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Forward−Backward Quantum Dynamics for Time Correlation Functions

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A novel quantum mechanical formulation of time correlation functions is derived, based on Bohmian trajectories integrated along a forward−backward time contour. The derived expression involves a smooth integrand amenable to Monte Carlo integration with a readily available position space density. The Bohmian potential governing the motion of the quantum trajectories is weak and well-behaved, facilitating the computation of Bohmian trajectories.

I. Introduction

Time correlation functions provide important information on the dynamics and spectroscopy of chemical systems. For example, the autocorrelation function of the dipole-moment operator leads directly to vibrational or electronic spectra, flux correlation functions provide reaction rate information, and velocity correlation functions yield diffusion constants in the bulk. The inclusion of quantum mechanical effects in the computation of time correlation functions presents a challenging problem that continues to receive much attention. At present, the dynamics of small molecules are treatable by a variety of basis-set or grid-based methods, and low-dimensional subsystems coupled to dissipative harmonic baths can be simulated via numerically exact path integral methods. In recent years, efforts to devise simulation tools capable of including quantum mechanical effects to the dynamics of polyatomic systems dominated by arbitrary anharmonic interactions have moved to the forefront of theoretical chemistry research. Among the most successful approaches currently available are the centroid molecular dynamics scheme, techniques based on surface hopping, and semiclassical initial value methods.

The semiclassical approximation to quantum mechanics[1,2] offers a rigorous and intuitively appealing way of including quantum effects via classical trajectory input. Semiclassical theory is based on classical trajectories and their stability properties, which can be obtained by inexpensive calculations even for very large systems.[3] These characteristics make semiclassical methods very appealing, as they can account for important quantum mechanical features of a system, while offering an intuitive understanding of dynamical processes.[4−7] In recent years, the semiclassical method has experienced a rebirth of interest with the development of semiclassical initial value representations (IVR),[4,8−20] which circumvent the troublesome “root-search” problem of the original formulation. Numerical calculations exploiting these advances have demonstrated the ability of the semiclassical approximation to provide an accurate description of essentially all types of quantum effects in chemical dynamics,[13,20−22] and a number of successful applications to polyatomic molecules have been presented.[19,20,23−31] To date, the highly oscillatory character of the semiclassical integrand remains the main drawback of semiclassical methods, preventing integration by Monte Carlo methods in condensed phase systems. A significant development in the past few years has been the formulation of forward−backward semiclassical dynamics (FBSD) methods,[32−48] which circumvent the problem by combining (and thus partially canceling) the phases of forward and reverse time trajectories entering the semiclassical representation of a correlation function, albeit with the loss of some quantum intereference.

In recent years, an intriguing formulation of quantum dynamics based on “quantum trajectories”[49−52] has been pursued by several groups.[53−67] The so-called Bohmian or hydrodynamic formulation of quantum mechanics[49−52] assumes a form very similar to the semiclassical approximation, and recent work[68] has discussed the apparent similarities and fundamental differences of the two formulations. Even though the wave function (or propagator) is written as an amplitude multiplied by a phase in both theories, the semiclassical method relies on cross terms between distinct trajectories in order to account for quantum interference, while the Bohmian prescription employs a single trajectory for each point in space whose motion is governed by a quantum potential. The neglect of such cross terms lies at the heart of FBSD[13,32−37,40,43,45] and quasiclassical methods,[44,69−72] making them feasible by avoiding oscillatory phases at the expense of neglecting quantum interference. In a recent paper by my group,[68] it was shown that the Bohmian expression for a time-dependent expectation value can take a similar quasiclassical (initial value) form, free of undesirable phases. Interestingly, no phase factors enter the Bohmian expectation value, and yet all quantum effects are fully accounted for! Provided that the quantum potential can be evaluated reliably along a quantum trajectory, this quasiclassical expression allows full quantum mechanical calculations via Monte Carlo sampling of a readily available initial density. However, accurate determination of the strong, rugged Bohmian force continues to present serious difficulties in bound anharmonic systems. Further, numerical determination of the quantum potential based on finite-difference or polynomial-fitting procedures requires the knowledge of trajectory information in the vicinity of the given phase space point. This interdependence of the Bohmian trajectories prevents the propagation of a single trajectory by itself. Recent work in my group has shown that this problem can be overcome in principle through the determination of the Bohmian force from the stability properties of a given quantum trajectory. The Bohmian trajectory stability (BTS) method[73] determines the quantum force along a trajectory “on the fly”,

