J. Phys. Chem. A **2007,** *111,* 10269−10283

A Hybrid Hydrodynamic−Liouvillian Approach to Mixed Quantum−Classical Dynamics: Application to Tunneling in a Double Well†

Keith H. Hughes* and Steven M. Parry

School of Chemistry, University of Wales Bangor, Bangor, Gwynedd LL57 2UW, U.K.

Gérard Parlant

Institut Charles Gerhardt, CNRS and Université Montpellier 2, Equipe CTMM, case courrier 1501, place Eugene Bataillon, 34095 Montpellier, France

Irene Burghardt*

Département de Chimie, Ecole Normale Supérieure, 24 rue Lhomond, F-75231, Paris, France

Received: April 4, 2007; In Final Form: June 20, 2007

The hybrid quantum−classical approach of Burghardt and Parlant [Burghardt, I.; Parlant, G. *J. Chem. Phys.* **2004**, *120,* 3055], referred to here as the quantum−classical moment (QCM) approach, is demonstrated for the dynamics of a quantum double well coupled to a classical harmonic coordinate. The approach combines the quantum hydrodynamic and classical Liouvillian representations by the construction of a particular type of moments (that is, partial hydrodynamic moments) whose evolution is determined by a hierarchy of coupled equations. For pure states, which are at the center of the present study, this hierarchy terminates at the first order. In the Lagrangian picture, the deterministic trajectories result in dynamics which is Hamiltonian in the classical subspace, while the projection onto the quantum subspace evolves under a generalized hydrodynamic force. Importantly, this force also depends upon the classical (Q, P) variables. The present application demonstrates the tunneling dynamics in both the Eulerian and Lagrangian representations. The method is exact if the classical subspace is harmonic, as is the case for the systems studied here.

I. Introduction

Quantum dynamics is recognized as a key area of science that is indispensable in developing our understanding of a wide range of processes and phenomena in all areas of science. In chemistry, it has been applied to diverse areas such as reactive collisions, photochemistry, and simulations of gas−surface encounters and has generally resulted in our development of a deeper understanding of most of the key processes that underpin the subject. In particular it is indispensable for understanding many of the observations made in ultrafast spectroscopy.[1,2] In principle, the dynamics of such processes can be understood within the single unifying framework of the time-dependent Schrödinger equation (for wave functions) and the Liouville−von Neumann equation (for density operators). However, although a fully quantum dynamical treatment may be desirable, for many systems of interest, this is unfeasible due to the enormous number of degrees of freedom involved. Often though, the quantum dynamics of only a few degrees of freedom are of interest, and the usual approach is to try to partition the global system to a relevant part that can be treated rigorously by quantum mechanics and an irrelevant part that can either be treated approximately or, as is often done, can even be ignored if the quantum subsystem interacts so weakly with the remaining degrees of freedom. In most cases, the interaction with the remaining degrees of freedom cannot be ignored. Typical examples include electron transfer in solvated molecules and intramolecular proton transfer. A number of approaches exists for the treatment of such complicated molecular systems. Among these are multiconfigurational methods,[3] semiclassical approaches,[4,5] reduced density matrix approaches and mixed quantum−classical approaches[6,7] (see ref 8 for a general review). The latter mixed quantum−classical approach is particularly appealing if the system can be described in terms of light "quantum" particles that couple to external heavy particles. The dynamics of the heavy degrees of freedom may then justifiably be treated explicitly in a classical mechanics framework. This is the perspective adopted in the present work.

The aim of mixed quantum−classical dynamics is to treat only a few degrees of freedom quantum mechanically, and the remaining degrees of freedom are treated classically, usually in a trajectory approach. The idea of treating a large number of degrees of freedom classically in a molecular dynamics type approach is an attractive one; however, it is not straightforward as to how a mixture of classical and quantum subsystems can be unified in a single framework. The two approaches are fundamentally different. Quantum mechanics is statistical/probabilistic and nonlocal in nature and is deterministic only insofar that the wave function, ψ, or the density operator, $\hat{\rho}$, can be determined for all time, provided the initial conditions and the Hamiltonian are known. Classical mechanics, on the other hand, is generally understood to be a local approach and, provided the initial conditions and the forces acting on the system are known, is completely deterministic. Several approaches have been developed to address this problem; most

---

† Part of the special issue "Robert E. Wyatt Festschrift".

* To whom correspondence should be addressed. E-mail: keith.hughes@bangor.ac.uk. (K.H.H.); irene.burghardt@ens.fr (I.B.).

10.1021/jp072642f CCC: $37.00

notably, the Ehrenfest mean-field approach,[9] surface hopping methods developed by Tully et al.,[10,11] and more recently, mixed quantum−classical Liouville methods[6,12−20] and the mixed quantum−classical Bohmian (MQCB) method[21,22] as well as the closely related formulation of ref 23.

The earliest attempt at formulating a mixed quantum−classical approach was by Ehrenfest, whose formulation of the relationship between the equations of motion for the quantum mechanical expectation values of position, $\langle q\rangle(t)$, and momentum, $\langle p\rangle(t)$, to Hamilton's classical equations of motion for $q(t)$ and $p(t)$ led to the mean-field approximation for mixed quantum−classical dynamics. In the mean-field approach, the quantum and classical systems are coupled by an interaction potential, $V(q, Q(t))$.[80] In the dynamical equations, the quantum part is influenced directly by the classical trajectory via $V(q, Q(t))$, but the classical trajectory is influenced by a force averaged over the quantum coordinate, $-\partial/\partial Q(\int \mathrm{d}q\psi^* V(q, Q(t))\psi)$ − the mean field. Since the classical part experiences only a mean field from the quantum part, this approach is often inadequate, particularly where nonadiabatic effects play an important role in the dynamics.[24,25] Surface hopping methods[10,11] are a slight improvement, where nonadiabatic effects are incorporated into classical trajectories by probabilities of hopping from one adiabatic potential to another, but this approach also has its limitations. As mentioned above, other approaches to mixed quantum−classical dynamics introduced more recently include mixed quantum−classical Liouville methods[6,12−20] and the MQCB method derived from Bohmian mechanics.[21,22,26] In the mixed quantum−classical Liouville method, a partial Wigner transform of the density operator, $\hat{\rho}$, is performed on the classical subspace, which maintains the operator form of the quantum part, and the classical part is defined by functions of the classical phase-space variables, Q and the momenta P. The equations of motion involve a linearized approximation to an exponential time evolution operator in the classical subspace that keeps terms to lowest order in $\hbar$. In the MQCB method, the dynamics of the composite system is defined in a Lagrangian trajectory framework. At the heart of Bohmian mechanics is the quantum potential;[27−31] this is a nonlocal potential that depends on the shape of the wave function and is the source of all quantum effects in the equations of motion. In the MQCB method, the quantum potential is neglected completely in the equations of motion for the classical subsystem. The resulting equations of motion consist of Newtonian equations for the classical subspace and a Bohmian hydrodynamic description of the quantum subspace, where the classical coordinate(s) appear as a parameter. This approach, however, lacks energy conservation, and its consistency has been questioned.[32,33]

