Iterative evaluation of the path integral for a system coupled to an anharmonic bath

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An iterative algorithm is presented for evaluating the path integral expression for the reduced density matrix of a quantum system interacting with an anharmonic dissipative bath whose influence functional is obtained via numerical methods. The method allows calculation of the reduced density matrix over very long time periods. © *1999 American Institute of Physics.*
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In spite of persistent efforts, the problem of calculating the quantum time evolution of a wave-function or density matrix in a multidimensional Hamiltonian remains unsolved. Recent work has revolved around methods based on mean field, quantum-classical, or semiclassical ideas. The most rigorous of these approaches, semiclassical evolution with the Van Vleck propagator,[1,2] is often highly accurate,[3–8] yet extremely demanding numerically because it requires multi-dimensional integration of oscillatory functions as well as evaluation of a prefactor that scales nonlinearly with the number of particles. Current efforts to make it practical exploit filtering techniques,[9–11] the self-cancellation achieved via combined forward–backward propagation,[12–16] or formulations which avoid calculation of the prefactor.[11,17–19] While these approaches appear promising, they are bound to fail at long propagation times or if tunneling effects are prominent.[20] Treatment at a higher level becomes necessary in such situations.

In a series of papers by our group, we have argued that the path integral-influence functional formulation of quantum dynamics[21,22] offers significant advantages when dealing with large-dimensional problems. One begins by identifying the observable ''system'' [the degree(s) of freedom s being probed in the calculation] and the remaining ''bath'' degrees of freedom $\mathbf{x}$ which interact with the system and thus affect its dynamics but whose precise state is not followed. Thus, the Hamiltonian is split into two terms,

$$H \equiv H_0(s, p_s) + H_b(\mathbf{x}, \mathbf{p}, s). \tag{1}$$

Expressing the full propagator as a path integral, and collecting all bath variables into an influence functional, one arrives at a formal path integral representation where only paths of the low-dimensional system are summed over. For example, the reduced density matrix of the system takes the form

$$\tilde{\rho}(s', s''; t) \equiv \mathrm{Tr}_b \langle s'' | \rho(t) | s' \rangle$$
$$= \int \mathscr{D}s_+ \int \mathscr{D}s_- \exp\left(\frac{i}{\hbar} S_0[s_+]\right)$$
$$\times \exp\left(-\frac{i}{\hbar} S_0[s_-]\right) F[s_+, s_-]. \tag{2}$$

Here, s_+, s_- are forward and backward paths of the observable system respectively, S_0 is the corresponding action, and the influence functional is given by the expression

$$F[s_+, s_-] = \mathrm{Tr}_b(U_b[s_+]\rho(0)U_b^{-1}[s_-]), \tag{3}$$

where U_b is the time evolution operator of the bath along a chosen system path. Note that the time parametrization of these paths makes the bath Hamiltonian time-dependent.

There are numerous advantages of this representation, as well as severe obstacles. The explicit form of the influence functional—an intrinsically quantum mechanical quantity not obtainable by classical molecular dynamics methods—is not available except in very restrictive situations, the most notable of which is the case of a harmonic bath.[22] Yet the simple structure of the influence functional, where the only operators appearing are the time propagators and the initial density matrix, implies that its evaluation may require less work than that required to obtain the full quantum dynamics for the same number of particles. Further, the consistency of the bath in terms of spectator coordinates implies that its dynamics may be treated at a less rigorous level than that of the observable system, i.e., errors due to approximate treatment of the influence functional are expected to affect the result in a less significant way compared to the error that would arise if a similar approximation were used to propagate the observable system. The semiclassical approximation lends itself naturally to this goal: it keeps track of quantum mechanical phases rather faithfully and its forward–backward version[12,13] is ideally suited. Thus, assuming that the influence functional from a sufficiently large environment can be computed numerically, one is confronted with the problem of evaluating the remaining path integral with respect to the system. Monte Carlo sampling of paths fails

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as the integrand is a highly oscillatory multidimensional function, while explicit enumeration of paths is feasible only for short times. The only remaining avenue seems to be an iterative formulation. The iterative evaluation of the path integral has proved a very fruitful method in the case of a harmonic dissipative bath;[23–26] its extension to general anharmonic environments is undertaken in the present letter.

