

Forward–Backward Semiclassical Dynamics with Linear Scaling

Jiushu Shao

School of Chemical Sciences, University of Illinois, 601 S. Goodwin Avenue, Urbana, Illinois 61801

Nancy Makri*

*School of Chemical Sciences, University of Illinois, 601 S. Goodwin Avenue, Urbana, Illinois 61801,
and Theoretical & Physical Chemistry Institute, National Hellenic Research Foundation,
48 Vassileos Constantinou Avenue, Athens, Greece 11635*

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A forward–backward semiclassical method is presented for calculating correlation functions of polyatomic systems. Unlike conventional semiclassical theories, this formulation does not require evaluation of the prefactor that contains a determinant with elements defined by the stability matrix. It is shown rigorously that the contribution of the semiclassical prefactor in the present formulation can be absorbed in the semiclassical phase and initial density if the momentum jump at the end of the forward propagation is chosen to be one-half of that dictated by the classical equations of motion. As a consequence, the number of equations of motion to be solved in its implementation is linearly proportional to the number of degrees of freedom. The method is applied to the dynamics of water clusters which involve strongly anharmonic interactions.

1. Introduction

Although large-scale computer simulations of many-body systems by means of classical molecular dynamics have become extremely common, fully quantum mechanical calculations on such systems remain far beyond the reach of current computational capability because their cost scales exponentially with the size of the system. An attractive compromise is the time-dependent semiclassical method in which Planck's constant is treated as a small parameter compared to the classical action. While the semiclassical propagator results from asymptotic analysis, it offers an accurate description of quantum evolution for short or intermediate times without requiring storage of multidimensional functions or diagonalization of large matrices. Since this time domain is relevant in many molecular dynamical processes, the semiclassical method is appealing as a numerical tool in theoretical chemistry.

The traditional analysis of semiclassical dynamics is based on the Van Vleck propagator.^{1,2} The accuracy of the semiclassical expression has been demonstrated in several calculations,^{3–6} including systems exhibiting quantum chaotic behavior.^{7,8} There are two main difficulties in implementing the Van Vleck propagator. First, one has to perform a root search in order to identify classical trajectories satisfying double-ended boundary conditions; and second, the expression diverges at caustics (see, for example, refs 9 and 10). Several insightful techniques have been devised to overcome these problems in the calculation of correlation functions. Initial value representations,⁴ which replace the integral over final coordinate to one involving the initial momentum of a trajectory, and coarse graining schemes based on cellular dynamics¹¹ or coherent state representations¹² are proven free of these difficulties. The semiclassical propagator involves a prefactor, a determinant whose elements are defined by the stability (monodromy) matrix. This means that in addition

to the $2n$ classical equations of motion in phase space for an n -dimensional system, one must also solve $(2n)^2$ differential equations determining the stability matrix, while evaluation of the determinant requires effort proportional to n^3 .

Because of the linear superposition principle inherent in quantum mechanics, both the quantum and the semiclassical propagators are oscillatory. This behavior results in the so-called sign problem when applied to the evaluation of physical observables or correlation functions. A solution toward this problem is offered by the introduction by our group of forward–backward semiclassical dynamics (FBS).¹³ A physical quantity can in general be cast into a form of an ensemble average which involves propagators in the forward and backward time directions. By combining the forward and backward propagations into a single semiclassical time evolution, the oscillations associated with these opposite in time motions can be canceled to a large extent and the resulting integrand is sufficiently smooth for treatment by Monte Carlo integration. The original formulation of FBS for the evaluation of influence functionals in the context of a path integral description of the observable system^{13,14} has been extended to schemes which treat all degrees of freedom semiclassically.^{15–17} The FBS representation of the influence functional arises if the integration connecting the forward and backward semiclassical propagators is evaluated by the stationary phase method and is thus completely consistent with the spirit of the semiclassical approximation. If the observable system is also treated semiclassically, the expression to which one should apply the final stationary phase procedure is not unique, leading to several versions of FBS. A number of studies to date have shown that the FBS scheme is sufficiently accurate for many situations of interest in chemical dynamics and feasible for systems of several atoms.^{13,14,16–19}

In a recent letter¹⁷ we described a new formulation of FBS for calculating semiclassical correlation functions. In this scheme, the prefactor is compensated for by the semiclassical phase and the expensive evaluation of the stability matrix and

* Address correspondence to School of Chemical Sciences, University of Illinois, 601 S. Goodwin Avenue, Urbana, Illinois 61801.

the corresponding determinant is no longer required. Compared to the full semiclassical treatment which deals with the forward and backward propagators separately, the new version of FBSD reduces by a factor of 2 the number of integration variables, guarantees a smooth integrand, and eliminates the calculation of the prefactor. For this reason, this FBSD scheme is practical for simulations on polyatomic systems. At the same time, owing to the partial neglect of interference between the forward and backward propagations (which seems to be more serious than the corresponding neglect inherent in the semiclassical propagator within a given time direction), one can expect FBSD to be less accurate than the fully semiclassical method. Nevertheless, model studies¹⁷ on multidimensional anharmonic systems have shown that FBSD gives very reasonable results over several oscillation periods, a time length often sufficient for important chemistry to take place. The loss of accuracy in FBSD may be roughly understood as follows: The semiclassical method is an asymptotic theory in which the absolute value of the classical action is assumed to be much larger than Planck's constant. In FBSD, the relevant quantity is the sum of actions along the forward and backward time contours, which are partially canceled out with each other. As a consequence, the effective action is not so large and the phase varies less rapidly than in the individual propagators.

This paper presents a more detailed derivation of the new FBSD for multidimensional systems and the results of its application to the dynamics of water clusters. As in ref 17, we focus on correlation functions of the type

$$C(t) = \text{Tr}(\rho(0)Ae^{iHt/\hbar}Be^{-iHt/\hbar}) \quad (1.1)$$

where H is the Hamiltonian of the n -dimensional system

$$H = \frac{1}{2}\mathbf{p}^T \cdot \mathbf{m}^{-1} \cdot \mathbf{p} + V(\mathbf{q}) \quad (1.2)$$

with \mathbf{m} being the mass matrix and the ordinary potential energy, A and B are two (scalar) Hermitian operators, and $\rho(0)$ is the initial density matrix. (The superscript denotes the transpose of a matrix or of a vector.) For simplicity we assume that B is a function of the position operator corresponding to the observable dynamical variable(s). It is straightforward to extend the following discussion to an arbitrary operator that is a general function of all phase space variables. Section II gives the rigorous derivation of the prefactor-free FBSD in the coherent state representation. In section III we discuss the implementation of FBSD to study the vibrational motion of a water molecule or cluster. Finally, section IV summarizes the present work.

