

Bohmian versus semiclassical description of interference phenomena

Yi Zhao^{a)} and Nancy Makri^{b)}

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

(Received 3 January 2003; accepted 25 March 2003)

The origin of quantum interference characteristic of bound nonlinear systems is investigated within the Bohmian formulation of time-dependent quantum mechanics. By contrast to time-dependent semiclassical theory, whereby interference is a consequence of phase mismatch between distinct classical trajectories, the Bohmian, fully quantum mechanical expression for expectation values has a quasiclassical appearance that does not involve phase factors or cross terms. Numerical calculations reveal that quantum interference in the Bohmian formulation manifests itself directly as sharp spatial/temporal variations of the density surrounding kinky trajectories. These effects are most dramatic in regions where the underlying classical motion exhibits focal points or caustics, and crossing of the Bohmian trajectories is prevented through extremely strong and rapidly varying quantum mechanical forces. These features of Bohmian dynamics, which constitute the hallmark of quantum interference and are ubiquitous in bound nonlinear systems, represent a major source of instability, making the integration of the Bohmian equations extremely demanding in such situations. © 2003 American Institute of Physics. [DOI: 10.1063/1.1574805]

I. INTRODUCTION

The theoretical prediction of the dynamics of polyatomic quantum mechanical systems remains a challenging problem. Currently, accurate numerical solutions are feasible in two limits: systems composed of a few atoms (including medium-size molecules with a level structure that gives rise to sparse matrices), which are generally tackled by matrix mechanics techniques, and low-dimensional (or few-level) subsystems interacting with simple (harmonic or otherwise separable) baths mimicking condensed phase environments, treatable by path integral methods. Progress toward numerically accurate solutions for large systems with many-body anharmonic interactions is hindered by the exponential scaling property of quantum mechanics, and this practical difficulty has motivated the development of a wide range of physically motivated approximate treatments.

The hydrodynamic picture of quantum mechanics, first developed fully by Bohm^{1,2} following earlier ideas^{3,4} has recaptured attention in recent years^{5–19} as an alternative to the conventional Schrödinger description. The main appeal of the Bohmian approach is its formulation in terms of “trajectories,” which allows a classical-like visualization of quantum mechanical events. In fact, the Bohmian wave function has a form very closely related to the time-dependent semiclassical approximation.^{20,21} The main difference is the presence of a “quantum potential” related to the local curvature of the instantaneous density. The latter amounts to an interdependence of the quantum trajectories, making the method nonlocal. While the scaling of Bohmian dynamics with dimension remains unclear, much recent work has focused on

the development of numerical procedures for solving the flow equations and graphical illustration of various features of the motion.^{5–12,14–16}

The most serious practical difficulty in the Bohmian methodology is the need for concurrent evaluation of the quantum force needed to update the density. In time-dependent semiclassical theory quantum interference effects arise from cross terms corresponding to distinct classical trajectories with fixed boundary conditions. Unlike in classical dynamics, it can be shown²² that Bohmian trajectories cannot cross in position space. As a consequence, the Bohmian wave function consists of a single term. The repulsive force necessary to prevent crossing events originates in the quantum potential. Accurate self-consistent determination of the rugged quantum potential and density poses a numerical challenge and can render the solution unstable. Successful calculation of Bohmian trajectories in such systems has been possible only by combining the hydrodynamic equations with a direct solution of the Schrödinger equation.^{13,19} An appealing application of the Bohmian trajectory method is its use to provide the nonadiabatic quantum force in curve-crossing problems and also in quantum-classical schemes.^{23–27} Finally, density matrix versions of the theory are available.^{16,17,28,29}

The present paper draws attention to the strikingly different ways in which the Bohmian and semiclassical formulations account for quantum mechanical effects. The Bohmian expression for an expectation value is written in an “initial value” form where *the quantum mechanical phase is entirely absent*. This form is contrasted with the analogous semiclassical expression, where off-diagonal phase differences between trajectories in the forward and backward propagation steps are entirely responsible for quantum interference. In fact, recent work has shown that elimination of such phase differences through forward–backward,^{30,31} linearization³² or similar stationary phase approximations^{33,34}

^{a)}Present address: Department of Chemistry, University of California, Berkeley, California 94720.

^{b)}Author to whom correspondence should be addressed. Electronic mail: nancy@makri.scs.uiuc.edu

produces quasiclassical expressions (in which a time-dependent classical variable is averaged with respect to an appropriate initial density) that are incapable of accounting for quantum interference. It is thus intriguing that the Bohmian, fully quantum mechanical method can assume a similar quasiclassical form.

How does the Bohmian method capture quantum mechanical interference in the absence of phase difference factors associated with multiple-bounce trajectories? This question is addressed by examining the quantum potential and the evolution of Lagrangian fields in a model bound anharmonic oscillator. Our analysis shows that quantum interference manifests itself directly as spatial variation of the density surrounding kinky trajectories that result from steep forces operating in regions where the corresponding classical solution exhibits focal points or caustics. The deviations of Bohmian trajectories from the underlying classical solution are extremely severe in the vicinity of such points, and this behavior represents the leading source of instability in the Bohmian methodology. Classical caustics are less common in barrier problems and entirely absent from the dynamics of quadratic Hamiltonians (except at times that are multiples of a half period) and thus the numerical difficulties encountered in such systems are not as severe.

Section II examines the Bohmian and semiclassical expressions for the evolution of expectation values. An extensive numerical analysis is given in Sec. III using a model one-dimensional oscillator with quartic anharmonicity. Finally, Sec. IV summarizes with a brief discussion and concluding remarks.

