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FORWARD-BACKWARD SEMICLASSICAL DYNAMICS

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Recent developments in semiclassical methodology for time-dependent properties of multi-dimensional systems are reviewed. Combining the time evolution operator and its adjoint into a single forward-backward propagator provides a natural smoothing of the semiclassical integrand, making the latter suitable for integration by Monte Carlo methods.

1 Introduction

Computing the time evolution of quantum systems composed of many coupled degrees of freedom presents serious challenges. Currently, simulations of time-dependent properties in polyatomic molecules, clusters, or condensed phases employ a variety of approximations, which are largely built around variational, quantum classical or semiclassical ideas. While approximate methods have proven extremely valuable in many situations, their regime of applicability is limited. Perhaps more importantly, checking the accuracy of the results is usually impractical, and thus reliability becomes a significant concern.

Numerical solution of the Schrödinger equation requires storage of the multi-dimensional wave function, which occupies a volume that grows exponentially with the number of particles. This limitation is circumvented in the path-integral formulation, where quantum mechanical amplitudes are expressed as sums over paths [1,2]. To reproduce quantum interference, the amplitude along each path must be a complex-valued phase. Because of the rapid oscillations of the latter, numerical evaluation of the real-time path

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integral by means of stochastic methods is plagued by severe numerical instabilities [3,4]. At the same time, explicit summation over all paths is far from feasible, as their number (if space and time are discretized) increases exponentially with the number of degrees of freedom and the total propagation time. Recently, exact evaluation of the path integral by virtue of an iterative algorithm became feasible in cases of a low-dimensional system coupled to a dissipative bath (for a review see Ref. [5]).

2 Semiclassical Dynamics with Forward-Backward Trajectories

The conventional time-dependent semiclassical approximation can be derived from the path-integral expression for the coordinate propagator [1,2],

$$\langle \mathbf{x}_2 | U(t_2,t_1) | \mathbf{x}_1 \rangle = \int \mathcal{D}\mathbf{x}(t) e^{iS[\mathbf{x}(t)]/\hbar} , \tag{1}$$

where U is the time evolution operator that propagates from time t_1 to t_2. The last equation is a functional integral over all paths $\mathbf{x}(t)$ with endpoints $\mathbf{x}(t_1) = \mathbf{x}_1$ and $\mathbf{x}(t_2) = \mathbf{x}_2$, and the amplitude contributed by each path is the classical action in units of Planck's constant. Taking the limit $\hbar \to 0$ and evaluating the functional integral by the stationary phase method (i.e. restricting the sum in Eq. (1) to paths that satisfy the Euler-Lagrange equations as well as quadratic fluctuations around them) leads to the Van Vleck expression for the semiclassical propagator [6,7]:

$$\langle \mathbf{x}_2 | U(t_2,t_1) | \mathbf{x}_1 \rangle_{\rm SC} = \sum_{\text{classical paths } \mathbf{x}(t)} D_{VV}(\mathbf{x}_2,\mathbf{x}_1)\, e^{iS[\mathbf{x}(t)]/\hbar} e^{-i\mu\pi/2} . \tag{2}$$

Here the prefactor D_{VV} is a determinant given by one of the elements of the stability matrix, and μ is the Maslov index which supplies the proper phase by keeping track of focusing characteristics of the classical trajectories. The sum in Eq. (2) arises because there are in general multiple solutions to the boundary value problem specified by the endpoint constraints imposed on the classical paths. An excellent presentation of the time-dependent semiclassical approximation and its relation to the path integral can be found in the books of Kleinert [8] and of Schulman [9].