Against this background, the present work focuses upon an approach that was recently introduced by Burghardt and Parlant;[34−36] in this approach, which we refer to as the quantum−classical moment (QCM) approach, the quantum subsystem is treated hydrodynamically, and the classical subsystem is described in a Liouville phase-space setting. Starting from the Wigner distribution of the composite system, $\rho_W(q, p, Q, P; t)$, the hybrid hydrodynamic Liouville mixed quantum−classical equations are defined in terms of a particular type of moments, obtained by integrating over the momentum p of the quantum part only, $\langle \mathscr{P}^n \rho\rangle_{qQP} = \int \mathrm{d}p p^n \rho_W(q, p; Q, P)$; see eq 1 below. We will refer to these moment quantities as partial moments. Exact equations of motion for the moments are then derived before a classical approximation is applied to the classical (QP) subsystem. By transforming the equations of motion to a Lagrangian framework, trajectory equations are obtained that involve a (qQP)-dependent generalized quantum force. Burghardt and Parlant demonstrated the approach for a completely harmonic composite system. In this study, we extend the QCM approach to demonstrate how the hybrid approach can be applied to more complicated systems such as the double well. Like the study of ref 34, the present application focuses on pure states (wave functions), even though the method naturally extends to mixed states (densities).

The remaining part of the paper is organized as follows. Section II develops the theory of the QCM approach. Section III illustrates the basic features of the method for the case of coupled harmonic oscillators. Section IV focuses on a double well system coupled to a classical harmonic coordinate; this system is at the center of the present study. Finally, Section V concludes. Several Appendices address background material regarding the Wigner representation and the quantum hydrodynamic picture, in addition to the explicit expressions used here for the hydrodynamic force for the double-well potential.

II. Theory

The present approach is based upon the hydrodynamic representation of quantum dynamics for mixed states, that is, density matrices, as described in refs 37−46. The hydrodynamic picture can be derived from the quantum Liouville equation for the density operator in the coordinate-space or Wigner phase-space representation[47,48] (see Appendix A for an introduction to Wigner phase space). The key ingredient of the hydrodynamic formulation is the decomposition of the Wigner density ρ_W in terms of its momentum moments, $\langle \mathscr{P}^n \rho\rangle(q) \equiv \langle \mathscr{P}^n \rho\rangle_q = \int \mathrm{d}p p^n \rho_W(q, p)$. A hierarchy of coupled equations for the q-dependent moments is thus obtained. The hydrodynamic representation corresponds to a "projection of the Wigner density onto coordinate space", as pointed out early on by Takabayasi.[49] A brief summary of the quantum hydrodynamic approach is given in Appendix B.

The mixed-state, quantum statistical hydrodynamic theory has coexisted since the 1940s with the pure-state de Broglie−Bohm theory.[27−29,50,51] Indeed, mixed-state hydrodynamics reduces to Bohmian mechanics in the pure-state limit, $\hat{\rho} = |\psi\rangle\langle\psi|$, with $\hat{\rho}$ as the density operator. Surprisingly, the pure/mixed-state connection has been largely ignored in the literature, both on the Bohmian mechanics side and on the mixed-state hydrodynamics side, with the exception of very few works, including refs 42, 44, 45,and 49; see also the recent overview in ref 31. Like its pure-state analogue, the mixed-state hydrodynamic theory leads to a dynamical description in terms of coupled equations for the local density $\langle\rho\rangle_q$ (that is, a continuity equation) and the momentum density $\langle \mathscr{P}\rho\rangle_q$; see eqs B2−B3. However, only in the pure-state case does this pair of coupled equations form a closed set;[44,52] in the general mixed-state case, approximate closure criteria at an appropriate level of the moment hierarchy have to be introduced.[53−55]

The hydrodynamic description of quantum dynamics is of great appeal in that it is associated with a trajectory dynamics in the Lagrangian hydrodynamic picture (see eqs B4−B5); this "moving with the flow" picture is complementary to the Eulerian picture of coupled hydrodynamic fields. Much effort has been invested over recent years to exploit this trajectory representation in a "quantum trajectory method" (QTM)[31,56] that would represent a promising alternative to conventional wavepacket propagation and would possibly overcome the ubiquitous exponential scaling problem.

Furthermore, the quantum trajectory picture immediately suggests the construction of a mixed quantum−classical trajectory scheme, whose purpose is to combine quantum and classical trajectory representations for high-dimensional systems. As pointed out in the Introduction, such an approach is designed for systems that feature a certain number of degrees of freedom that necessitates a quantum dynamical treatment and which is coupled to a large number of classical degrees of freedom. Building upon the mixed-state hydrodynamic theory,[37,38,41,43,44] we have proposed such a quantum−classical trajectory approach in refs 34 and 35.

The key idea of the method of refs 34 and 35 is to combine the quantum hydrodynamic trajectory representation with a classical Liouvillian trajectory representation. For the classical subspace, the Liouville phase-space representation is indeed the most natural picture, since it relates to conventional classical molecular dynamics schemes. For the quantum subspace, one could, in principle, envisage a quantum trajectory picture that derives from the Wigner representation, which yields the Liouville phase-space description as its classical limit (see Appendices A and C). However, such a "Wigner trajectory" representation[60,61,76] harbors various difficulties, as briefly addressed in Appendix C. We therefore focus here on a hydrodynamic, Lagrangian trajectory representation of the quantum subspace.

The central feature of the hybrid construction must be the correct connection between the hydrodynamic picture (for the quantum subspace) and the phase-space picture (for the classical subspace). As shown in refs 34 and 35, this connection can be established in the framework of the mixed-state hydrodynamic theory. The cornerstone of the method is the construction of the so-called partial hydrodynamic moments (see eq 1), which combine the hydrodynamic representation in the quantum subspace with a Liouvillian phase-space representation in the subspace, which is to be treated classically.

In the following, we will successively address the partial hydrodynamic moments in question (section A), the (exact) equations of motion for these moments (section B), the mixed quantum−classical (QCM) limit of these equations (section C), the Lagrangian trajectory dynamics derived for these mixed quantum−classical equations (section D), and the particular case of pure quantum states (section E).