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by solving a set of differential equations for the coordinates of the quantum trajectory, the quantum force, and the infinite-order stability properties. In the infinite hierarchy of BTS equations, the nonlocality of quantum mechanics manifests itself as an infinite set of quantum potential derivatives at any given point in space that provide information about the global properties of this function; thus, the BTS formulation is fully equivalent to the exact quantum mechanical problem. Under certain conditions, the BTS hierarchy can be truncated, leading to a *local* scheme for determining approximate Bohmian trajectories that can capture some quantum mechanical features of a process.[73] The possibility of integrating individual quantum trajectories allows the use of Monte Carlo methods to evaluate Bohmian initial value representations.

The present paper introduces a forward−backward *quantum* dynamical (FBQD) representation of time correlation functions based on Bohmian trajectories. The derived expression assumes an initial value form that contains a *slowly varying* phase. In this sense, the obtained FBQD result enjoys the main advantage of a smooth integrand characteristic of FBSD methods and yet is a fully quantum mechanical result that correctly accounts for quantum interference and tunneling. Another important feature of the FBQD correlation function is that the underlying quantum force is weak and well behaved, greatly facilitating the computation of Bohmian trajectories.

Section II presents the theoretical formulation of FBQD. Several analytic and numerical examples are given in section III, and section IV presents some concluding remarks.

II. Theory

For simplicity, the theory that follows is presented for a one-dimensional system. Extension of the formalism to many dimensions is straightforward.

For a general (possibly time-dependent) Hamiltonian, the Bohmian form of the solution to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\Psi(x;t) = \hat{H}(t)\Psi(x;t) \tag{2.1}$$

is written in the form

$$\Psi(x;t) = R(x;t)\,\mathrm{e}^{iS(x;t)/\hbar} \tag{2.2}$$

Here, $R(x;t)$ is a real-valued amplitude and the phase $S(x;t)$ satisfies the quantum Hamilton−Jacobi equation

$$-\frac{\partial S(x;t)}{\partial t} = \frac{1}{2m}\left(\frac{\partial S(x;t)}{\partial x}\right)^2 + V(x;t) + Q(x;t) \tag{2.3}$$

The latter differs from the ordinary equation of classical mechanics through the presence of a quantum potential that is proportional to the curvature of the amplitude

$$Q(x;t) = \frac{-\hbar^2}{2m} R(x;t)^{-1} \frac{\partial^2 R(x;t)}{\partial x^2} \tag{2.4}$$

The initial condition for eq 2.3 is the phase $S_0(x_0)$ of the initial wave function at the coordinate x_0, which reaches the position x at the time t upon integration according to the equations

$$\dot{x}(t') = m^{-1}p(t') \qquad \dot{p}(t') = -V'(x(t')) - Q'(x(t')) \tag{2.5}$$

with an initial momentum

$$p_0 = S_0{}'(x_0) \tag{2.6}$$

The amplitude obeys the following continuity equation

$$R(x;t) = R_0(x_0)\left|\frac{\partial x_0}{\partial x}\right|^{1/2} \tag{2.7}$$

with

$$R_0(x) = |\Psi_0(x)|$$

Consider the time correlation function for a pure state

$$C_{AB}(t) = \mathrm{Tr}(\hat{\rho}_0 \hat{A} e^{i\hat{H}t/\hbar} B e^{-i\hat{H}t/\hbar}) \tag{2.8}$$

where $\rho_0 = |\Psi_0\rangle\langle\Psi_0|$. For simplicity, it is assumed throughout this paper that the operators $\hat{A}$ and $\hat{B}$ are functions of position. Such correlation functions are of particular importance to the vibrational spectroscopy of polyatomic molecules, where one is interested in the autocorrelation function of the dipole moment operator $\hat{\mu} = \mu(\hat{x})$. The procedure that follows can easily be extended to correlation functions of more general operators and to mixed states (e.g., finite-temperature correlation functions).

