

Dynamics of reduced density matrices: Classical memory versus quantum nonlocality

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The nonlocality in the path integral description of the reduced density matrix for a system interacting with a classical harmonic bath can be eliminated through the introduction of auxiliary variables, leading to Markovian equations. By contrast, the presence of an imaginary part in quantum mechanical response functions appears to prohibit similar approaches, necessitating explicit treatment of quantum nonlocality. © 1998 American Institute of Physics.

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I. INTRODUCTION

Many situations in chemistry and physics invite partitioning the degrees of freedom into a low-dimensional system (e.g., a reaction coordinate) and a “bath” of uninteresting degrees of freedom which interacts with the observable system. Simple chemical reactions serve as a typical example, with the system chosen as the one-dimensional reaction coordinate (or a higher-dimensional reaction surface) while orthogonal molecular vibrations constitute the bath.¹ The system-bath decomposition is perhaps even more relevant in the case of condensed phase processes, where the large number of medium degrees of freedom prohibits explicit treatment. The goal of describing the evolution of a system in the presence of the coupled bath is best accomplished via reduced dimension approaches in which the uninteresting degrees of freedom are integrated out. In this context, the characteristics of the bath need to be specified only to the extent that they affect the dynamics of the system. In most theoretical descriptions the bath is modeled for simplicity as a collection of harmonic oscillators.

In spite of the dramatic simplification introduced through the elimination of the majority of participating degrees of freedom, the dynamics in the reduced dimension space of the system variables does not possess some of the appealing properties of the composite system-bath Hamiltonian. Perhaps the most obvious difference is the lack of energy conservation. Another distinct feature of reduced equations of motion is the loss of the Markovian character which governs the dynamics of the composite problem. In classical mechanics, Newton's differential equations are replaced upon integrating out the bath by the generalized Langevin equation (GLE).² Similarly, the quantum mechanical Schrödinger equation is replaced by expressions which are nonlocal in time³ and Markovian descriptions are obtained only by introducing approximations.⁴

An attractive, completely quantum mechanical description of the reduced density matrix (i.e., the density matrix averaged with respect to the harmonic bath) is obtained through Feynman's path integral formulation of time-dependent quantum mechanics.^{5,6} As a result of the interaction with the environment, the path integral for the quantum

particle of interest is augmented by an influence functional of system forward and backward paths which is nonlocal in time.³ This nonlocality, i.e., the effective range of the nonlocal influence functional interactions, is governed by the force autocorrelation function of the harmonic bath and prevents factorization of the path integral or, equivalently, conversion into a differential equation. In an illuminating paper⁷ Caldeira and Leggett showed that the influence functional interactions become delta functions of the time difference in the case of a strictly Ohmic dissipative bath⁷ at infinite temperature, such that one can recover the ordinary Langevin equation. Away from that limit the influence functional is nonlocal. If the bath corresponds to a macroscopic environment characterized by a continuous spectrum its correlation function decays to zero (typically as a power law), and thus the effective range of nonlocal interactions is for all practical purposes finite. Based on this feature, a decomposition of the path integral has been proposed⁸⁻¹² which leads to quasi-Markovian dynamics for an appropriate multitime reduced density matrix and thus to an iterative procedure. This scheme converges to the exact result as the correlation time treated explicitly increases. By contrast, a low-dimensional bath consisting of a few molecular normal mode vibrations cannot afford such treatment because of persisting recurrences in its correlation function.

This paper is concerned with the nature of memory effects in the quantum mechanics of reduced dimension quantities arising via elimination of a harmonic bath. Starting from the path integral formulation of the reduced density matrix, in which the effects of the bath enter via a nonlocal influence functional, we examine the character of the nonlocal interactions in the limit where the bath is treated classically. We show that the classical limit of the influence functional achieves a convenient decomposition which leads to a Markovian equation of motion for an augmented reduced density matrix that includes auxiliary variables. This property holds *exactly*, even though the characteristic correlation length of the bath is infinite. In this sense, memory effects arising from a classical bath are local, in contrast to those resulting from a bath of quantum mechanical nature.

The next section develops these ideas and describes pro-

cedures for classical memory elimination in the context of the path integral expression for the reduced density matrix. Brief concluding remarks appear in the last section.