II. SEMICLASSICAL AND BOHMIAN INITIAL VALUE REPRESENTATIONS

For a general Cartesian Hamiltonian H , the semiclassical approximation to the quantum mechanical propagator between two coordinates x_a and x_b is given by the well-known Van Vleck expression,²⁰

$$\langle x_b | e^{-iHt/\hbar} | x_a \rangle = \sum_{\substack{\text{all classical paths } x_{\text{cl}}^{(k)} \\ \text{with } x_{\text{cl}}^{(k)}(0)=x_a, x_{\text{cl}}^{(k)}(t)=x_b}} (2\pi\hbar)^{-1/2} \times \left| \frac{\partial^2 S_H^{(k)}}{\partial x_a \partial x_b} \right|^{1/2} e^{iS_H^{(k)}(x_a, x_b)/\hbar} e^{-i\mu^{(k)}\pi/2}. \quad (2.1)$$

Here $S_H^{(k)}$ is the action integral, i.e., the solution to the Hamilton–Jacobi equation

$$-\frac{\partial S_H(x;t)}{\partial t} = \frac{1}{2m} \left(\frac{\partial S_H(x;t)}{\partial x} \right)^2 + V(x;t) \quad (2.2)$$

along the classical path $x_{\text{cl}}^{(k)}$, and $\mu^{(k)}$ is the corresponding Maslov phase.³⁵ Using Eq. (2.1) the time-dependent wave function becomes

$$\Psi(x;t) = (2\pi\hbar)^{-1/2} \int dx_0 \Psi(x_0;0) \times \sum_{\substack{\text{all classical paths } x_{\text{cl}}^{(k)} \\ \text{with } x_{\text{cl}}^{(k)}(0)=x_0, x_{\text{cl}}^{(k)}(t)=x}} \left| \frac{\partial^2 S^{(k)}}{\partial x_0 \partial x} \right|^{1/2} e^{iS_H^{(k)}/\hbar} e^{-i\mu^{(k)}\pi/2}. \quad (2.3)$$

Thus, the semiclassical expression for the expectation value of an operator \hat{B} takes the form

$$\langle B(t) \rangle = \int dx |\Psi(x;t)|^2 B(x) = (2\pi\hbar)^{-1} \int dx_1 \int dx_2 \int dx \times \Psi^*(x_2;0) \Psi(x_1;0) B(x) \times \sum_{\substack{\text{all classical paths } x_{\text{cl}}^{(k)} \\ \text{with } x_{\text{cl}}^{(k)}(0)=x_1, x_{\text{cl}}^{(k)}(t)=x}} \left| \frac{\partial^2 S^{(k)}}{\partial x_1 \partial x} \right|^{1/2} e^{iS_H^{(k)}/\hbar} e^{-i\mu^{(k)}\pi/2} \times \sum_{\substack{\text{all classical paths } x_{\text{cl}}^{(n)} \\ \text{with } x_{\text{cl}}^{(n)}(0)=x, x_{\text{cl}}^{(n)}(t)=x_2}} \left| \frac{\partial^2 S^{(n)}}{\partial x_2 \partial x} \right|^{1/2} e^{-iS_H^{(n)}/\hbar} e^{+i\mu^{(n)}\pi/2}. \quad (2.4)$$

Nonlinear forces generally (at least at long times) give rise to multiple solutions to the boundary value problem of classical mechanics. The resulting cross terms lead to constructive or destructive phase interference. As is well known, the semiclassical approximation leads to an accurate description of quantum interference effects for problems of interest to chemical physics.³⁶ Initial value³⁷ or phase space³⁸ representations of Eq. (2.4) lead to similar expressions where semiclassical interference arises from phase cancellation (or enhancement) among distinct classical trajectories. For example, Eq. (2.4) can be written in the equivalent initial value form³⁷

$$\langle B(t) \rangle = (2\pi\hbar)^{-1} \int dx_{1i} \int dp_{1i} \int dp_{2i} \left| \frac{\partial x_{1f}}{\partial p_{1i}} \right|^{1/2} \left| \frac{\partial x_{2f}}{\partial p_{2i}} \right|^{1/2} \times \Psi^*(x_{2f};0) \Psi(x_{1i};0) B(x_{1f}) e^{i\Delta S/\hbar} e^{-i\Delta\mu\pi/2}. \quad (2.5)$$

Here x_{1i}, p_{1i} are the initial phase space coordinates of a trajectory that reaches the position x_{1f} at the time t , p_{2i} is the initial momentum of a new trajectory that originates at x_{1f} moving in the negative time direction, reaching the coordinate x_{2f} at the final time $-t$, and ΔS is the difference between forward and backward actions.

The expressions presented above can be simplified within the spirit of the semiclassical approximation. Performing the integral in Eq. (2.3) via the stationary phase method leads to the semiclassical approximation for the wave function,³⁹

$$\Psi(x;t) = (2\pi\hbar)^{-1/2} \sum_{\substack{\text{all classical paths } x_{\text{cl}}^{(k)} \\ \text{with } x_{\text{cl}}^{(k)}(t) = x, x_{\text{cl}}^{(k)}(0) = x_0^{(k)}, \\ p_{\text{cl}}^{(k)}(0) = S_0'(x_0^{(k)})}} R^{(k)}(x;t) \times e^{iS(x, x_0^{(k)}; t)/\hbar} e^{-i\mu^{(k)}\pi/2}. \quad (2.6)$$