Equation 2.8 can be written as

$$C(t) = \int \mathrm{d}x \langle\Psi_0|\hat{A}\,\mathrm{e}^{i\hat{H}t/\hbar}|x\rangle B(x)\langle x|^{-i\hat{H}t/\hbar}|\Psi_0\rangle \tag{2.9}$$

In principle, each of the time-evolution steps in eq 2.9 can be evaluated using the Bohmian prescription with an appropriate initial condition. Specifically, the initial state Ψ_0 is propagated to time t, and a different initial state given by $\hat{A}\Psi_0$ is propagated backward in time. However, the quantum potentials governing these two different dynamics are not the same because the initial states are different. As a result, forward and backward trajectories must be launched with different initial conditions in order to reach the same coordinate x. Changing the integration variable to the initial value x_0^{f} of the forward trajectory converts the correlation function to the form

$$C_{AB}(t) = \int \mathrm{d}x_0^{\mathrm{f}} \left|\frac{\partial x}{\partial x_0^{\mathrm{f}}}\right| \langle\Psi_0|A\,\mathrm{e}^{i\hat{H}t/\hbar}|x\rangle B(x)\langle x|\mathrm{e}^{-i\hat{H}t/\hbar}|\Psi_0\rangle \tag{2.10}$$

In this, quantum trajectories with initial position x_0^{f} (and a momentum derived from the derivative of the phase of Ψ_0) must be integrated forward in time, reaching the coordinate x at time t under the Bohmian potential mentioned above. However, one must solve a "root-search" problem to find the appropriate initial condition of the backward trajectory that reaches the same final position x. Solution of the boundary value problem is already impractical in the context of purely classical propagation and even more so in the present case where the dynamics is governed by the Bohmian quantum potential.

To alleviate the root-search problem, the correlation function is converted to a forward−backward representation. For this purpose, the initial wave function is propagated sequentially by the first three operators in the correlation function. Thus, we define the state

$$\Psi_{0\leftarrow t,\hat{B},t\leftarrow 0} \equiv \mathrm{e}^{i\hat{H}t/\hbar}\,\hat{B}\,\mathrm{e}^{-i\hat{H}t/\hbar}\Psi_0 \tag{2.11}$$

Using this definition, the correlation function becomes

$$C_{AB}(t) = \int \mathrm{d}x \langle\Psi_0|\hat{A}|x\rangle\langle x|\Psi_{0\leftarrow t,\hat{B},t\leftarrow 0}\rangle \tag{2.12}$$

which is readily converted to an initial value form

$$C_{AB}(t) = \int \mathrm{d}x_0 \left| \frac{\partial x}{\partial x_0} \right| \langle \Psi_0 | \hat{A} | x \rangle \langle \Psi_{0\leftarrow t,\hat{B},t\leftarrow 0} \rangle \tag{2.13}$$

Because all the dynamics is now included in the propagation of a single state, a single initial condition is involved, and thus evaluation of eq 2.13 does not require a root search.

Equation 2.11 involves three propagation steps, which are performed according to the Bohmian prescription. First, a trajectory launched from the position x_0 with a momentum satisfying eq 2.6 is propagated to the time t following the Bohmian dynamics specified by the Hamiltonian operator and the given initial state. At the end of this step, the wave function is given by the expression

$$\Psi_{t\leftarrow 0}(x_t) = R_\mathrm{f}(x_t;t)\, \mathrm{e}^{iS_\mathrm{f}(x_t:t)/\hbar} \tag{2.14}$$

where x_t is the coordinate reached by the Bohmian trajectory, and R_f and S_f are the amplitude and action specified by the dynamics along the forward trajectory. Subsequently, eq 2.14 is multiplied by $B(x_t)$, and the resulting function

$$\Psi_{\hat{B},t\leftarrow 0}(x_t) = B(x_t)\Psi_{t\leftarrow 0}(x_t) \tag{2.15}$$

serves as the "initial" condition for a new Bohmian propagation in the negative time direction. The initial momentum of the backward trajectory is given by $\partial S_\mathrm{f}/\partial x_t = p_t$. At the end of this backward time evolution, i.e., when the time equals zero, the Bohmian trajectory has reached the coordinate x, and the corresponding wave function is

