

# Monte Carlo Evaluation of Forward–Backward Semiclassical Correlation Functions with a Quantized Coherent State Density

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The derivative formulation of the forward–backward semiclassical dynamics (FBSD) representation of time correlation functions can be expressed as an integral with respect to trajectory initial conditions weighted by the coherent state transform of a corrected density operator. Expressions are derived for evaluating the relevant matrix elements for applications of particular interest, such as normal mode, bond stretching, and velocity correlation functions at zero and at finite temperature by employing the Gaussian approximation and the discretized path integral representation of the initial density operator, respectively. The obtained expressions lend themselves naturally to integration via Monte Carlo sampling techniques. The fully quantum mechanical representation of the appropriate density operator ensures a proper treatment of zero-point effects, and the use of the coherent state representation captures important imaginary components that are absent from purely classical trajectory methods. Applications to clusters of four water molecules at room temperature are presented.

## I. Introduction

For over three decades, classical trajectory methods have provided the most practical and versatile tool for studying the dynamics of polyatomic systems and can currently treat biological molecules with thousands of interacting atoms. Since its early days, the power of molecular dynamics has inspired persistent efforts to find ways of incorporating quantum mechanical effects within a classical trajectory setting. The most prominent quantum effects include nonadiabatic transitions, zero-point motion, and tunneling. These efforts have led to the development of quantum–classical methods. Perhaps the most widely used quantum–classical method is trajectory surface hopping, a development pioneered by Tully<sup>1</sup> and motivated by Pechukas' path integral analysis.<sup>2</sup>

In recent years, the semiclassical approximation<sup>3,4</sup> has reemerged as a powerful way of including quantum mechanical effects in classical trajectory simulations.<sup>5–55</sup> The appeal of that approach is evident because the time-dependent semiclassical approximation is entirely based on classical trajectories and their stability properties, yet it is usually sufficiently accurate in the parameter regime of chemical interest. Thus, the use of time-dependent semiclassical methods carries the potential for making accurate simulation of polyatomic reaction dynamics feasible.

However, progress toward that goal has been hampered by some serious difficulties. First, the original form of the semiclassical propagator involves a double-ended boundary condition that poses a difficult numerical problem. This situation is remedied through the development of initial value representations.<sup>5,9,17–23</sup> A more severe problem is the oscillatory nature of the semiclassical integrand, which renders Monte Carlo methods impractical. It appears that a successful treatment of quantum interference effects requires one's ability to handle oscillatory integrals, yet no stable method exists for such calculations in many dimensions. A compromise is offered by

forward–backward semiclassical dynamics methods.<sup>32–45</sup> The latter exploit the presence of a time-evolution operator and its adjoint in ensemble-averaged observables to express the dynamical part along a combined forward–backward time contour. This procedure is equivalent to an additional stationary-phase evaluation in all or just some of the degrees of freedom involved. The forward–backward implementation succeeds in tempering the phase at the expense of eliminating (partially or entirely) quantum interference effects, yet the resulting expressions are often sufficiently accurate for chemical calculations, as well as practical for application to large systems.<sup>48–50,52,55</sup>

Given one's inability to handle oscillatory integrands, forward–backward semiclassical dynamics (FBSD) methods are sufficiently stable for polyatomic calculations only if they eliminate phase cancellation to the largest extent possible. This requirement implies that quantum mechanical effects originating from phase interference will have to be neglected in such treatments. Yet, proper phase space representations and quantization of the initial condition offer the possibility of capturing other important nonclassical effects such as zero point motion and imaginary components. Miller and co-workers have developed a host of FBSD expressions for calculating time correlation functions<sup>36,39,43,44</sup> and have shown how the Wigner phase space quasiclassical method that has emerged in several different formulations<sup>26,56–58</sup> can be obtained as a linearized limit of the semiclassical representation.<sup>59</sup> Developments in our group have been largely based on a derivative identity,<sup>37,38,42,45</sup> which also leads to a quasiclassical form<sup>43,45,60</sup> that involves the Husimi or coherent state transform of the density operator. The capabilities and performance of these methods has been discussed and illustrated with several examples.

The present paper aims at the development of accurate methods for representing the initial density operator within the FBSD framework. In most cases of interest the molecular system is initially either in its ground vibrational state (and thus approximated by a Gaussian density in the normal mode coordinate system) or in thermal equilibrium described by the

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Boltzmann operator. Recent work showed that the Husimi transform of the Boltzmann density can be evaluated by employing the discretized path integral technique<sup>41</sup> or semiclassical theory.<sup>61</sup> In our earlier FBSD/path integral methodology the derivative associated with the trajectory jump at the end of the forward evolution was evaluated numerically.<sup>61</sup> Thus, the present paper extends those procedures to the derivative-free version, which utilizes trajectories only in the forward time direction. By avoiding integration of the equations of motion in the negative time direction allows one to extract results at all discrete time points employed in the trajectory calculation, leading to high efficiency. This initial value form requires the evaluation of additional matrix elements in the coherent state basis, which are derived in the sections that follow for multidimensional systems and for operators of particular interest in dynamics and spectroscopy.

Section II develops the discretized path integral formulation of derivative-FBSD in the initial value form and evaluates the relevant matrix elements. Monte Carlo procedures for evaluating the multidimensional integrals and for normalizing the sampling function are discussed in section III. Section IV presents numerical applications to water clusters, and section V concludes with a discussion and various remarks.

## II. Quasiclassical Expressions from Forward–Backward Semiclassical Dynamics

The focus of this paper is on quasiclassical expressions for two-time correlation functions of the type

$$C_{AB}(t) = \text{Tr}(\hat{\rho}_0 \hat{A}(0) \hat{B}(t)) = \text{Tr}(\hat{\rho}_0 \hat{A} e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}) \quad (2.1)$$

Here the Hamiltonian

$$H = \frac{1}{2} \mathbf{p} \cdot \mathbf{m}^{-1} \cdot \mathbf{p} + V(\mathbf{x}) = \sum_{s=1}^d \sum_{j=1}^3 \frac{p_{sj}^2}{2m_s} + V(\mathbf{r}_1, \dots, \mathbf{r}_d) \quad (2.2)$$

describes a system of  $d$  atoms with Cartesian positions  $\mathbf{r}_s \equiv \{r_{sj}\}$ ,  $j = 1, 2, 3$  in a potential field  $V$ . The coordinates and momenta of all the particles are denoted collectively by the  $3d$ -dimensional vectors  $\mathbf{x}$  and  $\mathbf{p}$ , respectively. The operators  $A$  and  $B$  in eq 2.1 are generally arbitrary, and  $\rho_0$  is the operator that specifies the initial density. Various quasiclassical expressions can be obtained by applying the stationary-phase approximation in some forward–backward form to eq 2.1. The particular expression considered here starts from an exponential derivative identity for the operator  $B$ ,

$$\hat{B} = -i \frac{\partial}{\partial \mu} e^{i\mu \hat{B}} \Big|_{\mu=0} \quad (2.3)$$

and applies the semiclassical approximation to the combined product of exponentials in the coherent state representation obtained by Herman and Kluk.<sup>17</sup> After several manipulations,<sup>37,38,42</sup> the Heisenberg operator in the correlation function takes the form

$$\begin{aligned} \hat{B}_H(t) &\equiv e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} = -i \frac{\partial}{\partial \mu} e^{i\hat{H}t/\hbar} e^{i\mu \hat{B}} e^{-i\hat{H}t/\hbar} \Big|_{\mu=0} \\ &= (2\pi\hbar)^{-3d} \frac{\partial}{\partial \mu} \int d\mathbf{x}_0 \int d\mathbf{p}_0 \\ &\quad \exp\left(\frac{i}{\hbar} S(\mathbf{x}_0, \mathbf{p}_0)\right) \Big| g(\mathbf{x}_f, \mathbf{p}_f) \Big| g(\mathbf{x}_0, \mathbf{p}_0) \Big|_{\mu=0} \quad (2.4) \end{aligned}$$