Here $R^{(k)}$ is a real-valued amplitude given by the relation

$$R^{(k)}(x;t) = R^{(k)}(x_0^{(k)}; 0) \left| \frac{\partial x_0^{(k)}}{\partial x^{(k)}} \right|^{1/2} \quad (2.7)$$

and

$$S(x, x_0; t) = S_0(x_0) + S_H^{(k)}, \quad (2.8)$$

where S_0 is the initial phase of the wave function. The sum in Eq. (2.6) is over classical paths that reach the position x at the specified time subject to an initial momentum given by the relation

$$p_0^{(k)} = S_0'(x_0^{(k)}).$$

One sees that if the initial wave function is real valued, all classical trajectories must start out with zero momentum. Again, there are in general multiple solutions to the boundary value classical mechanical problem and the superscript (k) labels the branch of the multivalued Lagrangian velocity field. By using the WKB wave function and performing the midpoint integral via the stationary phase method, we obtained in a recent paper³⁴ the following quasiclassical expression for an expectation value:

$$\langle B(t) \rangle = \int dx_0 |\Psi_0(x_0)|^2 B(x_t). \quad (2.9)$$

The Bohmian formulation expresses the wave function in a form similar to Eq. (2.6). However, the evolution is now such that the Lagrangian field remains single valued, and thus the wave function is given by a single term

$$\Psi(x;t) = R(x;t) e^{iS(x;t)/\hbar}. \quad (2.10)$$

Again $R(x;t)$ is a real-valued amplitude, but the phase $S(x;t)$ now satisfies the *quantum* Hamilton–Jacobi equation,

$$-\frac{\partial S(x;t)}{\partial t} = \frac{1}{2m} \left(\frac{\partial S(x;t)}{\partial x} \right)^2 + V(x;t) + Q(x;t). \quad (2.11)$$

The latter differs from the ordinary equation of classical mechanics through the presence of a quantum potential,

$$Q(x;t) = -\frac{\hbar^2}{2m} R(x;t)^{-1} \frac{\partial^2 R(x;t)}{\partial x^2}. \quad (2.12)$$

Just like its semiclassical analog, S in Eq. (2.10) incorporates the phase $S_0(x_0)$ of the initial wave function. The quantum trajectory follows the modified Hamilton equations:

$$\dot{x}(t') = m^{-1} p(t'), \quad \dot{p}(t') = -V'(x(t')) - Q'(x(t')) \quad (2.13)$$

with boundary conditions $x(t) = x$ and

$$p_0 = S_0'(x_0). \quad (2.14)$$

Both time-dependent semiclassical theory and the Bohmian formulation admit a hydrodynamic interpretation: one imagines a swarm of trajectories with the initial conditions

specified above which are integrated in time following the flow equations (2.13). The main difference is that in the Bohmian, fully quantum mechanical picture these equations do not form a closed set but require knowledge of the instantaneous quantum potential. The latter is obtained from the amplitude, which obeys the transport equation

$$R(x,t)^2 + \frac{d}{dx}(R(x,t)^2 \dot{x}(t)) = 0. \quad (2.15)$$

The last expression is recognized as the equation of continuity for a classical fluid and thus the amplitude satisfies the equation

$$R(x;t) = R_0(x_0) \left| \frac{\partial x_0}{\partial x} \right|^{1/2} \quad (2.16)$$

with $R_0(x) = |\Psi_0(x)|$. The presence of a quantum potential leads to an interdependence of the Bohmian trajectories, which obey a noncrossing law, and the corresponding Lagrangian field is single valued.

The expectation value of a coordinate-dependent operator \hat{B} is obtained from the time-dependent wave function according to the expression

$$\langle B(t) \rangle = \langle \Psi(t) | \hat{B} | \Psi(t) \rangle = \int dx |\Psi(x,t)|^2 B(x). \quad (2.17)$$

Using the Bohmian representation and performing a change of variables, one arrives at the following initial value representation:

$$\langle B(t) \rangle = \int dx_0 \left| \frac{\partial x_t}{\partial x_0} \right| R(x_t; t)^2 B(x_t). \quad (2.18)$$

Here x_t is the position reached by a Bohmian trajectory under the dynamics described above. Finally, use of Eq. (2.16) leads to the result

$$\langle B(t) \rangle = \int dx_0 |\Psi_0(x_0)|^2 B(x_t). \quad (2.19)$$

The last expression appears identical to the quasiclassical (stationary phase semiclassical) result³⁴ reproduced in Eq. (2.9). In spite of its quasiclassical appearance, where one averages the observable B at the time of interest with respect to a distribution specified by the initial density, the position x_t is obtained in the Bohmian expression from the quantum mechanical (rather than a classical) equation of motion. Thus, the presence of the appropriate quantum force in an otherwise *quasiclassical* expression is responsible for its exact treatment of quantum effects, including full inclusion of quantum interference, in spite of the absence of a phase factor from the integrand.

III. NUMERICAL ANALYSIS AND DISCUSSION

Here we analyze the features of the semiclassical and Bohmian formulations and investigate the ways in which both methods capture quantum mechanical interference in a model one-dimensional oscillator with quartic anharmonicity,

