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Semiclassical influence functionals for quantum systems in anharmonic environments ¹

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Abstract

A rigorous semiclassical methodology for calculating influence functionals arising from polyatomic anharmonic environments is presented. Integration of each trajectory forward and backward in time reduces the severity of the oscillations in the semiclassical propagator, namely those originating from the dynamics of the isolated environment, and leads to a convenient coherent state initial value representation which is amenable to Monte Carlo sampling. The advantages of this formulation are illustrated through an example employing a harmonic oscillator bath. © 1998. Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The development of simulation methods capable of correctly accounting for quantum mechanical effects continues to lie at the forefront of theoretical chemistry. With the exception of systems coupled to harmonic media, intramolecular energy transfer via sparse matrix techniques and limited applications of the maximum entropy method, rigorous quantum mechanical calculations are currently feasible on systems of only a few degrees of freedom. The main reason for this limitation is the exponential growth with dimension of basis set size required for solving the Schrödinger equation and the analogous prolifer-

ation of Feynman paths in the path integral formulation of quantum dynamics. The simulation of larger systems (clusters or condensed-phase processes) where interesting chemistry takes place has in the past relied on approximations, perhaps the most common of which are schemes combining quantum and classical methods.

An attractive alternative to a fully quantum mechanical description is offered by time-dependent semiclassical theory. The last few years have seen a revival of semiclassical ideas in time-dependent calculations formulated in terms of initial value representations [1–7]. Although approximate by nature, the Van Vleck expression for the propagator provides a rigorous alternative to the full time-dependent Schrödinger equation which is accurate to first order in Planck's constant. No ad hoc assumptions are introduced, and the method is often sufficiently

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accurate in regimes of chemical relevance even for long times. Practical implementation, however, requires multidimensional integration of oscillatory functions, which is plagued by the seemingly ubiquitous sign problem. Recently, Miller and co-workers [8] presented linearized semiclassical approximations for calculating canonical rate constants in polyatomic systems, which appear very promising.

In the present Letter we explore the possibility of performing rigorous quantum-semiclassical calculations for a particle of interest (the ‘system’) coupled to several nearly classical degrees of freedom (the ‘bath’). It is assumed that only the system is observable and the environment is treated only to the extent that it affects the properties of the system. Alternatively, the last assumption can be employed to define the partitioning of the coordinates into system plus bath. We show that the trace operation associated with the above definition of the environment can give rise to an advantageous semiclassical representation of the bath dynamics in which explicit phase cancellation is minimal. Exploiting that structure, we propose a numerical scheme for calculating semiclassical influence functionals arising from rather general atomic or molecular environments of several degrees of freedom.

The semiclassical formalism is developed in Section 2, along with an outline of suitable Monte Carlo sampling methods. To illustrate the advantages of the derived expression, we evaluate it analytically in Section 3 for a harmonic oscillator bath and show that the undesirable oscillations present in conventional semiclassical methods are largely eliminated. We also show Monte Carlo results for the incoherent relaxation of an initially localized two-level system interacting with a bath of ten harmonic oscillators. The last section concludes with a summary and a future outlook.

2. Formalism

2.1. Semiclassical representation of the influence functional

Consider a Hamiltonian

$$H(s, p_s, q, p) \equiv H_0(s, p_s) + H_b(s, q, p) \quad (1)$$

describing a system of interest with coordinate s interacting with a generally nonlinear bath. We use one-dimensional notation for simplicity and represent the coordinate of the bath oscillator as q . It is assumed that the system–bath interaction does not depend on momentum terms. Restricting attention to measurements that do not probe the precise state of the bath introduces a trace in expressions representing the observable system. Use of Feynman’s path integral formulation of quantum mechanics [9] allows observables at a time t (averaged with respect to a canonical ensemble at a temperature $T = 1/k_b \beta$) to be expressed in terms of the influence functional [10].

$$F[s_+, s_-] = Z_b^{-1} \text{Tr}_b(U_b[s_+]G[s_{\text{im}}]U_b^{-1}[s_-]). \quad (2)$$