Here the phase space variables  $\mathbf{x}_0, \mathbf{p}_0$  specify initial conditions

for classical trajectories, which are first integrated forward to time  $t$ . At that time, the trajectories incur position and momentum jumps given by the relations

$$\delta \mathbf{x}_t = -\frac{1}{2} \hbar \mu \frac{\partial}{\partial \mathbf{p}_t} B(\mathbf{x}_t, \mathbf{p}_t) \quad \delta \mathbf{p}_t = \frac{1}{2} \hbar \mu t \frac{\partial}{\partial \mathbf{x}_t} B(\mathbf{x}_t, \mathbf{p}_t) \quad (2.5)$$

while the action is incremented by the amount

$$\delta S_t = \hbar \mu B(\mathbf{x}_t, \mathbf{p}_t) + \mathbf{p}_t \cdot \delta \mathbf{x}_t \quad (2.6)$$

Subsequently, each trajectory is integrated back to time zero following the classical equations of motion, reaching the point  $\mathbf{x}_t, \mathbf{p}_t$  and the total accumulated action has the value  $S$ . Finally,  $g_{\mathbf{x}_0, \mathbf{p}_0}$  in eq 2.4 are coherent states described by complex-valued Gaussians,

$$\langle \mathbf{x} | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle = \left(\frac{2}{\pi}\right)^{3d/4} (\det \gamma)^{1/4} \exp\left[-(\mathbf{x} - \mathbf{x}_0) \cdot \gamma \cdot (\mathbf{x} - \mathbf{x}_0) + \frac{i}{\hbar} \mathbf{p}_0 \cdot (\mathbf{x} - \mathbf{x}_0)\right] \quad (2.7)$$

where  $\gamma$  is a  $3d \times 3d$  matrix with elements  $\gamma_{sj}$  ( $s = 1, \dots, d, j = 1, 2, 3$ ). The notable feature of eq 2.4 is the absence of the semiclassical prefactor. Elimination of the latter has been achieved by linearizing the final trajectory values and the action in the infinitesimal parameter  $\mu$  and rescaling the position and momentum jumps to compensate for the prefactor. For this reason, the trajectory increments given in eq 2.5 are equal to one-half of the values dictated by the classical equations of motion that correspond to the product of exponential operators (eq 2.4).

The infinitesimal character of the trajectory jumps at the end of the forward propagation implies that the cross terms between distinct forward and backward trajectories have been neglected. Thus, eq 2.4 cannot account for quantum interference effects. The above structure also allows the transformation of eq 2.4 to a derivative-free form that involves trajectories only in the forward time direction.<sup>43,60</sup> Thus, the Heisenberg operator takes the form

$$\begin{aligned} \hat{B}(t) &= (2\pi\hbar)^{-3d} \int d\mathbf{x}_0 \int d\mathbf{p}_0 B(\mathbf{x}(t), \mathbf{p}(t)) \\ &\quad \times \left\{ \left(1 + \frac{3}{2}d\right) \Big| g_{\mathbf{x}_0, \mathbf{p}_0} \Big| g_{\mathbf{x}_0, \mathbf{p}_0} \Big| - 2(\mathbf{x} - \mathbf{x}_0) \cdot \right. \\ &\quad \left. \gamma \Big| g_{\mathbf{x}_0, \mathbf{p}_0} \Big| g_{\mathbf{x}_0, \mathbf{p}_0} \Big| (\mathbf{x} - \mathbf{x}_0) \right\} \quad (2.8) \end{aligned}$$

where  $B(\mathbf{x}(t), \mathbf{p}(t))$  denotes the classical analogue of the operator. The correlation function then becomes

$$\begin{aligned} C_{AB}(t) &= (2\pi\hbar)^{-3d} \int d\mathbf{x}_0 \int d\mathbf{p}_0 B(\mathbf{x}(t), \mathbf{p}(t)) \\ &\quad \times \left[ \left(1 + \frac{3}{2}d\right) \langle g_{\mathbf{x}_0, \mathbf{p}_0} | \hat{\rho}_0 \hat{A} | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle - \right. \\ &\quad \left. 2 \langle g_{\mathbf{x}_0, \mathbf{p}_0} | (\mathbf{x} - \mathbf{x}_0) \cdot \hat{\rho}_0 \hat{A} \gamma \cdot (\mathbf{x} - \mathbf{x}_0) | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle \right] \quad (2.9) \end{aligned}$$

The correlation function of the inner product between two vectors is given by applying the last equation to each component of the Cartesian decomposition. For example, if both operators are  $3d$ -dimensional vectors, the correlation function is given by the expression

$$\begin{aligned}
C_{\mathbf{A}\cdot\mathbf{B}}(t) &= \text{Tr}(\hat{\rho}_0 \hat{\mathbf{A}}(0) \cdot \hat{\mathbf{B}}(t)) \\
&= (2\pi\hbar)^{-3d} \int d\mathbf{x}_0 \int d\mathbf{p}_0 \left(1 + \frac{3}{2}d\right) \\
&\quad \langle g_{\mathbf{x}_0, \mathbf{p}_0} | \hat{\rho}_0 \hat{\mathbf{A}} | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle \cdot \mathbf{B}(\mathbf{x}(t), \mathbf{p}(t)) \\
&\quad - 2(2\pi\hbar)^{-3d} \int d\mathbf{x}_0 \int d\mathbf{p}_0 \langle g_{\mathbf{x}_0, \mathbf{p}_0} | (\hat{\mathbf{x}} - \mathbf{x}_0) \hat{\rho}_0 [\hat{\mathbf{A}} \cdot \\
&\quad \mathbf{B}(\mathbf{x}(t), \mathbf{p}(t))] \cdot \gamma \cdot (\hat{\mathbf{x}} - \mathbf{x}_0) | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle \quad (2.10)
\end{aligned}$$

Throughout the rest of the paper, it is assumed for simplicity that the matrix  $\gamma$  is diagonal.

**A. Gaussian Density.** At zero temperature, the initial state is often approximated by a Gaussian wave function,

$$\Phi_0(\mathbf{x}) = \det\left(\frac{2\alpha}{\pi}\right)^{1/4} \exp[-(\mathbf{x} - \lambda) \cdot \alpha \cdot (\mathbf{x} - \lambda)^2] \quad (2.11)$$

where  $\alpha$  is a symmetric  $3d \times 3d$  matrix. The density operator is

$$\hat{\rho}_0 = |\Phi_0\rangle\langle\Phi_0| \quad (2.12)$$

and the correlation function of a scalar product takes the form

$$\begin{aligned}
C_{\mathbf{A}\cdot\mathbf{B}}(t) &= (2\pi\hbar)^{-3d} \int d\mathbf{x}_0 \int d\mathbf{p}_0 \left(1 + \frac{3}{2}d\right) \langle g_{\mathbf{x}_0, \mathbf{p}_0} | \Phi_0 \rangle \\
&\quad \langle \Phi_0 | \hat{\mathbf{A}} | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle \cdot \mathbf{B}(\mathbf{x}(t), \mathbf{p}(t)) \\
&\quad - 2(2\pi\hbar)^{-3d} \langle g_{\mathbf{x}_0, \mathbf{p}_0} | (\hat{\mathbf{x}} - \mathbf{x}_0) | \Phi_0 \rangle \langle \Phi_0 | [\hat{\mathbf{A}} \cdot \mathbf{B}(\mathbf{x}(t), \\
&\quad \mathbf{p}(t))] \cdot \gamma \cdot (\hat{\mathbf{x}} - \mathbf{x}_0) | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle \quad (2.13)
\end{aligned}$$