II. Theory

The dynamical part in the correlation function of eq 1.1 is the Heisenberg representation of the operator second operator, $B_H = e^{iHt/\hbar}Be^{-iHt/\hbar}$. For later use we rewrite B_H as a derivative of an operator with respect to a parameter μ , namely

$$B_H = -i \lim_{\mu \rightarrow 0} \frac{\partial}{\partial \mu} U(t; \mu) \quad (2.1)$$

where

$$U(t; \mu) = e^{iHt/\hbar} e^{i\mu B} e^{-iHt/\hbar} \quad (2.2)$$

is unitary and can be regarded as the evolution operator along a forward-backward time contour $0 \rightarrow t \rightarrow 0$ for the time-dependent Hamiltonian

$$H(t') = H - \hbar\mu\delta(t' - t)B \quad (2.3)$$

which includes an instantaneous “kick” at time t . In the semiclassical coherent state representation,¹² $U(t; \mu)$ takes the form

$$U(t; \mu) = (2\pi\hbar)^{-n} \int d\mathbf{q}_0 \int d\mathbf{p}_0 D(\mathbf{q}_0, \mathbf{p}_0; \mathbf{q}_f, \mathbf{p}_f) \times \exp\left(\frac{i}{\hbar} S(\mathbf{q}_0, \mathbf{p}_0; \mu)\right) |g(\mathbf{q}_f, \mathbf{p}_f)\rangle \langle g(\mathbf{q}_0, \mathbf{p}_0)| \quad (2.4)$$

Here $\mathbf{q}_f, \mathbf{p}_f$ denote the coordinates and momenta at the end of the forward-backward propagation, S is the corresponding classical action, and g is a coherent state described by the wave function

$$\langle g | g(\mathbf{q}_0, \mathbf{p}_0) \rangle = \left(\frac{2}{\pi}\right)^{n/4} (\det \Gamma)^{1/4} \exp\left[-(\mathbf{q}^T - \mathbf{q}_0^T) \cdot \Gamma \cdot (\mathbf{q} - \mathbf{q}_0) + \frac{i}{\hbar} \mathbf{p}_0^T \cdot (\mathbf{q} - \mathbf{q}_0)\right] \quad (2.5)$$

where the elements of Γ (a diagonal matrix) are arbitrary parameters representing the widths of the Gaussians. The prefactor D in eq 2.4 assumes the form

$$D(\mathbf{q}_0, \mathbf{p}_0; \mathbf{q}_f, \mathbf{p}_f) = 2^{-n/2} \left[\det \left(\frac{\partial \mathbf{q}_f}{\partial \mathbf{q}_0} + \Gamma^{-1} \cdot \frac{\partial \mathbf{p}_f}{\partial \mathbf{p}_0} \cdot \Gamma - 2i\hbar \frac{\partial \mathbf{q}_f}{\partial \mathbf{p}_0} \cdot \Gamma - \frac{1}{2i\hbar} \Gamma^{-1} \cdot \frac{\partial \mathbf{p}_f}{\partial \mathbf{q}_0} \right) \right]^{1/2} \quad (2.6)$$

The elements entering this determinant are determined from the stability matrix

$$\mathbf{M}(t') = \begin{pmatrix} \frac{\partial \mathbf{q}(t')}{\partial \mathbf{q}_0} & \frac{\partial \mathbf{q}(t')}{\partial \mathbf{p}_0} \\ \frac{\partial \mathbf{p}(t')}{\partial \mathbf{q}_0} & \frac{\partial \mathbf{p}(t')}{\partial \mathbf{p}_0} \end{pmatrix} \quad (2.7)$$

which obeys the differential equation

$$\frac{d}{dt'} \mathbf{M}(t') + \mathbf{F}(t') \cdot \mathbf{M}(t') = 0 \quad (2.8a)$$

with the initial condition

$$\mathbf{M}(0) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (2.8b)$$

where the matrix \mathbf{F} has the form

$$\mathbf{F}(t') = \begin{pmatrix} 0 & -\mathbf{m}^{-1} \\ \left. \frac{\partial^2 V}{\partial \mathbf{q}^2} \right|_{t'} & 0 \end{pmatrix} \quad (2.9)$$

The stability matrix is thus given from the solution of $(2n)^2$ coupled first-order differential equations. Furthermore, the numerical effort required for evaluation of the determinant is proportional to n^3 . For these reasons computation of the prefactor is prohibitive if the number of coupled degrees of freedom is large. It is argued in ref 17 that when FBSD is formulated in the above derivative form, one can arrange for the contribution of the prefactor to be compensated for by other terms. In the following we present a detailed analysis of this result, which eliminates the need for calculating the semiclassical determinant.

Note that the propagator $U(t;\mu)$ contains contributions from all classical trajectories in phase space. The classical dynamics is governed by Hamilton's equations, namely

$$\frac{d\mathbf{q}}{dt'} = \frac{\partial}{\partial \mathbf{p}} H(t') = \mathbf{m}^{-1} \cdot \mathbf{p} \quad (2.10a)$$

$$\begin{aligned} \frac{d\mathbf{p}}{dt'} &= -\frac{\partial}{\partial \mathbf{q}} H(t') \\ &= -\frac{\partial}{\partial \mathbf{q}} V(\mathbf{q}) + \hbar\mu\delta(t' - t)\frac{\partial}{\partial \mathbf{q}} B(\mathbf{q}) \end{aligned} \quad (2.10b)$$

and the equation of motion for the classical action is

$$\frac{dS}{dt'} = \frac{1}{2}\mathbf{p}^T \cdot \mathbf{m}^{-1} \cdot \mathbf{p} - V(\mathbf{q}) \quad (2.10c)$$

The classical forward-backward motion in phase space is simple. Starting from $(\mathbf{q}_0, \mathbf{p}_0)$ at time 0, the trajectory lands at $(\mathbf{q}_t, \mathbf{p}_t^F)$ at the time t and then evolves from $(\mathbf{q}_t, \mathbf{p}_t)$ backward to reach the phase point $(\mathbf{q}_f, \mathbf{p}_f)$ when the total time returns to zero. The essential physics lies in the dynamics in an infinitesimal time domain around the intermediate time t . According to the equations of motion, all coordinates and momenta evolve continuously except at time t . At that instant the momentum undergoes a jump equal to the amount

$$\delta\mathbf{p} = \hbar\mu\mathbf{B}'_t \quad (2.11)$$

where $\mathbf{B}'_t \equiv \partial B(\mathbf{q}_t)/\partial \mathbf{q}_t$. Finally, the action at the time t increments by the amount

$$\delta S = \hbar\mu B_t \quad (2.12)$$

where $B_t \equiv B(\mathbf{q}_t)$. If the operator B is a constant equal to B_0 , all trajectories return to their original point at the final time. In that case $U(t;\mu) = \exp(i\mu B_0)$, namely, the propagator is a multiplier independent of time.