Since we aim at a numerical propagation method, we switch to the discretized path integral representation, in which the reduced density matrix takes the form

$$\tilde{\rho}(s_N^-, s_N^+; t)$$

$$= \int ds_0^\pm \int ds_1^\pm \cdots \int ds_{N-1}^\pm \langle s_N^+ | e^{-iH_0\Delta t/\hbar} | s_{N-1}^+ \rangle \cdots$$

$$\times \langle s_1^+ | e^{-iH_0\Delta t/\hbar} | s_0^+ \rangle \langle s_0^- | e^{iH_0\Delta t/\hbar} | s_1^- \rangle \cdots$$

$$\times \langle s_{N-1}^- | e^{iH_0\Delta t/\hbar} | s_N^- \rangle F(s_0^\pm \ldots, s_N^\pm). \tag{4}$$

If the bath is harmonic, the influence functional is an exponential of a quadratic form.[22] In the case of a general anharmonic environment, F may contain multiple-site interactions, as described in the cumulant expansion of the influence functional,[27]

$$F(s_0^\pm s_1^\pm \ldots s_N^\pm) = \exp \left\{ - \sum_{k_1=0}^{N} (\alpha_{k_1}^+ s_{k_1}^+ + \alpha_{k_1}^- s_{k_1}^-) \right.$$

$$- \sum_{k_1=0}^{N} \sum_{k_2=0}^{N} (\beta_{k_1 k_2}^{++} s_{k_1}^+ s_{k_2}^+ + \beta_{k_1 k_2}^{+-} s_{k_1}^+ s_{k_2}^- + \cdots)$$

$$- \sum_{k_1=0}^{N} \sum_{k_2=0}^{N} \sum_{k_3=0}^{N} (\gamma_{k_1 k_2 k_3}^{+++} s_{k_1}^+ s_{k_2}^+ s_{k_3}^+$$

$$\left. + \gamma_{k_1 k_2 k_3}^{++-} s_{k_1}^+ s_{k_2}^+ s_{k_3}^- + \cdots) - \cdots \right\}. \tag{5}$$

As shown in Ref. 27, the coefficients in this expansion are given by multitime correlation functions of the force exerted on the system due to its interaction with the bath. Such correlation functions decay irreversibly if the environment is macroscopic. As a consequence, the nonlocal interactions in the influence functional arising from condensed media have finite range. If the expansion coefficients are known, it is a straightforward matter of extending the harmonic bath methodology developed in our group to devise an iterative procedure for evaluating the evolution of the reduced density matrix.

However, the expansion coefficients in Eq. (5) are not known in general. In a classical treatment of the bath, low-order terms in the series can be obtained by molecular dynamics simulations. The latter is costly and the evaluation of terms beyond the two-time correlation function is extremely demanding. Further difficulties are the required determination of imaginary parts and the inability to test the accuracy of the classical approximation. An alternative approach which we have considered is to evaluate the entire influence functional for each set of system paths numerically using forward-backward semiclassical dynamics (FBSD).[12,13] This approach is superior because it is not restricted to low-order terms in the cumulant expansion, is capable of describing the quantum behavior of the bath, and yields the real and imaginary parts of the influence functional in a single calculation. Although a numerically constructed influence functional does not assume the form of a systematic series expansion, it is shown below that it can still be cast in a form suitable for iterative propagation.

As in the case of a harmonic bath,[26] the scheme proceeds via multiplication of an array $\mathbf{R}$ of path segments that span the memory length by a propagator matrix $\mathbf{T}$. The memory length $\tau_m \equiv \Delta k_{\max} \Delta t$ (where $\Delta k_{\max}$ is an integer), given roughly by the decay time of the bath correlation functions, plays the role of a convergence parameter in the calculation. We define path segments

$$l_i^\pm \equiv \{s_1^\pm, s_2^\pm, \ldots, s_{\Delta k_{\max}}^\pm\}_i, \tag{6}$$

and the propagator matrix between the ''old'' path segment i and the ''new'' path segment j,