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 + 0.1x^4 \quad (2.20)$$

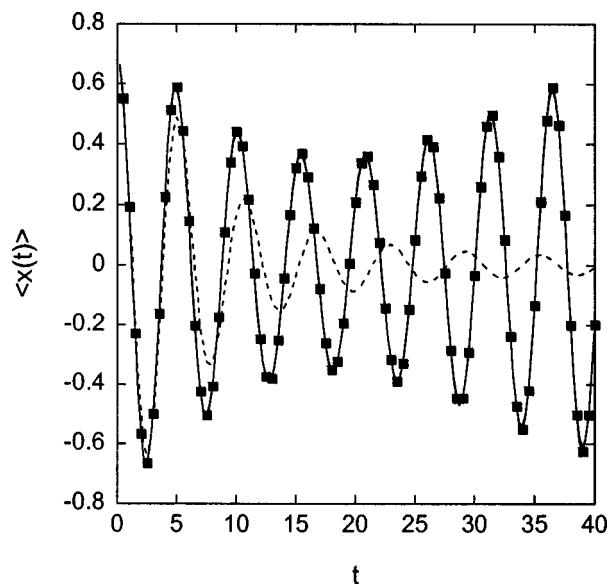


FIG. 1. Time evolution of the average position for a Gaussian centered at 0.7. Solid line, exact results obtained via the split operator method (Ref. 40). Filled squares, results of the Bohmian formulation, Eq. (2.19). The full semiclassical results using a coherent state semiclassical initial value representation (Ref. 38) are practically indistinguishable from those of the exact calculation. Dashed line, results of the quasiclassical (stationary phase semiclassical) expression (Ref. 34), Eq. (2.9).

with $m = \omega = 1$. The initial wave function is a Gaussian centered about $\langle x(0) \rangle = 0.7$. The strong nonlinearity of the system leads to rapid dephasing of the average position, followed by a period of rephasing, during which the expectation value regains its original amplitude. While the initial dephasing is a result of multiple frequencies over the phase space of interest, rephasing is a strictly nonclassical effect reflecting an underlying quantized energy level structure.

The semiclassical expression leads to a faithful description of quantum interference for this system, fully capturing the rephasing of the wave packet following an initial decay of the average position. The converged results of the Bohmian description, displayed in Fig. 1, coincide with those obtained through the split operator⁴⁰ solution of the time-dependent Schrödinger equation. The semiclassical approximation [e.g., the coherent state representation³⁸ of Eq. (2.5)] also leads to very accurate results that appear indistinguishable from those obtained through the fully quantum mechanical methods. (These results have been presented in earlier work³⁰ and are omitted from Fig. 1 for clarity.) As noted earlier, the observed wave packet rephasing in the semiclassical description is a consequence of interference between cross terms in the semiclassical propagator, Eq. (2.1). Neglect of these cross terms, as in forward-backward semiclassical^{30,31} or quasiclassical³²⁻³⁴ formulations, leads to inferior results that deteriorate over time, failing to account for the regaining of oscillation amplitude characterizing quantum mechanical motion. The numerical procedures employed in the Bohmian calculation are discussed later in this section.

How does the Bohmian picture capture phase interference through its quasiclassical form for the average position? To gain insight into this question we plot in Fig. 2(a) several

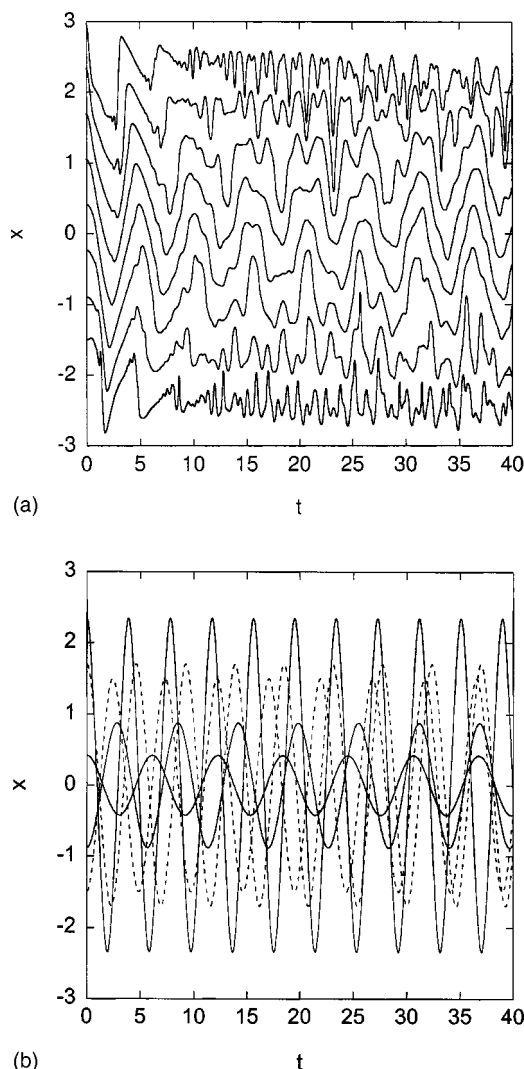


FIG. 2. (a) Bohmian and (b) classical trajectories for the system described in Sec. III. Some of the curves are shown as dashed lines for clarity.

Bohmian trajectories over a coordinate range of significant wave function amplitude. Classical trajectories with similar initial conditions are shown in Fig. 2(b) for comparison. (For clarity, only a few classical trajectories are shown in that figure.) All trajectories start out with zero momentum. While the classical trajectories exhibit the usual oscillatory pattern about the potential minimum with frequencies characteristic of their energies, the Bohmian trajectories execute smaller amplitude oscillations about their initial position, never intersecting one another. As eigenstates of the Hamiltonian give rise to Bohmian trajectories that do not evolve, the departure of quantum trajectories from their initial condition is a measure of the extent of translation/deformation of the wave packet. Another striking difference is the direction of motion immediately following initial preparation: classical trajectories always roll downhill toward the potential minimum, while all their quantum counterparts begin by moving toward the left. This trend is observed because the Gaussian wave packet initially tends to move nearly rigidly toward the left, having been displaced by a positive amount. Of particular interest is the fine structure of the Bohmian trajectories, characterized by high frequency components, and the sharp