At this point we return to eq 2.1, the derivative expression of the Heisenberg operator B_H . Because the final phase space variables as well as the action in eq 2.4 depend on the parameter μ , we may divide B_H into three parts corresponding to the derivatives of the prefactor $D(\mathbf{q}_0, \mathbf{p}_0; \mathbf{q}_f, \mathbf{p}_f)$, the action $S(\mathbf{q}_0, \mathbf{p}_0; \mu)$, and the final coherent state $|g(\mathbf{q}_f, \mathbf{p}_f)\rangle$, respectively. The correlation function eq 1.1 can also be partitioned into three terms accordingly

$$C(t) = C_1(t) + C_2(t) + C_3(t) \quad (2.13)$$

Using the fact that as μ approaches zero the trajectories become continuous at the midpoint, i.e., $(\mathbf{q}_f, \mathbf{p}_f) \rightarrow (\mathbf{q}_0, \mathbf{p}_0)$, $S \rightarrow 0$, and $D \rightarrow 1$, we readily obtain

$$\begin{aligned} C_1(t) &= -i(2\pi\hbar)^{-n} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \frac{\partial}{\partial \mu} D(\mathbf{q}_0, \mathbf{p}_0; \mathbf{q}_f, \mathbf{p}_f)|_{\mu=0} \\ &\quad \times \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_0, \mathbf{p}_0) \rangle \end{aligned} \quad (2.14a)$$

$$\begin{aligned} C_2(t) &= \frac{1}{\hbar}(2\pi\hbar)^{-n} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \frac{\partial}{\partial \mu} S(\mathbf{q}_0, \mathbf{p}_0; \mu)|_{\mu=0} \\ &\quad \times \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_0, \mathbf{p}_0) \rangle \end{aligned} \quad (2.14b)$$

and

$$\begin{aligned} C_3(t) &= -i(2\pi\hbar)^{-n} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \\ &\quad \frac{\partial}{\partial \mu} \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_f, \mathbf{p}_f) \rangle|_{\mu=0} \end{aligned} \quad (2.14c)$$

To proceed, we examine the stability matrix in the neighborhood of $\mu = 0$. Expanding through linear terms, one finds

$$\frac{\partial \mathbf{q}_f}{\partial \mathbf{q}_0} = \mathbf{1} + \mu \frac{\partial}{\partial \mathbf{q}_0} \left(\frac{\partial \mathbf{q}_f}{\partial \mathbf{p}_t} \frac{\partial \mathbf{p}_t}{\partial \mu} \right) \quad \frac{\partial \mathbf{q}_f}{\partial \mathbf{p}_0} = \mu \frac{\partial}{\partial \mathbf{p}_0} \left(\frac{\partial \mathbf{q}_f}{\partial \mathbf{p}_t} \frac{\partial \mathbf{p}_t}{\partial \mu} \right) \quad (2.15)$$

$$\frac{\partial \mathbf{p}_f}{\partial \mathbf{q}_0} = \mu \frac{\partial}{\partial \mathbf{q}_0} \left(\frac{\partial \mathbf{p}_f}{\partial \mathbf{p}_t} \frac{\partial \mathbf{p}_t}{\partial \mu} \right) \quad \frac{\partial \mathbf{p}_f}{\partial \mathbf{p}_0} = \mathbf{1} + \mu \frac{\partial}{\partial \mathbf{p}_0} \left(\frac{\partial \mathbf{p}_f}{\partial \mathbf{p}_t} \frac{\partial \mathbf{p}_t}{\partial \mu} \right) \quad (2.16)$$

where $\mathbf{1}$ is the $n \times n$ identity matrix. The derivatives $\partial \mathbf{q}_f / \partial \mathbf{p}_t$, etc. are elements of the stability matrix that corresponds to the backward evolution, i.e., the final point $(\mathbf{q}_f, \mathbf{p}_f)$ depends on the initial condition $(\mathbf{q}_t, \mathbf{p}_t)$ of the backward trajectory. At this stage we do not evaluate the derivative $\partial \mathbf{p}_f / \partial \mu$ explicitly, as we wish to allow an arbitrary momentum jump. By inserting these expressions into eq 2.6 and using the following relation

$$\det(\mathbf{R} + \delta\mathbf{R}) = \det \mathbf{R} (1 + \text{Tr}(\mathbf{R}^{-1} \cdot \delta\mathbf{R})) \quad (2.17)$$

which holds for any matrix \mathbf{R} and an infinitesimal variation $\delta\mathbf{R}$, the derivative of the prefactor takes the following form:

$$\begin{aligned} \frac{\partial}{\partial \mu} D(\mathbf{q}_0, \mathbf{p}_0; \mathbf{q}_f, \mathbf{p}_f) &= \frac{1}{4} \text{Tr} \left\{ \frac{\partial}{\partial \mathbf{q}_0} \left(\frac{\partial \mathbf{q}_f}{\partial \mathbf{p}_t} - \frac{1}{2i\hbar} \Gamma^{-1} \cdot \frac{\partial \mathbf{p}_f}{\partial \mathbf{p}_t} \right) \cdot \frac{\partial \mathbf{p}_t}{\partial \mu} \right. \\ &\quad \left. + \frac{\partial}{\partial \mathbf{p}_0} \left(\frac{\partial \mathbf{p}_f}{\partial \mathbf{p}_t} - 2i\hbar \frac{\partial \mathbf{q}_f}{\partial \mathbf{p}_t} \cdot \Gamma \right) \cdot \frac{\partial \mathbf{p}_t}{\partial \mu} \right\} \end{aligned} \quad (2.18)$$

Inserting this expression in eq 2.14a and integrating by parts, we obtain

$$\begin{aligned} C_1(t) &= \frac{i}{4}(2\pi\hbar)^{-n} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \frac{\partial \mathbf{p}_t^T}{\partial \mu} \Big|_{\mu=0} \\ &\quad \times \left[\left(\frac{\partial \mathbf{q}_f}{\partial \mathbf{p}_t} - \frac{1}{2i\hbar} \frac{\partial \mathbf{p}_f}{\partial \mathbf{p}_t} \cdot \Gamma^{-1} \right) \cdot \frac{\partial}{\partial \mathbf{q}_0} + \left(\frac{\partial \mathbf{p}_f}{\partial \mathbf{p}_t} - 2i\hbar \frac{\partial \mathbf{q}_f}{\partial \mathbf{p}_t} \cdot \Gamma \right) \cdot \frac{\partial}{\partial \mathbf{p}_0} \right] \\ &\quad \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_0, \mathbf{p}_0) \rangle \end{aligned} \quad (2.19)$$

where it is assumed that $\langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_0, \mathbf{p}_0) \rangle \rightarrow 0$ as one component of the coordinates or the momenta go to $\pm\infty$. Through some algebra one can show

$$\begin{aligned} \frac{\partial}{\partial \mathbf{q}_0} \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_0, \mathbf{p}_0) \rangle &= \\ -4\Gamma \cdot \mathbf{q}_0 \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_0, \mathbf{p}_0) \rangle &+ 2\Gamma \cdot \langle g(\mathbf{q}_0, \mathbf{p}_0) | \\ [\rho(0) A + \rho(0) A \mathbf{q}] g(\mathbf{q}_0, \mathbf{p}_0) \rangle \end{aligned} \quad (2.20)$$

and

$$\begin{aligned} \frac{\partial}{\partial \mathbf{p}_0} \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_0, \mathbf{p}_0) \rangle &= \\ \frac{i}{\hbar} \langle g(\mathbf{q}_0, \mathbf{p}_0) | [\rho(0) A \mathbf{q} - \mathbf{q} \rho(0) A] | g(\mathbf{q}_0, \mathbf{p}_0) \rangle \end{aligned} \quad (2.21)$$