The various matrix elements can be worked out using straightforward procedures. One finds

$$\begin{aligned}
\langle \Phi_0 | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle &= 2^{3d/2} \frac{\det(\alpha \cdot \gamma)^{1/4}}{\det(\alpha + \gamma)^{1/2}} \exp\{-(\mathbf{x}_0 - \lambda) \cdot [\gamma \cdot (\alpha + \\
&\quad \gamma)^{-1} \cdot \alpha] \cdot (\mathbf{x}_0 - \lambda) \\
&\quad - \frac{1}{4\hbar^2} \mathbf{p}_0 \cdot (\alpha + \gamma)^{-1} \cdot \mathbf{p}_0 - \frac{i}{\hbar} \mathbf{p}_0 \cdot (\alpha + \gamma)^{-1} \cdot \alpha \cdot \\
&\quad (\mathbf{x}_0 - \lambda)\} \quad (2.14)
\end{aligned}$$

$$\begin{aligned}
\langle \Phi_0 | \hat{\mathbf{x}} - \mathbf{x}_0 | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle &= -i\hbar \frac{\partial}{\partial \mathbf{p}_0} \langle \Phi_0 | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle \\
&= \left( -(\alpha + \gamma)^{-1} \cdot \alpha \cdot (\mathbf{x}_0 - \lambda) + \right. \\
&\quad \left. \frac{i}{2\hbar} (\alpha + \gamma)^{-1} \cdot \mathbf{p}_0 \right) \langle \Phi_0 | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle \quad (2.15)
\end{aligned}$$

and

$$\begin{aligned}
\langle \Phi_0 | (\hat{\mathbf{x}} - \mathbf{x}_0) \cdot \gamma \cdot (\hat{\mathbf{x}} - \mathbf{x}_0) | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle &= -\hbar^2 \frac{\partial}{\partial \mathbf{p}_0} \cdot \gamma \cdot \frac{\partial}{\partial \mathbf{p}_0} \\
&\quad \langle \Phi_0 | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle \\
&\times \left[ \frac{1}{2} \gamma \cdot (\alpha + \gamma)^{-1} + \left( -(\mathbf{x}_0 - \lambda) \cdot \alpha \cdot (\alpha + \gamma)^{-1} + \frac{i}{2\hbar} \mathbf{p}_0 \cdot \right. \right. \\
&\quad \left. \left. (\alpha + \gamma)^{-1} \right) \cdot \gamma \right. \\
&\left. \cdot \left( -(\alpha + \gamma)^{-1} \cdot \alpha \cdot (\mathbf{x}_0 - \lambda) + \frac{i}{2\hbar} (\alpha + \gamma)^{-1} \cdot \mathbf{p}_0 \right) \right] \langle \Phi_0 | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle \quad (2.16)
\end{aligned}$$

Using these, one can show that the expectation value of an operator is given by the expression

$$\begin{aligned}
\langle B(t) \rangle &= (2\pi\hbar)^{-3d/2} \int d\mathbf{x}_0 \int d\mathbf{p}_0 \langle g_{\mathbf{x}_0, \mathbf{p}_0} | \hat{\rho}_0 | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle B(\mathbf{x}(t), \mathbf{p}(t)) \\
&\times \left[ 1 + \frac{3d}{2} - 2(\mathbf{x}_0 - \lambda) \cdot \alpha \cdot (\alpha + \gamma)^{-1} \cdot \gamma \cdot (\alpha + \gamma)^{-1} \cdot \alpha \cdot \right. \\
&\quad \left. (\mathbf{x}_0 - \lambda) - \frac{1}{2\hbar^2} \mathbf{p}_0 \cdot (\alpha + \gamma)^{-1} \cdot \gamma \cdot (\alpha + \gamma)^{-1} \cdot \mathbf{p}_0 \right] \quad (2.17)
\end{aligned}$$

where

$$\langle g_{\mathbf{x}_0, \mathbf{p}_0} | \hat{\rho}_0 | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle = |\langle \Phi_0 | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle|^2 \quad (2.18)$$

is the Husimi (coherent state) transform of the Gaussian density. The matrix operations in eq 2.17 simplify if the matrix  $\alpha$  is diagonal. Furthermore, by working out the appropriate matrix element, one can obtain expressions for the correlation function for an operator  $\hat{A}$  of a polynomial form. For example, if the coordinate vector represents the normal modes of a molecule, the matrix  $\alpha$  has a diagonal form; then the equilibrium correlation function of the total normal mode vector  $\mathbf{Q}$  becomes

$$\begin{aligned}
C_{\mathbf{Q}\cdot\mathbf{Q}}(t) &= (2\pi\hbar)^{-(3d-6)/2} \prod_{j=1}^{3d-6} \int dQ_{j,0} \\
&\quad \int dP_{j,0} \langle g_{Q_{j,0}, P_{j,0}} | \hat{\rho}_0 | g_{Q_{j,0}, P_{j,0}} \rangle \\
&\times \left[ \left( 1 + \frac{3d-6}{2} \right) \xi^{T=0} - 2 \sum_{k=1}^{3d-6} \gamma_{kk} \xi^{T=0*}(Q_{k,0}, P_{k,0}) \right. \\
&\quad \left. \left( \frac{Q_k(t)}{2(\alpha_k + \gamma_k)} + \xi_k^{T=0}(Q_{j,0}, P_{j,0}) \xi^{T=0} \right) \right] \quad (2.19)
\end{aligned}$$

where

$$\xi^{T=0} = \sum_{k=1}^{3d-6} (f_k^{T=0}(Q_{k,0}, P_{k,0}) + Q_{k,0} Q_k(t)) \quad (2.20)$$

$$\begin{aligned}
f_j^{T=0}(Q_{j,0}, P_{j,0}) &\equiv \frac{\langle \Phi_0 | \hat{Q}_j - Q_{j,0} | g_{Q_{j,0}, P_{j,0}} \rangle}{\langle \Phi_0 | g_{Q_{j,0}, P_{j,0}} \rangle} = \\
&\quad - \frac{\alpha_j}{\alpha_j + \gamma_j} Q_{j,0} + \frac{i}{2\hbar} \frac{1}{\alpha_j + \gamma_j} P_{j,0} \quad (2.21)
\end{aligned}$$

**B. Finite Temperature.** At finite temperatures, systems often explore an appreciable domain of substantial potential nonlinearity. Although the quasiclassical expressions considered in this paper cannot account for quantum interference effects in the time evolution, it is possible and often extremely beneficial to treat the initial density by full quantum mechanics. It is well-known that quantization effects arising from zero-point vibrational energy can be large in systems with a small effective mass. In addition, a full quantum treatment of the time-independent component (i.e., the coherent state transform of the operator  $\hat{\rho}_0 \hat{A}$ ) is required to reproduce the imaginary part of a correlation function that is important in determining spectroscopic line shapes. A fully quantum mechanical treatment of this part is possible by resorting to the path integral representation of quantum statistical mechanics. Such a procedure was recently developed in our group for the derivative version of the FBSD formulation.<sup>41</sup> A derivative-free FBSD-

path integral methodology is presented below for expectation values and correlation functions of special interest.

In the present section, the density is given by the Boltzmann operator

$$\hat{\rho}_0 = Z^{-1} e^{-\beta \hat{H}} \quad (2.22)$$

where  $\beta = 1/k_B T$  is the reciprocal temperature in units of the Boltzmann constant and  $Z = \text{Tr } e^{-\beta \hat{H}}$  is the canonical partition function. For convenience, the derivation that follows is presented in one-dimensional notation, but its multidimensional extension to the correlation functions of an atom–atom distance (or force) vector and of the total position or velocity vectors is given at the end of the section.

There are two terms entering eq 2.9 that need to be evaluated quantum mechanically. Splitting the Boltzmann operator into a product of  $N$  imaginary time slices of length  $\Delta\beta = \beta/N$ ,

$$e^{-\beta H} = (e^{-\Delta\beta H})^N \quad (2.23)$$

and using the Trotter factorization of the exponential evolution operator

$$e^{-\Delta\beta \hat{H}} = e^{-\Delta\beta \hat{H}_0/2} e^{-\Delta\beta \hat{V}} e^{-\Delta\beta \hat{H}_0/2} \quad (2.24)$$

for sufficiently small  $\Delta\beta$ , one arrives at the following discretized path integral representation of the first coherent state factor entering the correlation function:

$$\begin{aligned} \langle g_{x_0, p_0} | e^{-\beta \hat{H}} \hat{A} | g_{x_0, p_0} \rangle &= \int dx_1 \cdots \int dx_N \\ &\langle g_{x_0, p_0} | e^{-\Delta\beta \hat{H}_0/2} | x_1 \rangle e^{-\Delta\beta V(x_1)} \langle x_1 | e^{-\Delta\beta \hat{H}_0} | x_2 \rangle \cdots \\ &\times e^{-\Delta\beta V(x_N)} \langle x_N | e^{-\Delta\beta \hat{H}_0/2} \hat{A} | g_{x_0, p_0} \rangle \end{aligned} \quad (2.25)$$

Note that the partitioning of the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V} \quad (2.26)$$

is in general arbitrary, but analytical expressions for the relevant short-time propagators are available only if  $\hat{H}_0$  has a simple (usually quadratic) form. In the present work, the reference Hamiltonian  $\hat{H}_0$  is chosen as the kinetic energy part of the Hamiltonian,

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} \quad (2.27)$$

and  $V$  is the potential function.