Here s_{\pm} are quantum or classical forward and backward paths for the system, s_{im} is a path in imaginary time and Z_b is the canonical partition function of the bath, while U_b and G are the real and imaginary time bath evolution operators along a chosen system path for propagation to time t and $-i\hbar\beta$, respectively. Evaluation of the trace in the coordinate representation and insertion of complete sets of position states brings Eq. (2) to the form

$$F[s_+, s_-] = Z_b^{-1} \int dq_0 \int dq \int dq' \langle q' | U_b[s_+] | q_0 \rangle \times \langle q_0 | G[s_{\text{im}}] | q \rangle \langle q | U_b^{-1}[s_-] | q' \rangle. \quad (3)$$

Rearrangement and elimination of the identity operator leads to the expression

$$F[s_+, s_-] = Z_b^{-1} \int dq_0 \int dq \langle q | U_b^{-1}[s_-] U_b[s_+] | q_0 \rangle \times \langle q_0 | G[s_{\text{im}}] | q \rangle. \quad (4)$$

It is convenient to describe the real time factor of the integrand in the above expression in terms of a single time evolution operator along the time contour displayed in Fig. 1. As time increments from zero to t , the bath evolves according to the Hamiltonian $H_b(q, p, s_+(t'))$ which is time-dependent by virtue of the coupling to the time-dependent forward system path. Subsequently, the time returns to zero as the bath dynamics follows $H_b(q, p, s_+(t'))$. In a

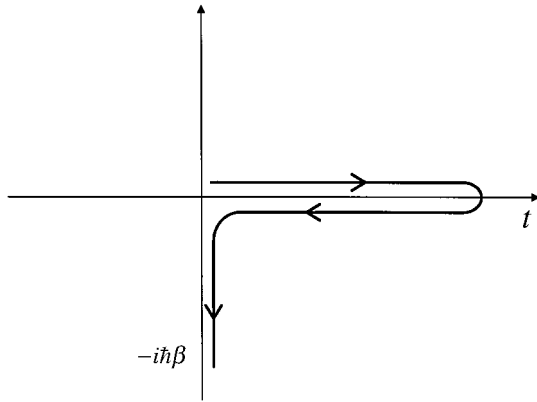


Fig. 1. Schematic representation of the time contour along which Eq. (4) is evaluated. The imaginary part of the contour is not included if the system and bath are initially uncorrelated.

numerical calculation where the real time system paths are discretized in terms of a small time step $\Delta t = t/N$ Eq. (4) becomes

$$\begin{aligned}
 F[s_+, s_-] &= Z_b^{-1} \int dq_0 \int dq \left\langle q \left| \exp\left(\frac{i}{\hbar} \frac{\Delta t}{2} H_b(s_-(0))\right) \right. \right. \\
 &\quad \times \exp\left(\frac{i}{\hbar} \Delta t H_b(s_-(\Delta t))\right) \\
 &\quad \times \exp\left(\frac{i}{\hbar} \frac{\Delta t}{2} H_b(s_-(N\Delta t))\right) \\
 &\quad \times \exp\left(-\frac{i}{\hbar} \frac{\Delta t}{2} H_b(s_+(N\Delta t))\right) \\
 &\quad \times \exp\left(-\frac{i}{\hbar} \Delta t H_b(s_+(\Delta t))\right) \\
 &\quad \times \exp\left(-\frac{i}{\hbar} \frac{\Delta t}{2} H_b(s_+(0))\right) \left. \right| q_0 \rangle \\
 &\quad \times \langle q_0 | G[s_{\text{im}}] | q \rangle, \tag{5}
 \end{aligned}$$

where only the parametric dependence of the Hamiltonian has been indicated explicitly.