$$T_{ij}(n\Delta k_{\max}) \equiv T((s_{n\Delta k_{\max}}^\pm, s_{n\Delta k_{\max}+1}^\pm, \ldots, s_{(n+1)\Delta k_{\max}-1}^\pm)_i, (s_{(n+1)\Delta k_{\max}}^\pm, \ldots, s_{(n+2)\Delta k_{\max}-1}^\pm)_j)$$

$$= \prod_{k=n\Delta k_{\max}+1}^{(n+1)\Delta k_{\max}} \langle s_{k-1}^+ | e^{-iH_0\Delta t/\hbar} | s_k^+ \rangle \langle s_k^- | e^{iH_0\Delta t/\hbar} | s_{k-1}^- \rangle$$

$$\times \frac{\tilde{F}(s_{n\Delta k_{\max}}^\pm, \ldots, s_{(n+1)\Delta k_{\max}-1}^\pm, s_{(n+1)\Delta k_{\max}}^\pm, \ldots, s_{(n+2)\Delta k_{\max}-1}^\pm)}{\tilde{F}(0, \ldots, 0, s_{(n+1)\Delta k_{\max}}^\pm, \ldots, s_{(n+2)\Delta k_{\max}-1}^\pm)}. \tag{7}$$

Here, the tilde indicates that the influence functionals must be evaluated with the proper boundary conditions: In order to include all the proper interactions for continued propagation, the old–new path pair is extended in one or both directions, i.e.,

$$\tilde{F}[l_i, l_j] \equiv \mathrm{Tr}_b(U^{(0)} U[l_j^+] U[l_i^+]$$

$$\times \rho(0) U^{-1}[l_i^-] U^{-1}[l_j^-] U^{(0)^{-1}}), \tag{8}$$

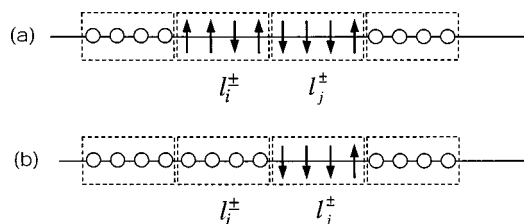where $U^{(0)}$ signifies time evolution with the bath Hamil-

FIG. 1. Schematic representation of two system path segments and additional memory erasing segments for constructing the influence functionals required for the (a) numerator and (b) denominator of the midtime propagator. The system has two states indicated as up- or down-arrows which determine the force exerted on the bath. The circles correspond to propagation with the isolated bath Hamiltonian.

tonian in the absence of system–bath interactions. According to Eq. (8), the influence functional entering the midtime propagator is given by evolving the initial density matrix by one memory length under the influence of the force along the system path segment l_i^+, subsequently evolving under the force due to l_i^+, followed by propagation with the isolated bath Hamiltonian by one more memory length and by the entire series of operations in reverse order in the backward time direction. The time lengths and forces involved in the calculation of $\widetilde{F}$ are shown in Fig. 1. Finally, the denominator in Eq. (7) involves the same sequence of operations but with $U[l_i^{\pm}]$ replaced by $U^{(0)}$. It is straightforward to show that successive multiplication with the propagator defined in Eq. (7) reproduces the exact dynamics of Eq. (4) subject to the assumption of finite memory length.

   After the first propagation step, the propagator matrix can be stored and used for successive iterations. This is so because the influence functional is *translationally invariant*, i.e., the $\widetilde{F}$ calculated from a given pair of path segments remains unchanged if additional zero-force segments are attached to either or both ends of Eq. (8), as long as $l_i^{\pm}$ are not too close to endpoints. This property is a consequence of dephasing and can be exploited to achieve dramatic computational savings.