The coordinate representation of the Boltzmann operator for the above reference Hamiltonian has the form

$$\langle x_{k-1} | e^{-\Delta\beta \hat{H}_0} | x_k \rangle = \left( \frac{m}{2\pi\hbar^2 \Delta\beta} \right)^{1/2} \exp \left( -\frac{m}{2\hbar^2 \Delta\beta} (x_k - x_{k-1})^2 \right) \quad (2.28)$$

The first coherent state matrix element can also be evaluated analytically. It is given by the expression

$$\begin{aligned} \langle g_{x_0, p_0} | e^{-\Delta\beta \hat{H}_0/2} | x_1 \rangle &= \left( \frac{2\gamma}{\pi} \right)^{1/4} \sqrt{\frac{m}{m + \hbar^2 \Delta\beta \gamma}} \\ &\times \exp \left\{ -\frac{m}{m + \hbar^2 \Delta\beta \gamma} \left( \gamma (x_1 - x_0)^2 + \frac{\Delta\beta}{4m} p_0^2 + \frac{i}{\hbar} p_0 (x_1 - x_0) \right) \right\} \end{aligned} \quad (2.29)$$

With simple choices of  $\hat{A}$ , the other coherent state matrix element can also be calculated. For  $\hat{A} = \hat{x}$ , one finds

$$\begin{aligned} \langle x_N | e^{-\Delta\beta \hat{H}_0/2} \hat{x} | g_{x_0, p_0} \rangle &= \left( \frac{2\gamma}{\pi} \right)^{1/4} \left( \frac{m}{m + \hbar^2 \Delta\beta \gamma} \right)^{3/2} \left[ x_N + \frac{\hbar^2 \Delta\beta}{m} \left( \gamma x_0 + \frac{i}{2\hbar} p_0 \right) \right] \\ &\times \exp \left\{ -\frac{m}{m + \hbar^2 \Delta\beta \gamma} \left( \gamma (x_N - x_0)^2 + \frac{\Delta\beta}{4m} p_0^2 - \frac{i}{\hbar} p_0 (x_N - x_0) \right) \right\} \end{aligned} \quad (2.30)$$

whereas for  $\hat{A} = \hat{p}$  the result is

$$\begin{aligned} \langle x_N | e^{-\Delta\beta \hat{H}_0/2} \hat{p} | g_{x_0, p_0} \rangle &= \left( \frac{2\gamma}{\pi} \right)^{1/4} \left( \frac{m}{m + \hbar^2 \Delta\beta \gamma} \right)^{3/2} [p_0 + 2i\hbar\gamma(x_N - x_0)] \\ &\times \exp \left\{ -\frac{m}{m + \hbar^2 \Delta\beta \gamma} \left( \gamma (x_N - x_0)^2 + \frac{\Delta\beta}{4m} p_0^2 - \frac{i}{\hbar} p_0 (x_N - x_0) \right) \right\} \end{aligned} \quad (2.31)$$

Equation 2.9 also depends on another term of the Husimi type. Its discretized path integral representation is

$$\begin{aligned} \langle g_{x_0, p_0} | (\hat{x} - x_0) e^{-\beta \hat{H}} \hat{A} (\hat{x} - x_0) | g_{x_0, p_0} \rangle &= \int dx_1 \cdots \int dx_N \langle g_{x_0, p_0} | (\hat{x} - x_0) e^{-\Delta\beta \hat{H}_0/2} | x_1 \rangle \\ &\times e^{-\Delta\beta V(x_1)} \langle x_1 | e^{-\Delta\beta \hat{H}_0} | x_2 \rangle \cdots e^{-\Delta\beta V(x_N)} \\ &\times \langle x_N | e^{-\Delta\beta \hat{H}_0/2} \hat{A} (\hat{x} - x_0) | g_{x_0, p_0} \rangle \end{aligned} \quad (2.32)$$

Again, the relevant coherent state factors can be evaluated. One finds

$$\langle x_1 | e^{-\Delta\beta \hat{H}_0/2} (\hat{x} - x_0) | g_{x_0, p_0} \rangle = -i\hbar \frac{\partial}{\partial p_0} \langle x_1 | e^{-\Delta\beta \hat{H}_0/2} | g_{x_0, p_0} \rangle \quad (2.33)$$

For  $\hat{A} = \hat{x}$ , the matrix element can be obtained by observing that

$$\langle x_N | e^{-\Delta\beta \hat{H}_0/2} (\hat{x} - x_0)^2 | g_{x_0, p_0} \rangle = -\hbar^2 \frac{\partial^2}{\partial p_0^2} \langle x_N | e^{-\Delta\beta \hat{H}_0/2} | g_{x_0, p_0} \rangle \quad (2.34)$$

Finally, for  $\hat{A} = \hat{p}$ , one finds

$$\langle x_N | e^{-\Delta\beta \hat{H}_0/2} \hat{p} (\hat{x} - x_0) | g_{x_0, p_0} \rangle = -i\hbar \frac{\partial}{\partial p_0} \langle x_N | e^{-\Delta\beta \hat{H}_0/2} \hat{p} | g_{x_0, p_0} \rangle \quad (2.35)$$

After some straightforward algebra, one arrives at the following expression for the FBSD-path integral expectation value or correlation function:

$$\begin{aligned} C(t) &= (2\pi\hbar)^{-1} \int dx_0 \int dp_0 \int dx_1 \cdots \int dx_N \\ &\Theta(x_0, p_0, x_1, \dots, x_N) B(x(t), p(t)) F(x_0, p_0, x_1, \dots, x_N) \end{aligned} \quad (2.36)$$

where

$$\begin{aligned} \Theta(x_0, p_0, x_1, \dots, x_N) &= \langle g_{x_0 p_0} | e^{-\Delta\beta\hat{H}_0/2} | x_1 \rangle e^{-\Delta\beta V(x_1)} \langle x_1 | e^{-\Delta\beta\hat{H}_0} | x_2 \rangle \dots \\ &\quad \times e^{-\Delta\beta V(x_N)} \langle x_N | e^{-\beta\hat{H}_0/2} | g_{x_0 p_0} \rangle \\ &= \left( \frac{2\gamma}{\pi} \right)^{1/2} \frac{m}{m + \hbar^2 \Delta\beta\gamma} \left( \frac{m}{2\pi\hbar^2 \Delta\beta} \right)^{(N-1)/2} \\ &\quad \times \exp \left\{ - \frac{m}{m + \hbar^2 \Delta\beta\gamma} \left( \gamma(x_1 - x_0)^2 + \gamma(x_N - x_0)^2 + \right. \right. \\ &\quad \left. \left. \frac{\Delta\beta}{2m} p_0^2 + \frac{i}{\hbar} p_0(x_1 - x_N) \right) \right. \\ &\quad \left. - \frac{m}{2\hbar^2 \Delta\beta} \sum_{k=2}^N (x_k - x_{k-1})^2 - \Delta\beta \sum_{k=1}^N V(x_k) \right\} \quad (2.37) \end{aligned}$$

is the integrand in the path integral representation of the Husimi transform of the Boltzmann operator and the function  $F$  is given by the following expressions in the three cases considered:

$$F_{\hat{A}=1}(x_0, p_0, x_1, \dots, x_N) = \frac{3}{2} - 2\gamma f^{\beta*}(x_0, p_0, x_1) f^{\beta}(x_0, p_0, x_N) \quad (2.38)$$

$$\begin{aligned} F_{\hat{A}=\hat{x}}(x_0, p_0, x_1, \dots, x_N) &= \frac{3}{2} (f^{\beta}(x_0, p_0, x_N) + x_0) \\ &\quad - 2\gamma f^{\beta*}(x_0, p_0, x_1) \left[ \frac{\hbar^2 \Delta\beta/2}{m + \hbar^2 \Delta\beta\gamma} + \right. \\ &\quad \left. f^{\beta}(x_0, p_0, x_N)^2 + x_0 f^{\beta}(x_0, p_0, x_N) \right] \quad (2.39) \end{aligned}$$

$$\begin{aligned} F_{\hat{A}=\hat{p}}(x_0, p_0, x_1, \dots, x_N) &= \frac{3}{2} w^{\beta}(x_0, p_0, x_N) \\ &\quad - 2\gamma f^{\beta*}(x_0, p_0, x_1) \left[ -i\hbar \frac{m}{m + \hbar^2 \Delta\beta\gamma} + \right. \\ &\quad \left. f^{\beta}(x_0, p_0, x_N) w^{\beta}(x_0, p_0, x_N) \right] \quad (2.40) \end{aligned}$$