Combining these results we may write $C_1(t)$ in the compact form

$$\begin{aligned} C_1(t) &= -i(2\pi\hbar)^{-n} \int d\mathbf{q}_0 \int d\mathbf{p}_0 [\langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | \\ &\quad | g(\mathbf{q}_0, \mathbf{p}_0) \rangle \mathbf{q}_0^T - \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A \mathbf{q}^T | g(\mathbf{q}_0, \mathbf{p}_0) \rangle] \\ &\quad \times \frac{\partial}{\partial \mathbf{p}_t} \left(\Gamma \cdot \mathbf{q}_f - \frac{1}{2i\hbar} \mathbf{p}_f \right) \cdot \frac{\partial \mathbf{p}_t}{\partial \mu} \Big|_{\mu=0} \end{aligned} \quad (2.22)$$

Thus, the term in the correlation function arising from the prefactor takes the form

$$C_1(t) = \int d\mathbf{q}_0 \int d\mathbf{p}_0 \mathbf{f}_1(\mathbf{q}_0, \mathbf{p}_0) \cdot \frac{\partial \mathbf{p}_t}{\partial \mu} \Big|_{\mu=0} \quad (2.23)$$

The derivative of the total action with respect to the parameter μ can be evaluated straightforwardly:

$$\frac{\partial S}{\partial \mu} \Big|_{\mu=0} = \hbar \frac{\partial \mathbf{p}_t}{\partial \mu} \Big|_{\mu=0} \cdot \frac{\partial \mathbf{q}_f}{\partial \mathbf{p}_t} \cdot \mathbf{p}_0 + \hbar B_t \quad (2.24)$$

which yields

$$\begin{aligned} C_2(t) &= (2\pi\hbar)^{-n} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \left(\frac{\partial \mathbf{p}_t}{\partial \mu} \Big|_{\mu=0} \cdot \frac{\partial \mathbf{q}_f}{\partial \mathbf{p}_t} \cdot \mathbf{p}_0 + \hbar B_t \right) \\ &\times \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_0, \mathbf{p}_0) \rangle \\ &\equiv \int d\mathbf{q}_0 \int d\mathbf{p}_0 \mathbf{f}_2(\mathbf{q}_0, \mathbf{p}_0) \cdot \frac{\partial \mathbf{p}_t}{\partial \mu} \Big|_{\mu=0} + C_{qc}(t) \end{aligned} \quad (2.25)$$

where the contribution $C_{qc}(t)$ due to the delta pulse in the effective Hamiltonian can be viewed as a quasiclassical correlation function, namely, the Heisenberg operator B_H is replaced by the classical counterpart $B(t)$ in the definition of $C(t)$ eq 1.1. The first term in eq 2.25 is proportional to the momentum jump, while the second quasiclassical term arises from the net increment of the action. In a similar manner we obtain an explicit formula for $C_3(t)$:

$$\begin{aligned} C_3(t) &= 2i\hbar(2\pi\hbar)^{-n} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \left\{ [\langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_0, \mathbf{p}_0) \rangle] \right. \\ &\times \left. \frac{\partial}{\partial \mathbf{p}_t} \left(\Gamma \mathbf{q}_f - \frac{1}{2i\hbar} \mathbf{p}_f \right) - \frac{1}{2i\hbar} \mathbf{p}_0^T \cdot \frac{\partial \mathbf{q}_f}{\partial \mathbf{p}_t} \right. \\ &\left. \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_0, \mathbf{p}_0) \rangle \right\} \cdot \frac{\partial \mathbf{p}_t}{\partial \mu} \Big|_{\mu=0} \end{aligned} \quad (2.26)$$

Again, the integrand is seen to be proportional to the derivative of the momentum jump, i.e.,

$$C_3(t) = \int d\mathbf{q}_0 \int d\mathbf{p}_0 \mathbf{f}_3(\mathbf{q}_0, \mathbf{p}_0) \cdot \frac{\partial \mathbf{p}_t}{\partial \mu} \Big|_{\mu=0} \quad (2.27)$$

Adding eqs 2.23, 2.25, and 2.27 one sees that

$$\begin{aligned} C(t) &= \int d\mathbf{q}_0 \int d\mathbf{p}_0 [\mathbf{f}_1(\mathbf{q}_0, \mathbf{p}_0) + \mathbf{f}_2(\mathbf{q}_0, \mathbf{p}_0) + \mathbf{f}_3(\mathbf{q}_0, \mathbf{p}_0)] \\ &\times \frac{\partial \mathbf{p}_t}{\partial \mu} \Big|_{\mu=0} + C_{qc}(t) \end{aligned} \quad (2.28)$$

Furthermore, comparison of the above results reveals that

$$-\frac{1}{2}[\mathbf{f}_2(\mathbf{q}_0, \mathbf{p}_0) + \mathbf{f}_3(\mathbf{q}_0, \mathbf{p}_0)] = \mathbf{f}_1(\mathbf{q}_0, \mathbf{p}_0) \quad (2.29)$$

from which it follows that

$$\begin{aligned} C(t) &= \frac{1}{2} \int d\mathbf{q}_0 \int d\mathbf{p}_0 [\mathbf{f}_2(\mathbf{q}_0, \mathbf{p}_0) + \mathbf{f}_3(\mathbf{q}_0, \mathbf{p}_0)] \\ &\times \frac{\partial \mathbf{p}_t}{\partial \mu} \Big|_{\mu=0} + C_{qc}(t) \end{aligned} \quad (2.30)$$

It is thus possible to eliminate the contribution of the prefactor from the correlation function. To compensate for this omission, the part of the correlation function that arises from the momentum increment at the time t must be multiplied by 1/2.

As that part cannot be separated from the one arising from the quasiclassical contribution associated with the change in the action, this must be achieved by multiplying the momentum increment by a factor of 1/2.

Equation 2.30 is the main result outlined in ref 17. The correlation function is given by the expression

$$\begin{aligned} C(t) &= -i(2\pi\hbar)^{-n} \frac{\partial}{\partial \mu} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \exp\left(\frac{i}{\hbar} S(\mathbf{q}_0, \mathbf{p}_0; \mu)\right) \\ &\times \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho(0) A | g(\mathbf{q}_f, \mathbf{p}_f) \rangle \Big|_{\mu=0} \end{aligned} \quad (2.31)$$

The trajectories follow the classical equations of motion with the Hamiltonian H up to the time t , at which point the momentum component jumps by the amount

$$\delta \mathbf{p}_{opt} = \frac{1}{2} \hbar \mu \mathbf{B}'_t \quad (2.32)$$

for a small value of the finite difference parameter μ . At the same time, the action increments by the full amount given by eq 2.12. Subsequent evolution takes place in the negative time direction, and the integrand is evaluated when the time parameter reaches zero once again.