The main advantage arising from the pairing of the two time evolution operators in Eq. (4) is elimination of the fast oscillations in the corresponding propagator. This is so because the backward propagation cancels approximately the terms originating from the bare bath propagator which are responsible

for rapidly changing phases. The remaining oscillations are associated with system–bath potential interactions. Still, in the classical limit where these paths coincide the corresponding time evolution operators cancel exactly, producing a delta function. This numerically undesirable singularity will be removed in the initial value representation adopted below. For simplicity we now assume that the system and bath are initially uncorrelated, so that Eq. (4) becomes

$$\begin{aligned}
 F[s_+, s_-] &= Z_{b,0}^{-1} \int dq_0 \int dq \langle q | U_b^{-1}[s_-] U_b[s_+] | q_0 \rangle \\
 &\quad \times \langle q_0 | e^{-\beta H_{b,0}} | q \rangle, \tag{6}
 \end{aligned}$$

where $H_{b,0}$ is the Hamiltonian of the isolated bath and $Z_{b,0}$ is the corresponding partition function. The general case of a bath that is equilibrated with respect to the system of interest can be treated via a straightforward (though slightly more cumbersome) extension of the procedure described below.

The goal is to evaluate the Boltzmann factor entering Eq. (6) quantum mechanically or via an acceptable approximation and to use the semiclassical expression for the real time component. To this end we seek an initial value representation of the influence functional. Noting that Eq. (6) can be rewritten formally in the form of a sum over bath eigenstates Φ_n with eigenvalues E_n ,

$$\begin{aligned}
 F[s_+, s_-] &= Z_{b,0}^{-1} \int dq_0 \sum_{n=0}^{\infty} e^{-\beta E_n} \langle \Phi_n | q_0 \rangle \\
 &\quad \times \langle q_0 | U_b^{-1}[s_-] U_b[s_+] | \Phi_n \rangle, \tag{7}
 \end{aligned}$$

and using the semiclassical coherent state representation of Herman and Kluk [2] for each basis function the influence functional becomes

$$\begin{aligned}
 F[s_+, s_-] &= Z_{b,0}^{-1} (2\pi\hbar)^{-1} \\
 &\quad \times \sum_{n=0}^{\infty} e^{-\beta E_n} \int dq_0 \int dp_0 \langle \Phi_n | G(q_f, p_f) \rangle \\
 &\quad \times D(q_0, p_0) \exp\left(\frac{i}{\hbar} S(q_0, p_0)\right) \\
 &\quad \times \langle G(q_0, p_0) | \Phi_n \rangle. \tag{8}
 \end{aligned}$$

Here q_f and p_f are the final coordinate and momentum for a classical trajectory with initial conditions

(q_0, p_0) which evolves under the action of the combined forward–backward time evolution operators that appear in Eq. (7), S is the corresponding action, and D is the coherent state analog of the Van Vleck determinant, given by expression [3].

$$D(q_0, p_0) = \frac{1}{\sqrt{2}} \left(\frac{\partial q_f}{\partial q_0} + \frac{\partial p_f}{\partial p_0} - 2i\hbar\gamma \frac{\partial q_f}{\partial p_0} + \frac{i}{2\hbar\gamma} \frac{\partial p_f}{\partial q_0} \right)^{1/2}. \quad (9)$$

Finally,

$$\langle q|G(q_0, p_0)\rangle = \sqrt{\frac{2\gamma}{\pi}} \exp\left(-\gamma(q - q_0)^2 + \frac{i}{\hbar}p_0(q - q_0)\right) \quad (10)$$

is a coherent state of momentum p_0 centered about q_0 . The width parameter γ is at this stage completely arbitrary.

The classical trajectories entering Eq. (8) obey Hamilton's equations

$$\dot{q}(t) = \frac{\partial H_b(t)}{\partial p}, \quad \dot{p}(t) = -\frac{\partial H_b(t)}{\partial q} \quad (11)$$

in the time-dependent bath Hamiltonian along the real time contour shown in Fig. 1 defined as

$$H_b(t') = \begin{cases} H_b(q, p, s_+(t')), & t' \uparrow \\ H_b(q, p, s_-(t')), & t' \downarrow \end{cases} \quad (12)$$

and the action is given by

$$S(q_0, p_0) = \int_0^t (p(t')\dot{q}(t') - H_b(t'))dt' + \int_t^0 (p(t')\dot{q}(t') - H_b(t'))dt'. \quad (13)$$