Equation (2) is formulated in terms of the classical solution(s) to a double-ended boundary value problem and thus is impractical. In addition, the Van Vleck prefactor diverges at caustics, and its rapidly growing rate in the vicinity of such points gives rise to numerical instabilities. Miller has shown that

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both of these problems can be overcome by switching to an initial value representation [10], provided that one is interested in an observable rather than the propagator itself. This is achieved by changing the integration variable associated with the final position of a trajectory to that specifying its initial momentum and absorbing the Van Vleck determinant and the Jacobian into a single prefactor. The most favorable representation is obtained in terms of coherent states, which introduce a natural weight factor for sampling the initial conditions of classical trajectories. Inserting overcomplete sets of coherent states and applying repeatedly the stationary phase approximation, Herman and Kluk showed [11,12] that the semiclassical propagator can also be brought into the form

$$\langle \mathbf{x}_2|U(t_2,t_1)|\mathbf{x}_1\rangle_{\rm SC} = \int d\mathbf{x}_0 \int d\mathbf{p}_0 \, \langle \mathbf{x}_2|g(\mathbf{x}_f,\mathbf{p}_f)\rangle D_{HK}(\mathbf{x}_0,\mathbf{p}_0) \times e^{iS(\mathbf{x}_0,\mathbf{p}_0)]/\hbar} \langle g(\mathbf{x}_0,\mathbf{p}_0)|\mathbf{x}_1\rangle \, . \tag{3}$$

Here $\mathbf{x}_f, \mathbf{p}_f$ stand for the final coordinate and momentum of a classical trajectory with initial conditions $\mathbf{x}_0$ and $\mathbf{p}_0$, and the coherent state wave functions are defined by the usual relation

$$\langle \mathbf{x}|g(\mathbf{x}_0,\mathbf{p}_0)\rangle = \sqrt{\det \frac{2\boldsymbol{\gamma}}{\pi}} \exp\left[-(\mathbf{x}-\mathbf{x}_0)\cdot\gamma\cdot(\mathbf{x}-\mathbf{x}_0) + \frac{i}{\hbar}\mathbf{p}_0\cdot(\mathbf{x}-\mathbf{x}_0)\right] . \tag{4}$$

The semiclassical propagator is capable of reproducing semiquantitatively all aspects of quantum mechanics [10,13,14]. In spite of these appealing features, rigorous semiclassical theory has found little practical utility in the past. As in the case of the real time path integral, evaluation of ensemble-averaged observables by means of the semiclassical propagator is plagued by the problem of severe phase cancellation, which now occurs due to interfering classical trajectories. Persistent efforts in the last few years have led to some methodological advances, which have enabled calculations in several models and small molecular systems [11,12,15-34].

Systems of many atoms are usually characterized in terms of ensemble-averaged quantities, such as correlation functions or the reduced density matrix. In these, the dynamical quantity of interest (usually an operator that depends on a few degrees of freedom of direct interest, the "system"), propagated to the desired time, is traced over all unprobed coordinates (those of the "bath") subject to a distribution function that characterizes the particular

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ensemble. Such expressions have the general structure

$$\mathrm{Tr}\left(\rho_0 \cdots U_{\mathrm{back}}^{-1}(t,0) \cdots U_{\mathrm{for}}(t,0)\right) , \tag{5}$$

where ρ_0 is the equilibrium density matrix and U_{for}, U_{back} are time evolution operators corresponding to the dynamics generated by the same or two distinct Hamiltonians, that may also be explicitly time-dependent. This structure can be exploited to reduce the severity of the sign problem.

The conventional semiclassical procedure for evaluating Eq. (5) is to approximate each of the two propagators by the semiclassical (Van Vleck or coherent state) expression and attempt to perform the resulting multidimensional integrals by Monte Carlo methods. In the coordinate representation, this procedure produces an expression of the form

$$\int d\mathbf{x}_0 \int d\mathbf{x}_f \int d\mathbf{x}_t e^{-iS_{\mathrm{back}}(\mathbf{x}_t,\mathbf{x}_f)/\hbar} \cdots e^{iS_{\mathrm{for}}(\mathbf{x}_0,\mathbf{x}_t)/\hbar} \cdots . \tag{6}$$

According to this, one integrates trajectories from $(\mathbf{x}_0, 0)$ to $(\mathbf{x}_t, t)$ and also from $(\mathbf{x}_t, t)$ to $(\mathbf{x}_f, 0)$. With the exception of very short times, each of the action integrals in the above equation is large relative to $\hbar$ and thus the integrand is highly oscillatory.

