Monte Carlo Bohmian Dynamics from Trajectory Stability Properties

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It is shown that the quantum force in the Bohmian formulation of quantum mechanics can be related to the stability properties of the given trajectory. In turn, the evolution of the stability properties is governed by higher order derivatives of the quantum potential, leading to an infinite hierarchy of coupled differential equations whose solution specifies completely all aspects of the dynamics. Neglecting derivatives of the quantum potential beyond a certain order allows truncation of the hierarchy, leading to approximate Bohmian trajectories. Use of the method in conjunction with Bohmian initial value formulations [*J. Chem. Phys.* **2003,** *119,* 60] gives rise to simple position-space representations of observables or time correlation functions. These are analogous to approximate quasiclassical expressions based on the Wigner or Husimi phase space density but involve lower dimensional integrals with smoother integrands and avoid the costly evaluation of phase space transforms. The lowest-order version of the truncated hierarchy can capture large corrections to classical mechanical treatments and yields (with fewer trajectories) results that are somewhat more accurate than those based on quasiclassical phase space treatments.

I. Introduction

The Bohmian theory of time evolution[1–3] is an alternative formulation of quantum mechanics. The main appeal of Bohmian dynamics is its formulation in terms of "trajectories", a familiar concept from classical physics, which can lead to insightful pictures of quantum phenomena. The Bohmian trajectories obey classical-like equations of motion with an additional force arising from a "quantum potential" that is proportional to the local wave function curvature. Apart from interest in Bohmian theory as an interpretational tool, the close resemblance of the Bohmian formulation to that of classical mechanics raises the intriguing prospect of using it to develop new numerical tools applicable to multidimensional systems that are too large to treat via conventional quantum mechanical methods. Of course quantum mechanics is a nonlocal theory, and the Bohmian formulation is not expected to beat the scaling laws that apply to basis set or grid based methods. Yet, approximate versions of Bohmian dynamics may lead to sufficiently accurate results in some systems with many degrees of freedom. Another attractive approach is the construction of practical quantum-classical (or even quantum-semiclassical) descriptions of the dynamics based on trajectories where the quantum force acts only on designated degrees of freedom (e.g., those corresponding to light particles).[4–8]

Considerable effort has been invested in Bohmian dynamics since the late 1990s by several groups.[4–25] Much of that work has focused on visual investigation of quantum trajectories in model systems and on the development of numerical methods for evaluating the required quantum force. The latter is given by the third derivative of the instantaneous density, and its accurate determination has been the stumbling block in Bohmian methodology. Most methods have used moving weighted least-squares fitting schemes,[10,15] distributed approximating functionals,[14] or Gaussian expansions[25] for evaluating the derivatives necessary to obtain the quantum force from density information in the neighborhood of a quantum trajectory. Despite their success in treating barrier and dissociation problems, these methods have proven elusive in systems that exhibit strong quantum interference effects. The dynamics of such systems is characterized by strong and rugged force fields, whose accurate evaluation continues to pose a serious numerical problem that tends to render the solution unstable.[26] To date, accurate calculation of Bohmian trajectories in systems with strong quantum interference has been possible only by utilizing eigenstate information obtained by solving the full quantum mechanical problem by conventional methods.[17,23,26]

The approach presented in the present manuscript was motivated by our desire to avoid evaluation of the quantum force via numerical derivative procedures, thereby circumventing the stability problem in the calculation of Bohmian trajectories and the need for simultaneous propagation. Starting from the equation of continuity for the quantum density,[27] we show that the quantum force along a given trajectory can be obtained from the stability properties of the same trajectory. These, in turn, satisfy differential equations that involve derivatives of the stability matrix familiar from classical mechanics, which require knowledge of derivatives of the quantum potential. This resulting procedure, which is based on information contained in the Bohmian trajectory stability (BTS) matrix, leads to an infinite hierarchy of differential equations whose solution yields simultaneously the density, quantum potential, and trajectory coordinates. This way each quantum trajectory can be propagated *independently*, avoiding the need for concurrent propagation of surrounding trajectories required for derivative evaluation by numerical schemes.

Recent work by our group has shown that useful dynamical properties can be cast in initial value representations with smooth integrands,[26,28] so the independent evaluation of quantum

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trajectories in the BTS approach allows the use of Monte Carlo methods in order to select initial conditions in Bohmian calculations. In practice, however, a solution of these differential equations is possible only if the hierarchy terminates. Although this occurs naturally in special cases, in most systems, it is necessary to truncate the hierarchy by neglecting derivatives of the quantum potential beyond a certain order. This procedure gives rise to approximate Bohmian dynamics whose accuracy depends on the system and the property in question. Quantum interference phenomena (which arise from cross terms in the analogous semiclassical formulation of time-dependent quantum mechanics) are a signature of nonlocality and thus probably cannot be captured by low-order versions of the BTS hierarchy. On the other hand, truncation of the BTS hierarchy at the second order gives rise to exact quantum trajectories in parabolic potentials, and thus low-order BTS approximations can account reasonably well for near-barrier-top tunneling.

Section II describes the theory and develops the BTS hierarchy. That section also discusses various features of the BTS scheme and its use in conjunction with Monte Carlo sampling techniques. Several numerical examples are presented in section III, illustrating the capabilities and limitations of the BTS methodology. Finally, some concluding remarks appear in section IV.

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 solution to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(x;t) = \hat{H}(t)\Psi(x;t) \tag{1}$$

is written in the form

$$\Psi(x;t) = R(x;t)e^{iS(x;t)/\hbar} \tag{2}$$

Here $R(x;t)$ is a real-valued amplitude (which may be negative) and the phase $S(x;t)$ satisfies the quantum Hamilton-Jacobi equation

$$-\frac{\partial S(x;t)}{\partial t} = \frac{1}{2m}\left(\frac{\partial S(x;t)}{\partial x}\right)^2 + V(x;t) + Q(x;t) \tag{3}$$

The latter differs from the ordinary equation of classical mechanics through the presence of a quantum potential proportional to the local wave function curvature

$$Q(x;t) = -\frac{\hbar^2}{2m} R(x;t)^{-1} \frac{\partial^2 R(x;t)}{\partial x^2} = \\ -\frac{\hbar^2}{8m}\left(2\frac{\rho(x;t)\rho''(x;t)}{\rho(x;t)^2} - \frac{\rho'(x;t)^2}{\rho(x;t)^2}\right) \tag{4}$$