$$\Psi_{0\leftarrow t,\hat{B},t\leftarrow 0}(x) = R_\mathrm{b}(x;0)e^{iS_\mathrm{b}(x:0)/\hbar} \tag{2.16}$$

where R_b and S_b are the amplitude and action specified by the dynamics along the backward Bohmian trajectory. Use of the hydrodynamic continuity equation implies that

$$R_\mathrm{b}(x;0) = R_\mathrm{b}(x_t;t) \left| \frac{\partial x_t}{\partial x} \right|_\mathrm{b}^{1/2} \tag{2.17}$$

where the subscript "b" indicates that the derivative is evaluated at points along the backward trajectory. Recalling that the initial amplitude of the backward trajectory is

$$R_\mathrm{b}(x_t;t) = B(x_t)R_\mathrm{f}(x_t;t) \tag{2.18}$$

and making use of the continuity relation along the forward trajectory

$$R_\mathrm{f}(x_t;t) = R_\mathrm{f}(x_0;0) \left| \frac{\partial x_0}{\partial x_t} \right|_\mathrm{f}^{1/2} = \Psi_0(x_0)\, \mathrm{e}^{-iS_0(x_0)/\hbar} \left| \frac{\partial x_0}{\partial x_t} \right|_\mathrm{f}^{1/2} \tag{2.19}$$

leads to the following expression for the correlation function

$$C_{AB}(t) = \int \mathrm{d}x_0 \left| \frac{\partial x}{\partial x_0} \right| \langle \Psi_0 | \hat{A} | x \rangle B(x_t) \langle x_0 | \Psi_0 \rangle \left| \frac{\partial x_0}{\partial x_t} \right|_\mathrm{f}^{1/2} \left| \frac{\partial x_t}{\partial x} \right|_b^{1/2} \mathrm{e}^{iS(x)/\hbar} \tag{2.20}$$

where $S(x) = S_\mathrm{f}(x_t;t) + S_\mathrm{b}(x;0) - S_0(x_0)$ is the net action accumulated along the forward–backward trajectory. Finally, the product of stability elements can be simplified, leading to the expression

$$C_{AB}(t) = \int \mathrm{d}x_0 \langle \Psi_0 | \hat{A} | x \rangle B(x_t) \langle x_0 | \Psi_0 \rangle \left| \frac{\partial x}{\partial x_0} \right|^{1/2} \mathrm{e}^{iS(x)/\hbar} \tag{2.21}$$

Equation 2.21 is the main result of this paper. The correlation function is obtained from a forward–backward quantum trajectory procedure, which involves a trajectory propagated along forward and reverse time directions, interrupted by the action of the operator $\hat{B}$. Its attractive features can be summarized as follows:

(i) The FBQD correlation function represents an *exact quantum mechanical result* and thus leads to an exact description of tunneling, interference, and zero-point energy effects.

(ii) Equation 2.21 is an *initial value representation*. As such, it does not require numerical generation and storage of the time-dependent wave function on a grid (as long as the Bohmian force can be generated by a local or semilocal procedure)[73] nor does it involve a root search problem.

(iii) The correlation function is expressed as the result of a forward–backward time propagation. In this sense, it enjoys all the attractive features of forward–backward semiclassical dynamics (FBSD). Specifically, *the phase arising from the forward–backward action is a smooth function of the integration variables* and thus amenable to Monte Carlo procedures. Unlike FBSD expressions, which cannot account for quantum interference effects, the present FBQD formulation incorporates quantum interference results exactly.

(iv) FBQD can also be compared to the full semiclassical representation of a correlation function expressed in terms of two separate semiclassical propagators for the forward and backward evolution parts, usually referred to as "double IVR". Such expressions are capable of accounting for nonclassical interference effects through off-diagonal contributions from distinct forward and backward classical trajectories, but the classical nature of the dynamics does not allow for the inclusion of deep tunneling. As is well-known, the phase arising from the combined action integrals is a highly oscillatory function that prevents the use of Monte Carlo methods for the evaluation of semiclassical correlation functions. By contrast, the FBQD expression contains the net action along forward–backward quantum trajectories, which (as argued above) is a smooth function. Thus, FBQD is not only superior to the full semiclassical (double IVR) correlation function in its ability to describe strictly quantum mechanical effects but also easier for Monte Carlo methods.