In these expressions,  $f^{\beta}$  is the finite temperature version of a similar quantity defined in the Gaussian density section,

$$\begin{aligned} f^{\beta}(x_0, p_0, x_k) &= \frac{\langle x_k | e^{-\Delta\beta H_0/2} (\hat{x} - x_0) | g_{x_0 p_0} \rangle}{\langle x_k | e^{-\Delta\beta H_0/2} | g_{x_0 p_0} \rangle} = \\ &\quad \frac{m}{m + \hbar^2 \Delta\beta\gamma} (x_k - x_0 + i\hbar \frac{\Delta\beta}{2m} p_0) \quad (2.41) \end{aligned}$$

and

$$\begin{aligned} w^{\beta}(x_0, p_0, x_k) &= \frac{\langle x_k | e^{-\Delta\beta H_0/2} \hat{p} | g_{x_0 p_0} \rangle}{\langle x_k | e^{-\Delta\beta H_0/2} | g_{x_0 p_0} \rangle} = \\ &\quad \frac{m}{m + \hbar^2 \Delta\beta\gamma} [p_0 + 2i\hbar\gamma(x_k - x_0)] \quad (2.42) \end{aligned}$$

The multidimensional generalization of the expressions obtained so far are given below. The correlation function of an inner product becomes

$$\begin{aligned} C_{\mathbf{A}\cdot\mathbf{B}}(t) &= Z^{-1} \text{Tr}(e^{-\beta H} \mathbf{A} \cdot e^{iHt/\hbar} \mathbf{B} e^{iHt/\hbar}) \\ &= (2\pi\hbar)^{-3d} \int d\mathbf{x}_0 \int d\mathbf{p}_0 \int d\mathbf{x}_1 \dots \int d\mathbf{x}_N \\ &\quad \Theta(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) \Lambda_{\mathbf{A}\cdot\mathbf{B}}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) \quad (2.43) \end{aligned}$$

Here the two functions in the integrand are again the multidimensional extensions of those defined through eqs 2.37, 2.39, and 2.40, but  $\Lambda$  now includes a portion that comes from the operator  $B$ . For example, the autocorrelation function of the 3d-dimensional position vector  $\mathbf{x}$  is given by the expression

$$\begin{aligned} C_{\mathbf{x}\cdot\mathbf{x}}(t) &= Z^{-1} \text{Tr}(e^{-\beta H} \hat{\mathbf{x}} \cdot e^{iHt/\hbar} \hat{\mathbf{x}} e^{-iHt/\hbar}) \\ &= (2\pi\hbar)^{-3d} \int d\mathbf{x}_0 \int d\mathbf{p}_0 \int d\mathbf{x}_1 \dots \int d\mathbf{x}_N \\ &\quad \Theta(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) \Lambda_{\mathbf{x}\cdot\mathbf{x}}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) \quad (2.44) \end{aligned}$$

with

$$\begin{aligned} \Lambda_{\mathbf{x}\cdot\mathbf{x}}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) &= \left( 1 + \frac{3}{2} \right) \xi - 2 \sum_{s=1}^d \sum_{j=1}^3 \gamma_{sj} f_{sj}^{\beta*}(x_{sj,0}, p_{sj,0}, x_{sj,1}) \\ &\quad \times \left( \frac{\hbar^2 \Delta\beta/2}{m_s + \hbar^2 \Delta\beta\gamma_{sj}} x_{sj}(t) + \xi f_{sj}^{\beta}(x_{sj,0}, p_{sj,0}, x_{sj,N}) \right) \quad (2.45) \end{aligned}$$

The autocorrelation function of the total momentum vector has a similar form,

$$\begin{aligned} C_{\mathbf{p}\cdot\mathbf{p}}(t) &= Z^{-1} \text{Tr}(e^{-\beta H} \hat{\mathbf{p}} \cdot e^{iHt/\hbar} \hat{\mathbf{p}} e^{-iHt/\hbar}) \\ &= (2\pi\hbar)^{-3d} \int d\mathbf{x}_0 \int d\mathbf{p}_0 \int d\mathbf{x}_1 \dots \int d\mathbf{x}_N \Theta \\ &\quad (\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) \Lambda_{\mathbf{p}\cdot\mathbf{p}}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) \quad (2.46) \end{aligned}$$

where

$$\begin{aligned} \Lambda_{\mathbf{p}\cdot\mathbf{p}}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) &= \left( 1 + \frac{3}{2} d \right) \theta \\ &\quad - 2 \sum_{s=1}^d \sum_{j=1}^3 \gamma_{sj} f_{sj}^{\beta*}(x_{sj,0}, p_{sj,0}, x_{sj,1}) \\ &\quad \times \left( -i\hbar \frac{m_j}{m_j + \hbar^2 \Delta\beta\gamma_{sj}} p_{sj}(t) + \right. \\ &\quad \left. \theta f_{sj}^{\beta}(x_{sj,0}, p_{sj,0}, x_{sj,N}) \right) \quad (2.47) \end{aligned}$$

In these equations

$$\xi = \sum_{s=1}^d \sum_{j=1}^3 (f_{sj}^{\beta}(x_{sj,0}, p_{sj,0}, x_{sj,N}) + x_{sj,0} x_{sj}(t)) \quad (2.48)$$

and

$$\theta = \sum_{s=1}^d \sum_{j=1}^3 w_{sj}(x_{sj,0}, p_{sj,0}, x_{sj,N}) p_{sj}(t) \quad (2.49)$$

Finally, we derive below an expression for the correlation function of the relative position vector between two atoms. This type of information is useful for calculating dipole moment and force correlation functions, which encode important information for infrared spectroscopy and relaxation dynamics. Upon



stretching, the relative position vector between two atoms  $k_1$  and  $k_2$  is displaced from its equilibrium value by the amount

$$\Delta \mathbf{r}(t) = \mathbf{r}_{k_1}(t) - \mathbf{r}_{k_2}(t) - \mathbf{a}(t) \quad (2.50)$$

where  $\mathbf{a}(t)$  is the equilibrium bond distance vector in the direction of the line connecting the two atoms:

$$\mathbf{a}(t) = \sigma_{k_1 k_2} \frac{\mathbf{r}_{k_1}(t) - \mathbf{r}_{k_2}(t)}{|\mathbf{r}_{k_1}(t) - \mathbf{r}_{k_2}(t)|} \quad (2.51)$$

$\sigma_{k_1 k_2}$  is the equilibrium bond length. The correlation function of the atom–atom distance vector becomes

$$C_{\mathbf{r}_{k_1}, \mathbf{r}_{k_2}}(t) = \text{Tr} \{ \rho_0 [\hat{\mathbf{r}}_{k_1} - \hat{\mathbf{r}}_{k_2} - \mathbf{a}(0)] e^{iHt/\hbar} \cdot [\hat{\mathbf{r}}_{k_1} - \hat{\mathbf{r}}_{k_2} - \mathbf{a}(t)] e^{-iHt/\hbar} \} \quad (2.52)$$