The corresponding quantum force can be written in the form

$$-Q'(x;t) = \frac{\hbar^2}{4m}\left(\frac{\rho^{(3)}(x;t)}{\rho(x;t)} - 2\frac{\rho'(x;t)\rho''(x;t)}{\rho(x;t)^2} + \frac{\rho'(x;t)^3}{\rho(x;t)^3}\right) \tag{5}$$

where $\rho(x;t) = R(x;t)^2$ is the local density. The initial condition for eq 3 is the phase $S_0(x_0)$ of the initial wave function at the coordinate x_0. The trajectory reaches the position x_t at the time

t upon integration according to the equations

$$\dot{x}_{t'} = m^{-1}p_{t'}, \quad \dot{p}_{t'} = -V'(x_{t'}) - Q'(x_{t'}) \tag{6}$$

with an initial momentum

$$p_0 = S'_0(x_0) \tag{7}$$

The dynamics of the Bohmian trajectories resembles fluid flow, and the density obeys the following continuity equation:

$$\rho(x;t) = \rho_0(x_0)\frac{\partial x_0}{\partial x} \tag{8}$$

To obtain the quantum force at a given point along a quantum trajectory one must know the first three derivatives of the density. Numerical evaluation of these derivatives from the evolving grid of Bohmian particles (the "Lagrangian field") is a demanding and often unstable task, as small errors in the determination of the quantum force can destroy the stability of the method. Further, the storage and propagation of the full Bohmian grid is impractical for systems of many particles, where Monte Carlo methods provide the only option. Recent work has indicated that Bohmian expressions can be cast in an initial value form with a smooth integrand.[26,28] This possibility raises the question of whether the quantum force necessary to propagate an individual Bohmian trajectory can be evaluated from the trajectory itself and its stability properties, in the absence of information from neighboring trajectories.

To proceed, we notice that the continuity equation can be exploited to obtain spatial derivatives of the density. Indeed, repeated differentiation of eq 8 and use of the chain rule leads to the equations

$$\rho'_t(x_t) = \rho'_0(x_0)\left(\frac{\partial x_0}{\partial x_t}\right)^2 + \rho_0(x_0)\frac{\partial^2 x_0}{\partial x_t^2}$$

$$\rho''_t(x_t) = \rho''_0(x_0)\left(\frac{\partial x_0}{\partial x_t}\right)^3 + 3\rho'_0(x_0)\frac{\partial x_0}{\partial x_t}\frac{\partial^2 x_0}{\partial x_t^2} + \rho_0(x_0)\frac{\partial^3 x_0}{\partial x_t^3}$$

$$\rho_0^{(3)}(x_t) = \rho_0^{(3)}(x_0)\left(\frac{\partial x_0}{\partial x_t}\right)^4 + 6\rho''_0(x_0)\left(\frac{\partial x_0}{\partial x_t}\right)^2 \frac{\partial^2 x_0}{\partial x_t^2} + \\ \rho'_0(x_0)\left(4\frac{\partial x_0}{\partial x_t}\frac{\partial^3 x_0}{\partial x_t^3} + 3\left(\frac{\partial^2 x_0}{\partial x_t^2}\right)^2\right) + \rho_0(x_0)\frac{\partial^4 x_0}{\partial x_t^4} \tag{9}$$

Here all derivatives are evaluated subject to fixed initial conditions, as specified by eq 7. For a real-valued initial wave function, $p_0 = 0$ and the derivatives are evaluated with fixed initial momentum. Similar expressions can be obtained for higher order derivatives.

The derivatives of the initial density are assumed known. The other derivatives are brought into the form of derivatives of position x_t reached by a trajectory with respect to its initial value

$$\frac{\partial x_0}{\partial x_t} = \left(\frac{\partial x_t}{\partial x_0}\right)^{-1}, \quad \frac{\partial^2 x_0}{\partial x_t^2} = -\frac{\partial^2 x_t}{\partial x_0^2}\left(\frac{\partial x_t}{\partial x_0}\right)^{-3},$$

$$\frac{\partial^3 x_0}{\partial x_t^3} = \left[3\left(\frac{\partial^2 x_t}{\partial x_0^2}\right)^2 - \frac{\partial x_t}{\partial x_0}\frac{\partial^3 x_t}{\partial x_0^3}\right]\left(\frac{\partial x_t}{\partial x_0}\right)^{-5} \tag{10}$$

etc. These equations require knowledge of derivatives of the coordinate reached by a quantum trajectory with respect to its

initial condition. The first of these derivatives is related to one of the elements of the stability matrix

$$\mathbf{M}_t = \begin{pmatrix} \dfrac{\partial x_t}{\partial x_0} & \dfrac{\partial x_t}{\partial p_0} \\[2mm] \dfrac{\partial p_t}{\partial x_0} & \dfrac{\partial p_t}{\partial p_0} \end{pmatrix} \qquad (11)$$

This matrix is known to satisfy the following differential equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\mathbf{M}_t = \mathbf{T}_t \cdot \mathbf{M}_t \qquad (12)$$

where

$$\mathbf{T}_t = \begin{pmatrix} 0 & m^{-1} \\ -V''_{\mathrm{tot}} & 0 \end{pmatrix} \qquad (13)$$

In the last equation $V_{\mathrm{tot}}(x_t;t) = V(x_t;t) + Q(x_t;t)$ is the sum of the classical and quantum potentials acting on the Bohmian particle.

To calculate the required higher order derivatives, we differentiate eq 12 repeatedly with respect to x_0. This procedure leads to the following differential equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathbf{M}_t}{\partial x_0} = \mathbf{T}_t \frac{\partial \mathbf{M}_t}{\partial x_0} + \frac{\partial \mathbf{T}_t}{\partial x_0}\mathbf{M}_t,$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial^2 \mathbf{M}_t}{\partial x_0{}^2} = \mathbf{T}_t \frac{\partial^2 \mathbf{M}_t}{\partial x_0{}^2} + 2\frac{\partial \mathbf{T}_t}{\partial x_0}\frac{\partial \mathbf{M}_t}{\partial x_0} + \frac{\partial^2 \mathbf{T}_t}{\partial x_0{}^2}\mathbf{M}_t \quad (14)$$

etc. These equations require knowledge of derivatives of $V''_{\mathrm{tot}}(x_t)$ with respect to its initial position x_0. One finds

$$\frac{\partial V''_{\mathrm{tot}}(x_t;t)}{\partial x_0} = V^{(3)}_{\mathrm{tot}}(x_t;t)\left(\frac{\partial x_t}{\partial x_0}\right),$$

$$\frac{\partial^2 V''_{\mathrm{tot}}(x_t;t)}{\partial x_0{}^2} = V^{(4)}_{\mathrm{tot}}(x_t;t)\left(\frac{\partial x_t}{\partial x_0}\right)^2 + V^{(3)}_{\mathrm{tot}}(x_t;t)\left(\frac{\partial^2 x_t}{\partial x_0{}^2}\right) \quad (15)$$

and the procedure can be repeated to obtain higher order derivatives.