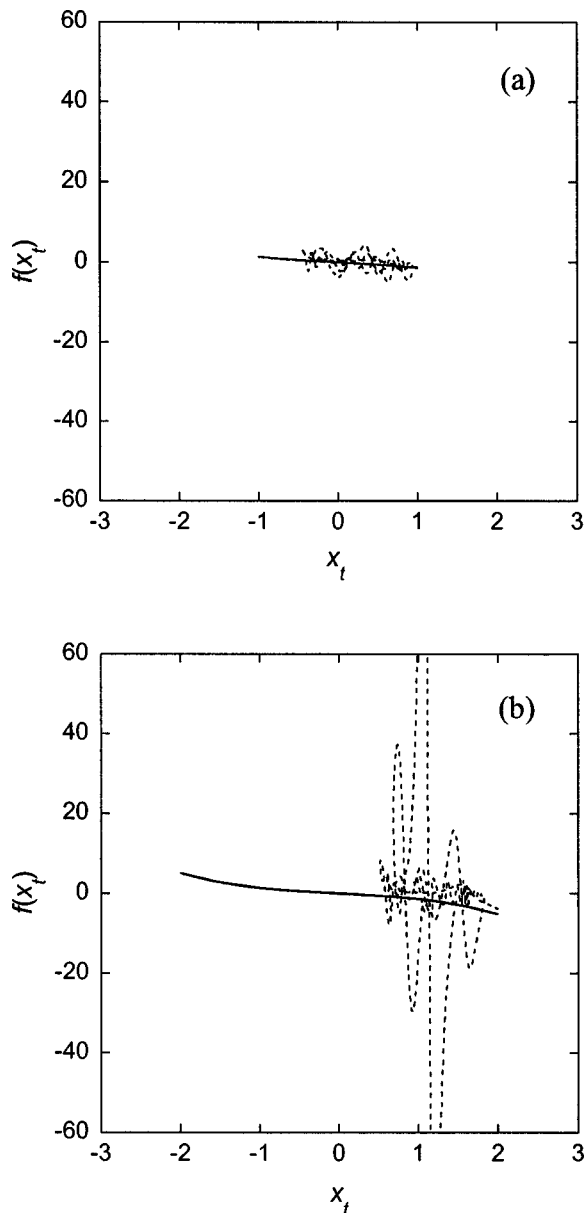


FIG. 3. Classical (solid lines) and Bohmian (dashed lines) forces along trajectories with initial positions (a) $x_0=1$ and (b) $x_0=2$. The total time is $t_{\max}=10$. Note the magnitude of the quantum force compared to its Newtonian counterpart.

shifts in their direction. These features are particularly prominent in the outer coordinate regions where the potential nonlinearity is felt most strongly. Such solutions characterize stiff differential equations and necessitated the use of time steps smaller than 10^{-4} (i.e., nearly 10^5 time steps per period of motion) to achieve stability.

The observed qualitatively different nature of classical and quantum mechanical motion arises from strong time-dependent quantum force fields. The quantum potential essentially dominates the dynamics and is responsible for shifting the direction of trajectories away from that dictated by the classical force field. It also guarantees that Bohmian trajectories do not cross. Thus, the motion is altered qualitatively near classical caustics, and correct propagation in the vicinity of such points requires a delicate treatment. Figures

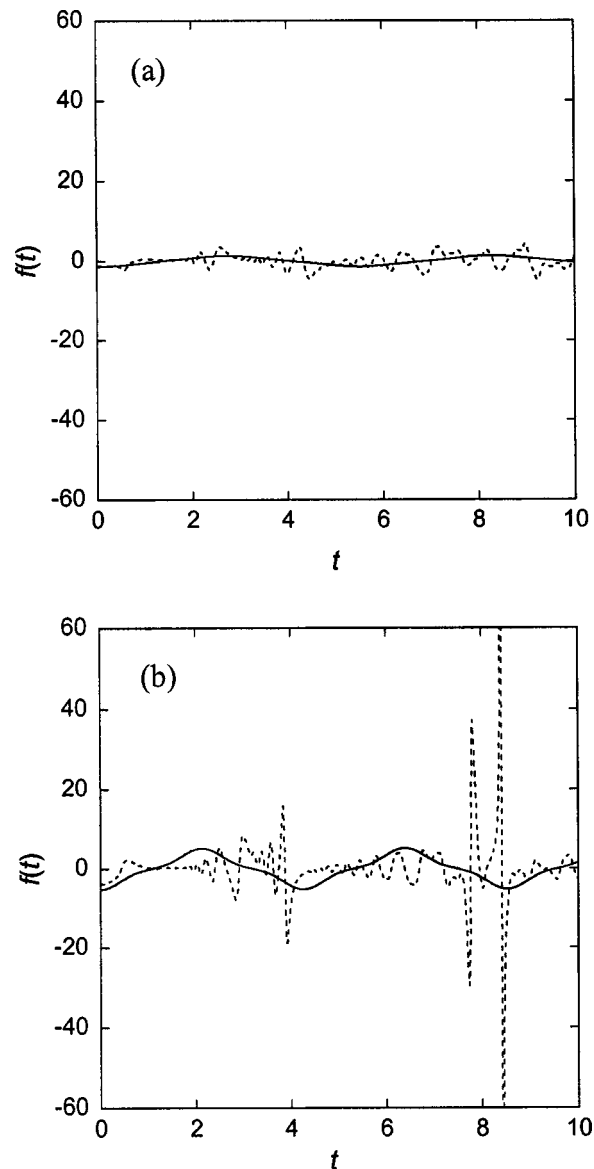


FIG. 4. Classical (solid lines) and Bohmian (dashed lines) forces vs time for trajectories with initial positions (a) $x_0=1$ and (b) $x_0=2$. The total time is $t_{\max}=10$.