By working out the coherent state matrix elements, it is possible to show that the FBSD-path integral expression for the correlation function of an atom–atom distance vector is again given by eq 2.46 with

$$\begin{aligned} \Lambda_{\mathbf{r}_{k_1}, \mathbf{r}_{k_2}}(\mathbf{x}_0, \mathbf{p}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) \\ = \left(1 + \frac{3d}{2}\right) \xi_{k_1 k_2} \\ - 2 \sum_{s=1}^d \sum_{j=1}^3 \gamma_{sj} f_{sj}^*(r_{sj,0}, p_{sj,0}, r_{sj,1}) f_{sj}(r_{sj,0}, p_{sj,0}, r_{sj,N}) \xi_{k_1 k_2} \\ - \hbar^2 \Delta \beta \sum_{j=1}^3 [r_{k_1 j}(t) - r_{k_2 j}(t) - a_j(t)] \\ \times \left( \frac{\gamma_{k_1 j} f_{k_1 j}^*(r_{k_1 j,0}, p_{k_1 j,0}, r_{k_1 j,1})}{m_{k_1} + \hbar^2 \Delta \beta \gamma_{k_1 j}} - \frac{\gamma_{k_2 j} f_{k_2 j}^*(r_{k_2 j,0}, p_{k_2 j,0}, r_{k_2 j,1})}{m_{k_2} + \hbar^2 \Delta \beta \gamma_{k_2 j}} \right) \end{aligned} \quad (2.53)$$

### III. Monte Carlo Procedures

This section describes Monte Carlo algorithms that can be used to evaluate the correlation function. To achieve good statistics, one should use the modulus of the exponential function in the integrand of each expression as the sampling function. Note that in all cases considered above the exponential part of the integrand arises solely from the Husimi transform of the density operator. Note also that the imaginary components of the integral arise from the coherent state functions and thus are associated with the phase space treatment of the quantum density.

**A. Gaussian Density.** It is straightforward to develop a Monte Carlo methodology for evaluating eqs 2.17 and 2.19, which employ a Gaussian density. One simply uses the Husimi density as the sampling function,

$$\begin{aligned} P(\mathbf{x}_0, \mathbf{p}_0) = |\langle \Phi_0 | g_{\mathbf{x}_0, \mathbf{p}_0} \rangle|^2 = 2^{3d} \frac{\det(\alpha \cdot \gamma)^{1/2}}{\det(\alpha + \gamma)} \\ \times \exp \left\{ -2(\mathbf{x}_0 - \lambda) \cdot [\gamma \cdot (\alpha + \gamma)^{-1} \cdot \alpha] \cdot \right. \\ \left. (\mathbf{x}_0 - \lambda) - \frac{1}{2\hbar^2} \mathbf{p}_0 \cdot (\alpha + \gamma)^{-1} \cdot \mathbf{p}_0 \right\} \end{aligned} \quad (3.1)$$

By virtue of the closure property of coherent states, the integral of this function is equal to  $(2\pi\hbar)^{3d}$ , and thus the weight function is normalizable analytically.

**B. Finite Temperature.** Even though the expressions considered here have a quasiclassical structure, the coherent state treatment of the Boltzmann operator has introduced an oscillatory component in the integrand of eq 2.36. The resulting phase cancellation is not severe, but it is nonetheless extremely important to employ as efficient a sampling method as possible. Optimal sampling is achieved by choosing the sampling function as the absolute value of the entire exponential part (i.e., the modulus of the integrand of the Husimi density):

$$\begin{aligned} P(x_0, p_0, x_1, \dots, x_N) \propto |\langle g_{x_0, p_0} | e^{-\Delta \beta \hat{H}_0/2} | x_1 \rangle e^{-\Delta \beta V(x_1)} \\ \langle x_1 | e^{-\Delta \beta \hat{H}_0} | x_2 \rangle \cdots e^{-\Delta \beta V(x_N)} \\ \times \langle x_N | e^{-\Delta \beta \hat{H}_0/2} | g_{x_0, p_0} \rangle | \end{aligned} \quad (3.2)$$

In eq 3.2, one-dimensional notation has been used again for the sake of clarity. Because the acceptance criterion in the Metropolis procedure is based on the relative weights at each attempted step, constant factors are of no significance. The sampling function takes the form

$$\begin{aligned} P(x_0, p_0, x_1, \dots, x_N) \\ = \exp \left\{ - \frac{m}{m + \hbar^2 \Delta \beta \gamma} (\gamma(x_1 - x_0)^2 + \gamma(x_N - x_0)^2 + \frac{\Delta \beta}{2m} p_0^2) \right. \\ \left. - \frac{m}{2\hbar^2 \Delta \beta} \sum_{k=2}^N (x_k - x_{k-1})^2 - \Delta \beta \sum_{k=1}^N V(x_k) \right\} \end{aligned} \quad (3.3)$$

The standard Metropolis procedure employs a sampling function to generate configurations at which the remaining part of the integrand is evaluated. For this purpose, the sampling function must be a nonnegative probability distribution normalized to unity. Thus, one must be able to evaluate the integral of the sampling function. In the general case of a nonlinear multidimensional potential, the integral must be calculated by a separate Monte Carlo random walk. Such a procedure was developed recently in the context of forward–backward semiclassical influence functionals or the derivative formulation of semiclassical correlation functions<sup>41</sup> and is summarized here for completeness.

As a starting point, notice that the integrals with respect to the trajectory initial conditions are of the Gaussian type and can be evaluated analytically. Therefore, the normalization integral takes the form

$$\begin{aligned} \int d\mathbf{x}_0 \int d\mathbf{p}_0 \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N P(x_0, p_0, x_1, \dots, x_N) = \\ \pi \frac{m + \hbar^2 \Delta \beta \gamma}{\sqrt{m \gamma \Delta \beta}} \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N \sigma(x_1, \dots, x_N) \end{aligned} \quad (3.4)$$

where

$$\begin{aligned} \sigma(x_1, \dots, x_N) = \exp \left\{ - \frac{m \gamma / 2}{m + \hbar^2 \Delta \beta \gamma} (x_1 - x_N)^2 - \right. \\ \left. \frac{m}{2\hbar^2 \Delta \beta} \sum_{k=2}^N (x_k - x_{k-1})^2 - \Delta \beta \sum_{k=1}^N V(x_k) \right\} \end{aligned} \quad (3.5)$$

It is thus sufficient to calculate the normalization integral of this function. To proceed, note that the canonical partition function at the same level of approximation (i.e., expressed as a discretized path integral with  $N$  imaginary time slices) takes the form

$$Z = \text{Tr} e^{-\beta H} = \left( \frac{m}{2\pi\hbar^2\Delta\beta} \right)^{N/2} \int dx_1 \cdots \int dx_N \times \exp \left\{ -\frac{m}{2\hbar^2\Delta\beta} \left[ \sum_{k=2}^N (x_k - x_{k-1})^2 + (x_1 - x_N)^2 \right] - \Delta\beta \sum_{k=1}^N V(x_k) \right\} \quad (3.6)$$

The partition function is now expressed in terms of the function entering the normalization integral,

$$Z = \left( \frac{m}{2\pi\hbar^2\Delta\beta} \right)^{N/2} \int dx_1 \cdots \int dx_N \sigma(x_1, \dots, x_N) \exp[-\lambda(x_1 - x_N)^2] \quad (3.7)$$

where

$$\lambda \equiv \frac{m}{2\pi\hbar^2\Delta\beta} - \frac{m\gamma/2}{m + \hbar^2\Delta\beta\gamma} \quad (3.8)$$

is a positive constant.