II. THEORY

Throughout this article we restrict attention to the following system-bath Hamiltonian:

$$H = \frac{p_s^2}{2m_0} + V_0(s) + \sum_{j=1}^n \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 x_j^2 - c_j s x_j. \quad (2.1)$$

Here s is the coordinate of the system of interest which is coupled to a harmonic bath of n degrees of freedom x_j characterized by the frequencies ω_j . The system-bath interaction is chosen to be bilinear.

The object of interest is the reduced density matrix of the quantum system,

$$\langle s'' | \tilde{\rho}(t) | s' \rangle \equiv \text{Tr}_b \langle s'' | e^{-iHt/\hbar} \rho(0) e^{+iHt/\hbar} | s' \rangle. \quad (2.2)$$

Here $\rho(0)$ is the initial density operator of the composite system and the trace is with respect to the bath. For a bath at a temperature $T = 1/k_B\beta$, and if the system and bath are initially uncorrelated, i.e., assuming that

$$\rho(0) = \tilde{\rho}(0) \frac{e^{-\beta H_b}}{Z}, \quad (2.3)$$

where Z is the canonical partition function, the reduced density matrix of the system can be brought into the following path integral form:

$$\begin{aligned} \langle s'' | \tilde{\rho}(t) | s' \rangle &= \int \mathcal{D}s^+ \int \mathcal{D}s^- \exp(i\Phi_0[s^+]/\hbar) \\ &\times \exp(-i\Phi_0[s^-]/\hbar) \langle s_0^+ | \tilde{\rho}(t) | s_0^- \rangle F[s^+, s^-]. \end{aligned} \quad (2.4)$$

Here s^+ and s^- are system forward and backward paths with end points $s^\pm(0) = s_0^\pm$, $s^+(t) = s''$ and $s^-(t) = s'$ arising from the path integral representation of the positive- and negative-time evolution operators in Eq. (2.2), Φ_0 is the action of the isolated system and F is an influence functional which contains the effects on the system due to its interaction with the bath:³

$$\begin{aligned} F[s^+, s^-] &= \exp\left(-\frac{1}{\hbar} \int_0^t dt' \int_0^{t'} dt'' (s^+(t') - s^-(t')) \right. \\ &\quad \left. \times (\alpha(t' - t'') s^+(t'') - \alpha^*(t' - t'') s^-(t''))\right) \end{aligned} \quad (2.5)$$

The function α entering the exponent of the influence functional is the force autocorrelation function of the harmonic bath:

$$\begin{aligned} \alpha(t' - t'') &= \frac{1}{\hbar} \sum_{j=1}^n \langle c_j x_j(t') c_j x_j(t'') \rangle_\beta \\ &= \sum_{j=1}^n \frac{c_j^2}{2m_j \omega_j} \left(\coth\left(\frac{1}{2}\hbar\omega_j\beta\right) \cos \omega_j(t' - t'') \right. \\ &\quad \left. - i \sin \omega_j(t' - t'') \right). \end{aligned} \quad (2.6)$$

This function couples the two time integration variables in Eq. (2.5), such that the reduced density matrix does not obey Markovian dynamics. Equations (2.4)–(2.6) are exact.

Finally, it is useful to express the path integral in discrete time form. In the limit $N \rightarrow \infty$ Eqs. (2.4) and (2.5) take the form

$$\begin{aligned} \langle s_N^+ | \tilde{\rho}(t) | s_N^- \rangle &= \int ds_0^+ \int ds_1^+ \cdots \int ds_{N-1}^+ \langle s_N^+ | e^{-iH_0\Delta t/\hbar} | s_{N-1}^+ \rangle \cdots \langle s_1^+ | e^{-iH_0\Delta t/\hbar} | s_0^+ \rangle \langle s_0^+ | \rho_0 | s_0^- \rangle \langle s_0^- | e^{iH_0\Delta t/\hbar} | s_1^- \rangle \cdots \\ &\quad \times \langle s_{N-1}^- | e^{iH_0\Delta t/\hbar} | s_N^- \rangle \exp\left(-\frac{1}{\hbar} \sum_{k'=0}^{N-1} \sum_{k''=0}^{k'} (s_{k'}^+ - s_{k''}^-) (\alpha_{k'k''} s_{k''}^+ - \alpha_{k'k''}^* s_{k''}^-)\right), \end{aligned} \quad (2.7)$$

where for notational simplicity the reduced density matrix is given as a function of the path end points s_N^\pm . Here $\Delta t = t/N$ is the time step and $\alpha_{k'k''}$ are coefficients that result from discretization of the double integral in Eq. (2.4). As will be seen below, the nonlocality in time can be eliminated if the bath is treated classically.

