free) bath trajectory still provides an excellent approximation to the actual trajectory under classical-like conditions.

Writing

\[
x(t) = x_{\text{free}}(t) + x_{\text{inter}}(t),
\] (3.14)

one may separate the action into similar terms

\[
\Phi_b^{\text{class}}(x_0, p_0; [s^+]) = \Phi_b^{\text{free}}(x_0, p_0; [s^+]) + \Phi_b^{\text{inter}}(x_0, p_0; [s^+]),
\] (3.15)

where

\[
\Phi_b^{\text{free}}(x_0, p_0; [s^+]) = -\int_0^t \left[ V(s^+(t'), x_{\text{free}}(t')) - V(s^-(t'), x_{\text{free}}(t')) \right] dt'
\] (3.16)

is a local (memory-free) action. All time nonlocality is in the “quantum” part \(\Phi_b^{\text{inter}}\). Upon integration, this part will give rise to a quantum mechanical contribution to the influence functional. In the case of a harmonic bath linearly coupled to the quantum system, this term is independent of initial conditions, leading to a temperature-independent contribution. Of course this term will not be independent of initial conditions in the case of a nonlinear bath, thus its contribution to the influence functional is generally expected to be (mildly) temperature-dependent.

The system-independent (“free bath”) trajectory, which leads to a local action, should provide an excellent approximation whenever the effects of the quantum system on the classical particle (the “back reaction”) are weak. As argued above, this is the case at high temperature, which causes the phase space density of the classical particle to be very broad and thus the energy and amplitude of oscillation to be very large for the majority of trajectories. Indeed, such a system-free trajectory treatment is commonly employed to simulate the effects of the radiation field as long as the number of photons (i.e., the field’s quantum number) is large, validating the treatment of the quantum field as a classical oscillating dipole for the purpose of studying absorption or stimulated emission of light. In the context of chemical dynamics, this approximation is often referred to as the classical path model.

At a fixed temperature and with specific bath parameters, the degree of trajectory deviation from the free bath limit depends on the magnitude of the system-bath coupling. Thus, even at relatively low temperatures, the system-free part of the solution to the classical equation of motion still dominates if the system-bath coupling is weak. In this situation, the classical path approximation (with different trajectories for each
positive and the Monte Carlo evaluation of the integral conditions the quantum influence function remains mostly positive, allowing efficient evaluation by Monte Carlo methods. The above remarks do not apply to a nonclassical path or random hop approximations. This implies that one must include explicitly the dependence of a classical trajectory on system paths beyond a single step. It is possible to devise such an iterative methodology, where the detailed force on a trajectory by the quantum system is felt up to \( m \) time steps, by iterating the matrix of the \( M^2 \times M^2 \) propagator matrix which amounts to the same computational effort as that required to propagate the quantum system. This random hop approximation is somewhat reminiscent of surface hopping methods, although the hops occur at specified times and no momentum/energy adjustment is made to the trajectory.

Nevertheless, when the effects of nonlocality are substantial, it will be necessary to include them beyond the classical path or random hop approximations. This implies that one must include explicitly the dependence of a classical trajectory on system paths beyond a single step. It is possible to devise such an iterative methodology, where the detailed force on a trajectory by the quantum system is felt up to \( m \) time steps, by iterating the matrix of the \( M^2 \times M^2 \) propagator matrix which amounts to the same computational effort as that required to propagate the quantum system. This random hop approximation is somewhat reminiscent of surface hopping methods, although the hops occur at specified times and no momentum/energy adjustment is made to the trajectory.

In light of the above analysis, we comment again on the dependence of the quantum influence function on the initial phase space coordinates. In the limit of a classical bath (or, equivalently, within the classical path QCPI approximation), this function is equal to the density matrix of the quantum system driven by a time-dependent external field which arises from the free bath trajectory. Thus, the trace of the quantum influence function equals unity in this approximation, and its diagonal elements are non-negative and cannot exceed unity. As a result, the integrand of Eq. (2.16) is smooth and positive, allowing efficient evaluation by Monte Carlo methods. The above remarks do not apply to a nonclassical bath. When quantum nonlocality is significant, the quantum influence function can have values that are negative or exceed unity, although its trace is always conserved. The larger spread of the integrand can lead to slower convergence of the Monte Carlo average. In practice, we find that under common conditions the quantum influence function remains mostly positive and the Monte Carlo evaluation of the integral converges very well.

IV. NUMERICAL ILLUSTRATIONS

In this section, we illustrate the nature of the dynamics in the near-classical or weak coupling limit, the effectively local character of the dominant influence functional contribution and the relatively minor role of nonlocality, which allow efficient evaluation of the QCPI expression. The observed behaviors are relevant to any (classical or semiclassical) QCPI formulation where the quantum system is treated by a full path integral while the dynamics of the bath particles is captured via classical trajectories. In this paper, we are not concerned with the relative accuracy of classical, quasiclassical or semiclassical treatments of the bath. Such comparisons will be reported in future work.