A. Partial Hydrodynamic Moments. The moments in question are constructed by introducing a hydrodynamic projection for selected degrees of freedom. In particular, starting from the Wigner representation for two degrees of freedom, we choose to integrate only over one of the phase-space momentum variables, here p

$$\langle\mathscr{P}^n\rho\rangle_{qQP} = \int \mathrm{d}p\, p^n \rho_W(q, p; Q, P) \tag{1}$$

The resulting three index quantities can be understood as hydrodynamic moments in q, which are parametrized in the phase-space variables (Q, P). These moments appear as the coefficients in a Taylor expansion of the mixed coordinate-space−phase-space density

$$\rho(q, r; Q, P) = \sum_n \frac{1}{n!}\langle\mathscr{P}^n\rho\rangle_{qQP}\left(\frac{ir}{\hbar}\right)^n \tag{2}$$

Here, the distribution $\rho(q, r; Q, P)$ acts as a generating function; it is related to $\rho_W(q, p; Q, P)$ by a Fourier transform, $\rho_W(q, p; Q, P) = 1/2\pi\hbar \int \mathrm{d}r \rho(q, r; Q, P)\exp(-ipr/\hbar)$.

Depending on the structure of the quantum density, the moments $\langle\mathscr{P}^n\rho\rangle_{qQP}$ can carry redundant information. For example, for pure states, all information is contained in the first two partial moments (see section E below). Similarly, a Gaussian mixed-state density is determined by the first three partial moments.[35,36] In general, an infinite number of moments are required to characterize the time-evolving system, and truncation schemes have to be designed to approximately terminate the moment hierarchy at a certain order.[53−55]

B. Exact Equations of Motion. Equations of motion for the partial moments of eq 1 can be derived from the quantum Liouville equation, either in the coordinate-space representation or else in the phase-space Wigner representation. In the following, we consider a Hamiltonian of the form $H = p^2/2m + P^2/2M + V(q, Q)$, with $V(q, Q) = V_q(q) + V_{\mathrm{int}}(q, Q) + V_Q(Q)$.

As shown in ref 35, exact equations of motion can be obtained in the following form

$$\frac{\partial\langle\mathscr{P}^n\rho\rangle_{qQP}}{\partial t} = \langle\mathscr{P}^n\{H, \rho_W\}_{qp}\rangle_{qQP} + \{H, \langle\mathscr{P}^n\rho\rangle_{qQP}\}_{QP} + \mathscr{C}_{\mathrm{qu}} \tag{3}$$

where $\{,\}_{qp}$ represents the Poisson bracket (see Appendix A), and $\mathscr{C}_{\mathrm{qu}}$ denotes quantum correction terms as defined below. As one would intuitively expect from the partial moment construction, eq 3 comprises (i) a "classical" hydrodynamic part in the (q, p) subspace

$$\langle\mathscr{P}^n\{H, \rho_W\}_{qp}\rangle_{qQP} = -\frac{1}{m}\frac{\partial}{\partial q}\langle\mathscr{P}^{n+1}\rho\rangle_{qQP} - n\,\frac{\partial[V_q(q) + V_{\mathrm{int}}(q,Q)]}{\partial q}\langle\mathscr{P}^{n-1}\rho\rangle_{qQP} \tag{4}$$

(ii) a classical Liouvillian part in the (Q, P) subspace

$$\{H, \langle\mathscr{P}^n\rho\rangle_{qQP}\}_{QP} = -\frac{P}{M}\frac{\partial\langle\mathscr{P}^n\rho\rangle_{qQP}}{\partial Q} + \frac{\partial[V_Q(Q) + V_{\mathrm{int}}(q, Q)]}{\partial Q}\frac{\partial\langle\mathscr{P}^n\rho\rangle_{qQP}}{\partial P} \tag{5}$$

and (iii) a mixed hydrodynamic−Liouvillian "quantum correction" part

$$\mathscr{C}_{\mathrm{qu}} = \sum_{l_1+l_2\geq 3}(-1)^{l_2+1}\frac{1}{l_2!}\binom{n}{l_1}\left(\frac{\hbar}{2i}\right)^{l_1+l_2-1} \times \left(\frac{\partial^{l_1+l_2}[V_q(q) + V_{\mathrm{int}}(q, Q) + V_Q(Q)]}{\partial q^{l_1}\partial Q^{l_2}}\right)\frac{\partial^{l_2}}{\partial P^{l_2}}\langle\mathscr{P}^{n-l_1}\rho\rangle_{qQP} \tag{6}$$

where the summation runs over odd values of the sum of indices $l_1 + l_2$ and $l_1 \leq n$.

The hydrodynamic and quantum correction parts couple the nth order moment $\langle\mathscr{P}^n\rho\rangle_{qQP}$ to the orders $\langle\mathscr{P}^{n\pm 1}\rho\rangle_{qQP}$ and $\langle\mathscr{P}^{n-l_1}\rho\rangle_{qQP}$, respectively. By contrast, the Liouvillian part acts exclusively on a given order $\langle\mathscr{P}^n\rho\rangle_{qQP}$. The "quantum correction" part is closely related to the Wigner−Weyl series expansion; it collects all terms that carry an explicit $\hbar$ dependence and involve third- and higher-order derivatives of the potential. Hence, this part is nonzero for moments of all orders, except for systems described by potentials that are, at most, second-order polynomials. The fact that the equations of motion for the zeroth- and first-order moments carry explicit $\hbar$ contributions, which are absent in a purely hydrodynamic description, highlights the mixed hydrodynamic−Liouvillian nature of the partial moments. Indeed, for the zeroth moment $\langle\rho\rangle_{qQP}$ ($l_1 = n = 0$), the explicit

$\hbar$ terms originate entirely in the (Q, P) subspace, while the equation of motion for the first moment $\langle \mathscr{P}\rho\rangle_{qQP}$ ($l_1 = 0{,}1$) contains correction terms involving mixed q/Q derivatives.