Consider first the case of a monochromatic bath ($n = 1$) of mass m_1 and frequency ω_1 coupled to the quantum mechanical system via the coupling coefficient c_1 . In the

limit $\hbar \rightarrow 0$ (or, equivalently, in the infinite temperature limit) the response function in Eq. (2.6) is purely real:

$$\lim_{\hbar \rightarrow 0} \langle c_1 x_1(t') c_1 x_1(t'') \rangle_\beta = \frac{c_1^2}{\beta m_1 \omega_1^2} \cos \omega_1(t' - t''). \quad (2.8)$$

Expanding the cosine of the time difference, the exponent of the influence functional becomes

$$\begin{aligned}
& - \frac{c_1^2}{m_1 \omega_1^2 \hbar^2 \beta} \int_0^t dt' \int_0^{t'} dt'' (\cos \omega_1 t' \cos \omega_1 t'' + \sin \omega_1 t' \sin \omega_1 t'') (s^+(t') - s^-(t')) (s^+(t'') - s^-(t'')) \\
& = - \frac{c_1^2}{2m_1 \omega_1^2 \hbar^2 \beta} \left[\left(\int_0^t (s^+(t') - s^-(t')) \cos \omega_1 t' dt' \right)^2 + \left(\int_0^t (s^+(t') - s^-(t')) \sin \omega_1 t' dt' \right)^2 \right]. \quad (2.9)
\end{aligned}$$

Due to the assumption of a monochromatic bath, the correlations in the classical influence functional span an infinite time length. However, by virtue of the above factorization, evaluation of the path integral does not require explicit treatment of nonlocal interactions; knowledge of the time-integrated weighted path difference determines its contribution to the path integral. This fact implies Markovian dynamics for an appropriate function. For convenience we return to the discrete time representation of the reduced density matrix, which using Eq. (2.9) becomes

$$\begin{aligned}
\langle s_N^+ | \tilde{\rho}(t) | s_N^- \rangle &= \int ds_0^\pm \int ds_1^\pm \cdots \int ds_{N-1}^\pm \langle s_N^+ | e^{-iH_0 \Delta t / \hbar} | s_{N-1}^+ \rangle \cdots \langle s_1^+ | e^{-iH_0 \Delta t / \hbar} | s_0^+ \rangle \langle s_0^+ | \rho_0 | s_0^- \rangle \langle s_0^- | e^{iH_0 \Delta t / \hbar} | s_1^- \rangle \cdots \\
&\quad \times \langle s_{N-1}^- | e^{iH_0 \Delta t / \hbar} | s_N^- \rangle \exp \left[- \frac{c_1^2}{2m_1 \omega_1^2 \hbar^2 \beta} \left(\sum_{k=1}^{N-1} \lambda_k (s_k^+ - s_k^-) + \frac{1}{2} \lambda_0 (s_0^+ - s_0^-) + \frac{1}{2} \lambda_N (s_N^+ - s_N^-) \right)^2 \right] \\
&\quad \times \exp \left[- \frac{c_1^2}{2m_1 \omega_1^2 \hbar^2 \beta} \left(\sum_{k=1}^{N-1} \mu_k (s_k^+ - s_k^-) + \frac{1}{2} \mu_0 (s_0^+ - s_0^-) + \frac{1}{2} \mu_N (s_N^+ - s_N^-) \right)^2 \right], \quad (2.10)
\end{aligned}$$

where

$$\lambda_k = \cos k \omega_1 \Delta t \quad \text{and} \quad \mu_k = \sin k \omega_1 \Delta t$$

are coefficients arising from a trapezoid rule discretization of the integrals. We define the function