3 and 4 show the total force acting on the classical and Bohmian trajectories emanating from the same initial position. While the classical force is uniquely determined by the trajectory's instantaneous position, the Bohmian force varies with time, following the local density fluctuations. In particular, Figs. 3(b) and 4(b) show that trajectories exploring a substantially nonlinear part of the potential experience extremely large forces following an initial mildly oscillatory period where the quantum force is comparable in magnitude to the classical one. A very large quantum force opposes the classical motion near classical caustics, thus turning the trajectory away from crossing points.

Figure 5 shows the classical and Bohmian Lagrangian fields, i.e., the instantaneous momentum versus position, at select times. The classical momentum field wraps around itself in an intricate fashion: since the energy increases as the fourth power of position, trajectories with large values of x_0 are able to bounce many times, leading to multiple branches

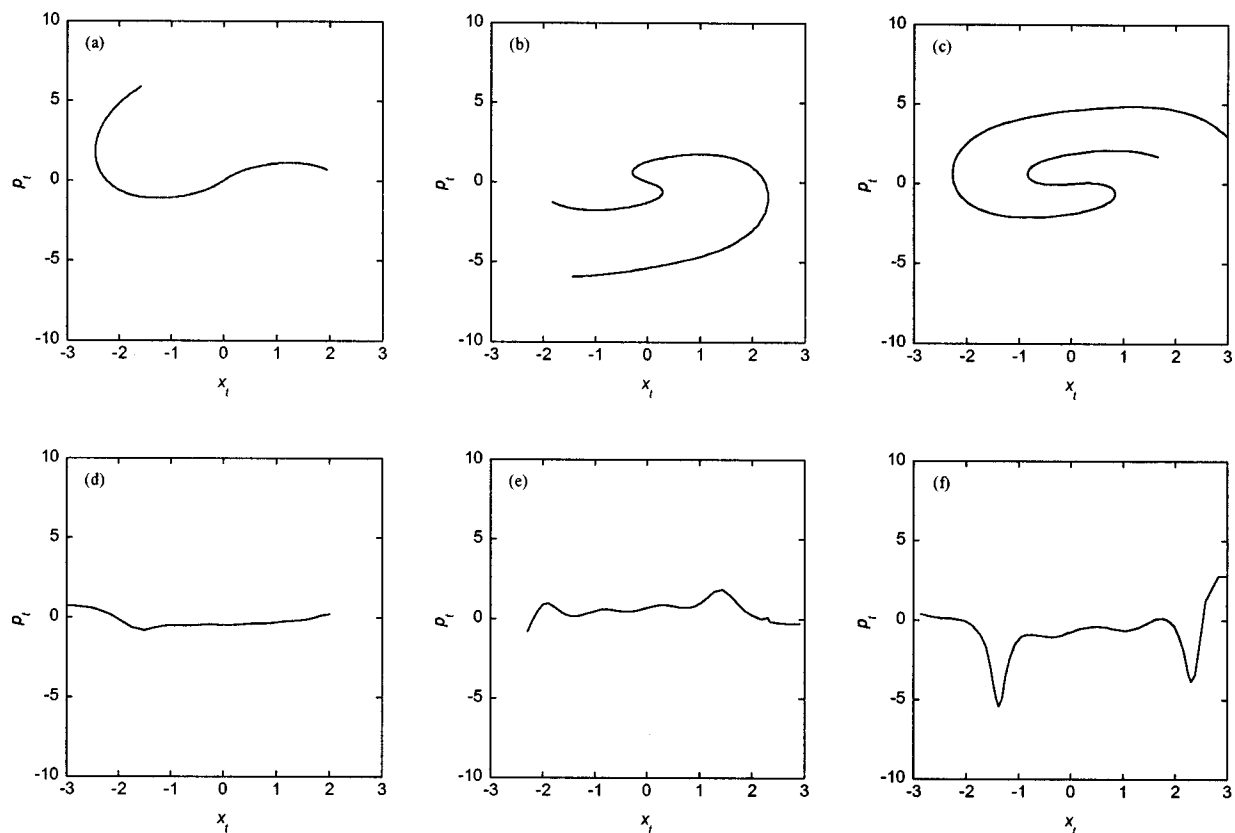


FIG. 5. (a)–(c) Classical and (d)–(f) Bohmian Lagrangian fields for the system described in Sec. III.

of the momentum field. (In fact, the Lagrangian field for this system wraps around itself an infinite number of times if the entire coordinate axis is considered.) The intersections of this field with the constant x_t line give the final momenta of the classical trajectories entering the Van Vleck expression, Eq. (2.1). On the other hand, the Lagrangian field of the Bohmian trajectories remains single valued, and there is a single trajectory reaching any given position. Snapshots of the total (classical plus quantum) potential for this system are given in Fig. 6. The sharp variations and very deep sinks lead to extremely large forces.