C. Quantum−Classical (QCM) Approximation. In view of defining a mixed quantum−classical dynamics, a classical approximation is introduced in the (Q, P) subspace. To this end, only those quantum correction terms of eq 6 are retained, which involve derivatives of order $l_2 = 0, 1$, that is, we neglect in the equations of motion for the partial moments all terms involving multiple order derivatives with respect to the coordinate Q. This is the same "classical" approximation as the one made when obtaining the classical Poisson bracket from the quantum Lie bracket.[6,17,18] The quantum−classical equations of QCM thus read as follows[35]

$$\frac{\partial\langle \mathscr{P}^n\rho\rangle^c_{qQP}}{\partial t} = \langle \mathscr{P}^n\{H_q + V_{\text{int}}, \rho_W\}_{qp}\rangle^c_{qQP} + \{H_Q + V_{\text{int}}, \langle \mathscr{P}^n\rho\rangle^c\}_{QP} + \mathscr{C}^c_{\text{qu}} \quad (7)$$

with the approximate quantum correction part

$$\mathscr{C}^c_{\text{qu}} = -\sum_{\substack{l_1=3\\ \text{odd}}}^{n}\binom{n}{l_1}\left(\frac{\hbar}{2i}\right)^{l_1-1}\frac{\partial^{l_1}V}{\partial q^{l_1}}\langle \mathscr{P}^{n-l_1}\rho\rangle^c_{qQP} + \sum_{\substack{l_1=2\\ \text{even}}}^{n}\binom{n}{l_1}\left(\frac{\hbar}{2i}\right)^{l_1}\frac{\partial^{l_1+1}V}{\partial q^{l_1}Q}\frac{\partial}{\partial P}\langle \mathscr{P}^{n-l_1}\rho\rangle^c_{qQP} \quad (8)$$

The index c (that is, the classical limit) indicates the approximate nature of the quantities evolving under the above equation of motion.

In contrast to eqs 3−6, the approximation of eq 7 entails that the equations of motion for the first two partial moments do not carry any quantum correction terms, that is

$$\begin{aligned}\frac{\partial\langle\rho\rangle^c_{qQP}}{\partial t} &= \langle\{H_q + V_{\text{int}}, \rho_W\}_{qp}\rangle^c_{qQP} + \{H_Q + V_{\text{int}}, \langle\rho\rangle^c_{qQP}\}_{QP}\\ &= -\frac{1}{m}\frac{\partial\langle \mathscr{P}\rho\rangle^c_{qQP}}{\partial q} + \{H_Q + V_{\text{int}}, \langle\rho\rangle^c_{qQP}\}_{QP}\end{aligned} \quad (9)$$

and

$$\begin{aligned}\frac{\partial\langle \mathscr{P}\rho\rangle^c_{qQP}}{\partial t} &= \langle \mathscr{P}\{H_q + V_{\text{int}}, \rho_W\}_{qp}\rangle^c_{qQP} + \{H_Q + V_{\text{int}}, \langle \mathscr{P}\rho\rangle^c\}_{QP}\\ &= -\frac{1}{m}\frac{\partial\langle \mathscr{P}^2\rho\rangle^c_{qQP}}{\partial q} - \frac{\partial}{\partial q}(V_q(q) + V_{\text{int}}(q, Q))\langle\rho\rangle^c_{qQP} + \{H_Q + V_{\text{int}}, \langle \mathscr{P}\rho\rangle^c_{qQP}\}_{QP}\end{aligned} \quad (10)$$

This will turn out to have important implications for the Lagrangian trajectory dynamics of eq 14; see section D. If the potentials in the classical subspace are harmonic and the coupling between the quantum and classical subspaces is, at most, linear in the classical variables, eq 7 is exact. This is, in fact, the case for the systems which will be considered in this paper.

Importantly, eqs 7−8 are closely related to the quantum−classical Liouville equation.[6,12−20] Indeed, the above equations are found to be identical to the partial moment equations one would obtain from the quantum−classical Liouville equation.[35]

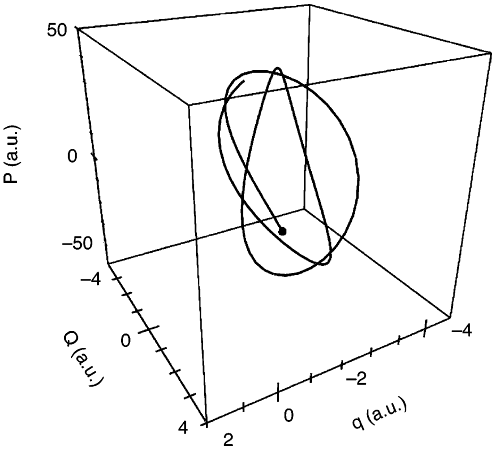

Figure 1. Mixed quantum−classical trajectory according to the Lagrangian picture, eq 12, for the three independent variables (q,Q,P). The hydrodynamic fields $\langle \mathscr{P}^n\rho\rangle_{qQP}$ are constructed along the fluid dynamical path.

D. Lagrangian Trajectory Dynamics. In order to obtain coupled quantum−classical trajectory equations, the Eulerian QCM equations eq 7−10 for the mixed quantum−classical moments have to be translated to the Lagrangian frame (see also Appendix B). If the equation for the zeroth-order moment $\langle\rho\rangle^c_{qQP}$ is interpreted as a hybrid hydrodynamic−Liouvillian continuity equation, the fluid−particle dynamics follows from the definition of a three-component current $\mathbf{j}_{qQP}$

$$\begin{aligned}\frac{\partial\langle\rho\rangle^c_{qQP}}{\partial t} &= -\frac{1}{m}\frac{\partial\langle \mathscr{P}\rho\rangle^c_{qQP}}{\partial q} + \{H_Q + V_{\text{int}}, \langle\rho\rangle^c_{qQP}\}_{QP}\\ &\equiv -\nabla_{qQP}\cdot\mathbf{j}_{qQP}\end{aligned} \quad (11)$$

with $\nabla_{qQP} = (\partial/\partial q, \partial/\partial Q, \partial/\partial P)$ and the current

$$\frac{\mathbf{j}_{qQP}}{\langle\rho\rangle^c_{qQP}} = \begin{pmatrix}\dot{q}\\ \dot{Q}\\ \dot{P}\end{pmatrix} = \begin{pmatrix}p_{qQP}/m\\ (\partial H/\partial P)\\ -(\partial H/\partial Q)\end{pmatrix} \quad (12)$$

where the momentum field p_{qQP} was introduced via the first moment, $\langle \mathscr{P}\rho\rangle^c_{qQP} = p_{qQP}\langle\rho\rangle^c_{qQP}$. The quantity p_{qQP} represents the average momentum derived from the underlying Wigner distribution for a given combination of independent variables (q, Q, P).