Imagine, however, that one finds a way to combine the two time evolution operators in Eq. (5) into a single propagator. Various ways of doing this are discussed in the subsections that follow, but notice that the presence of the operator B in the correlation function prevents the combined exponentials from producing the identity (and thus eliminating all dynamics). Applying the semiclassical approximation to the new forward-backward propagator would lead to an expression with a *single* semiclassical amplitude [25]:

$$\int d\mathbf{x}_0 \int d\mathbf{x}_f \cdots e^{iS(\mathbf{x}_0,\mathbf{x}_f)/\hbar} \cdots . \tag{7}$$

Here the classical trajectories run from $(\mathbf{x}_0, 0)$ to $(\mathbf{x}_t, t)$ and subsequently backwards in time to $(\mathbf{x}_f, 0)$, and S is the combined forward-backward action.

The pairing of the two evolution operators has accomplished two tasks. First, the midpoint integral has been eliminated. In fact, Eq. (7) can be viewed as the result of evaluating the midpoint integral of Eq. (6) by the stationary phase method. Second, and more important, the action entering Eq. (7) is the *net* result of forward and backward propagation. If the trajectory simply reversed its steps during the backward part, the overall action would be equal to zero. As will become clear in the following, the presence of

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an operator between the two propagators alters somewhat the course of the backward trajectory; nevertheless, the net forward-backward action generally remains small. The significance of this fact is obvious: the rapid oscillations of the integrand have been eliminated and Monte Carlo methods should be applicable. Phrased differently, the advantage of forward-backward semiclassical dynamics (FBSD) is that the phase cancellation which plagues the multi-dimensional integrals of Eq. (6) is shifted naturally to a cancellation between forward and backward actions.

The smoothing achieved by combining the forward and backward propagation steps are illustrated in Figs. 1 and 2 which show the semiclassical integrand as a function of the trajectory initial conditions for a harmonic potential after (a) propagation in the forward direction only (Fig. 1) and (b) combined forward-backward propagation (Fig. 2). In multi-dimensional space, the oscillatory character of the integrand depicted in Fig. 1 is responsible for the failure of Monte Carlo methods. On the other hand, the smooth forward-backward integrand of Fig. 2 is perfectly suitable for stochastic sampling.

The numerical advantages achieved by combining the forward and backward evolution operators into a single semiclassical step are not without consequences. Consider two classical trajectories satisfying the boundary conditions of the forward and backward propagators in Eq. (6). As no constraint is imposed on these trajectories, they may join with different slopes (and thus different momenta) at the midpoint $\mathbf{x}_t$. Now imagine evaluating the midpoint integral by the stationary phase method in order to arrive at the FBSD expression, Eq. (7). The stationary phase condition is [26]

$$\left.\frac{\partial S_{\rm for}(\mathbf{x}_0,\mathbf{x}_t)}{\partial \mathbf{x}_t}\right|_{\mathbf{x}_0} - \left.\frac{\partial S_{\rm back}(\mathbf{x}_t,\mathbf{x}_f)}{\partial \mathbf{x}_t}\right|_{\mathbf{x}_f} = \mathbf{p}_t^{\rm for} - \mathbf{p}_t^{\rm back} = 0\,, \tag{8}$$

where $\mathbf{p}_t^{\rm for}$ is the final momentum of the forward trajectory and $\mathbf{p}_t^{\rm back}$ is the initial momentum of the backward trajectory. Thus, the forward and backward trajectories in FBSD are no longer independent but are constrained to maintain momentum continuity at all times. This restriction can lead to loss of interference.