Equation 2.31 (along with the momentum and action jumps given by eqs 2.32 and 2.12, respectively) is a rigorous semiclassical formulation of correlation functions that uses trajectories in combined forward–backward time for all degrees of freedom. Its main advantage is that the contribution from the prefactor is eliminated. As a consequence, the number of equations to be solved scale linearly with the number of degrees of freedom in the Hamiltonian. Note that the elimination of the prefactor is achieved via an *exact* transformation of the derivative form of the correlation function, resulting in an expression where *the momentum jump is one-half of that dictated by the classical equations of motion*. This transformation was feasible because the derivative formulation in terms of a small parameter allows linearization of the equations. It should be noted that the prefactor is equal to the negative of the total contribution from terms arising directly from the momentum jump; these terms are extremely important, as the remaining term is merely a quasiclassical contribution.

The combined forward–backward treatment of the correlation function amounts to a stationary phase evaluation of the full semiclassical expression, in which the individual forward and backward time-evolution operators are treated via the Van Vleck propagator. That full semiclassical formulation takes the form

$$\begin{aligned} C(t) &= (2\pi\hbar)^{-2n} \int d\mathbf{q}_F \int d\mathbf{p}_F \int d\mathbf{q}_B \int d\mathbf{p}_B D_F(\mathbf{q}_F, \mathbf{p}_F) \\ &\times D_B(\mathbf{q}_B, \mathbf{p}_B) \exp\left(\frac{i}{\hbar} S(\mathbf{q}_F, \mathbf{p}_F; \mathbf{q}_B, \mathbf{p}_B)\right) \langle g(\mathbf{q}_F, \mathbf{p}_F) | \rho(0) A | g(\mathbf{q}_B, \mathbf{p}_B) \rangle \langle g(\mathbf{q}_B, \mathbf{p}_B) | B | g(\mathbf{q}_F, \mathbf{p}_F) \rangle \end{aligned} \quad (2.33)$$

where $\mathbf{q}_F, \mathbf{p}_F$ and $\mathbf{q}_B, \mathbf{p}_B$ are the endpoints of the forward and backward trajectories. Often A and B are operators that depend on only a few observable degrees of freedom (the “system”) while the remaining coordinates constitute the environment (or “bath”). Treating the intermediate integrations associated with the bath components of $\mathbf{q}_B, \mathbf{p}_B$ via the stationary phase method leads¹⁶ to an FBSD expression where the trajectories evolve continuously in the space of the bath, while their system component jumps at the intermediate time t . That procedure amounts to an enormous simplification, as the cancellation between the forward and the backward parts corresponding to the dynamics of the solvent gives rise to small actions and thus

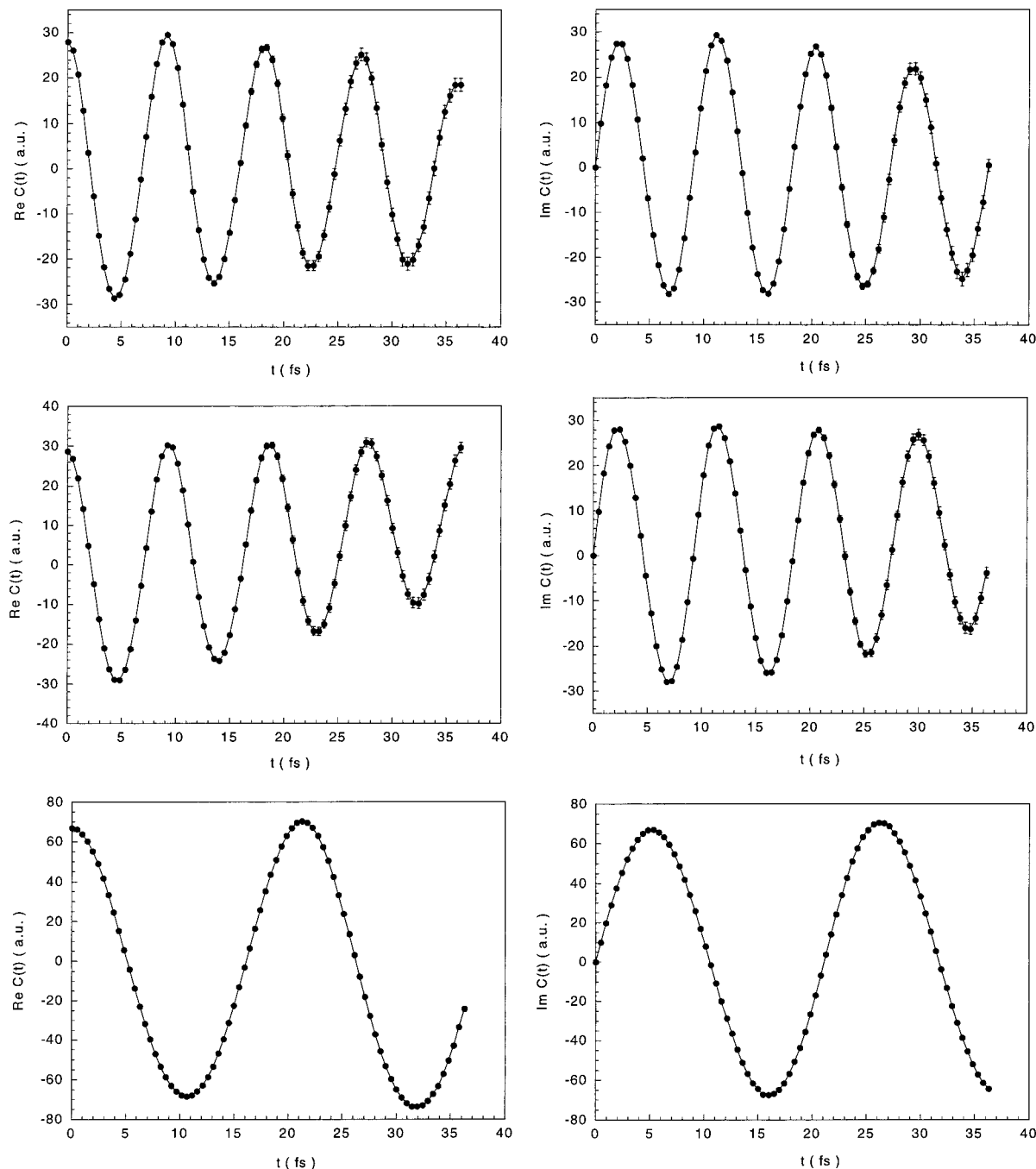


Figure 1. (a) Real and imaginary parts of the correlation function of the O–H asymmetric stretch as obtained from the FBSD calculations. Error bars indicate one standard deviation. Solid lines are guides to the eye only. (b) Real and imaginary parts of the correlation function of the O–H symmetric stretch. (c) Real and imaginary parts of the correlation function of the H–O–H bend.