The strong, rapidly changing nature of the quantum force makes Bohmian calculations extremely demanding and often numerically unstable. At each time step, calculation of the quantum force requires accurate knowledge of the density, which itself requires trajectory input in the form of velocity gradients or stability properties. Several groups have developed optimal procedures involving adaptive grids from which trajectories, density and quantum forces are to be propagated simultaneously.^{6,11,13} In the present case, however, even very small errors along the evolution led to incorrect forces, rendering the scheme unstable. We were unable to obtain stable results using numerical procedures to compute the quantum potential from derivatives of the density by solving only the hydrodynamic equations. Instead, we first obtained the quantum force field as a function of time on a fixed grid using a basis set expansion of the time-dependent wave function and interpolated the quantum force at the position values required in the Bohmian calculation. Since our procedure utilized the exact solution of the Schrödinger

equation, the results presented in this section should not be viewed as evidence for stability of Bohmian calculations in bound nonlinear systems. The failure of highly optimized schemes for Bohmian trajectories can be traced to the abundance of caustics in this system, where the quantum force becomes large and accidental crossings destroy the stability of the algorithm. Unfortunately, classical caustics constitute the rule rather than the exception in bound anharmonic systems over times that exceed half a period of motion; at the same time, caustics give rise to multiple terms in the semiclassical propagator and thus are intimately connected with quantum interference effects. Thus, it appears that the Bohmian method is extremely hard to stabilize in systems where quantum phase interference is significant.

IV. CONCLUDING REMARKS

The quantum trajectory method is without doubt an intriguing formulation of time-dependent quantum mechanics. Perhaps its most attractive feature is the concept of “quantum trajectories,” along with its apparent similarity to semiclassical theory. Apart from these seemingly classical features, however, the Bohmian flow differs dramatically from that of classical mechanics. The analysis presented in this work shows the dramatic role of the quantum potential in systems where the underlying classical dynamics is dominated by focal points or caustics. Crossing of the quantum trajectories is prevented through application of steep force fields, and the resulting distribution of trajectories leads to the correct probability density without the cross terms re-

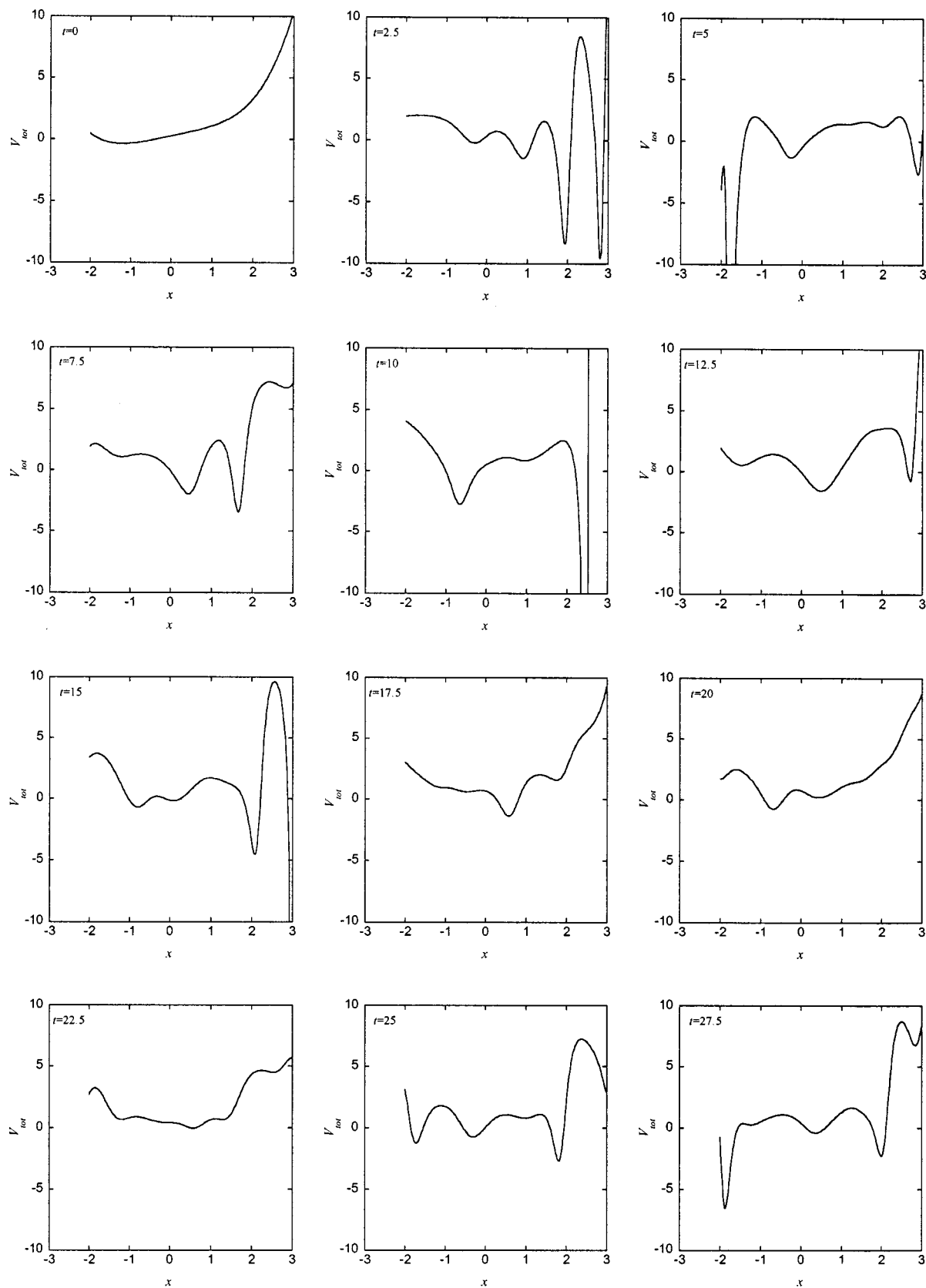


FIG. 6. Snapshots of the total (classical plus quantum) potential at various times.

quired in the semiclassical solution. This feature leads to fully quantum mechanical expressions for expectation values that assume an appealing quasiclassical form where quantum mechanical phases are entirely absent.