Equations 4, 6, and 8−15 form a set of differential equations from which the density, quantum potential, and Bohmian trajectories can be propagated simultaneously in time. These equations are not closed but form an infinite hierarchy. (For example, evaluation of the quantum force according to eq 4 requires knowledge of the first three derivatives of the density; these, in turn, require knowledge of the fourth derivative of the trajectory position, which obeys a differential equation whose right-hand-side depends on the fifth derivative of the quantum potential.) In certain situations the hierarchy terminates at a given order, and the solution of this set of differential equations yields exact Bohmian trajectories. More often, the above procedure yields an infinite set of equations. Depending on the problem at hand, truncation of these equations may lead to reasonable approximations to the dynamics or to physically incorrect results. The remainder of this section discusses these situations, and section III illustrates them with analytic and numerical examples.

While the present manuscript was in preparation, an article by Trahan et al.[29] appeared that describes an infinite differential equation hierarchy for the real and imaginary parts of the logarithm of a wave function. These equations are obtained directly by expressing the evolving wave function in exponential form and substituting in the time-dependent Schrödinger equation. Thus, that approach is an exponential derivative scheme for propagating a wave function and is (in its more general form) no easier than solving the time-dependent Schrödinger equation in its conventional form. Of course, once the full wave function has been determined from the solution to the Schrödinger equation, it is a straightforward task to evaluate the quantum potential and explore the properties of Bohmian trajectories; but we emphasize that the approach described in ref 29 does not solve the Bohmian equations of quantum mechanics as a way of generating the desired dynamics.

Solution of the differential equations for the logarithm of a wave function is facilitated by adopting a particular *ansatz* for the evolving function. Some celebrated choices include Gaussian superpositions,[30] the time-dependent WKB expansion in powers of $\hbar$, local quadratic approximations,[31] and expansions in powers of time.[32] (The last two of these methods have been implemented in the context of the quantum mechanical propagator.) The article by Trahan et al. truncates the hierarchy by neglecting derivatives of the wave function logarithm beyond a certain (typically the second) order. The validity of that assumption is debated later in this section, but we note here that the neglect of derivatives higher than second order is not necessarily equivalent to full quantum mechanical propagation subject to a local Gaussian *ansatz* for the wave function. The assumed exponential form implies that the scheme cannot account for nodes that develop in the course of the evolution nor can it be used to propagate excited states. If a locally Gaussian wave function approximation is used to generate a quantum potential, the latter will have only two nonzero derivatives at any point.

The BTS approach described in the present paper generates the Bohmian trajectories exclusively from knowledge of the quantum forces, which are, in turn, obtained from the instantaneous stability properties of an individual trajectory. Implementation of this scheme requires in most cases of interest the neglect of high order derivatives of the quantum potential. Note, however, that no assumptions are made for the form of the wave function, and thus, the present methodology can be used to propagate excited-state functions with spatial nodes.

The question that arises naturally in conjunction with any truncated hierarchy is whether the derivatives of the function actually exist and, assuming they do, whether they vanish beyond a certain order. A function f can be accurately represented by a Taylor series in the neighborhood of a given point x_0, provided that $f^{(n+1)}(\bar{x})(x-x_0)^{n+1}/(n+1)!$ (where $f^{(k)}$ denotes the kth derivative of the function and $\bar{x}$ lies between x and x_0) is sufficiently small. For smooth functions, this condition can always be satisfied by constraining x to be as close to x_0 as necessary. However, these facts do not imply that $f^{(n+1)}$ vanishes. Although the use of a Taylor expansion of the function through nth order may lead to an excellent approximation, the neglect of derivatives of order higher than n in a differential equation hierarchy may not lead to an accurate solution. These remarks apply to the derivative propagation method of Trahan et al.[29] (which truncates the exponent of the evolving wave function) and also to the BTS approach developed in this paper (which truncates the quantum potential).

Focusing on the formulation presented in this section, whether derivatives of the quantum potential are small and thus can be neglected beyond a certain order depends on the physical system under consideration. Clearly, quadratic Hamiltonians, as well

as certain special wave functions in nonlinear systems (see section IIIb) are amenable to such truncations without approximation. For other situations, such as short duration scattering events, truncation of the quantum potential may lead to excellent approximations to the dynamics. Equations 4, 6, and 8−15 allow propagation of an individual quantum trajectory, without any reference to neighboring trajectory information. Yet, this set of equations is formally exact precisely because the hierarchy is an infinite one. By virtue of Taylor's theorem, knowledge of an infinite set of derivatives at a given point is equivalent to global knowledge of a smooth function. Thus, the nonlocality of quantum mechanics manifests itself in the infinite hierarchy of coupled equations in the present formalism: the infinite set of sensitivity characteristics of a Bohmian trajectory (i.e., all derivatives of the type $\partial^n x_t/\partial x_0{}^n$) contains information equivalent to that carried by all other Bohmian trajectories and the underlying quantum potential. In strongly nonlinear systems where strong interference is observed, the dynamics cannot be made local by truncating the differential equation hierarchy. Truncation of such schemes will in such cases lead to significant errors in the propagation of the Bohmian trajectories and a loss of important quantum interference. Dynamical observables that exhibit strong quantum interference effects are not described accurately by low-order versions of the BTS methodology.