To proceed, one samples the function  $\exp[-\lambda(x_1 - x_N)^2]$  in a Metropolis random walk using  $\sigma$  as the weight function. This procedure yields the integral

$$\kappa \equiv \mu^{-1} \int dx_1 \cdots \int dx_N \sigma(x_1, \dots, x_N) \exp[-\lambda(x_1 - x_N)^2] \quad (3.9)$$

where

$$\mu = \int dx_1 \cdots \int dx_N \sigma(x_1, \dots, x_N) \quad (3.10)$$

is the desired integral. In terms of these equations, the partition function takes the form

$$Z = \left( \frac{m}{2\pi\hbar^2\Delta\beta} \right)^{N/2} \mu \kappa \quad (3.11)$$

Finally,

$$Z^{-1} \int dx_0 \int dp_0 \int dx_1 \cdots \int dx_N P(x_0, p_0, x_1, \dots, x_N) = \pi \frac{m + \hbar^2\Delta\beta\gamma}{\sqrt{m\Delta\beta\gamma}} \left( \frac{m}{2\pi\hbar^2\Delta\beta\gamma} \right)^{-N/2} \kappa^{-1} \quad (3.12)$$

Combining this relation with the remaining constants in the expression for the correlation function leads to the result

$$C(t) = \kappa^{-1} \int dx_0 \int dp_0 \int dx_1 \cdots \int dx_N P_{\text{norm}}(x_0, p_0, x_1, \dots, x_N) B(x_i, p_i) \times \exp \left( -\frac{i}{\hbar} \frac{m}{m + \hbar^2\Delta\beta\gamma} p_0(x_1 - x_N) \right) F(x_0, p_0, x_1, \dots, x_N) \quad (3.13)$$

where  $P_{\text{norm}}$  is a normalized sampling function proportional to eq 3.3.

To summarize, one calculates by Monte Carlo the integral  $\kappa$  of the function  $\exp[-\lambda(x_1 - x_N)^2]$  using the sampling function defined in eq 3.3. The result is the inverse of the overall prefactor in the quasiclassical expression for the correlation function.

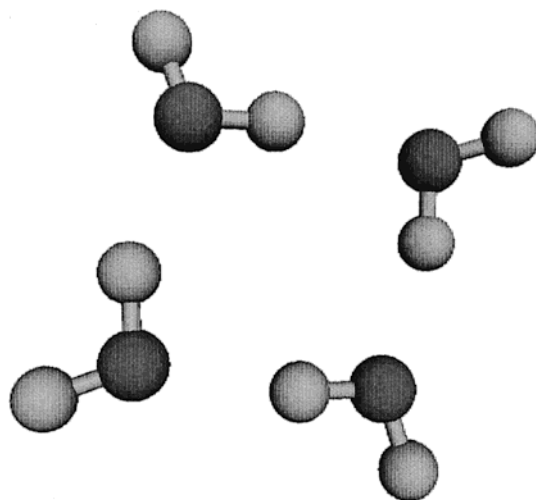


Figure 1. Lowest-energy structure of the water tetramer.

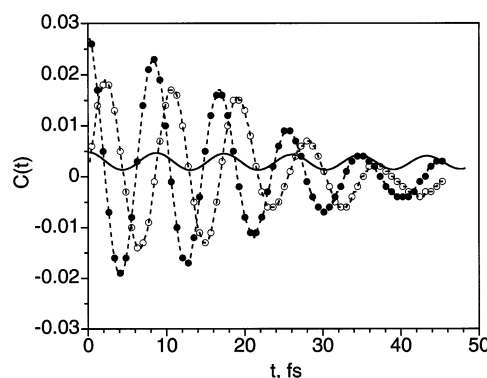


Figure 2. Correlation function of the hydrogen-bonded OH distance, eq 2.52, for the water tetramer at 300 K. Open and solid circles: real and imaginary parts of the FBSD/path integral results with  $N = 6$ . Solid line: classical (real-valued) results.

Extension of this procedure to systems with many degrees of freedom is entirely straightforward.

#### IV. Application

The methodology presented in the preceding sections is illustrated by calculating the correlation function of the hydrogen-bonded OH vibration in a cluster of four water molecules. The minimum-energy configuration of the cluster, a structure of  $S_4$  symmetry, is depicted in Figure 1. The dynamics of the water tetramer is studied at room temperature using the Toukan–Rahman potential<sup>62</sup> to model the various atom–atom interactions. This potential is a modified version of the simple point-charge (SPC) model of Berendsen et al.,<sup>63</sup> which allows for flexible molecules and has been deemed successful in its prediction of various structural properties of bulk water. One of the two hydrogen atoms of each water molecule is hydrogen bonded in the cyclic arrangement of the molecules in the four-water cluster; the corresponding OH equilibrium distance is elongated by 0.03 Å according to the Toukan–Rahman force field, in good agreement with the prediction of accurate electronic structure calculations.<sup>64</sup>

Figure 2 shows the bond displacement correlation function for the hydrogen-bonded OH vibration (referenced with respect to the OH bond length of the monomer) at 300 K. The calculation was performed in the space of the Cartesian coordinates for all 12 atoms and thus involved evaluation of a 72-dimensional integral. The difference in the equilibrium bond length of the tetramer compared to that of the monomer causes

the correlation function to oscillate about a small positive value rather than about zero. Converged path integral results were obtained with  $N = 6$ . It is seen that the quantum correction captured in the FBSD-path integral methodology exceeds one order of magnitude. In addition, the method presented in this paper produces an imaginary part that is similar in magnitude to the real part of the correlation function. Finally, the FBSD-path integral result exhibits a slow decay that is absent from the classical correlation function. As FBSD cannot account for quantum mechanical phase interference, the observed dephasing is a purely classical effect arising from the anharmonicity of the potential describing the hydrogen bond. The absence of dephasing from the classical correlation function depicted in Figure 2 is a consequence of its neglect of zero-point motion. The latter, which is fully accounted for in the present treatment through proper quantization of the Boltzmann density, shifts the energy of the phase space distribution to the strongly nonlinear part of the cluster potential, causing the observed dephasing.

## V. Discussion and Summary

The combination of FBSD dynamics in the derivative formulation with an imaginary time-path integral treatment of the density operator gives rise to a rigorous way of quantizing the initial condition while treating the dynamics via inexpensive classical trajectory calculations. As shown in the preceding sections, a fully quantum mechanical treatment of the Boltzmann density within the context of FBSD is both feasible and practical because it can be implemented with existing path integral techniques combined with routine Monte Carlo sampling. It was shown that optimal sampling can be achieved by choosing the entire absolute value of the integrand as the weight function whose normalization involves integration of a well-behaved function. The path integral representation of the density ensures a proper treatment of zero-point motion, thereby allowing the trajectories to explore the appropriate potential regions and thus capturing frequency shifts and many other effects that are neglected in purely classical mechanical treatments.

While the treatment of the real-time dynamics is based exclusively on classical trajectories and thus is incapable of accounting for quantum interference, the coherent state treatment of the density introduces nonclassical effects in the time evolution. The latter are responsible for the imaginary part of the correlation function and are observed even in the crudest high-temperature ( $N = 1$ ) limit of the imaginary time path integral representation of the Boltzmann operator. This advantage is characteristic of semiclassical phase space treatments of the density operator (i.e., methods based on the coherent state or the Wigner<sup>65</sup> transform). Such imaginary components would not be observed in calculations employing a coordinate state representation or a purely classical phase space treatment of the density. Consider, for example, a position space treatment of the operator  $\hat{\rho}_0 \hat{A}$  in which a correlation function is given by the expression<sup>45</sup>

$$C(t) = Z^{-1} \int dx_0 \langle x_0 | \hat{\rho}_0 \hat{A} | x_0 \rangle B(x_t, p_t) \quad (3.14)$$

which can be derived from the semiclassical expression through a series of stationary-phase integrations. Equation 3.14 is similar to the working expression of section II, eq 2.8, but employs the coordinate matrix element of the density rather than a coherent state transform of a corrected operator. It is straightforward to see that if the operator  $\hat{A}$  is a function of position eq 3.14 can yield only purely real-valued results and therefore is

incapable of reproducing the imaginary time component of a correlation function. The same is true of the purely classical approximation of that operator (i.e., the conventional classical correlation function)

$$C(t) = Z_{cl}^{-1} \int dx_0 \int dp_0 e^{-\beta H_{cl}(x_0, p_0)} A(x_0, p_0) B(x_t, p_t) \quad (3.15)$$

where  $A(x, p)$  is the classical (not semiclassical) analogue of the corresponding operator. It is thus apparent that the coherent state-based FBSD expression (as well as its Wigner<sup>56,65</sup> or linearized semiclassical<sup>30</sup> analog) goes beyond a purely classical treatment of the dynamics because it can fully account for imaginary contributions that are very important at low temperatures. Thus, the methodology described in the present paper can be thought of as “quantum semiclassical”, employing a fully quantum mechanical treatment of the initial density and a consistent semiclassical treatment of the dynamics at the stationary phase (FBSD) level that neglects quantum-phase interference.