In the Lagrangian picture, the hydrodynamic fields are evaluated along the fluid−particle trajectories (or, more precisely, along the characteristics of eq 11[57]), as defined by eq 12; see the illustration in Figure 1. The temporal evolution in the Lagrangian frame is expressed via the total time derivative, $\mathrm{d}/\mathrm{d}t = \partial/\partial t + \mathbf{v}_{qQP}\cdot\nabla_{qQP}$. Thus, the continuity equation eq 11, which describes the local density balance at each point (q, Q, P), translates to the Lagrangian form

$$\frac{\mathrm{d}\langle\rho\rangle^c_{qQP}}{\mathrm{d}t} = -\frac{\langle\rho\rangle^c_{qQP}}{m}\frac{\partial p_{qQP}}{\partial q} \quad (13)$$

The Lagrangian picture is completed by combining eq 12 with an equation for the fluid−particle acceleration $\mathrm{d}p_{qQP}/\mathrm{d}t$ as obtained from the equation eq 10 for the first moment, $\langle \mathscr{P}\rho\rangle^c_{qQP} = p_{qQP}\langle\rho\rangle^c_{qQP}$; this equation involves a generalized hydrodynamic force term derived from the second moment.[35] The overall picture is the one of a correlated dynamics of the quantum hydrodynamic variables (q, $p = p_{qQP}$) and classical variables (Q, P)[34,35]

$$\dot{q} = \frac{p}{m}$$

$$\dot{p} = -\frac{\partial}{\partial q}(V_q(q) + V_{\mathrm{int}}(q, Q)) + F_{\mathrm{hyd}}(q, Q, P)$$

$$\dot{Q} = \frac{P}{M}$$

$$\dot{P} = -\frac{\partial}{\partial Q}\,(V_Q(Q) + V_{\mathrm{int}}(q, Q)) \tag{14}$$

with $p \equiv p_{qQP}$ and the hydrodynamic force

$$F_{\mathrm{hyd}}(q, Q, P) = -\frac{1}{m\langle\rho\rangle^c_{qQP}}\frac{\partial \sigma_{qQP}}{\partial q} \tag{15}$$

obtained as the spatial derivative with respect to q of the generalized variance

$$\sigma_{qQP} = \langle\mathscr{P}^2\rho\rangle^c_{qQP} - p^2_{qQP}\langle\rho\rangle^c_{qQP} \tag{16}$$

The quantity σ_{qQP} reflects the width in p, for given (q, Q, P), of the (approximate) phase-space distribution $\rho^c_W(q, p; Q, P)$, and it is the spatial variation of σ_{qQP} with respect to the hydrodynamic coordinate q which gives rise to F_{hyd}. Apart from its dependence upon the classical phase-space variables (Q, P), eq 15 is entirely analogous to the quantum hydrodynamic equation obtained for a single quantum degree of freedom[44,45] and reduces to this equation in the absence of the classical subspace. Furthermore, if the isolated quantum subsystem corresponds to a pure state, one recovers the Bohmian quantum force $F_{\mathrm{hyd}} = -\partial V_{\mathrm{qu}}/\partial q$,[30,42,44] where V_{qu} is the Bohmian quantum potential.

The trajectories of the QCM evolving under the equations of motion, eq 14, can be associated with a phase-space distribution function of the form[34,35] (see also eq B8 of Appendix B)

$$\rho_{\mathrm{hybrid}}(q, p; Q, P) = \langle\rho\rangle^c_{qQP}\delta(p - p_{qQP}) \tag{17}$$

This distribution preserves the features of the underlying Liouville phase-space distribution in the classical subspace but is single-valued in p in the quantum subspace, that is, a unique value of the hydrodynamic momentum p_{qQP} is assigned to each combination of variables (q, Q, P). As shown in ref 35, a Liouville equation can be formulated for the distribution eq 17, which involves the hydrodynamic force along with the external force term. Importantly, the distribution ρ_{hybrid} determines the initial sampling of the trajectories which are subsequently propagated using eq 14, that is, trajectories are sampled from the full (Q, P) Liouville phase-space distribution in the classical sector, while the sampling is restricted to the q axis of the quantum sector.

The deterministic, Lagrangian trajectory representation eq 14 is a result of the classical nature of the first two moment equations eqs 9 and 10, within the quantum−classical approximation. The representation eq 14 is rather unique in several respects. First, the dynamics of the coupled hydrodynamic and classical trajectories is nonstochastic, in contrast to the trajectory dynamics usually associated with the quantum−classical Liouville equation.[17,18] Furthermore, the fact that the dynamics is purely Hamiltonian in the classical subspace is in contrast to the Wigner phase-space representation,[58−61] which would entail quantum correction terms in the classical sector which are entirely due to the quantum−classical coupling. By "localizing" the quantum subsystem, the hydrodynamic representation leads to a remarkably simple form of the coupled trajectory equation, eq 14.

E. Pure States. For pure states, $\hat{\rho}_{\mathrm{pure}} = |\psi\rangle\langle\psi|$, certain relations can be shown to hold between the hydrodynamic moments of $\rho^{\mathrm{pure}}_W(q, p; Q, P)$, thus simplifying the moment hierarchy. In particular, the second moment $\langle\mathscr{P}^2\rho\rangle_{qQP}$ can be expressed in terms of the zeroth- and first-order moments, such that the pair of equations eqs 9 and 10 decouple from the rest of the moment hierarchy.[35] Indeed, all information on the state of the system is contained in the first two moments (apart from a piecewise constant phase factor).[34,35] This is entirely analogous to the conventional hydrodynamic moment description;[44] see also Appendix B. In the following, we consider the explicit form of the partial moment quantities for the pure-state case.

Our starting point is the Wigner function, which takes the following form

$$\rho_W(q,p) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \mathrm{d}r\rho_{\mathrm{pure}}\left(q + \frac{r}{2}, q - \frac{r}{2}\right)\exp\left(-\frac{ipr}{\hbar}\right) \tag{18}$$

with

$$\rho_{\mathrm{pure}}\left(q + \frac{r}{2}, q - \frac{r}{2}\right) = \psi\left(q + \frac{r}{2}\right)\psi^*\left(q - \frac{r}{2}\right) \tag{19}$$

In order to calculate the moments of $\rho^{\mathrm{pure}}_W(q,p,Q,P)$, it can be advantageous to rewrite eq 1 so as to apply a differentiation with respect to the difference coordinate r

$$\begin{aligned}
&\langle\mathscr{P}^n\rho_{\mathrm{pure}}\rangle_{qQP}\\
&= \int \mathrm{d}pp^n\rho^{\mathrm{pure}}_W(q, p; Q, P)\\
&= \left(\frac{\hbar}{i}\right)^n\frac{\partial^n}{\partial r^n}\,\rho^{\mathrm{pure}}_W(q, r; Q, P)\bigg|_{r=0}\\
&= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\mathrm{d}R\,\exp\left(-\frac{iPR}{\hbar}\right)\times\\
&\qquad \left(\frac{\hbar}{i}\right)^n\frac{\partial^n}{\partial r^n}\left[\psi\left(q + \frac{r}{2}, Q + \frac{R}{2}\right)\psi^*\left(q - \frac{r}{2}, Q - \frac{R}{2}\right)\right]_{r=0}
\end{aligned} \tag{20}$$

These relations will be used below in order to calculate the pure-state moments in conjunction with a basis set expansion.