It is useful to note that all four terms entering Eq. (9) are elements of the stability matrix. If the second derivative of the bath potential is independent of the system coordinate the stability matrix returns to its initial value (the total elapsed time is equal to zero) and $D(q_0, p_0) = 1$. A Maslov phase arises in Eq. (8) if the quantity inside the square root of Eq. (9) turns

negative. For statistically significant combinations of forward and backward paths and/or for system–bath interaction forms that are only moderately nonlinear the backward part of the evolution cancels the largest change in the stability matrix, leading to a prefactor that is close to unity and an accompanying Maslov index that is equal to zero. Rearranging Eq. (8) and removing the bath eigenstates leads to the result

$$F[s_+, s_-] = Z_{b,0}^{-1}(2\pi\hbar)^{-1} \int dq_0 \int dp_0 D(q_0, p_0) \exp\left(\frac{i}{\hbar}S(q_0, p_0)\right) \times \langle G(q_0, p_0) | e^{-\beta H_{b,0}} | G(q_f, p_f) \rangle. \quad (14)$$

Eq. (14) is a rigorous semiclassical representation of the influence functional. For the reasons discussed below, this expression is in general amenable to Monte Carlo evaluation. Although the integrand of Eq. (14) is not strictly positive, the dominant terms in the action arising from the dynamics of the isolated bath (which are responsible for the highly oscillatory nature of the semiclassical propagator) cancel approximately because of the backward propagation. Most importantly, one can show that the oscillations are mild for statistically significant system paths. Indeed, if the forward and backward paths coincide, each trajectory simply retraces its steps during the second part of the time contour and returns to its initial phase space location and the total action integral equals zero. These advantageous features are a consequence of formulating the problem in the spirit of the improved propagator approach [11] in which only important interaction terms are treated explicitly.

2.2. Evaluation of the coherent state Boltzmann factor

To complete the prescription for evaluating the influence functional one needs an expression for the coherent state transform of the Boltzmann operator appearing in Eq. (14). Below we outline three meth-

ods which correspond to different levels of approximation:

2.2.1. High-temperature approximation

Using the Trotter splitting of the Boltzmann operator, the coherent state matrix element takes the form

$$\begin{aligned} & \langle G(q_0, p_0) | e^{-\beta H_{b,0}} | G(q_f, p_f) \rangle \\ & \approx \int dq \langle G(q_0, p_0) | e^{-\beta T_b/2} | q \rangle e^{-\beta V_b(q)} \\ & \quad \times \langle q | e^{-\beta T_b/2} | G(q_f, p_f) \rangle, \end{aligned} \quad (15)$$

where T_b is the bath kinetic energy operator and V_b is the potential for the isolated bath. The kinetic energy factors in Eq. (15) can be evaluated analytically, leading to the expression

$$\begin{aligned} & \langle G(q_0, p_0) | e^{-\beta H_{b,0}} | G(q_f, p_f) \rangle \\ & \approx \sqrt{\frac{2\gamma}{\pi}} \frac{m}{\hbar^2 \beta \gamma + m} \int dq \exp \left(-\frac{m}{\hbar^2 \beta \gamma + m} \right. \\ & \quad \times (\gamma(q - q_0)^2 + \gamma(q - q_f)^2 \\ & \quad + \frac{\beta}{4m}(p_0^2 + p_f^2) + \frac{i}{\hbar}(p_0 - p_f)q \\ & \quad \left. - \frac{i}{\hbar}(p_0 q_0 - p_f q_f) \right) - \beta V(q). \end{aligned} \quad (16)$$

2.2.2. Steepest descent evaluation of the high-temperature expression

If the coherent state parameter γ is sufficiently large, the Gaussian factor in the above equation decays much faster than the high-temperature potential part. Further, if $\gamma^{-1/2} \gg |q_0 - q_f|$ the two Gaussians overlap almost completely and one can expand the integrand about the midpoint $\frac{1}{2}(q_0 + q_f)$, leading to the result

$$\begin{aligned} & \langle G(q_0, p_0) | e^{-\beta H_{b,0}} | G(q_f, p_f) \rangle \\ & \approx \sqrt{\frac{m}{\hbar^2 \beta \gamma + m}} \exp \left(-\frac{m}{\hbar^2 \beta \gamma + m} \right. \\ & \quad \times \left(\frac{\beta}{4m}(p_0^2 + p_f^2) + \frac{i}{\hbar}(p_0 + p_f) \frac{q_0 - q_f}{2} \right. \\ & \quad \left. \left. - \beta V \left(\frac{q_0 + q_f}{2} \right) \right) \right). \end{aligned} \quad (17)$$