To this date, the Bohmian methodology has not found adequate solutions to the instability problem encountered near classical trajectory crossing points. (In a recent paper¹⁹ on wave packet propagation in a double well potential such

difficulties were avoided by employing a direct solution of the time-dependent Schrödinger equation in the interference region.) Such events are ubiquitous in bound anharmonic systems and represent the signature of quantum interference. It is evident that new, more powerful numerical treatments are necessary before the Bohmian formulation becomes a robust and practically useful method for obtaining strongly nonclassical solutions of the time-dependent Schrödinger equation.

ACKNOWLEDGMENTS

This work has been supported by the National Science Foundation under Award No. NSF CHE-02-12640 and by the Camille and Henry Dreyfus Foundation through a Camille Dreyfus Teacher-Scholar Award.

- ¹D. Bohm, Phys. Rev. **85**, 166 (1952).
- ²D. Bohm, Phys. Rev. **85**, 180 (1952).
- ³L. de Broglie, C. R. Acad. Sci. URSS, Ser. A **183**, 447 (1926).
- ⁴E. Madelung, Z. Phys. **40**, 322 (1926).
- ⁵B. K. Dey, A. Askar, and H. Rabitz, J. Chem. Phys. **109**, 8770 (1998).
- ⁶C. L. Lopreore and R. E. Wyatt, Phys. Rev. Lett. **82**, 5190 (1999).
- ⁷F. S. Mayor, A. Askar, and H. A. Rabitz, J. Chem. Phys. **111**, 2423 (1999).
- ⁸R. E. Wyatt, Chem. Phys. Lett. **313**, 189 (1999).
- ⁹E. R. Bittner, J. Chem. Phys. **112**, 9703 (2000).
- ¹⁰R. E. Wyatt, D. J. Kouri, and D. K. Hoffman, J. Chem. Phys. **112**, 10730 (2000).
- ¹¹C. L. Lopreore and R. E. Wyatt, Chem. Phys. Lett. **325**, 73 (2000).
- ¹²D. Nerukh and J. H. Frederick, Chem. Phys. Lett. **332**, 145 (2000).
- ¹³R. E. Wyatt and E. R. Bittner, J. Chem. Phys. **113**, 8898 (2000).
- ¹⁴O. V. Prezhdo and C. Brooksby, Phys. Rev. Lett. **86**, 3215 (2001).
- ¹⁵Z. S. Wang, G. R. Darling, and S. Holloway, J. Chem. Phys. **115**, 10373 (2001).
- ¹⁶J. B. Maddox and E. R. Bittner, J. Chem. Phys. **115**, 6309 (2001).
- ¹⁷J. B. Maddox and E. R. Bittner, Phys. Rev. E **65**, 026143 (2002).
- ¹⁸R. E. Wyatt and K. Na, Phys. Rev. E **65**, 016702 (2002).
- ¹⁹R. E. Wyatt, J. Chem. Phys. **117**, 9569 (2002).
- ²⁰J. H. Van Vleck, Proc. Natl. Acad. Sci. U.S.A. **14**, 178 (1928).
- ²¹C. Morette, Phys. Rev. **81**, 848 (1952).
- ²²P. R. Holland, *The Quantum Theory of Motion* (Cambridge University Press, Cambridge, MA, 1993).
- ²³J. C. Burant and J. C. Tully, J. Chem. Phys. **112**, 6097 (2000).
- ²⁴E. Gindensperger, C. Meier, and J. A. Beswick, J. Chem. Phys. **113**, 9369 (2000).
- ²⁵C. S. Guiang and R. E. Wyatt, J. Chem. Phys. **112**, 3580 (2000).
- ²⁶C. L. Lopreore and R. E. Wyatt, J. Chem. Phys. **116**, 1228 (2002).
- ²⁷E. Gindensperger, C. Meier, and J. A. Beswick, J. Chem. Phys. **116**, 8 (2002).
- ²⁸I. Burghardt and L. S. Cederbaum, J. Chem. Phys. **115**, 10303 (2001).
- ²⁹I. Burghardt and L. S. Cederbaum, J. Chem. Phys. **115**, 10312 (2001).
- ³⁰J. Shao and N. Makri, J. Phys. Chem. **103**, 7753 (1999).
- ³¹J. Shao and N. Makri, J. Phys. Chem. **103**, 9479 (1999).
- ³²X. Sun, H. Wang, and W. H. Miller, J. Chem. Phys. **109**, 7064 (1998).
- ³³R. Gelabert, X. Giménez, M. Thoss, H. Wang, and W. H. Miller, J. Chem. Phys. **114**, 2572 (2001).
- ³⁴Y. Zhao and N. Makri, Chem. Phys. **280**, 135 (2002).
- ³⁵V. P. Maslov and M. V. Fedoriouk, *Semiclassical Approximation in Quantum Mechanics* (Reidel, Boston, MA, 1981).
- ³⁶W. H. Miller, in *The Physics of Electronic and Atomic Collisions*, edited by B. C. Cobic and M. V. Kurepa (Institute of Physics, Belgrade, 1973).
- ³⁷W. H. Miller, Adv. Chem. Phys. **25**, 69 (1974).
- ³⁸M. F. Herman and E. Kluk, Chem. Phys. **91**, 27 (1984).
- ³⁹P. A. Dirac, Proc. Cambridge Philos. Soc. **26**, 376 (1930).
- ⁴⁰M. D. Feit, J. A. J. Fleck, and S. A. Steiger, J. Comput. Phys. **47**, 412 (1982).