On the other hand, trajectories generated via the BTS methodology can penetrate classically forbidden regions. Propagation of a Gaussian wave packet in a parabolic barrier gives rise to a quadratic quantum potential, and thus, the BTS scheme truncates rigorously at the second potential derivative in this case. BTS trajectories can also penetrate nonquadratic potential barriers and can lead to reasonable (albeit not exact) descriptions of tunneling effects. The ability of the truncated BTS scheme to account for tunneling is an important practical advantage of the methodology described in this paper and can be exploited to allow barrier penetration for select light particles in a mixed quantum-semiclassical (or quantum-classical) calculation on a polyatomic system.

Assuming that neglect of high order derivatives is possible, the BTS method decouples the quantum trajectories from one another and thus can be implemented in conjunction with Monte Carlo methods. Such methods provide the only viable approach for evaluating integrals of high dimension and their use will be necessary in order to apply Bohmian dynamics to polyatomic systems such as molecule−surface scattering. Recent papers by our group[26,28] have derived initial value representations for observables and time correlation functions that are ideally suited to Monte Carlo integration. For example, the expectation value of a coordinate-dependent operator $\hat{A}$ is given by the expression[26]

$$\langle A \rangle_t \equiv \langle \Psi(t)|\hat{A}|\Psi(t)\rangle = \int \mathrm{d}x_0 |\Psi_0(x_0)|^2 A(x_t) \quad (16)$$

This exact quantum mechanical result has a deceptively simple quasiclassical appearance, where the dynamical observable of interest evaluated at a point along a Bohmian trajectory is averaged with respect to a distribution specified by the initial wave function density. Equation 16 does not contain oscillatory phase factors, and thus, the integrand is a smooth function suitable for integration by Monte Carlo techniques. Implementation of such methods is entirely straightforward since the sampling function given by the initial density $|\Psi_0(x_0)|^2$ is by definition readily available.

Below we summarize the equations that are propagated in the 2nd order BTS scheme. It is easy to show that all derivatives of the stability matrix vanish in this approximation. This leads to the following compact expressions for the first two derivatives of the quantum potential:

$$Q'(x_t;t) = Q'(x_0;0)\left(\frac{\partial x_t}{\partial x_0}\right)^{-3}, \quad Q''(x_t;t) = Q''(x_0;0)\left(\frac{\partial x_t}{\partial x_0}\right)^{-4} \quad (17)$$

The position, momentum, and stability matrix elements along each quantum trajectory are obtained by solving the following set of six first-order differential equations:

$$\frac{\mathrm{d}x_t}{\mathrm{d}t} = m^{-1}p_t, \quad \frac{\mathrm{d}p_t}{\mathrm{d}t} = -V'_{\mathrm{tot}}(x_t), \quad \frac{\mathrm{d}\mathbf{M}_t}{\mathrm{d}t} = \mathbf{T}_t \cdot \mathbf{M}_t \quad (18)$$

Several examples presented in the next section show that the simple 2nd order BTS approximation often provides a reasonably accurate and inexpensive approximation to the dynamics.

Extension of the BTS methodology to multidimensional systems is in principle straightforward. Derivation of the relevant equations can be easily performed with the aid of symbolic algebra software. For a system of N degrees of freedom, the 2nd order BTS methodology leads to $4N^2 + 2N$ coupled differential equations; this is the same number of equations required by phase space semiclassical formulations[33] (where all elements of the stability matrix must be propagated concurrently), and thus, the integration of BTS trajectories in multidimensional systems (with a second order truncation of the quantum potential) should not be computationally prohibitive.

III. Examples

(a) Quadratic Hamiltonians. It is always instructive to consider application of a new method to a simple harmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \quad (19)$$

Here we choose $m = \omega = 1$. First we consider a Gaussian initial state described by the wave function

$$\Psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(-\frac{\alpha}{2}(x - x_0)^2\right) \quad (20)$$

It is easy to show that the quantum potential is at all times a quadratic function in this case, and thus, the hierarchy of differential equations terminates at the second derivative of the total potential.

Figure 1 shows quantum trajectories obtained with various values of α for the initial condition specified by $x_0 = 4$. These trajectories were propagated independently of one another by using the methodology presented in section II. The Bohmian trajectory corresponding to the center of the Gaussian wave packet evolves completely classically, oscillating about the potential minimum. When $\alpha = m\omega/\hbar$, the wave packet oscillates rigidly about the potential minimum, and the Bohmian trajectories display the simple behavior observed in Figure 1b. For $\alpha \neq m\omega/\hbar$, there is an additional "breathing" motion, where the width of the wave packet exhibits an oscillatory pattern about the ground-state value, and the quantum trajectories exhibit more complex behaviors.

The observable of interest is the width (root-mean-square deviation) of the evolving Gaussian wave packet

$$w(t) = \sqrt{\langle x^2 \rangle_t - \langle x \rangle_t^2} \quad (21)$$

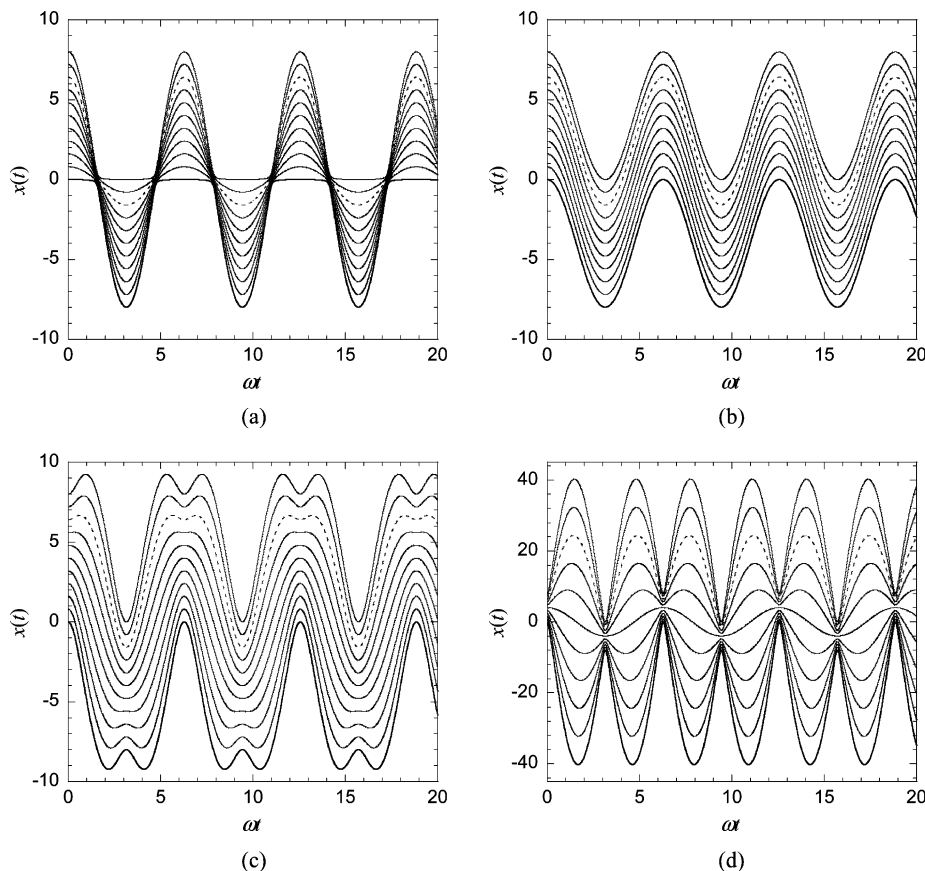as a function of time. The expectation values entering this