Furthermore, by writing the wave function in the polar form[81]

$$\psi(q, Q) = A(q, Q)\exp\left(\frac{iS(q, Q)}{\hbar}\right) \tag{21}$$

it can be shown that the Wigner density is entirely determined by its first two moments $\langle\mathscr{P}^n\rho_{\mathrm{pure}}\rangle_{qQP}$, $n = 0, 1$. That is, all higher-order moments can be expressed in terms of the first two moments or, alternatively, in terms of the following local-in-space quantities[35]

$$\tilde{\rho}(q, Q) = A^2(q, Q)$$

$$\tilde{p}(q, Q) = \frac{\partial S(q, Q)}{\partial q} \tag{22}$$

These quantities can be obtained from the three index partial moments by integrating over the classical phase-space coordinate, $\tilde{\rho}(q,Q) = \int\mathrm{d}P\langle\rho\rangle_{qQP}$ and $\tilde{p}(q, Q) = \int\mathrm{d}P\langle\mathscr{P}\rho\rangle_{qQP}/\tilde{\rho}(q, Q)$.

In particular, one obtains for the pure-state hydrodynamic momentum[35]

$$p_{qQP}^{\mathrm{pure}} = \frac{1}{2\pi\hbar}\int \mathrm{d}P \exp\left(-\frac{iPR}{\hbar}\right)\frac{1}{2}\left\{\tilde{p}\left(q, Q+\frac{R}{2}\right) + \tilde{p}\left(q, Q-\frac{R}{2}\right) - \frac{i\hbar}{2}\frac{\partial}{\partial q}\left[\ln\tilde{\rho}\left(q, Q+\frac{R}{2}\right) - \ln\tilde{\rho}\left(q, Q-\frac{R}{2}\right)\right]\right\} \tag{23}$$

and for the generalized variance[35]

$$\sigma_{qQP}^{\mathrm{pure}} = -\frac{1}{2\pi\hbar}\int \mathrm{d}P \exp\left(-\frac{iPR}{\hbar}\right)\frac{1}{2}\left\{\frac{\hbar^2}{4}\frac{\partial^2}{\partial q^2}\left[\ln\tilde{\rho}\left(q, Q+\frac{R}{2}\right) + \ln\tilde{\rho}\left(q, Q-\frac{R}{2}\right)\right] + \frac{i\hbar}{2}\frac{\partial}{\partial q}\left[\tilde{p}\left(q, Q+\frac{R}{2}\right) - \tilde{p}\left(q, Q-\frac{R}{2}\right)\right]\right\}\langle\rho\rangle_{q,Q+R/2,Q-R/2} \tag{24}$$

with the coordinate-domain local density (zeroth partial moment)

$$\langle\rho\rangle_{q,Q+R/2,Q-R/2} = A\left(q, Q+\frac{R}{2}\right)A\left(q, Q-\frac{R}{2}\right)\exp\left(\frac{i}{\hbar}\left[S\left(q, Q+\frac{R}{2}\right) - S\left(q, Q-\frac{R}{2}\right)\right]\right) \tag{25}$$

Using eq 24, the pure-state hydrodynamic force can be constructed in accordance with eq 15, within the quantum−classical approximation

$$F_{\mathrm{hyd}}(q, Q, P) = -\frac{1}{m\langle\rho\rangle_{qQP}}\frac{\partial\sigma_{qQP}^{\mathrm{pure}}}{\partial q} \tag{26}$$

From eqs 24 and 26, this force term involves third-order derivatives of the density with respect to the quantum coordinate q, similar to the conventional Bohmian quantum force.[30,31] Indeed, eq 26 reduces to the Bohmian quantum force in the absence of the classical QP subspace (see the following section for an example relating to a harmonic oscillator system).

To summarize, the pure-state case leads to a termination of the hydrodynamic hierarchy with the first two moment equations, that is, eqs 9 and 10 in the Eulerian frame or eqs 13 and 14 in the Lagrangian frame. The hydrodynamic force of eq 26 can be constructed from the pure-state variance eq 24. Alternatively, if the wave function itself is known, one can construct the variance from eq 18−20 for the pure-state moments. In the following, two examples will be discussed, for which either of these strategies was applied.

Two aspects should be pointed out regarding the pure-state approximation to the moment equations. (i) When evolving an initial pure state under the QCM equations eqs 9 and 10, the pure-state property is not conserved. (ii) The generalized variance eq 24 is obtained from the exact wave function eq 21 and is therefore not consistent with the quantum−classical approximation. Hence, the Wigner−Fourier transform eq 24 should be truncated; this is analogous to a (semi-)classical approximation for the Wigner density.[62,63] Since the systems considered here reduce to a harmonic form in the classical subspace, these two issues are not of direct relevance for our discussion; they will be addressed in detail in our future work including anharmonic potentials in the classical subspace.

III. Coupled Harmonic Oscillators

Here, we illustrate the workings of the method for a system of coupled harmonic oscillators, using analytical expressions for the hydrodynamic quantities. We, in part, recapitulate results which were previously obtained in the context of analyzing the vibrationally nonadiabatic behavior of this system for a pair of light ("quantum") and heavy ("classical") oscillators.[34,36] Indeed, this apparently simple system poses a considerable challenge for mixed quantum−classical methods, notably the Ehrenfest and surface hopping method[24] and the MQCB method.[21] In ref 34, we demonstrated that this system is described exactly by the QCM approach.

We consider the potential

$$V(q, Q) = V_2 q^2 + V_5 Q^2 + V_6 qQ \tag{27}$$

representing two harmonic oscillators with a bilinear coupling term. The potential parameters are (in atomic units) $V_2 = 2.5$ for the light oscillator, $V_5 = 10$ for the heavy oscillator, and $V_6 = -1.25$ for the bilinear coupling. (This choice of parameters differs slightly from refs 34 and 24.) The masses for the light and heavy oscillator were taken as $m = 1$ and $M = 10$, respectively. The state of the system at all times corresponds to a pure-state two-dimensional Gaussian wave function

$$\psi(\mathbf{q}, t) = \exp\left(\frac{i}{\hbar}[(\mathbf{q} - \langle\mathbf{q}\rangle_t)\cdot\mathbf{a}_t\cdot(\mathbf{q} - \langle\mathbf{q}\rangle_t) + \langle\mathbf{p}\rangle_t\cdot(\mathbf{q} - \langle\mathbf{q}\rangle_t) + \gamma_t]\right) \equiv A(\mathbf{q}, t)\exp\left(\frac{iS(\mathbf{q}, t)}{\hbar}\right) \tag{28}$$