Our test model is the standard two-level system (TLS) coupled to a dissipative bath of harmonic oscillators, for which the system and bath terms of Eq. (2.1) are given by the expressions

\[
H_0 = -\hbar \Omega \sigma_x
\]

and

\[
H_b = \sum_j \left( \frac{\beta_j^2}{2m} + \frac{1}{2} m \omega_j^2 \hat{x}_j^2 - c_j \sigma_z \hat{x}_j \right),
\]

where \( \sigma_x \) and \( \sigma_z \) are the standard 2 \( \times \) 2 Pauli spin matrices. This Hamiltonian serves as a rich model for condensed phase tunneling and is frequently employed in the description of charge transfer between two equivalent sites. In this case, the two diagonal terms of the 2 \( \times \) 2 Hamiltonian matrix correspond to the two coupled diabatic potentials, which are assumed to be quadratic functions by virtue of the linear response approximation. The dynamics of the dissipative TLS (or a multi-level system interacting with a harmonic dissipative bath) can be evaluated efficiently to arbitrary accuracy using the iterative tensor multiplication methodology which is based on a finite-memory decomposition of the influence functional with the quasidiabatic partitioning of the system-bath propagators. We use the dissipative TLS model here only for convenience because it is amenable to accurate treatment for comparison, but it should be clear that the trajectory-based QCPI method is completely general and applicable to any anharmonic polyatomic bath. We choose the factorized initial condition

\[
\hat{\rho}(0) = |1\rangle \langle 1| \frac{e^{-\beta \hat{H}_b^{\text{free}}}}{\text{Tr} e^{-\beta \hat{H}_b^{\text{free}}}},
\]

where \( \hat{H}_b^{\text{free}} \) is the Hamiltonian of the bath in the absence of coupling to the system.

The parameters of the bath are collectively described by the spectral density function

\[
J(\omega) = \frac{\pi}{2} \sum_j \frac{\bar{c}_j^2}{m_j \omega_j} \delta(\omega - \omega_j).
\]

We use the common Ohmic form

\[
J(\omega) = \frac{1}{2} \pi \hbar \xi \omega e^{-\omega/\omega_c}.
\]

The dimensionless Kondo parameter \( \xi \) provides a measure of the dissipation strength (i.e., the magnitude of the system-bath coupling) and the maximum of the spectral density occurs at \( \omega_c \). The continuous bath is discretized into a sum of 60 oscillators whose frequencies and coupling coefficients are evaluated using a logarithmic discretization of
the iterative scheme described in detail in Paper II. Converged iterative QCPI calculation with quantum nonlocality spanning 5 path integral time steps. (Black line) Exact results obtained via the iterative path integral methodology based on the analytical Feynman-Vernon influence functional. The results of the classical path approximation and the random hop model are almost indistinguishable in this case.

The random hop QCPI calculation leads to values that spread somewhat outside this interval. The full inclusion of quantum nonlocality, obtained via the iterative QCPI methodology presented in Paper II. It is seen that the simple random hop model captures approximately half of the quantum correction with minor effort. Inclusion of these nonlocal interactions corrects the classical path approximation in a quantitative manner, and the converged QCPI results are in excellent agreement with those of the exact path integral calculation.

Figure 3 shows the quantum influence function corresponding to the population of state 1 at the phase space coordinates sampled during the Monte Carlo random walk. It is seen that the quantum influence function is always between zero and unity within the classical path QCPI approximation. The random hop QCPI calculation leads to values that spread somewhat outside this interval. The full inclusion of quan-
V. CONCLUDING REMARKS

Quantum-classical treatments may offer the only pragmatic approach for simulating the dynamics of complex condensed phase or biological systems with hundreds or thousands of atoms. The main theoretical challenge in this endeavor is to devise theoretical treatments that are rigorous, consistent, and practical. The difficulty in this regard lies in the nature of quantum mechanics, which is nonlocal and invokes delocalized wavefunctions, while classical theory is based on the local characteristics of trajectories. In this regard, Feynman’s path integral formulation of quantum mechanics provides the perfect common ground for the development of theoretically sound quantum-classical treatments that do not invoke any approximations beyond the use of Newton’s laws for the classical particles. However, evaluation of the path integral generally seems to present unsurmountable difficulties.

In this work, we have presented an analysis of the quantum-classical path integral, which suggests that the very nature of the classical assumption should make such calculations feasible. In the limit of a purely classical environment, a QCPI expression reduces to the ensemble average of a driven quantum system, which can be evaluated straightforwardly and efficiently. Quantum effects in the solvent manifest themselves as nonlocal contributions to the action, which lead to a proliferation of trajectories and seem to obviate an iterative evaluation of the path sum. If such quantum effects are minor, simple treatments such as a random hop model are able to capture some of these corrections. In the companion paper, we describe an iterative decomposition of the path sum, which allows full evaluation of the path integral with modest amounts of effort. Based on the excellent starting point offered by the form of the fully classical limit (i.e., the classical path approximation to the QCPI result), we suspect that simple and powerful tools for such calculations will become available. Work along these lines is in progress in our group.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation (NSF) under Award No. CHE 11-12422.

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