Figure 1. Quantum trajectories for a displaced Gaussian state with (a) $\alpha = (1/10)m\omega/\hbar$, (b) $\alpha = m\omega/\hbar$, (c) $\alpha = 2m\omega/\hbar$, and (d) $\alpha = 10m\omega/\hbar$. One of these trajectories in each figure is shown as a dashed line for clarity. Notice the different scale in d.
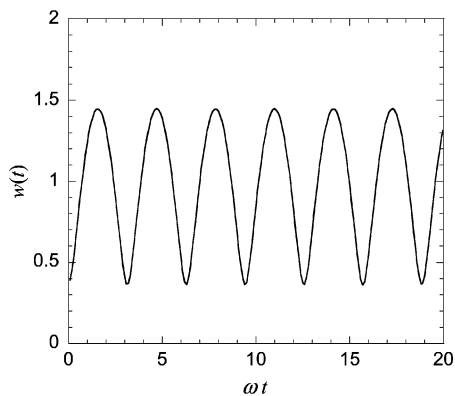

Figure 2. Width of a Gaussian wave packet with $\alpha = 4m\omega/\hbar$, $x_0 = 4$ in a harmonic potential. Solid circles: Monte Carlo results obtained with 5000 BTS trajectories. The error bars are smaller than the size of the markers. The solid line shows the exact quantum mechanical result.

Figure 3. Quantum trajectories for a displaced excited state of a harmonic potential (cf. eq 22). The dotted line shows the trajectory of the center, for which the quantum force vanishes.

expression were obtained from eq 16 with $\hat{A} = \hat{x}$ or $\hat{x}^2$. This initial value representation of Bohmian dynamics,[26] eq 16, is an exact result that can be straightforwardly extended to multidimensional systems. Figure 2 shows the oscillating width of the wave packet centered at $x_0 = 4$ in the case $\alpha = 4m\omega/\hbar$ obtained via Monte Carlo integration of eq 16 with the initial probability density as the sampling function. These results were obtained with 5000 BTS trajectories.

Finally, we demonstrate the application of this methodology to the evolution of a non-Gaussian state. The initial wave function has the form

$$\Psi_0(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4}(x - x_0)\exp\left(-\frac{\alpha}{2}(x - x_0)^2\right) \quad (22)$$
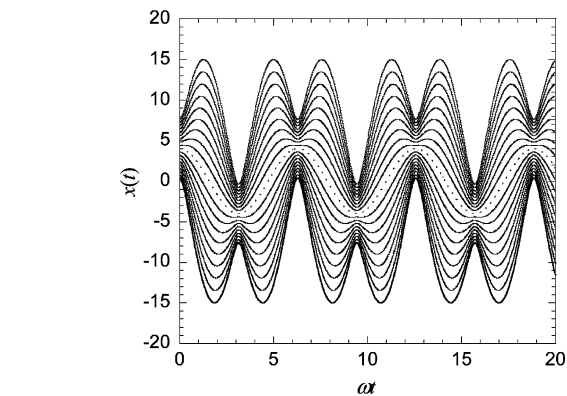
with $\alpha = 2m\omega/\hbar$ and $x_0 = 4$. This function corresponds to the first excited state for a harmonic potential with frequency 2ω and a minimum at x_0. Again, truncation of the quantum potential at the second order leads to exact dynamics. It is easy to show that the Bohmian force of a displaced harmonic oscillator state is identical to the one corresponding to a shifted Gaussian of the same width. Figure 3 shows the quantum trajectories for this wave function. Excluding nodes, which lead to zero denominators and thus cannot be propagated, all other trajectories were propagated using a straightforward application of the BTS scheme. It can be seen from Figure 3 that the BTS trajectories do not pass through the nodal line.

(b) Eigenstates of Anharmonic Systems. Eigenstates of a general time-independent Hamiltonian give rise to Bohmian forces that precisely cancel their classical counterparts. To see

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this, consider a Bohmian wave function whose amplitude function at $t = 0$ satisfies the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}R''(x;0) + V(x)R(x;0) = ER(x;0) \qquad (23)$$

It follows that $R(x;t) = R(x;0)$ and $S(x;t) = -Et$. The Bohmian potential is

$$Q(x;t) = -\frac{\hbar^2}{2m}\frac{R''(x;t)}{R(x;t)} = E - V(x) \qquad (24)$$

Thus, $V(x) + Q(x;t) = E$, and the total force equals zero. As a result, the Bohmian particles do not evolve. However, these features require a delicate (in principle, exact) cancellation of classical and quantum forces, and thus, the propagation of eigenstates in anharmonic potentials using methods based on numerical derivatives encounters similar challenges to those discussed in the Introduction.

Because the quantum potential equals exactly the negative of the classical one, these two functions must have the same Taylor series expansion (with opposite signs). One can thus truncate the quantum potential at any given order, and provided that the classical potential is also truncated at the same order, the forces will balance exactly, leading to correct time evolution.

These features are illustrated by propagating the first excited state of a strongly anharmonic oscillator corresponding to the potential

$$V(x) = \frac{1}{2}m\omega^2 x^2 + 0.1x^4 \qquad (25)$$

with $m = \omega = 1$. The excited state wave function and its derivatives were evaluated via a basis set expansion. The BTS scheme was applied with the quantum potential truncated at the fourth order, consistent with the quartic form of the classical potential. The BTS trajectories displayed in Figure 4 are seen to be perfectly straight lines, a consequence of exact cancellation between classical and quantum forces.