smooth integrands; at the same time, the integrand is more oscillatory along the direction of the variables associated with the probed system, and thus these integration variables must be treated via a combination of Monte Carlo and quadrature methods. Replacing the exact integration by the stationary phase result wipes out the interference between multiple bounce contributions across the forward and backward parts of the dynamics and thus may degrade the accuracy if the potential of the bath degrees of freedom is very anharmonic. However, important interference between system trajectories is fully accounted for in that scheme. Another way of arriving at FBSD expressions where the system component of the momentum jumps at the intermediate time while the trajectories remain continuous in the space of the bath involves¹⁵ expressing the operator B in exponential form by invoking the Wigner–Weyl

representation^{20,21} and implementing FBSD for all degrees of freedom. While the system components of $\mathbf{q}_B, \mathbf{p}_B$ are also treated within the stationary phase method in that approach, the finite-size momentum jumps permitted in the space of the system allow for some interference between multiple bounce trajectories. The present formulation, which uses a derivative method to exponentiate the operators, is simpler than all of the above in that no additional integrations are introduced and, most importantly, there is no prefactor to be computed. At the same time, the prefactor-free FBSD described here cannot account for interference between distinct trajectories of the forward and reverse time propagators as the momentum jump performed at the time t is infinitesimal in magnitude. As a consequence, the present method is similar in spirit to the linearization approximation of Miller and co-workers,^{22,23} although the math-

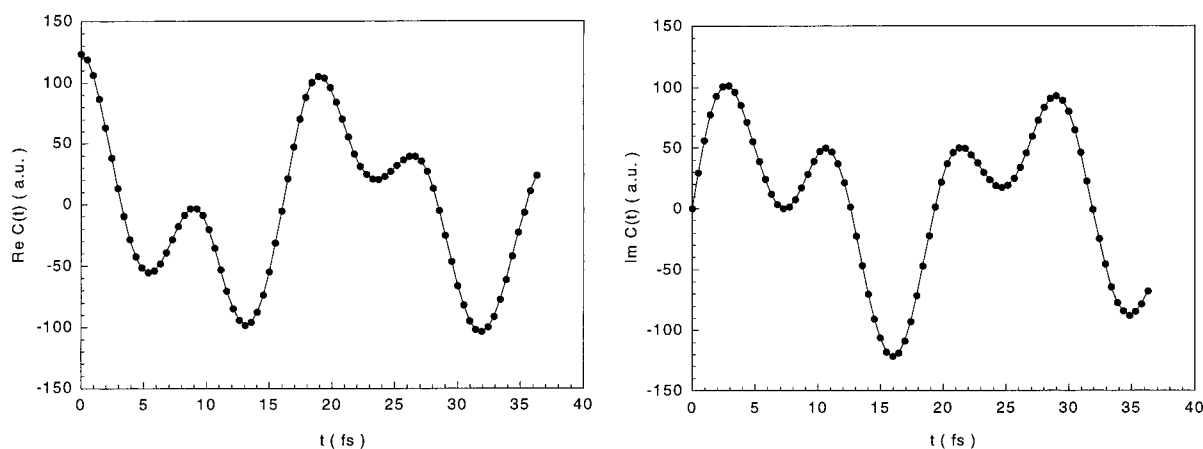


Figure 2. Real and imaginary parts of the sum of the three correlation functions.

emational details differ and the present prefactor-free FBSD was obtained via a rigorous semiclassical procedure. Sun et al.²⁴ have found that their linearization approximation, which also neglects similar interference terms, captures the short time, transition-state-like features of thermal rate constants correctly but fails to describe nonclassical aspects of the recrossing dynamics resulting from quantum interference on the time scale of two or more vibrational periods. Our tests¹⁷ have demonstrated that the prefactor-free FBSD leads to reasonably accurate results for correlation functions in multidimensional potentials where relaxation and dissipative effects tend to weaken interference phenomena.

III. Application: Vibrational Dynamics of Water

The FBSD developed above is a general technique for investigating dynamical properties of a system. In addition to correlation functions, the quantum average at time t of any observable corresponding to the operator B can be evaluated via eq 1.1 in which A is set equal to the identity operator. In the following we consider molecular vibrations of a molecule or small cluster at low temperatures. Because vibrations are collective motions, we focus on the numerical implementation of the FBSD for calculating correlation functions of the type

$$C(t) = \text{Tr}(\rho(0)Q_k e^{iHt/\hbar} Q_k e^{-iHt/\hbar}) \quad (3.1)$$

where Q_k is one of the normal modes of the system with respect to the global potential minimum. It is a straightforward matter to extend the procedure to the calculation of the dipole correlation function if the functional form of the dipole moment operator is available.

The initial density is constructed in terms of the ground vibrational state, $\rho(0) = |\Psi_0\rangle\langle\Psi_0|$, which factorizes in the normal mode representation

$$\langle\mathbf{Q}|\Psi_0\rangle = \prod_{j=1}^n \left(\frac{\omega_j}{\pi}\right)^{1/4} \exp\left(-\frac{\omega_j}{2\hbar} Q_j^2\right) \quad (3.2)$$

where $n = 3N - 6$, N being the total number of atoms and ω_j the normal-mode frequencies. We take Γ as a diagonal matrix with elements equal to $\omega_j/2\hbar$. Carrying out the Gaussian integrals, one readily obtains

$$\begin{aligned} \langle g(\mathbf{Q}_0, \mathbf{P}_0) | \rho(0) Q_k | g(\mathbf{Q}_f, \mathbf{P}_f) \rangle &= \frac{1}{2} \left(Q_{kf} + i \frac{P_{kf}}{\omega_k} \right) \prod_{j=1}^n \\ &\times \exp \left[-\frac{\omega_j}{4\hbar} (Q_{j,0}^2 + Q_{j,f}^2) - \frac{1}{4\hbar\omega_j} (P_{j,0}^2 + P_{j,f}^2) \right. \\ &\left. - \frac{1}{2i\hbar} (Q_{j,0}P_{j,0} - Q_{j,f}P_{j,f}) \right] \end{aligned} \quad (3.3)$$

and

$$\begin{aligned} \langle g(\mathbf{Q}_0, \mathbf{P}_0) | \rho(0) Q_k | g(\mathbf{Q}_0, \mathbf{P}_0) \rangle &= \frac{1}{2} \left(Q_{k,0} + i \frac{P_{k,0}}{\omega_k} \right) \prod_{j=1}^n \\ &\times \exp \left(-\frac{\omega_j}{2\hbar} Q_{j,0}^2 - \frac{1}{2\hbar\omega_j} P_{j,0}^2 \right) \end{aligned} \quad (3.4)$$

These expressions are inserted into eq 2.28 in numerical calculations.