Note that although the above approximate evaluation follows the idea of the steepest descent method, the

quadratic nature of the rapidly decaying terms ensures uniqueness of the roots and the result can become arbitrarily accurate by choosing the coherent state parameter in the appropriate range.

2.2.3. Path integral evaluation

Finally, the coherent state Boltzmann factor can be expressed in terms of an imaginary time path integral in coordinate space. This procedure introduces additional integration variables which are to be treated (along with the phase space variables of Eq. (14)) via stochastic sampling. Because the high-temperature Boltzmann factors are real-valued in the coordinate representation, the auxiliary path integral variables are not expected to affect significantly the convergence of the sampling procedure.

2.3. Monte Carlo sampling

In the general case of a bath consisting of several coupled degrees of freedom Eq. (14) must be evaluated via Metropolis sampling. For concreteness we restrict attention to the high-temperature regime and adopt the first approach, Eq. (16). In this approximation the influence functional becomes

$$\begin{aligned} F[s_+, s_-] &= (2\pi\hbar)^{-1} \sqrt{\frac{2\gamma}{\pi}} \frac{m}{\hbar^2 \beta \gamma + m} Z_{b,0}^{-1} \\ & \quad \times \int dq_0 \int dp_0 \int dq D(q_0, p_0) \\ & \quad \times \exp \left(-\frac{m}{\hbar^2 \beta \gamma + m} (\gamma(q - q_0))^2 \right. \\ & \quad + \gamma(q - q_f)^2 + \frac{\beta}{4m}(p_0^2 + p_f^2) \\ & \quad + \frac{i}{\hbar}(p_0 - p_f)q - \frac{i}{\hbar}(p_0 q_0 - p_f q_f) \\ & \quad \left. - \beta V(q) + \frac{i}{\hbar} S(q_0, p_0) \right). \end{aligned} \quad (18)$$

It is convenient to employ a sampling function that depends only on the initial conditions of the bath trajectories; here we choose the function

$$\begin{aligned} \rho(q_0, p_0, q) &= \exp \left(-\frac{m}{\hbar^2 \beta \gamma + m} (\gamma(q - q_0))^2 \right. \\ & \quad \left. + \frac{\beta}{4m} p_0^2 \right) - \beta V(q). \end{aligned} \quad (19)$$

Performing the phase space integrals analytically and noting that the integral over q is proportional to the

partition function in the high-temperature approximation, one obtains the following expression for the normalization integral of the sampling function:

$$\int dq_0 \int dp_0 \int dq \rho(q_0, p_0, q) = 2\pi \frac{m + \hbar^2 \beta \gamma}{\sqrt{m \beta \gamma}} \sqrt{\frac{2\pi \hbar^2 \beta}{m}} Z_{b,0}. \quad (20)$$

Multiplying Eq. (18) by the normalization integral and changing the q_0 integration variable to $y \equiv q_0 - q$ in order to facilitate sampling leads to the final result for the influence functional of a high-temperature bath oscillator:

$$F[s_+, s_-] = 2 \int dy \int dp_0 \int dq \rho_{\text{norm}}(q_0, p_0, q) \times D(q_0, p_0) \exp\left(-\frac{m}{\hbar^2 \beta \gamma + m} \times \left(\gamma(q - q_f)^2 + \frac{\beta}{4m} p_f^2 + \frac{i}{\hbar}(p_0 - p_f)q - \frac{i}{\hbar}(p_0 q_0 - p_f q_f) + \frac{i}{\hbar}S(q_0, p_0)\right)\right), \quad (21)$$

where ρ_{norm} is a normalized sampling function proportional to Eq. (19). The multidimensional generalization of Eq. (21) is straightforward.