(c) Barrier Transmission. As a third paradigm, we consider transmission through a one-dimensional barrier. The transmission coefficient $P(E)$ at a given translational energy E was calculated from the expression

$$P(E) = \lim_{t \to \infty} P_E(t) \qquad (26)$$

Here $P_E(t)$ is the time-dependent transmission probability at the translational energy E

$$P_E(t) = \int_0^\infty |\Psi(x;t)|^2 \, dx_t = \int_{-\infty}^\infty |\Psi(x;t)|^2 h(x_t) \, dx_t = \\ \langle \Psi_0 | e^{i\hat{H}t/\hbar} \hat{h} e^{-i\hat{H}t/\hbar} | \Psi_0 \rangle \quad (27)$$

where $h(x)$ is a step function. Using again eq 16, the transmission probability takes the form

$$P_E(t) = \int_{-\infty}^\infty |\Psi_0(x_0)|^2 h(x_t) dx_0 \qquad (28)$$

This expression integrates the initial probability density over the coordinate interval that leads to reactive trajectories. Since there is no recrossing for this simple barrier problem, it suffices to find the coordinate x_{div} which separates Bohmian trajectories that cross the barrier from those that remain nonreactive. This can be done iteratively with a small number of trajectories: initially, one sets up a sparse grid to find an approximate value
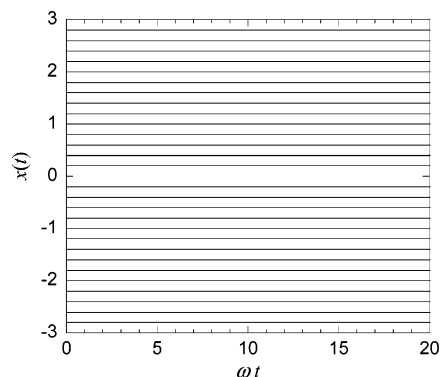

Figure 4. BTS trajectories corresponding to the first excited state of an anharmonic oscillator with the potential given in eq 25. The quantum potential was truncated at the fourth order.

of x_{div}, which is subsequently refined by propagating trajectories on a finer grid spanning the vicinity of that coordinate value. The same procedure can be implemented within a Monte Carlo setting. Once the critical position is found, calculation of the transmission probability involves evaluating an integral of a time-independent positive function

$$P_E(t) = \int_{x_{\text{div}}}^\infty |\Psi_0(x_0)|^2 \, dx_0 \qquad (29)$$

which in the present case of a Gaussian density is given by an error function and more generally can be evaluated by quadrature or conventional Monte Carlo procedures. We emphasize again that sampling is straightforward and efficient, as the integrand is positive everywhere and the sampling function is given by the initial density.

Below we present results for an Eckart barrier

$$V(x) = \frac{V_0}{\cosh(ax)^2} \qquad (30)$$

with $a = 1.3624$ au, $V_0 = 0.016$ au $= 0.425$ eV, and mass $m = 1061$ au. These parameters correspond roughly to the H + H$_2$ reaction and have been employed in model calculations by other groups. The imaginary frequency at the barrier top is $\omega_0 = (2a^2V_0/m)^{1/2}$. The initial wave packet has a Gaussian form

$$\Psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(-\frac{\alpha}{2}(x - x_{\text{in}})^2 + \frac{i}{\hbar}p_{\text{in}}(x - x_{\text{in}})\right) \quad (31)$$

with $\alpha = 4$, $x_{\text{in}} = -1$, and $p_{\text{in}} = (2mE)^{1/2}$.

Bohmian trajectories were propagated in time according to the 2nd order BTS methodology described in the previous section, along with the stability matrix elements, their derivatives, and the density. The time-dependent transmission probability for $E = 0.002$ au is shown in Figure 5 and compared to accurate quantum mechanical results.

Figure 6 shows the transmission coefficient as a function of translational energy for the one-dimensional H + H$_2$ model specified above. The transmission probability varies by a factor of 300 over the energy range displayed in the figure. It is seen that the 2nd order BTS results are in reasonable agreement with those obtained through exact quantum mechanical propagation. The same figure also compares the results to those for a parabolic barrier with the same curvature at $x = 0$. The transmission probability obtained with the parabolic approximation differs significantly from that of the Eckart potential. One observes that the 2nd order BTS scheme leads to reasonably
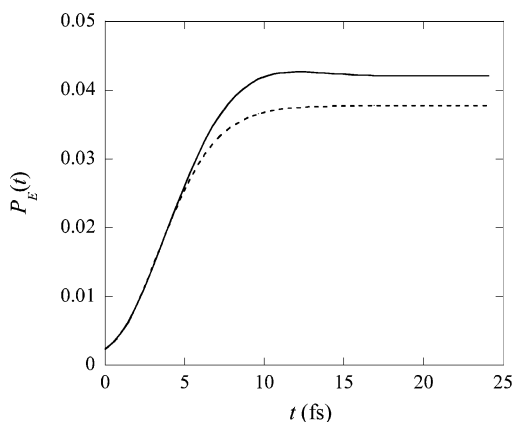
Figure 5. Transmission probability as a function of time for the Eckart barrier with $E = 0.002$ au. Solid line: exact quantum mechanical results. Dashed line: results of 2nd order BTS method.
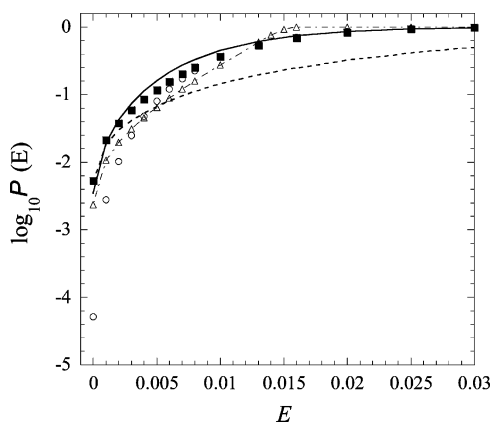

Figure 6. Transmission probability as a function of energy for the Eckart barrier described in eq 30. Solid line: basis set results. Solid squares: results of the 2nd order BTS scheme. Hollow circles: classical results obtained from eq 33. Chain-dotted line and triangles: position-space classical results using eq 28 with classical trajectories. The dashed line shows the transmission probability for a parabolic barrier with the same curvature at the potential maximum.

accurate results for barrier transmission even though the effects of potential anharmonicity are quite sizable.