   The details of the algorithm will be presented in a future publication.[28] Here, we illustrate the scheme by presenting the long-time dynamics of a two-level system (TLS) coupled to a nonlinear bath of 50 two-level systems according to the Hamiltonian

$$H = -\hbar\Omega\sigma_x^0 - \sum_{i=1}^{n} \frac{1}{2}\hbar\omega_i\sigma_x^i - \sigma_z^0\sum_{i=1}^{n} c_i \sqrt{\frac{\hbar}{2\omega_i}}\sigma_z^i. \quad (9)$$

In the last equation, σ_x and σ_z are the usual Pauli spin matrices, the tunneling splittings are $2\hbar\Omega$ and $\hbar\omega_i$ for the bare system and the bath spins, respectively, and the parameters of the bath are specified from the spectral density function of the Ohmic form,[29]

$$J(\omega) = \frac{\pi}{2}\sum_{i=1} \frac{c_i^2}{\omega_i}\delta(\omega-\omega_i) = \frac{\pi}{2}\hbar\xi\omega e^{-\omega/\omega_c},$$

with $\omega_c = 6\Omega$. Further, we assume that the interaction between system and bath is turned on at $t=0$, at which time the system is in the ''up'' state and that the bath is prepared at the temperature $1/k_B\beta$. The discrete character of H_0 turns
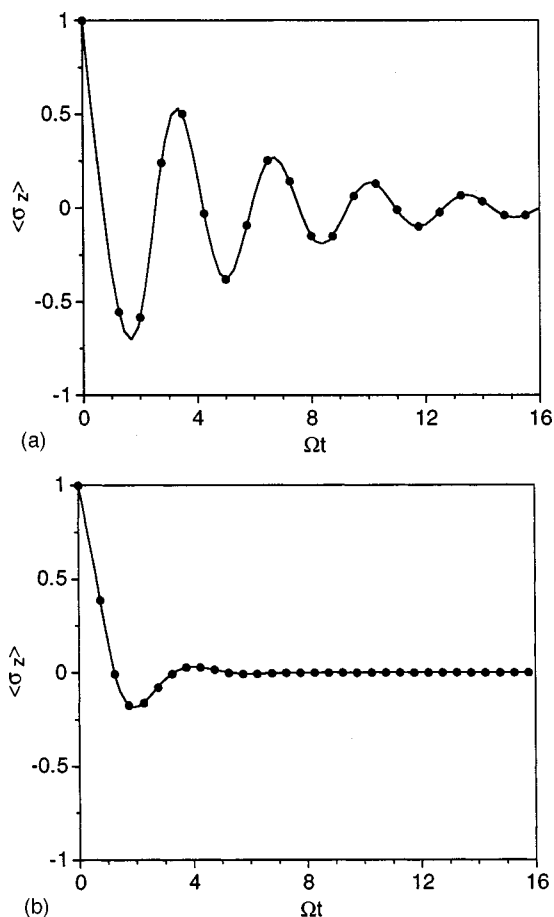

FIG. 2. Expectation value of the TLS position as a function of time as obtained with the iterative scheme described in this letter. (a) $\hbar\Omega\beta=2$, $\xi=0.1$ and $\hbar\Omega\beta=0.05$, $\xi=0.5$.

the integrals in Eq. (4) into sums. In the present situation, the influence functional factorizes and is computed exactly by the matrix multiplication method.[30]

   Figure 2 shows the evolution of the average position of the observable TLS as calculated by iterative evaluation of the path integral for $\hbar\Omega\beta=2$, $\xi=0.1$ and $\beta=0.05$, $\xi=0.5$. The path integral time step is $\Delta t = 0.25 \ \Omega^{-1}$ and the memory length is $\tau_m = 3\Delta t$. The total propagation time equals 60 elementary time steps. At these long times, full evaluation of the path integral by global summation is not feasible, but at short times the present results are in good agreement with those reported in Ref. 31.

   In summary, it is possible to formulate an iterative scheme for evaluating the path integral of a low-dimensional system coupled to a general dissipative bath if the influence functional of the latter can be calculated at some level of approximation. Use of this idea in conjunction with the FBSD methodology for evaluating anharmonic influence functionals will lead to a powerful approach to the dynamics of polyatomic chemical systems. The combined path integral-semiclassical treatment offers two distinct advantages compared to fully semiclassical schemes: it avoids treating the important, highly quantum mechanical system of interest via the semiclassical approximation; and the semiclassical evaluation of the influence functional requires only short-time dynamics, over which FBSD is likely to be ex-

tremely accurate. Future publications will exploit these ideas in the context of solvation dynamics.

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