(v) FBQD is a coordinate-space formulation and thus does not require the use of coherent states[9] or Wigner transforms[69] to obtain a sampling function for the initial conditions of the trajectories. Thus the difficult numerical issue of evaluating these phase space representations is avoided. An added bonus is the reduction in the dimension of the integrals compared to quasiclassical or full semiclassical expressions.

(vi) The FBQD formulation closely resembles FBSD expressions and thus *can be combined with a FBSD treatment* in a single calculation. As a result, FBQD may be employed to upgrade a semiclassical forward–backward treatment of a large system by including important quantum effects (such as interference and tunneling) originating from a small number of light particles.

(vii) Finally, the form of eq 2.21 *greatly facilitates computation of the quantum potential*. The initial density in an equilibrium correlation function commutes with the system's time evolution operator. In the specific case of a pure state, the forward part of the time evolution involves propagation of an eigenstate of the Hamiltonian. It can be shown that Bohmian trajectories remain stationary under the action of the quantum force arising from eigenstates of the Hamiltonian, and thus quantum trajectories remain fixed at their initial positions during the forward part of the dynamics. Subsequently, the eigenstate is multiplied by the operator $\hat{B}$. If the latter is the dipole operator responsible for vibrational transitions, this process produces a state that is to a first approximation similar to an excited state of the same Hamiltonian. Thus, evolution of that state is mild, leading to a *soft, slowly varying quantum force* that is free of sharp variations, and the dynamics does not suffer from the instability problems that plague the Bohmian method when applied to bound anharmonic potentials.

The desirable features outlined above make the FBQD formulation of time correlation functions a very attractive one. It should be emphasized, however, that numerical evaluation of the quantum trajectories entering the FBQD expression requires the concurrent generation of the underlying Bohmian force. Circumventing the various numerical difficulties surrounding the latter is not within the scopes of the present paper, but it is hoped that the dramatic smoothing and weakening of the Bohmian potential achieved through the propagation of FBQD trajectories corresponding to near eigenstates of the Hamiltonian will enable this task in a variety of systems of practical interest.

The next section illustrates these promising features of the FBQD formulation with analytic and numerical examples.

III. Examples

The attractive features of the FBQD representation of a time correlation function are illustrated with two examples. The first example involves the position autocorrelation function $\hat{A} = \hat{B} = \hat{x}$ for a system described by a harmonic potential of frequency ω and eigenstates Φ_n at zero temperature. During the forward part of the dynamics, the ground-state wave function evolves to time t by acquiring a phase

$$\Psi_{t\leftarrow 0}(x_t) = \Phi_0(x_0)\ \mathrm{e}^{-i\omega t/2} \tag{3.1}$$

During this stage the quantum potential is easily found to be

$$Q_{\mathrm{f}}(x) = -\frac{1}{2}m\omega^2x^2 + \frac{1}{2}\hbar\omega \tag{3.2}$$

Because the total (classical plus quantum) force equals zero, the Bohmian particles remain stationary ($x_t = x_0$, $p_t = p_0 = 0$) and the forward action is $S_{\mathrm{f}} = -{}^1/_2\hbar\omega t$. At the end of the forward propagation, the position operator acts on the wave function, changing it to the first excited state of the Hamiltonian

$$\Psi_{\hat{B},t\leftarrow 0}(x) = \sqrt{\frac{\hbar}{2m\omega}}\Phi_1(x) \tag{3.3}$$

The backward propagation is governed by the quantum force generated by this wave function, so again trajectories remain fixed, such that $x = x_0$, while the backward action is

$$S_{\mathrm{b}} = \frac{3}{2}\hbar\omega t$$

Substitution of these relations in eq 2.21 gives

$$C_{xx}(t) \equiv \langle\Phi_0|\hat{x}\ \mathrm{e}^{i\hat{H}t/\hbar}\hat{x}\ \mathrm{e}^{-i\hat{H}t/\hbar}|\Phi_0\rangle = \sqrt{\frac{\hbar}{2m\omega}}\int \mathrm{d}x_0\Phi_1(x)x_0\Phi_0(x_0)\ \mathrm{e}^{i\omega t} = \frac{\hbar}{2m\omega}\ \mathrm{e}^{i\omega t} \tag{3.4}$$

which is recognized as the exact result. In this idealized model, the total force acting on the Bohmian particles remained equal to zero at all times, and the phase was independent of coordinates.