The finite width of the wave packet leads to a momentum spread. The probability distribution in momentum space for the initial Gaussian wave function is given by the expression

$$|\tilde{\Psi}(p)|^2 = \sqrt{\pi \alpha \hbar^2} \exp\left(-\frac{(p - p_{\text{in}})^2}{\hbar^2 \alpha}\right) \qquad (32)$$

The classical transmission probability is given by the expression

$$P_{\text{cl}}(E) = \int_0^\infty |\tilde{\Psi}(p_0)|^2 h(p^2/2m + V(x_{\text{in}}) - V_0) \, \mathrm{d}p_0 \quad (33)$$

One can see from Figure 6 that the results of eq 33 underestimate the transmission probability by almost 2 orders of magnitude at low energies.

In a recent paper,[34] it was shown that a stationary phase evaluation of the semiclassical expression for an expectation value leads to an alternative classical expression identical to eq 28 but where the coordinate x_t is the value reached by a classical trajectory. The results of this classical approximation are of particular interest here, as any differences from the BTS results must reveal the role of the approximate quantum potential on the trajectories. Figure 6 also shows this position space classical result for the same system. This classical transmission coefficient
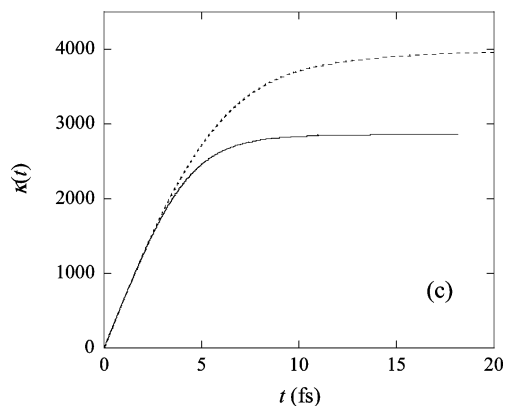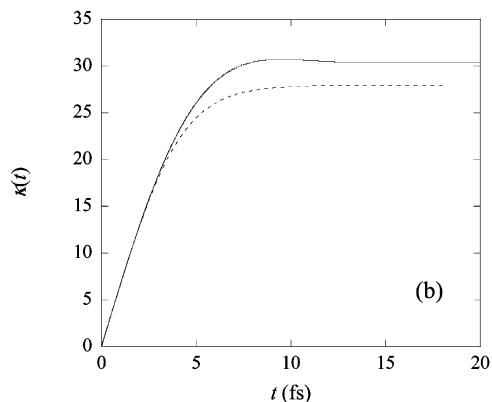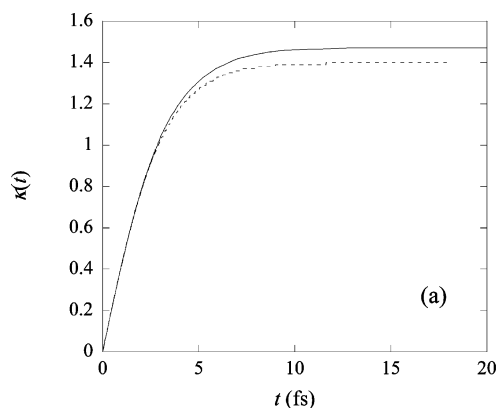

Figure 7. Time-dependent quantum correction factor for the Eckart model. Solid line: exact quantum mechanical results. Dashed line: 2nd order BTS results. (a) $T = 1000$ K. (b) $T = 300$ K. (c) $T = 200$ K.

shows a steep rise at a translational energy that satisfies the energy conservation relation $E + V(x_{\text{in}}) = V_0$ (which corresponds to $E \approx 0.012$ au). This result resembles an S-shape curve when plotted on a linear scale. (The deviation of this classical result from a step function can be attributed to the energy spread of the wave packet.) The results of this classical position−space treatment are also inferior to those obtained via the 2nd order BTS approximation, as they underestimate the transmission probability at low energies and overestimate it at higher energies. Both sets of trajectories start from the same positions and momenta for a given value of the translational energy; yet, the proper fraction of BTS trajectories reach the product side of the barrier at low energies, where the vast majority of classical trajectories are nonreactive (and the converse is true at high energies). Apparently, inclusion of the approximate BTS potential can guide trajectories to the appropriate long-time distribution.

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In conclusion, the 2nd order BTS results show a much better agreement with the exact quantum mechanical results compared to both the momentum-based and position-based classical approximations. More elaborate phase space formulations (e.g., the Wigner prescription,[35,36] recently rederived[37,38] through linearization of the semiclassical expression and forward−backward semiclassical approximations[39]) must be used to improve the accuracy of the classical results. When compared to the results of these phase space representations for the same system, the 2nd order BTS results generally show small improvements. Such comparisons are discussed in more detail in the next subsection. However, phase space formulations require the integration of oscillatory functions, which poses significant challenges to Monte Carlo methods.[40] Further, phase space representations of the quantum density are available analytically only in simple cases where the wave function has a Gaussian form and more generally require numerical evaluation of a Wigner or coherent state transform, which can be very demanding tasks.[41] By contrast, the 2nd order BTS methodology is implemented fully in position space (where the density is readily available) and involves evaluation of positive definite integrals.