It is thus apparent that the FBSD approach should be implemented with caution. Depending on the nature of the problem at hand and the desired degree of accuracy it may be advantageous to treat all of just some of the degrees of freedom by FBSD. Various situations that emerge are described

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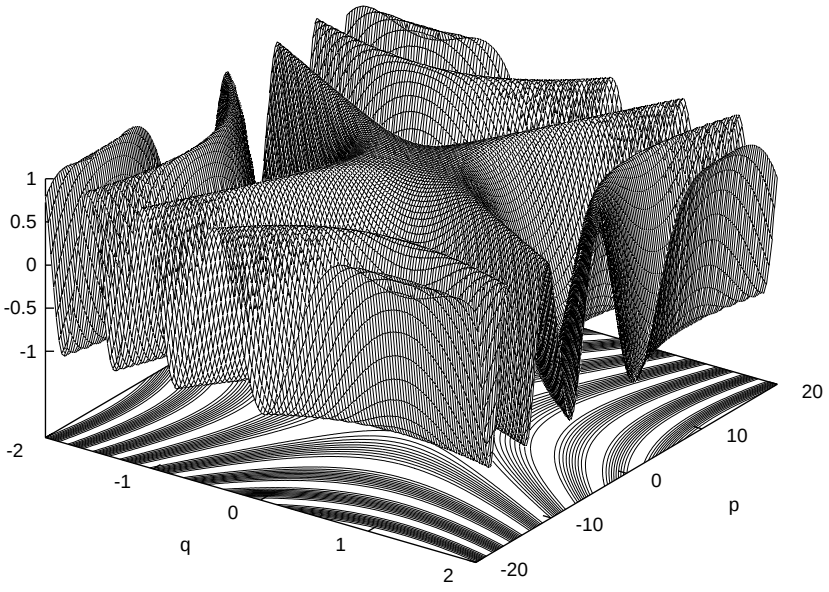

Figure 1. The real part of the semiclassical propagator as a function of initial position and momentum for a one-dimensional harmonic oscillator driven by a time-dependent force arising from its coupling to a quantum system for the action arising from a path in the conventional forward time direction. The total propagation time is $\omega t = 1$.

below.

Perhaps the most straightforward and unambiguous use of FBSD is in the evaluation of influence functionals [35] in the context of the path-integral representation of time-dependent quantum mechanics. Consider, for example, the reduced density matrix for a system described by the Hamiltonian $H_0(r, p_r)$ in contact with an n-dimensional environment of coordinates $\mathbf{x}, \mathbf{p}$ whose force field and interaction with the solute are given by the Hamiltonian $H_b(\mathbf{x}, \mathbf{p}, r)$. Using the path-integral representation for each of the two propagators, the reduced density matrix can be brought in the form

$$\langle r''|\rho(t)|r'\rangle = \int dr_0^+ \int dr_0^- \int \mathcal{D}r^+ \int \mathcal{D}r^- e^{iS_0[r^+]/\hbar} e^{-iS_0[r^-]/\hbar} F[r^+, r^-]\,, \quad (9)$$

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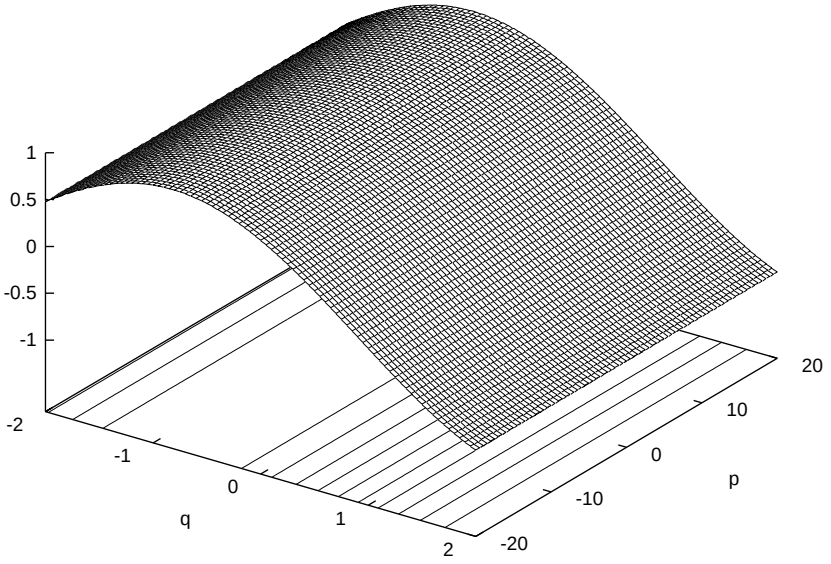