with the amplitude and phase

$$A(\mathbf{q}, t) = \exp\left(-\frac{1}{\hbar}[(\mathbf{q} - \langle\mathbf{q}\rangle_t)\cdot\mathrm{Im}\,\mathbf{a}_t\cdot(\mathbf{q} - \langle\mathbf{q}\rangle_t) + \mathrm{Im}\,\gamma_t]\right)$$

$$S(\mathbf{q}, t) = (\mathbf{q} - \langle\mathbf{q}\rangle_t)\cdot\mathrm{Re}\,\mathbf{a}_t\cdot(\mathbf{q} - \langle\mathbf{q}\rangle_t) + \langle\mathbf{p}\rangle_t\cdot(\mathbf{q} - \langle\mathbf{q}\rangle_t) + \mathrm{Re}\,\gamma_t \tag{29}$$

with $\mathbf{q} = (q, Q)$. The wavepacket is centered initially on ($\langle q\rangle_{t=0} = -0.75$, $\langle Q\rangle_{t=0} = -0.75$), as in ref 24. The harmonic form of the potential function guarantees that the wave function will keep its Gaussian shape during the system's time evolution. The position and momentum expectation values $\langle\mathbf{q}\rangle_t$ and $\langle\mathbf{p}\rangle_t$ evolve classically, while the phase γ_t (a complex number) and the width matrix $\mathbf{a}_t = ((a_{qq}, a_{qQ}), (a_{qQ}, a_{QQ}))$ (a complex symmetric matrix) contain all nonclassical information.[64] The off-diagonal elements of the width matrix describe $q-Q$ correlations and therefore measure the nonseparability of the system.

For the particular case of the Gaussian pure state, eq 28, the expression for the three index local density $\langle\rho\rangle_{qQP}$ is obtained by inserting the amplitude and phase expressions eqs 29 in 25 for the coordinate-domain local density $\langle\rho\rangle_{q,Q+R/2,Q-R/2}$, and subsequently carrying out a $(Q, R) \rightarrow (Q, P)$ Fourier transform. The final expression for $\langle\rho\rangle_{qQP}$ reads

$$\langle\rho\rangle_{qQP}(t) = \left(\frac{2\det(\mathrm{Im}\,\mathbf{a}(t))}{\pi^3\,\mathrm{Im}\,a_{QQ}(t)}\right) \times \exp\{-(1/2\mathrm{Im}\,a_{QQ}(t))[r_{qq}(t)(q - \langle q\rangle_t)^2 + r_{QQ}(t)(Q - \langle Q\rangle_t)^2 + r_{PP}(t)(P - \langle P\rangle_t)^2 + r_{qQ}(t)(q - \langle q\rangle_t)(Q - \langle Q\rangle_t) + r_{qP}(t)(q - \langle q\rangle_t)(P - \langle P\rangle_t) + r_{QP}(t)(Q - \langle Q\rangle_t)(P - \langle P\rangle_t)]\} \tag{30}$$

where the time-dependent coefficients derive from the width matrix

$$r_{qq} = 4[\mathrm{Im}\,a_{qq}\mathrm{Im}\,a_{QQ} + (\mathrm{Re}\,a_{qQ})^2]$$

$$r_{QQ} = 4[(\mathrm{Re}\, a_{QQ})^2 + (\mathrm{Im}\, a_{QQ})^2]$$

$$r_{PP} = 1$$

$$r_{qQ} = 8(\mathrm{Im}\, a_{qQ}\mathrm{Im}\, a_{QQ} + \mathrm{Re}\, a_{qQ}\mathrm{Re}\, a_{QQ})$$

$$r_{qP} = -4\mathrm{Re}\, a_{qQ}$$

$$r_{QP} = -4\mathrm{Re}\, a_{QQ}$$

Note that the parameters $\langle p\rangle_t$ and Re a_{qq} do not appear in the expression for $\langle\rho\rangle_{qQP}$ since the phase components depending entirely on the quantum coordinate q cancel out in the construction of $\langle\rho\rangle_{q,Q+R/2,Q-R/2}$ of eq 25. Thus, the quantity $\langle\rho\rangle_{qQP}$ is determined by eight real parameters overall (that is, three coordinate or momentum expectation values and five real width parameters).

Using the pure-state expressions eqs 23−25, with $\tilde{\rho}(q, Q) = A^2(q, Q)$ and $\tilde{p}(q, Q) = \partial S(q,Q)/\partial q$ from eq 29, we obtain for the (exact) mixed hydrodynamic−classical momentum

$$p_{qQP}(t) = \langle p\rangle_t + c_q(t)(q - \langle q\rangle_t) + c_Q(t)(Q - \langle Q\rangle_t) + c_P(t)(P - \langle P\rangle_t) \quad (31)$$

that is, a linear function of (q, Q, P), which reduces to $p_{qQP}(t) = \langle p\rangle_t$ for the trajectory describing the center motion of the wavepacket, $q = \langle q\rangle_t$, $Q = \langle Q\rangle_t$, $P = \langle P\rangle_t$. The coefficients (c_q, c_Q, c_P) are again derived from the time-dependent width matrix

$$c_q = 2\mathrm{Re}\, a_{qq} - 2\,\frac{\mathrm{Im}\, a_{qQ}\mathrm{Re}\, a_{qQ}}{\mathrm{Im}\, a_{QQ}}$$

$$c_Q = 2\mathrm{Re}\, a_{qQ} - 2\,\frac{\mathrm{Im}\, a_{qQ}\mathrm{Re}\, a_{QQ}}{\mathrm{Im}\, a_{QQ}}$$

$$c_P = \frac{\mathrm{Im}\, a_{qQ}}{\mathrm{Im}\, a_{QQ}} \quad (32)$$

Further, using the expression for the generalized variance eq 24, we obtain $\sigma_{qQP}^{\mathrm{pure}} = \det(\mathrm{Im}\,\mathbf{a})/a_{QQ}\langle\rho\rangle_{qQP}$, from which follows for the hydrodynamic force of eq 26[34]

$$F_{\mathrm{hyd}}(q, Q, P; t) = f_q(t)(q - \langle q\rangle_t) + f_Q(t)(Q - \langle Q\rangle_t) + f_P(t)(P - \langle P\rangle_t) \quad (33)$$

with the time-dependent coefficients

$$f_q = \frac{4}{m}\,\frac{\det(\mathrm{Im}\,\mathbf{a})}{(\mathrm{Im}\, a_{QQ})^2}\,[\mathrm{Im}\, a_{qq}\mathrm{Im}\, a_{QQ} + (\mathrm{Re}\, a_{qQ})^2]$$

$$f_Q = \frac{4}{m}\,\frac{\det(\mathrm{Im}\,\mathbf{a})}{(\mathrm{Im}\, a_{QQ})^2}\,[\mathrm{Im}\, a_{qQ}\mathrm{Im}\, a_{QQ} + \mathrm{Re}\, a_{qQ}\mathrm{Re}\, a_{QQ}]$$

$$f_P = -\frac{2}{m}\,\frac{\det(\mathrm{Im}\,\mathbf{a})}{(\mathrm{Im}\, a_{QQ})^2}\,\mathrm{Re}\, a_{qQ} \quad (34)$$

Like the hydrodynamic momentum, the force F_{hyd} is a linear function of the three (q, Q, P) variables. A noteworthy feature is that these three independent variables appear on an equal footing in the force acting in the quantum subspace. This indicates that $q-Q$ and $q-P$ correlations are “fully resolved” by our method. These conclusions carry over to the mixed-state case, which is addressed in more detail in refs 36, 65, and 66.