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## References and Notes

- (1) Tully, J. C.; Preston, R. K. *J. Chem. Phys.* **1971**, *55*, 562.
- (2) Pechukas, P. *Phys. Rev.* **1969**, *181*, 166.
- (3) Van Vleck, J. H. *Proc. Nat. Acad. U.S. Sci.* **1928**, *14*, 178.
- (4) Morette, C. *Phys. Rev.* **1952**, *81*, 848.
- (5) Miller, W. H. *Adv. Chem. Phys.* **1974**, *25*, 69.
- (6) Miller, W. H. *Adv. Chem. Phys.* **1975**, *30*, 77.
- (7) Heller, E. J.; Reimers, J. R.; Drolshagen, G. *Phys. Rev. A* **1987**, *36*, 2613.
- (8) Child, M. S. *Semiclassical mechanics with molecular applications*; Clarendon: Oxford, 1991.
- (9) Heller, E. J. *J. Chem. Phys.* **1991**, *94*, 2723.
- (10) Tomsovic, S.; Heller, E. J. *Phys. Rev. Lett.* **1991**, *67*, 664.
- (11) Sepulveda, M. A.; Tomsovic, S.; Heller, E. J. *Phys. Rev. Lett.* **1992**, *69*, 402.
- (12) Sepulveda, M. A.; Grossmann, F. *Adv. Chem. Phys.* **1996**, *XCVI*, 191.
- (13) Cao, J.; Voth, G. A. *J. Chem. Phys.* **1996**, *104*, 273.
- (14) Grossmann, F. *Phys. Rev. A* **1999**, *60*, 1791.
- (15) Garashchuk, S.; Grossmann, F.; Tannor, D. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 781.
- (16) Garashchuk, S.; Light, J. C. *J. Chem. Phys.* **2000**, *113*, 9390.
- (17) Herman, M. F.; Kluk, E. *Chem. Phys.* **1984**, *91*, 27.
- (18) Kluk, E.; Herman, M. F.; Davis, H. L. *J. Chem. Phys.* **1986**, *84*, 326.
- (19) Campolieti, G.; Brumer, P. *Phys. Rev. A* **1994**, *50*, 997.
- (20) Wilkie, J.; Brumer, P. *Phys. Rev. A* **2001**, *61*, 064101.
- (21) Kay, K. G. *J. Chem. Phys.* **1994**, *100*, 4377.
- (22) Kay, K. G. *J. Chem. Phys.* **1994**, *100*, 4432.
- (23) Kay, K. *J. Chem. Phys.* **1997**, *107*, 2313.
- (24) Walton, A. R.; Manolopoulos, D. E. *Mol. Phys.* **1996**, *84*, 961.
- (25) Brewer, M. L.; Hulme, J. S.; Manolopoulos, D. E. *J. Chem. Phys.* **1997**, *106*, 4832.
- (26) Hernandez, R.; Voth, G. A. *Chem. Phys.* **1998**, *233*, 243.
- (27) McQuarrie, B. R.; Brumer, P. *Chem. Phys. Lett.* **2000**, *319*, 27.
- (28) Wang, H.; Manolopoulos, D. E.; Miller, W. H. *J. Chem. Phys.* **2001**, *115*, 6317.
- (29) Sun, X.; Miller, W. H. *J. Chem. Phys.* **1997**, *106*, 916.
- (30) Wang, H.; Sun, X.; Miller, W. H. *J. Chem. Phys.* **1998**, *108*, 9726.
- (31) Sun, X.; Wang, H.; Miller, W. H. *J. Chem. Phys.* **1998**, *109*, 4190.
- (32) Makri, N.; Thompson, K. *Chem. Phys. Lett.* **1998**, *291*, 101.
- (33) Miller, W. H. *Faraday Discuss.* **1998**, *110*, 1.
- (34) Thompson, K.; Makri, N. *J. Chem. Phys.* **1999**, *110*, 1343.
- (35) Thompson, K.; Makri, N. *Phys. Rev. E* **1999**, *59*, R4729.
- (36) Sun, X.; Miller, W. H. *J. Chem. Phys.* **1999**, *110*, 6635.
- (37) Shao, J.; Makri, N. *J. Phys. Chem.* **1999**, *103*, 7753.
- (38) Shao, J.; Makri, N. *J. Phys. Chem.* **1999**, *103*, 9479.
- (39) Wang, H.; Thoss, M.; Miller, W. H. *J. Chem. Phys.* **2000**, *112*, 47.
- (40) Shao, J.; Makri, N. *J. Chem. Phys.* **2000**, *113*, 3681.
- (41) Jezek, E.; Makri, N. *J. Phys. Chem.* **2001**, *105*, 2851.



- (42) Makri, N. Forward-backward semiclassical dynamics. In *Fluctuating paths and fields*; Janke, W., Pelster, A., Schmidt, H.-J., Bachmann, M., Eds.; World Scientific: Singapore, 2001.
- (43) Wang, H.; Thoss, M.; Sorge, K. L.; Gelabert, R.; Gimenez, X.; Miller, W. H. *J. Chem. Phys.* **2001**, *114*, 2562.
- (44) Thoss, M.; Wang, H.; Miller, W. H. *J. Chem. Phys.* **2001**, *114*, 9220.
- (45) Zhao, Y.; Makri, N. *Chem. Phys.* **2002**, in press.
- (46) Sun, X.; Miller, W. H. *J. Chem. Phys.* **1998**, *108*, 8870.
- (47) Batista, V.; Zanni, M. T.; Greenblatt, J.; Neumark, D. M.; Miller, W. H. *J. Chem. Phys.* **1999**, *110*, 3736.
- (48) Zanni, M. T.; Batista, V. S.; Greenblatt, J.; Miller, W. H.; Neumark, D. M. *J. Chem. Phys.* **1999**, *110*, 3748.
- (49) Skinner, D. E.; Miller, W. H. *J. Chem. Phys.* **1999**, *111*, 10787.
- (50) Thoss, M.; Miller, W. H.; Stock, G. *J. Chem. Phys.* **2000**, *112*, 10282.
- (51) Coronado, E. A.; Batista, V. S.; Miller, W. H. *J. Chem. Phys.* **2000**, *112*, 5566.
- (52) Guallar, V.; Batista, V. S.; Miller, W. H. *J. Chem. Phys.* **2000**, *113*, 9510.
- (53) Miller, W. H. *J. Phys. Chem.* **2001**, *105*, 2942.
- (54) Gelabert, R.; Giménez, X.; Thoss, M.; Wang, H.; Miller, W. H. *J. Chem. Phys.* **2001**, *114*, 2572.
- (55) Ovchinnikov, M.; Apkarian, V. A.; Voth, G. A. *J. Chem. Phys.* **2001**, *114*, 7130.
- (56) Heller, E. J. *J. Chem. Phys.* **1976**, *65*, 1289.
- (57) Brown, R. C.; Heller, E. J. *J. Chem. Phys.* **1981**, *75*, 186.
- (58) Cline, R. E., Jr.; Wolynes, P. G. *J. Chem. Phys.* **1988**, *88*, 4334.
- (59) Sun, X.; Wang, H.; Miller, W. H. *J. Chem. Phys.* **1998**, *109*, 7064.
- (60) Makri, N.; Shao, J. Semiclassical time evolution in the forward-backward stationary phase limit. In *Accurate description of low-lying electronic states and potential energy surfaces*; Hoffmann, M., Ed.; Oxford University Press: 2002.
- (61) Makri, N.; Miller, W. H. *J. Chem. Phys.* in press.
- (62) Toukan, K.; Rahman, A. *Phys. Rev. B* **1985**, *31*, 2643.
- (63) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; Hermans, J. In *Intermolecular forces*; Pullman, B., Ed.; Reidel: Dordrecht, 1981.
- (64) Xantheas, S. S. *J. Chem. Phys.* **1995**, *102*, 4505.
- (65) Wigner, E. J. *J. Chem. Phys.* **1937**, *5*, 720.