Figure 2. Same as Fig. 1, but for combined action along the forward-backward time contour for an arbitrary choice of distinct forward and backward paths.

where

$$F[r^+, r^-] = \mathrm{Tr}_b \left(U_{\mathrm{for}}(t,0) \rho_0 U^{-1}_{\mathrm{back}}(t,0) \right) \tag{10}$$

is the influence functional that contains all the effects of the environment on the dynamics of the particle of interest. Here $U_{\mathrm{for}}(t,0)$ and $U_{\mathrm{back}}(t,0)$ are operators that propagate the bath in the presence of a potential that is time-dependent by virtue of the time-parameterization of the system coordinate:

$$H_{\mathrm{for}}(t') = H_b(\mathbf{x}, \mathbf{p}, r^+(t')), \qquad H_{\mathrm{back}}(t') = H_b(\mathbf{x}, \mathbf{p}, r^-(t')). \tag{11}$$

Noting that the trace operation allows a cyclic rearrangement of the two arguments brings the influence functional in a form suitable for FBSD. Its coherent state representation becomes [25]

$$F[r^+, r^-] = \int d\mathbf{x}_0 \int d\mathbf{p}_0 \, D_{HK}(\mathbf{x}_0, \mathbf{p}_0) \, e^{iS(\mathbf{x}_0, \mathbf{p}_0)]/\hbar}$$

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$$\times \langle g(\mathbf{x}_0, \mathbf{p}_0)|\rho_0|g(\mathbf{x}_f, \mathbf{p}_f)\rangle \, . \tag{12}$$

Consider now the evaluation of general correlation functions of the type

$$C(t) = \mathrm{Tr}\left(\rho_0 A e^{iHt/\hbar} B e^{-iHt/\hbar}\right) , \tag{13}$$

where A and B are general operators. In this case, the forward-backward structure of the integrand is disrupted by the presence of these operators and formulating a semiclassical forward-backward scheme is neither straightforward nor unique.

The most straightforward treatments involve bringing the operator B into an exponential form and applying FBSD to the resulting evolution operator. Miller and coworkers have proposed the use of the Weyl identity,

$$B_W(\mathbf{x}, \mathbf{p}) = \int d\mathbf{p}' \int d\mathbf{x}' W_{\rho_0 B}(\mathbf{x}', \mathbf{p}') e^{i\mathbf{p}'\cdot\mathbf{x}/\hbar} e^{-i\mathbf{p}\cdot\mathbf{x}'/\hbar} , \tag{14}$$

where $W_{\rho_0 B}$ is the Wigner transform [36] of the operator $\rho_0 B$. The correlation function is brought in the form [29,30]

$$\begin{aligned} C(t) = \int d\mathbf{x}_0 \int d\mathbf{p}_0 \int d\mathbf{x}' \int d\mathbf{p}' W_{\rho_0 A}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_f, \mathbf{p}_f) B(\mathbf{x}_t, \mathbf{p}_t) \\ \times D_W(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_t, \mathbf{p}_t) e^{iS(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}', \mathbf{p}')/\hbar} , \end{aligned} \tag{15}$$

where the phase space variables with initial conditions $\mathbf{x}_0, \mathbf{p}_0$ and the action follow the classical equations of motion forward and backward in time to the final values $\mathbf{x}_f$, $\mathbf{p}_f$, changing discontinuously at the time t by the amounts

$$\delta\mathbf{x} = \mathbf{x}', \quad \delta\mathbf{p} = \mathbf{p}' . \tag{16}$$