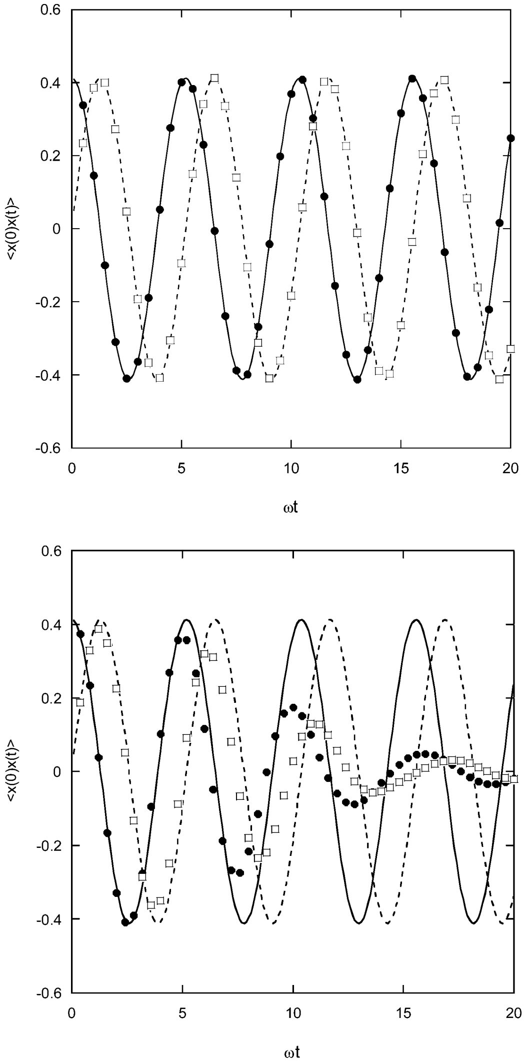

Figure 1. The position autocorrelation function for the quartic oscillator described by eq 3.5. Filled circles and hollow squares show real and imaginary parts, respectively. (a) FBQD results using a basis set method to evaluate the quantum potential. (b) FBSD results. The solid and dashed lines display the real and imaginary parts of the exact results obtained by a basis set calculation.

The second example involves a one-dimensional oscillator with quartic anharmonicity

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2x^2 + 0.1x^4 \tag{3.5}$$

with $m = \omega = 1$. The three lowest energy levels in this system have values equal to 0.559, 1.769, and 3.139$\hbar\omega$. Comparison with the eigenvalues of the corresponding harmonic potential (equal to 0.5, 1.5, and 2.5$\hbar\omega$) reveals the very significant role of the anharmonic term in this system. The quantum potential required to integrate the Bohmian trajectories was calculated accurately via a basis-set method. The FBQT correlation function shown in Figure 1 is seen to be in excellent agreement with that obtained via a basis-set method. Despite the regularity of the oscillations observed in this figure, it should be emphasized again that the potential in eq 3.5 is a strongly anharmonic one, and the frequency of the 0 → 1 and 1 → 2 transitions exceed ω by 21 and 37%, respectively. The effects