It is convenient to retain the normal mode coordinates for the representation of the FBSD correlation function. The RWK2 potential²⁵ which has been designed for calculating vibrational spectra of water clusters is adopted in our work. That potential consists of the Morse oscillator potential from the intramolecular interaction plus atom–atom interactions and Coulomb terms between point charges from the intermolecular interaction. The classical equations of motion are solved in normal mode coordinates. Our previous work¹⁷ showed that it is feasible to sample the initial conditions via a Metropolis procedure with the absolute value of eq 3.4 being the weight function. Here for fast convergence we invoke the Genz–Monahan algorithm developed specifically for higher dimensional integrals over unbounded regions with Gaussian weight.²⁶ Their approach is based on the stochastic spherical–radial rules for integrations. We report the results of the method described in the previous section for a single water molecule as well as two- and four-molecule clusters using 2500 trajectories for each degree of freedom. The largest of these systems has 30 active degrees of freedom and thus the calculation involves a 60-dimensional integral which is evaluated with a total of 150 000 trajectories.

Figure 1 shows the correlation functions of the three vibrational modes of a water molecule, namely the O–H asymmetric stretch, O–H symmetric stretch, and H–O–H bend, obtained via the prefactor-free FBSD scheme described in section II. Figure 2 shows the sum of the three correlation functions. Since rotational degrees of freedom evolve on a

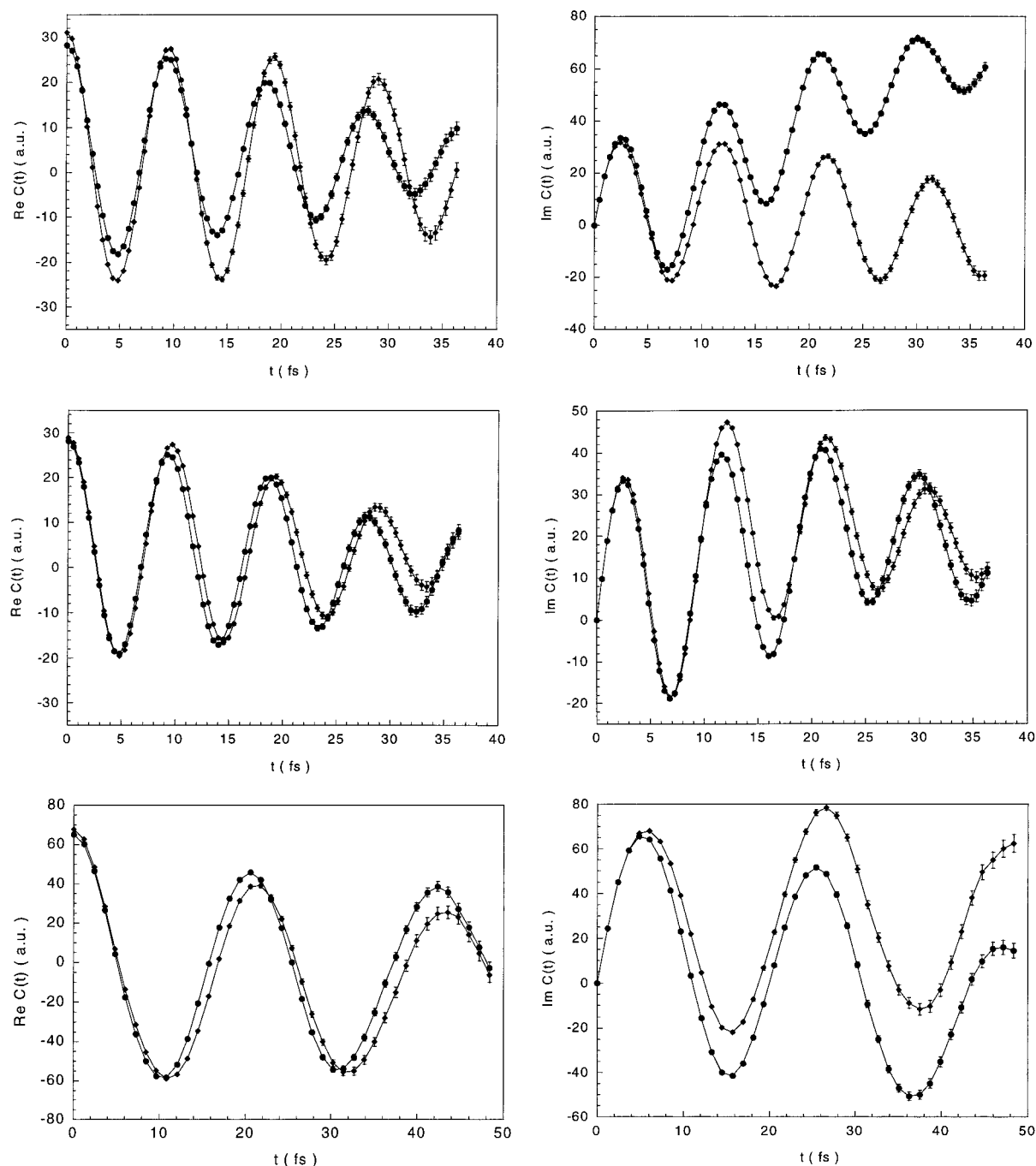


Figure 3. (a) Real and imaginary parts of the correlation functions: the two O–H stretches of the donor in the water dimer. (b) Real and imaginary parts of the correlation functions: the two O–H stretches of the acceptor in the water dimer. (c) Real and imaginary parts of the correlation functions of the two H–O–H bends in the water dimer.

slower time scale, this sum represents a good approximation to the correlation function for the normal mode vector of water.

The fundamental frequencies of vibrations can be estimated from these figures. The frequencies for the O–H asymmetric stretch, O–H symmetric stretch, and H–O–H bend are about 3658, 3573, and 1576 cm^{-1} , respectively. Comparing with the results of the normal-mode analysis, which are 3922, 3817, and 1639 cm^{-1} , respectively, we see strong red shifts due to the anharmonicity of the system. It is clearly shown in these figures that anharmonic interactions affect the dynamics within about 10 fs. In addition, one observes energy transfer from the O–H asymmetric stretch to the nearly resonant O–H symmetric stretch during the initial 40 fs. This time is still short for the H–O–H bend to be involved in the process of energy redistribution in the molecule.