A very practical scheme arises by using a derivative identity to convert the operators to an exponential form and evaluating the resulting expression by FBSD. The correlation function is written as

$$C(t) = -i\frac{\partial}{\partial\mu}\mathrm{Tr}\left(\rho_0 A e^{iHt/\hbar} e^{i\mu B} e^{-iHt/\hbar}\right)\Big|_{\mu=0} . \tag{17}$$

By applying the semiclassical approximation to the product of exponentials in this expression and manipulating the resulting equation, Shao and Makri have shown in Refs. [33,34] that Eq. (17) leads to the expression

$$C(t) = -i\hbar^{-n}\frac{\partial}{\partial\mu}\int d\mathbf{x}_0 \int d\mathbf{p}_0 \, \exp\left(\frac{i}{\hbar}S(\mathbf{x}_0, \mathbf{p}_0)\right)$$

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$$\times \langle g(\mathbf{x}_0, \mathbf{p}_0) | \rho_0 A | g(\mathbf{x}_f, \mathbf{p}_f) \rangle |_{\mu=0} \,, \tag{18}$$

where the coordinates and action increment at time t by the infinitesimal amounts to

$$\delta \mathbf{x}_t = -\hbar\mu \frac{\partial B(\mathbf{x}_t, \mathbf{p}_t)}{\partial \mathbf{p}_t}, \quad \delta \mathbf{p}_t = \frac{1}{2}\hbar\mu \frac{\partial B(\mathbf{x}_t, \mathbf{p}_t)}{\partial \mathbf{x}_t}, \quad \delta S = \hbar\mu B(\mathbf{x}_t) \,. \tag{19}$$

Note that Eq. (18) contains no prefactor, and that the momentum jump in this expression is exactly one half of that dictated by Hamilton's equations for the effective potential governing the dynamics. This way, the semiclassical prefactor is accounted for by the combined contribution of the action and initial density. The absence of a prefactor from Eq. (18) leads to nearly linear scaling of the required computer time with the number of degrees of freedom. Miller and coworkers have shown that Eq. (18) can also be expressed in a form involving only forward propagation.

Equation (18) is the rigorous stationary phase limit of Eq. (17). However, because the stationary phase approximation with respect to the midpoint integral is applied here to *all* degrees of freedom, it is clear that the interference arising from distinct forward and backward trajectories will be missed, and thus Eq. (18) is not as accurate as semiclassical expressions employing two separate propagators. In fact, the overall behavior of Eq. (18) is similar to that of the Wigner approximation [37,38]

$$C(t) = \hbar^{-n} \int d\mathbf{x}_0 \int d\mathbf{p}_0 W_{\rho_0 A}(\mathbf{x}_0, \mathbf{p}_0) B(\mathbf{x}_t, \mathbf{p}_t) \,, \tag{20}$$

which involves a quasiclassical trajectory average with the Wigner function replacing the classical density. Here W is the Wigner transform of the operator ρ_0. Sun and Miller have shown that the Wigner quasiclassical method can also be obtained from the full semiclassical expression by linearizing the action difference of the forward and backward trajectories [21].

As a test, Shao and Makri applied Eq. (18) to a model of an initially displaced quartic oscillator coupled to a bath of 30 harmonic oscillators [33] and compared the resulting average position to exact solutions [39]. As seen in Fig. 3, for zero coupling the prefactor-free expression reproduces the first several oscillations of the average position semiquantitatively but fails to capture the rephasing of the wavepacket. When a small amount of dissipation is included, the average position decays irreversibly, and both prefactor-free expressions follow closely the exact results.