$$\begin{aligned}
R_{\text{mc}}(s_{N-1}^\pm, q_1, q_2; N \Delta t) &= \int ds_0^\pm \int ds_1^\pm \cdots \int ds_{N-2}^\pm \langle s_{N-1}^+ | e^{-iH_0 \Delta t / \hbar} | s_{N-2}^+ \rangle \cdots \langle s_{N-2}^+ | e^{-iH_0 \Delta t / \hbar} | s_0^+ \rangle \langle s_0^+ | \rho_0 | s_0^- \rangle \\
&\quad \times \langle s_0^- | e^{iH_0 \Delta t / \hbar} | s_1^- \rangle \cdots \langle s_{N-2}^- | e^{iH_0 \Delta t / \hbar} | s_{N-1}^- \rangle \exp \left[- \frac{c_1^2}{2m_1 \omega_1^2 \hbar^2 \beta} \left(\sum_{k=1}^{N-1} \lambda_k (s_k^+ - s_k^-) + \frac{1}{2} \lambda_0 (s_0^+ \right. \right. \\
&\quad \left. \left. - s_0^-) + q_1 \right)^2 \right] \exp \left[- \frac{c_1^2}{2m_1 \omega_1^2 \hbar^2 \beta} \left(\sum_{k=1}^{N-1} \mu_k (s_k^+ - s_k^-) + \frac{1}{2} \mu_0 (s_0^+ - s_0^-) + q_2 \right)^2 \right], \quad (2.11)
\end{aligned}$$

which yields upon integration the reduced density matrix:

$$\begin{aligned}
\langle s_N^- | \tilde{\rho}(N \Delta t) | s_N^+ \rangle &= \int ds_{N-1}^\pm \langle s_N^+ | e^{-iH_0 \Delta t / \hbar} | s_{N-1}^+ \rangle \langle s_{N-1}^- | e^{iH_0 \Delta t / \hbar} | s_N^- \rangle \\
&\quad - 1 - | e^{iH_0 \Delta t / \hbar} | s_N^- \rangle \\
&\quad \times R_{\text{mc}} \left(s_{N-1}^\pm, \frac{1}{2} \lambda_N (s_N^+ \right. \\
&\quad \left. - s_N^-), \frac{1}{2} \mu_N (s_N^+ - s_N^-); N \Delta t \right). \quad (2.12)
\end{aligned}$$

Examination of Eq. (2.11) reveals that the function R_{mc} can be propagated forward in time according to the integral relation

$$\begin{aligned}
R_{\text{mc}}(s_N^\pm, q_1, q_2; (N+1) \Delta t) &= \int ds_{N-1}^\pm \langle s_N^+ | e^{-iH_0 \Delta t / \hbar} | s_{N-1}^+ \rangle \langle s_{N-1}^- | e^{iH_0 \Delta t / \hbar} | s_N^- \rangle \\
&\quad \times R_{\text{mc}}(s_{N-1}^\pm, q_1 + \lambda_N (s_N^+ - s_N^-), q_2 \\
&\quad + \mu_N (s_N^+ - s_N^-); N \Delta t). \quad (2.13)
\end{aligned}$$

Note that, in spite of the introduction of two auxiliary variables, the integrations involved in Eq. (2.13) are the same as those required to propagate the density matrix of the bare system.

Equations (2.12) and (2.13) are *exactly* equivalent to the discretized path integral expression, Eq. (2.10). The only error entering these equations is associated with the use of a

finite time step in the splitting of the system-bath time evolution operator. As a consequence, Eq. (2.12) with R_{mc} propagated according to Eq. (2.13) approaches the exact result with decreasing time step.

According to Eq. (2.13), the function R_{mc} , defined as an extension of the reduced density matrix which depends on two auxiliary variables, obeys Markovian dynamics. The apparent time nonlocality of the influence functional in the full path integral expression has been replaced by spatial nonlocality in the new variables. In fact, the effective range of the auxiliary variables may be substantial, although by virtue of

Eq. (2.11) it exhibits Gaussian decay for any finite value of the system-bath coupling. In the special case where the bath is not coupled to the system, the q_1 and q_2 variables are redundant and Eq. (2.11) can be solved on any finite range for these variables.