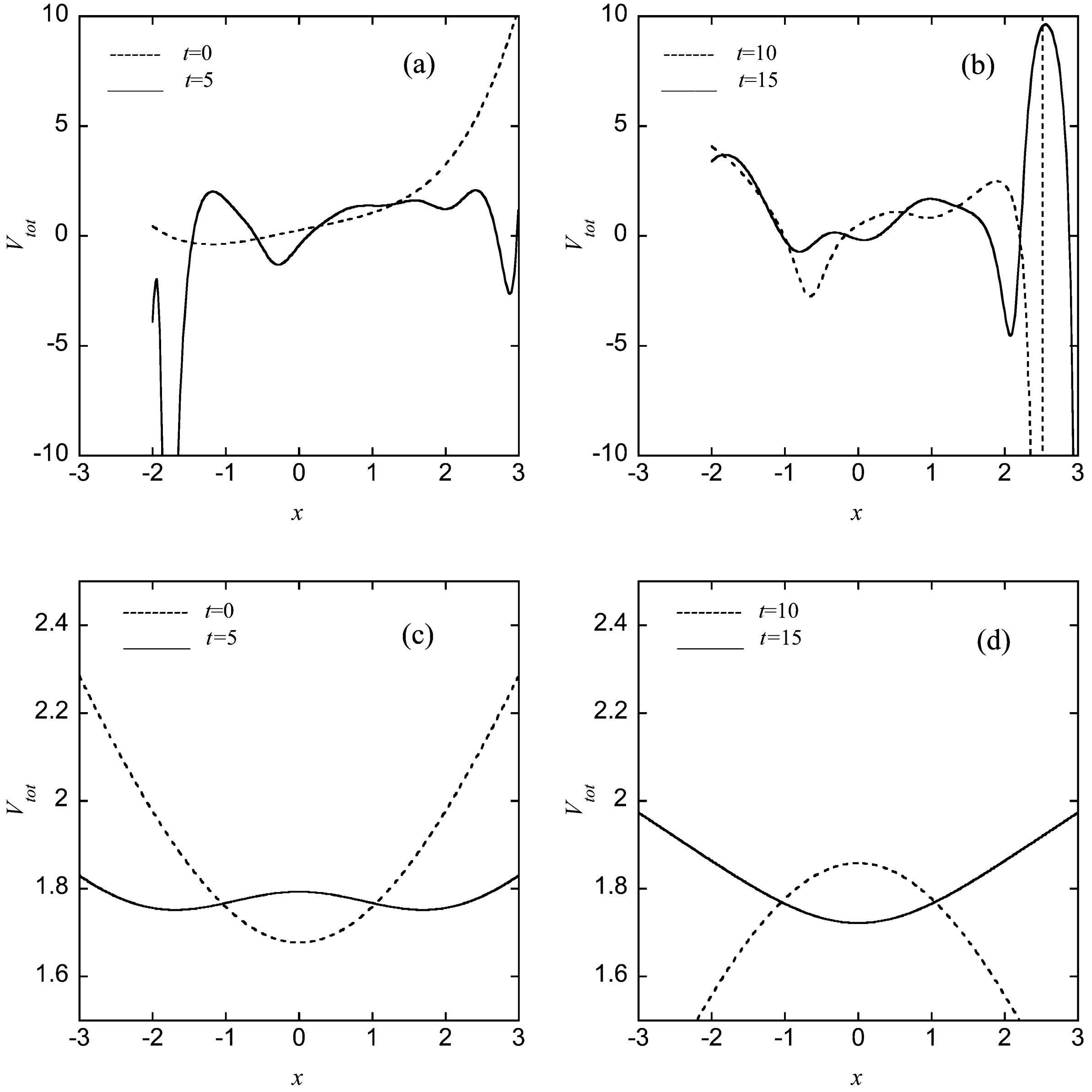

Figure 2. Total (classical plus quantum) potentials for the quartic oscillator described by eq 3.5. (a) and (b) Forward evolution of a Gaussian wavepacket displaced by 0.7 units from the potential minimum. (c) and (d) FBQD evolution for the zero-temperature position autocorrelation function. (The legend measures elapsed time from the beginning of the backward propagation.) Notice the smaller range of FBQD potential axis.

of nonlinearity are strongly felt in the evolution of most relevant trajectories. To further substantiate this claim, Figure 1 also displays the results of the derivative FBSD formulation,[36] where the correlation function takes the form

$$C_{AB}^{\mathrm{FBSD}}(t) = \int \mathrm{d}x_0 \int \mathrm{d}p_0\, f_A(x_0, p_0) B(x_t, p_t) \tag{3.6}$$

where f_A is a complex-valued function related to the initial wave function and the operator $\hat{A}$. Equation 3.6 is similar in appearance to the FBQD expression, as it is also an initial value form lacking an oscillatory phase. The observed dephasing of the FBSD result is a consequence of strong quantum interference for this system.