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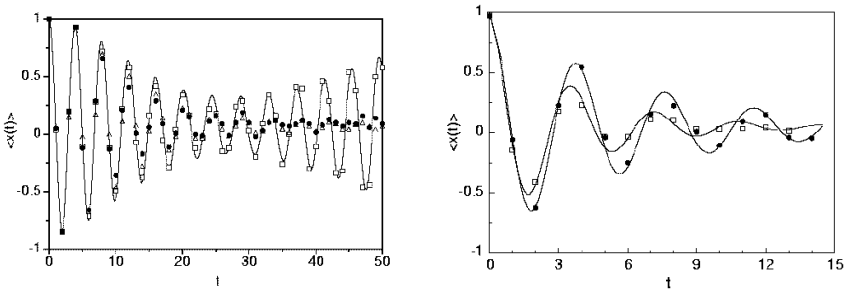

Figure 3. Average position for a one-dimensional quartic oscillator coupled to a bath of 30 harmonic degrees of freedom at zero temperature. Solid line: exact results. Solid circles and hollow squares: FBSD without prefactor, Eq. (18). Hollow triangles: linearized (Wigner) approximation; *left:* no system-bath coupling, *right:* weak and moderate system-bath coupling.

3 Discussion

Shao and Makri used the derivative version of the FBSD formulation summarized in equations (18) and (19) and calculated correlation functions of various normal modes in clusters of two and four water molecules at zero temperature. The largest of these clusters has 30 active degrees of freedom and the calculation involves a 60-dimensional integral which was evaluated with only 2,500 sampling points per integration variable, i.e. a total of 150,000 trajectories. Representative results are shown in Fig. 4 for the water tetramer [34]. The large imaginary parts of these correlation functions is of purely quantum mechanical origin. It is concluded that the prefactor-free FBSD is capable of describing the vibrational dynamics of sizable systems with numerical effort that is comparable to that required in conventional molecular dynamics, while capturing important quantum mechanical effects.

To improve the accuracy of FBSD, one should express the correlation function in a form that includes some explicit interference between forward and backward trajectories. One way to do this is to apply the stationary phase technique to the coordinates of the bath, but evaluate the midpoint integral with respect to the system coordinate numerically [27]. Another possibility is to start from the full semiclassical expression but introduce damping factors that bias sampling around stationary phase paths, with adjustable weights [40]. Both of these approaches lead to improved results where important quantum features can be captured accurately, but at considerably higher

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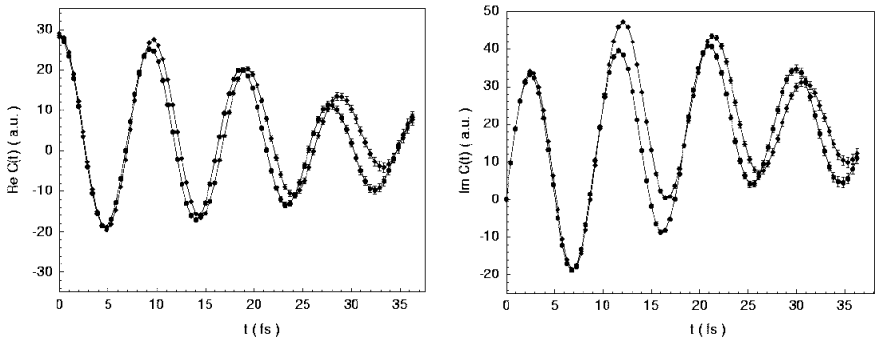

Figure 4. Real and imaginary parts of the correlation function for the acceptor OH stretching vibrations in the water tetramer as obtained by the derivative version of the FBSD procedure.

computational cost.

In summary, the FBSD approach and its numerous variants have tremendously enhanced the feasibility of semiclassical calculations in chemical systems. However, the most practical of these schemes are accurate only for short times and/or when dephasing effects due to multi-dimensional environments quench quantum coherence fairly rapidly. The more accurate versions of FBSD remain computationally expensive and even prohibitive in some cases. Devising semiclassical approximations that are capable of capturing quantum interference effects, while being routinely applicable to large systems, remains the focus of intense efforts in the dynamics community.

Acknowledgments

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