Figures 3 and 4 show similar results for the water dimer and tetramer, respectively. The stable configuration of the tetramer is cyclic. We also find red shifts (mainly due to intramolecular vibrations) for the studied normal modes. This observation is in agreement with the results from the self-consistent field calculations by Jung and Gerber.²⁷ In the dimer, the hydrogen bond induces an increment of the amplitude and a decrement of the frequency for one of the OH stretches in the donor. In general, the larger number of degrees of freedom leads to stronger mixing among the normal modes during evolution. All figures exhibit imaginary parts comparable in size to the real parts of the correlation functions. This behavior is a manifestation of the quantum mechanical aspect of the dynamics at zero temperature. It is remarkable that the error bars are small in all cases, even though the number of samples per integration

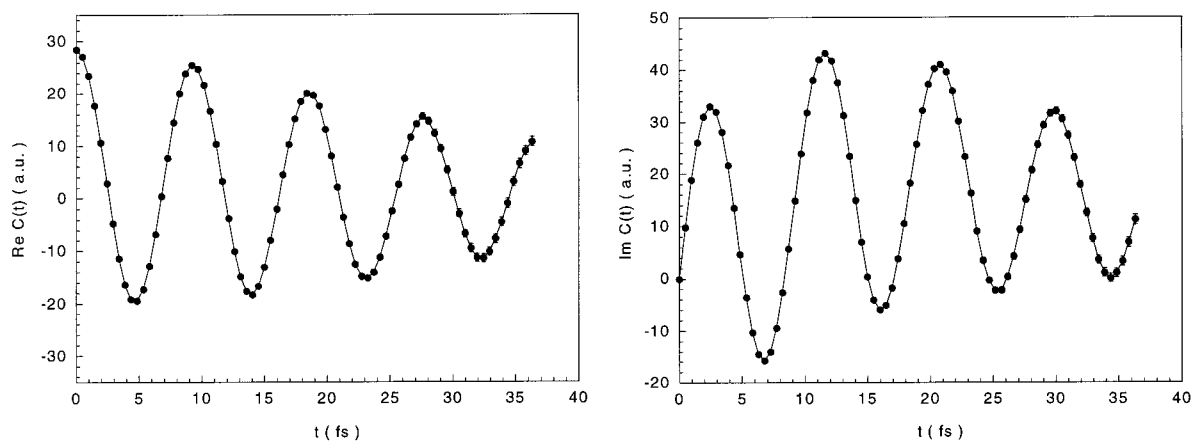


Figure 4. Real and imaginary parts of the correlation function of the O-H stretch with the highest frequency in the water tetramer.

variable is rather small. Most importantly, the size of the error bars is seen to be a slowly varying function of cluster size. This is very encouraging for performing FBSD calculations with truly large systems.

IV. Concluding Remarks

We have presented a rigorous, yet practical methodology for calculating semiclassical correlation functions or expectation values. The key features of this approach are (a) the combined treatment of the forward and backward time evolution operators, which guarantee a smooth integrand amenable to Monte Carlo sampling, and (b) the absence of a semiclassical prefactor which leads to linear scaling. Starting from a derivative formulation of the correlation function, it was shown that the prefactor amounts to *exactly one-half* of the combined semiclassical phase and initial density terms proportional to the momentum jump at the end of the forward evolution. As a consequence, using momentum increments of half the magnitude dictated from the classical equations of motion cancels the contribution from the semiclassical determinant. Given the near elimination of the sign problem and the linear scaling with system size, the prefactor-free FBSD opens the way to large-scale simulations in real time.

Implementation of the prefactor-free methodology is straightforward. If the coherent state matrix element involving the initial density is known, one uses its absolute value as a sampling function to carry out a stochastic procedure for the integrals, say, selecting initial conditions via a Metropolis random walk. After integrating to the desired propagation time t , trajectories incur an instantaneous discontinuity and subsequently continue in the backward time direction until the time origin is reached. Evaluation of the required derivative by a two-point finite difference formula requires a single calculation. As the finite difference parameter is infinitesimal, the corresponding momentum jump and resulting forward-backward action are small. These facts ensure excellent Monte Carlo statistics with modest numbers of samples.

Application to the vibrational dynamics of a water molecule was employed to illustrate the practicality of the scheme. The correlation functions of the normal modes were computed for several oscillation periods. The calculations give rise to a large imaginary component of the correlation functions. Such imagi-

nary components are of purely quantum mechanical origin, as classical correlation functions are always real-valued. If the dipole moment operator is known to a reasonable approximation, the real part of correlation function can be used to extract spectral line shapes. Future work in our group will deal with similar investigations in molecular clusters.

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References and Notes

- (1) Van Vleck, J. H. *Proc. Nat. Acad. Sci. U.S.A.* **1928**, *14*, 178.
- (2) Morette, C. *Phys. Rev.* **1952**, *81*, 848.
- (3) Miller, W. H. *J. Chem. Phys.* **1970**, *53*, 3578.
- (4) Miller, W. H. *Adv. Chem. Phys.* **1974**, *25*, 69.
- (5) Eu, B. C. *Semiclassical theory of molecular scattering*; Springer-Verlag: Berlin, 1984.
- (6) Child, M. S. *Semiclassical mechanics with molecular applications*; Clarendon: Oxford, 1991.
- (7) Tomsovic, S.; Heller, E. J. *Phys. Rev. Lett.* **1991**, *67*, 664.
- (8) Sepulveda, M. A.; Tomsovic, S.; Heller, E. J. *Phys. Rev. Lett.* **1992**, *69*, 402.
- (9) Gutzwiller, M. C. *Chaos in classical and quantum mechanics*; Springer-Verlag: New York, 1990.
- (10) Schulman, L. S. *Techniques and applications of path integration*; John Wiley and Sons: New York, 1981.
- (11) Heller, E. J. *J. Chem. Phys.* **1991**, *94*, 2723.
- (12) Herman, M. F.; Kluk, E. *Chem. Phys.* **1984**, *91*, 27.
- (13) Makri, N.; Thompson, K. *Chem. Phys. Lett.* **1998**, *291*, 101–109.
- (14) Thompson, K.; Makri, N. *J. Chem. Phys.* **1999**, *110*, 1343.
- (15) Miller, W. H. *Faraday Discuss.* **1998**, *110*, 1.
- (16) Thompson, K.; Makri, N. *Phys. Rev.* **1999**, *E 59*, R4729.
- (17) Shao, J.; Makri, N. *J. Phys. Chem.* **1999**, in press.
- (18) Batista, V.; Zanni, M. T.; Greenblatt, J.; Neumark, D. M.; Miller, W. H. *J. Chem. Phys.* **1999**, *110*, 3736–3747.
- (19) Kühn, O.; Makri, N. *J. Phys. Chem.*, submitted.
- (20) Wigner, E. J. *Chem. Phys.* **1937**, *5*, 720.
- (21) Weyl, H. *Z. Phys.* **1927**, *46*, 1.
- (22) Wang, H.; Sun, X.; Miller, W. H. *J. Chem. Phys.* **1998**, *108*, 9726.
- (23) Sun, X.; Wang, H.; Miller, W. H. *J. Chem. Phys.* **1998**, *109*, 7064.
- (24) Sun, X.; Wang, H.; Miller, W. H. *J. Chem. Phys.* **1998**, *109*, 4190.
- (25) Coker, D. F.; Watts, R. O. *J. Phys. Chem.* **1987**, *91*, 2513.
- (26) Genz, A.; Monahan, J. *J. Comput. Appl. Math.*, to be published. We thank Prof. Genz for providing his program RANRTH.
- (27) Jung, J. O.; Gerber, R. B. *J. Chem. Phys.* **1996**, *105*, 10332.