(d) Thermal Flux Correlation Functions. Last, we focus on the calculation of flux correlation functions, which can be used to obtain thermal rate constants. The flux−flux auto-correlation function[42] can be written in several forms, one of which is[43]

$$C_{\text{ff}}(t) = Tr(\text{e}^{-\beta\hat{H}/2}\hat{F}\text{e}^{-\beta\hat{H}/2}\text{e}^{i\hat{H}t/\hbar}\hat{F}\text{e}^{-i\hat{H}t/\hbar}) \quad (34)$$

Here $\beta = 1/k_{\text{B}}T$ is the inverse temperature and

$$\hat{F} = \frac{i}{\hbar}[\hat{H},\hat{h}] \quad (35)$$

where $\hat{h}$ is a projection operator corresponding to the Heaviside step function ($h(x) = 1$ for $x > 0$ only). The time integral of the flux−flux autocorrelation function yields the thermal rate constant for the reaction. Evaluating the trace in the coordinate representation and inserting a complete set of position states, eq 34 becomes

$$C_{\text{ff}}(t) = \int \text{d}x \int \text{d}x' \langle x|\text{e}^{-i\hat{H}t/\hbar}\hat{F}\text{e}^{-\beta\hat{H}/2}|x'\rangle\langle x'|\text{e}^{i\hat{H}t/\hbar}\hat{F}e^{-\beta\hat{H}/2}|x\rangle \quad (36)$$

Each factor in this expression requires propagation of the state $\hat{F}\text{e}^{-\beta\hat{H}/2}|x\rangle$ forward (or backward) to time t, a task that is to be performed using the Bohmian methodology. Before proceeding, one can exploit the presence of the flux operators in eq 36 to eliminate both integrals. Simple algebra leads to the final expression

$$C_{\text{ff}}(t) =$$
$$-\frac{\hbar^2}{2m^2}\frac{\partial}{\partial x_1}\langle 0|\text{e}^{-i\hat{H}t/\hbar}\text{e}^{-\beta\hat{H}/2}|x_1\rangle|_{x_1=0}\frac{\partial}{\partial x_2}\langle x_2|\text{e}^{-i\hat{H}t/\hbar}\text{e}^{-\beta\hat{H}/2}|0\rangle|_{x_2=0} +$$
$$\frac{\hbar^2}{2m^2}\frac{\partial^2}{\partial x_1 \partial x_2}\langle x_2|\text{e}^{-i\hat{H}t/\hbar}\text{e}^{-\beta\hat{H}/2}|x_1\rangle|_{x_1=x_2=0}\langle 0|\text{e}^{-i\hat{H}t/\hbar}\text{e}^{-\beta\hat{H}/2}|0\rangle \quad (37)$$

To evaluate eq 37, the "thermal wave function" (i.e., the x-representation) corresponding to the state $\text{e}^{-\beta\hat{H}}|x_1\rangle$ is constructed and used as required to propagate the Bohmian equations to the desired time. Because only low-order derivatives are involved, differentiation with respect to x_1 in eq 37 is

accurately evaluated by finite difference using a total of two x_1 values symmetrically placed around the barrier top. Differentiation with respect to the "final" position x_2 was performed using a 5-point least-squares interpolation formula and requires propagation of only a few Bohmian trajectories that remain in the vicinity of the barrier region. Finally, we note that propagation of a "thermal wave function" to the longest desired time contains all of the necessary information to allow evaluation of the correlation function at many intermediate time points.

BTS trajectories for three thermal wave functions corresponding to x_1 values symmetrically placed with respect to the barrier top were integrated for the Eckart potential described above. In the present case, the first term in eq 37 vanishes due to potential symmetry. We calculate the time dependent quantum correction factor, obtained by dividing the time-integrated flux−flux autocorrelation function by the classical transition state theory value

$$\kappa(t) = \left(\frac{\text{e}^{-\beta V_0}}{2\pi\hbar\beta}\right)^{-1} \int_0^t C_{\text{ff}}(t')\, \text{d}t' \quad (38)$$

at various temperatures. The long-time limit of this quantity yields the quantum correction factor to the thermal rate constant. Figure 7 shows $\kappa(t)$ obtained with the second-order BTS approximation and compares to accurate quantum mechanical results obtained through a basis set method at various temperatures. The BTS results are seen to be nearly quantitative at 1000 K and give an error of about 30% at the lowest temperature considered where the quantum mechanical effects are very large.

Although the 2nd order BTS approximation does not capture accurately all quantum dynamical features of the motion in this strongly anharmonic system, its performance is still remarkably good given the computational advantages discussed earlier, namely, the coordinate space representation of BTS and the absence of integrals with oscillatory functions, which lead to results with small numbers of trajectories. Quasiclassical approximations, most notably the Wigner formulation of time correlation functions[35,36] (recently rederived[37,38] through a linearization of the semiclassical expression) and forward−backward semiclassical dynamics (FBSD) techniques[39] also avoid highly oscillatory phase factors associated with quantum or semiclassical dynamics, but the numerical evaluation of the phase space transform and the lack of a positive definite integrand can be major obstacles in their application. The 2nd order BTS results shown in Figure 7, which were obtained with $2 \times 5 + 1 = 11$ trajectories, are slightly closer to the exact results than those obtained with the most accurate implementation of the Wigner method for the same system,[43] which required much larger numbers of trajectories for convergence. In light of this performance, the 2nd BTS methodology appears to provide an attractive (though still approximate) alternative.

IV. Concluding Remarks

We have presented a procedure for obtaining the quantum force in the Bohmian formulation of quantum mechanics concurrently with the instantaneous density and the stability properties along a given quantum trajectory. The quantities of interest are given from an infinite hierarchy of coupled differential equations. The scheme does not require knowledge of the density or other properties of surrounding trajectories, and thus, the BTS may appear to become a local methodology. However, just as an infinite set of derivatives of an analytic (Taylor-expandable) function at a given point fully specifies the entire function, knowledge of the stability characteristics

of a trajectory to *all* orders can provide sufficient nonlocal information to reproduce exactly quantum interference effects. Truncation of the quantum potential at a specific order closes the hierarchy, leading to a local and practical approximate scheme for calculating the quantum force and density along a quantum trajectory. The truncated BTS scheme makes no assumptions for the time-dependent wave function or density. In many situations, the numerical solution of the coupled BTS equations with low-order truncations of the quantum potential leads to accurate approximations to the dynamics. However, the truncated BTS hierarchy generally cannot reproduce interference effects of a purely quantum mechanical nature.

The independent nature of the BTS trajectories invites the use of Monte Carlo methods to sample initial conditions. Recent work has shown that initial value representations of expectation values or time correlation functions are possible and take a particularly simple form, with integrands that are smooth functions, free of rapidly oscillatory phase factors. In the present paper, we have demonstrated the first use of Monte Carlo methods to calculate time-dependent observables using the Bohmian formulation of quantum mechanics. The results presented in section III are very encouraging and indicate that low-order BTS approximations with Monte Carlo sampling of initial conditions provide a useful, often more accurate and more economical alternative to quasiclassical methods based on phase space representations.

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