The above procedure can be extended to a dissipative bath characterized by a spectral density

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{m_j \omega_j} \delta(\omega - \omega_j) \quad (2.14)$$

by replacing the variables q_1, q_2 by functions:

$$\begin{aligned} R(s_{N-1}^\pm, q_1(\omega), q_2(\omega); N\Delta t) = & \int ds_0^\pm \int ds_1^\pm \cdots \int ds_{N-2}^\pm \langle s_{N-1}^+ | e^{-iH_0\Delta t/\hbar} | s_{N-2}^+ \rangle \cdots \langle s_1^+ | e^{-iH_0\Delta t/\hbar} | s_0^+ \rangle \langle s_0^+ | \rho_0 | s_0^- \rangle \\ & \times \langle s_0^- | e^{iH_0\Delta t/\hbar} | s_1^- \rangle \cdots \langle s_{N-2}^- | e^{iH_0\Delta t/\hbar} | s_{N-1}^- \rangle \exp \left[-\frac{1}{2\pi\hbar} \int_0^\infty d\omega J(\omega) \coth \left(\frac{1}{2} \hbar \omega \beta \right) \right. \\ & \times \left(\sum_{k=1}^{N-1} \lambda_k(\omega) (s_k^+ - s_k^-) + \frac{1}{2} \lambda_0(\omega) (s_0^+ - s_0^-) + q_1(\omega) \right)^2 \left. \right] \exp \left[-\frac{1}{2\pi\hbar} \right. \\ & \times \left. \int_0^\infty d\omega J(\omega) \coth \left(\frac{1}{2} \hbar \omega \beta \right) \left(\sum_{k=1}^{N-1} \lambda_k(\omega) (s_k^+ - s_k^-) + \frac{1}{2} \lambda_0(\omega) (s_0^+ - s_0^-) + q_2(\omega) \right)^2 \right], \end{aligned} \quad (2.15)$$

where

$$\lambda_k(\omega) = \cos k\omega\Delta t \quad \text{and} \quad \mu_k(\omega) = \sin k\omega\Delta t.$$

Propagation follows Eq. (2.13).

In the classical limit the bath response function becomes proportional to the friction kernel $\eta(t)$ entering the generalized Langevin equation,

$$\lim_{\hbar \rightarrow 0} \alpha(t) = \frac{1}{\hbar\beta} \eta(t). \quad (2.16)$$

In certain situations, further factorization of the dissipative influence functional is possible which reduces R to a simple function. Consider, for example, a bath characterized by a friction kernel of the type

$$\eta(t) = 1 - \frac{t^2}{\tau^2} \quad (2.17)$$

for $t \ll \tau$. A procedure similar to that described for a monochromatic bath leads again to iterative propagation for a function that depends on a small number of auxiliary variables. Finally, in the limit of a frozen bath ($\omega_j \rightarrow 0$) the response function becomes independent of time as the bath loses its dynamical character¹³ and iterative dynamics is achieved with the aid of a single auxiliary variable.

III. CONCLUDING REMARKS

The main point of this work concerns the character of nonlocal interactions entering the equation of motion characterizing the dynamics of reduced dimension quantities. In

classical mechanics, the position of the observable system obeys the generalized Langevin equation which involves the history of the trajectory weighted by the friction kernel. In the special case of a truly Ohmic bath the friction kernel becomes a delta function and the equation of motion reverts to the memoryless Langevin equation. However, it is known that memory effects can be formally eliminated under certain circumstances even if the memory kernel spans a nonzero time interval. This is accomplished by coupling the system to auxiliary classical variables.^{14,15}

Similar conclusions hold for the memory interactions originating from a classical bath coupled to a quantum mechanical system. Even when the range of the nonlocal interactions is very large, Markovian equations result for a bath composed of a sum of single-frequency modes and also for baths characterized by appropriate spectral densities. Note that Markovian evolution results for a reduced density matrix which is augmented by spectator variables that are not integrated over.

By contrast to this situation, the nonlocal interactions associated with the imaginary part of the response function, which arise from a quantum mechanical bath, do not appear to be amenable to such treatment. Even in the case of a classically memoryless, strictly Ohmic bath, reduction to a local equation is feasible only in the infinite-temperature limit.

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