3. Example: harmonic oscillator bath

We illustrate the advantageous features of the formalism presented in Section 2 by applying it to the case of a harmonic oscillator linearly coupled to a one-dimensional system. The bath Hamiltonian has the form

$$H_b = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 - csq. \quad (22)$$

Using the well-known forced harmonic oscillator expressions for the forward and backward branches, one finds

$$q_f = q_0 - \frac{c}{m\omega} \int_0^t \Delta s(t') \sin \omega t' dt' \quad (23a)$$

and

$$p_f = p_0 + c \int_0^t \Delta s(t') \cos \omega t' dt', \quad (23b)$$

where

$$\Delta s(t') \equiv s_+(t') - s_-(t'). \quad (24)$$

Evaluation of the forward–backward action yields the result

$$S(q_0, p_0) = cq_0 \int_0^t \Delta s(t') \cos \omega t' dt' + c^2 g[s_+, s_-], \quad (25)$$

where g depends on the forward and backward system paths alone. Notice that the quadratic terms present in the harmonic oscillator action for forward time evolution have been eliminated. Interestingly, the dependence on initial momentum has also disappeared, a consequence of linearity for the model at hand. As a result, the rapid oscillations in the semiclassical propagator are largely diminished: no oscillations occur in p_0 and the oscillations in the q_0 variable are relatively mild as the action now depends on that variable only linearly with a prefactor which, according to Eq. (25), is proportional to the net force experienced by the bath. In the classical limit, where the forward and backward paths are the same the action is independent of both integration variables. These features are illustrated in Fig. 2, which shows the semiclassical propagator for a particular combination of forward–backward paths and compares to the bare forward–time propagator. It is clear that the propagator arising from Eq. (25) is much better suited to Monte Carlo integration.

Using the above equations it is straightforward (though rather tedious) to show that Eq. (18) leads to the result

$$F[s_+, s_-] = \exp\left(-\frac{c^2}{m\omega\hbar} \int_0^t dt' \int_0^{t'} dt'' (s_+(t') - s_-(t'))(\alpha(t' - t'')s_+(t'') - \alpha^*(t' - t'')s_-(t''))\right), \quad (26)$$

where

$$\alpha(t) = \frac{2}{\hbar\omega\beta} \cos(\omega t) - i \sin(\omega t) \quad (27)$$

is the $\beta \rightarrow 0$ limit of the bath response function, thus reproducing the high-temperature limit of the Feynman–Vernon influence functional [9].

Since the scheme presented in Section 2 is exact in the case of a harmonic bath, the key question is

whether the reduction of phase oscillations achieved via the combined forward–backward evolution is sufficient to yield stable results with reasonable

numbers of Monte Carlo steps. To illustrate the practicality of our approach we present in Fig. 3 numerical results for the average position of a two-