As discussed in recent work, the influence of the strong quartic term in this system leads to a classical dynamics that is dominated by caustic (focal) points. This feature leads to sharp variations of the quantum potential corresponding to wave packets undergoing forward time evolution. The resulting extremely strong forces render propagation unstable.[68] The quantum potential (calculated via basis set methods) corresponding to propagation of a Gaussian wave packet in this anharmonic system displaced by 0.7 units from the potential minimum is shown in parts a and b of Figure 2. Shown in parts c and d of Figure 2 is the quantum potential arising in the FBQD calculation of the position autocorrelation function for the same system. (The position operator is again chosen as a rough approximation of the dipole-moment function for a diatomic molecule.) Even though this operator does not promote the wave function of an anharmonic system exclusively to the first excited eigenstate, the wave function generated this way bears close resemblance to the eigenfunction, such that the resulting quantum potential is smooth and well behaved. As a result, the Bohmian trajectories employed in the calculation of Figure 1 were integrated with a time step comparable to that for integration of purely classical trajectories, whereas forward wave packet propagation for the same system became possible only by decreasing the time step by a factor of 200. It is emphasized, however, that the quantum potential employed in the calculation shown in Figure 1 was obtained by using a nonlocal basis set expansion. The dramatic smoothing of the quantum potential

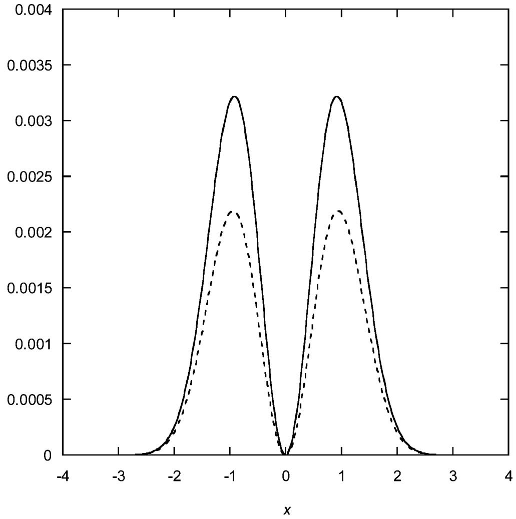

Figure 3. The integrand of the FBQD expression for the quartic oscillator model at $\omega t = 0.5$. Solid and dashed lines show the real and imaginary parts of the integrand, respectively.

achieved in the FBQD formulation is encouraging and suggests that its determination by local schemes may become possible in the near future.

Finally, Figure 3 shows the real and imaginary parts of the integrand of eq 2.21 at a specific time. The real and imaginary parts are seen to be smooth functions free of oscillatory components. This feature is a result of the slow variation of the net forward−backward action in the FBQD expression. The absence of a rapid oscillatory phase from the integrand implies that Monte Carlo methods, which provide the only viable approach for systems of several degrees of freedom, are suitable for the evaluation of FBQD correlation functions.

IV. Concluding Remarks

In summary, the FBQD formulation introduced in this paper offers an attractive, fully quantum mechanical representation of time correlation functions. Because the FBQD integrand is a smooth function, the present formulation enjoys the advantages of forward−backward semiclassical approximations without the neglect of quantum mechanical features such as phase interference and tunneling. Unlike FBSD, which requires the calculation of an appropriate phase space transform of the density operator, FBQD is implemented directly in position space with a density directly obtainable from the raw wave function (or density matrix) describing the initial condition. Last, a very important feature of FBQD correlation functions is the smoothness and small magnitude of the quantum potential governing the dynamics. Bohmian calculations on bound anharmonic systems have encountered severe difficulties in the past because of the strong quantum force and rugged shape of the quantum potential. The absence of these undesirable features from the present formulation suggests that the numerical issues surrounding the evaluation of the quantum force may become sufficiently mild to make Bohmian calculations with a self-consistent determination of the quantum force practical. Finally, the attractive features of FBQD also apply to correlation functions of more general operators and to systems at thermal equilibrium.[74]

Given the advantageous features of the FBQD formulation, the problem of accurate determination of the quantum force is the single most serious obstacle that currently prevents application of this methodology to general multidimensional systems. Efforts to overcome this problem are currently underway.[73,74]

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