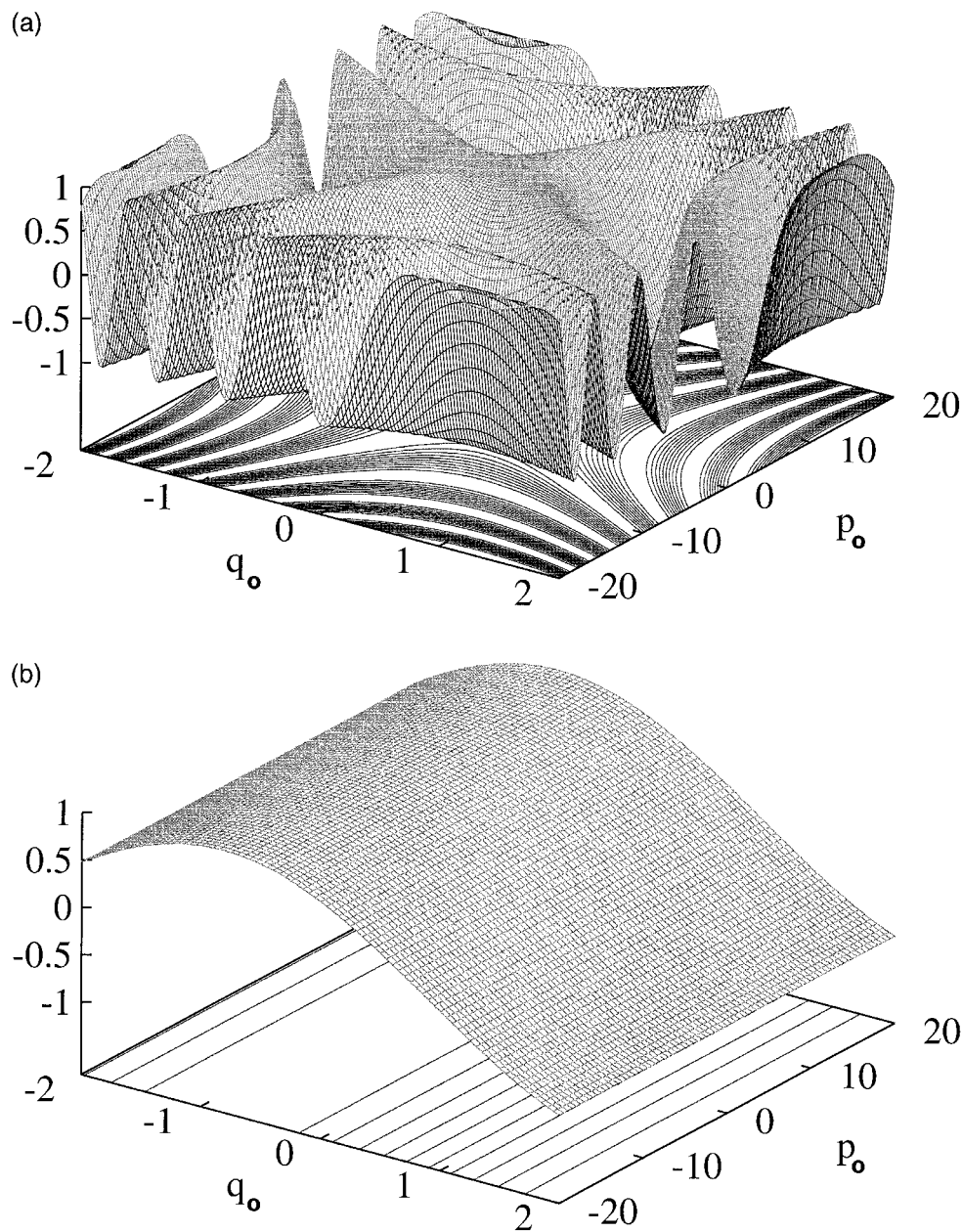


Fig. 2. The real part of the semiclassical propagator, $\text{Re exp}(iS/\hbar)$, as a function of initial position and momentum for a one-dimensional harmonic oscillator driven by a time-dependent force arising from its coupling to a quantum system. The total propagation time is $\omega t = 10$. (a) Action arising from a path in the conventional forward time direction. (b) Combined action in the present formulation for an arbitrary choice of distinct forward and backward paths.

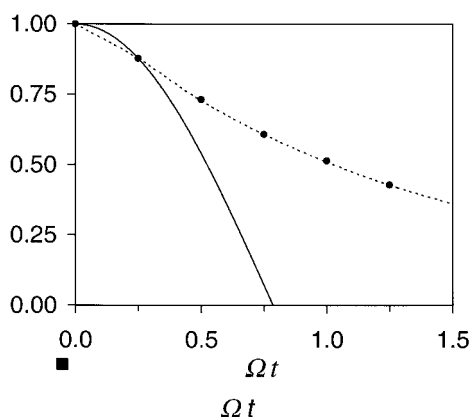


Fig. 3. Average position of a two-level system coupled to a bath of ten harmonic oscillators. The parameters are given in the text. The path integral time step is $\Delta t = 0.25 \Omega^{-1}$. Markers: results obtained using the semiclassical influence functional formalism. The Monte Carlo error bars are smaller than the markers. Dashed line: exact results, generated using the Feynman–Vernon influence functional. Solid line: dynamics of the bare two-level system.

level system coupled to a dissipative harmonic bath [12] of Ohmic spectral density,

$$J(\omega) = \frac{1}{2} \pi \hbar \xi \omega e^{-\omega/\omega_c}, \quad (28)$$

with $\xi = 0.25$ and $\omega_c = 3 \Omega$ at a temperature equal to $20 \hbar \Omega$ (where 2Ω is the tunneling splitting of the bare system). The sum over system paths was carried out explicitly using up to five path integral time steps. The semiclassical evaluation of the influence functional employed ten discrete bath modes of frequencies distributed to reproduce a density of states proportional to $J(\omega)/\omega$. The results shown in Fig. 3 were generated by using 5000 Monte Carlo points per bath degree of freedom for each influence functional evaluation. The small size of the statistical error reflects the smoothness of the integrand for statistically significant path pairs. Note that the influence functional calculation does not exploit the independent mode character of the bath but rather samples the full 3×10 -dimensional space of the integration variables shown in Eq. (21). Comparison with exact results generated via full path summation with the Feynman–Vernon influence functional for an infinite-dimensional bath demonstrates that the method is essentially exact at this temperature. It is also seen that coupling to ten bath degrees of free-

dom results in dynamics which is qualitatively different from that of the isolated two-level system; the semiclassical Monte Carlo calculation captures this effect quite successfully.

4. Concluding remarks

The semiclassical formalism developed in Section 2 of this Letter possesses several appealing features. First, evaluation of the forward and backward time propagation in a single step through trajectories that return to zero time eliminates the dominant terms from the classical action, leading to smooth propagators that are well-suited to numerical integration. This way the interference between the two time evolution operators is accounted for exactly, circumventing the need for an explicit treatment that would entail numerical instabilities. A coherent state initial value representation is adopted which cuts off the momentum range while introducing a prefactor that is generally close to unity. Further, for most statistically significant combinations of forward and backward system paths the accumulated Maslov index is zero, and thus no additional phase variation is introduced. Three procedures are suggested for evaluating the resulting coherent state transform of the Boltzmann operator, including a closed-form high-temperature approximation and a numerical path integral representation. Although the coherent state Boltzmann factor introduces mild oscillations in the integrand, examination of Eq. (14) or Eq. (18) reveals that in the most important limit where the system forward and backward paths coincide the oscillatory terms cancel exactly and the entire integrand is positive definite. Finally, a Monte Carlo scheme is described which employs a normalized sampling function to generate initial phase space conditions for the classical trajectories.

Application to the model of a harmonic oscillator bath yields a semiclassical propagator that is independent of p_0 and which exhibits slow oscillations in q_0 , in contrast to the forward-only propagator which is a rapidly oscillatory function of both phase space variables. Although the precise cancellation of the initial momentum is a consequence of linearity in this case, we expect the integrand to exhibit only

mild oscillations with this variable in the case of an anharmonic bath. Further, the harmonic bath model gives rise to a prefactor which is exactly equal to unity for all trajectories. We emphasize again that the integrand is by construction completely positive in the classical limit of identical system paths for which the influence functional takes on its largest value.

Last, a very appealing feature of the present influence functional formulation is its simplicity. The normalized sampling function constructed for the high-temperature case is ideally suited for direct phase space sampling in the spirit of classical molecular dynamics. Finally, if the system–bath interaction terms are linear in the bath coordinate the prefactor in Eq. (14) is unity and one does not need to worry about following the dynamics of the stability matrix or keeping track of Maslov phases.

The highly desirable features of the semiclassical influence functional formulation developed in this Letter suggest that rigorous quantum-semiclassical simulations of processes in polyatomic environments such as clusters or atomic/molecular fluids may become feasible. At present, the method is limited to short time calculations because of the usual proliferation of system paths at longer time intervals. Overcoming this problem requires the construction of an iterative scheme for evaluating the path integral in the general case where the influence functional is not known analytically. Another attractive possibility is to use the influence functional scheme presented in

this Letter in conjunction with a semiclassical treatment of the observable particle. Extensions and applications of this methodology are currently in progress in our group.

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