In the absence of $q-Q$ correlations, that is, for $a_{qQ} = 0$, the above quantities reduce to the one-dimensional hydrodynamic quantities

$$p_q(t) = \langle p\rangle_t + 2\mathrm{Re}\, a_{qq}(t)(q - \langle q\rangle_t)$$

$$F_{\mathrm{hyd}}(q, t) = \frac{4}{m}\,(\mathrm{Im}\, a_{QQ}(t))^2(q - \langle q\rangle_t) \quad (35)$$

for a single harmonic oscillator in the hydrodynamic description.[30,31]

As described in ref 34, the continuity equation eq 13 and trajectory equations eq 14 are solved on a three-dimensional moving (q, Q, P) grid. The calculation is initiated by choosing an ensemble of N_{traj} values $\{q_i, Q_i, P_i\}$, $i = 1, \ldots N_{\mathrm{traj}}$, as well as the corresponding N_{traj} values $\langle\rho\rangle_{q_iQ_iP_i}$ of the density. The ensemble $\{q_i, Q_i, P_i\}$ forms a three-dimensional grid that moves and changes shape as the system evolves in time. Note that the generalized momentum p_{qQP} eq 32, although it figures in the Hamiltonian equations eq 14, does not constitute a fourth dimension of this grid because it is a function in the three-dimensional space (q, Q, P).

In the particular case considered here, a very small number of grid points, or trajectories, is required to follow the time evolution of the system. The density $\langle\rho\rangle_{qQP}$ of eq 30, which is known to remain Gaussian during the propagation, is fitted to a general 3D Gaussian expression. As mentioned above, $\langle\rho\rangle_{qQP}$ is determined by eight real parameters. These parameters are used to construct the time-evolving quantum force F_{hyd} of eq 33. A batch of 27 trajectories were run − although only 8 trajectories would be required, in principle − and were found to give converged results. The updated generalized momentum p_{qQP} was obtained from the Lagrangian equation eq 14 and was, in turn, used in the propagation equation for the density eq 13. The ensemble of equations, four Hamiltonian equations and one equation for the density, was propagated using an adaptive-step fourth-order Runge−Kutta algorithm.[67]

Figure 2 illustrates the ensemble of time-evolving quantum−classical trajectories in a space−time picture. In the absence of coupling between the two subsystems (panel a), decoupled hydrodynamic versus Liouvillian sub-ensembles are obtained. When the coupling is present (panel b), the hydrodynamic and Liouvillian projections are correlated; this generates a deformation of the hydrodynamic ensemble and creates q-dependent manifolds of trajectories in the classical sub-ensemble (which is here chosen to correspond to a single initial point for illustration). Figure 3 illustrates the time-dependent hydrodynamic force experienced by a chosen mixed quantum−classical trajectory in the quantum subspace.

The present propagation scheme specifically draws on the analytical form (eq 33) of the hydrodynamic force and is consequently very efficient. In a more general approach, the hydrodynamic force is obtained by numerically calculating the generalized variance σ_{qQP} and its spatial derivatives, as exemplified by the double-well system addressed in the next section. The overall propagation method then closely resembles Wyatt’s quantum trajectory method QTM,[31,56] with an additional dependence on the time-evolving classical variables Q, P.

IV. Double Well Coupled to a Harmonic Oscillator

The dynamics of a wide range of processes are subject to double-well potentials. Effects attributable to double-well potentials have been identified in many aspects of the behavior of a wide range of systems that involve small-sized molecules to large biological-sized molecules and in all of the phases of matter. In chemistry, many isomerizations are characterized by

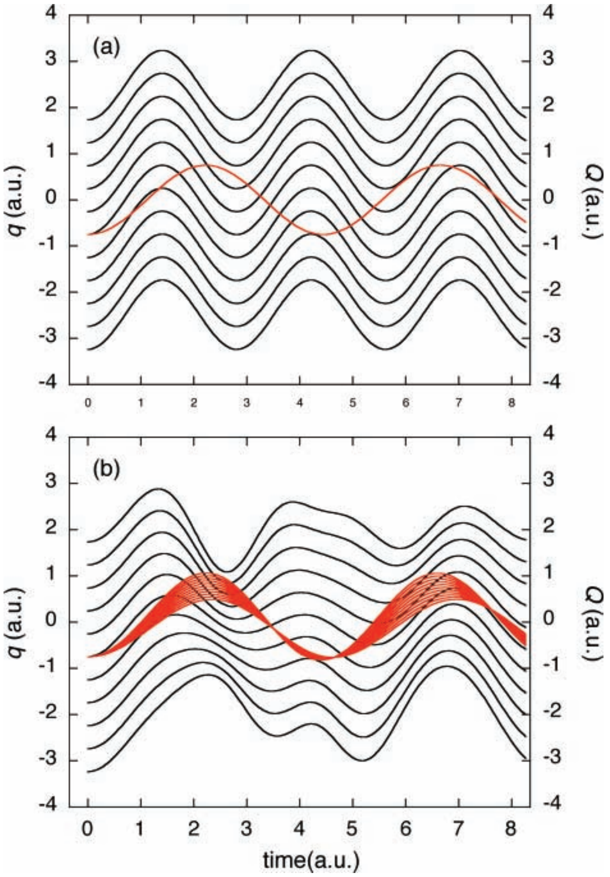

Figure 2. Hybrid quantum-classical trajectory ensembles, for the coupled harmonic-oscillator system of Sec. III. For purposes of illustration, the initial ensemble is chosen as a delta function in the classical subspace, $\rho_{\text{hybrid}}(q,p;Q,P) = P(q)\delta(p-p_0)\delta(Q-Q_0)\delta(P-P_0)$. Panel (a) shows the evolution of the system in the absence of coupling between the oscillators, while panel (b) shows the evolution for a nonzero value of the bilinear coupling. In this case, the hydrodynamic ensemble in the quantum subspace (black lines) is deformed, while the classical projection (red lines) splits up due to the $q-Q$ interaction.

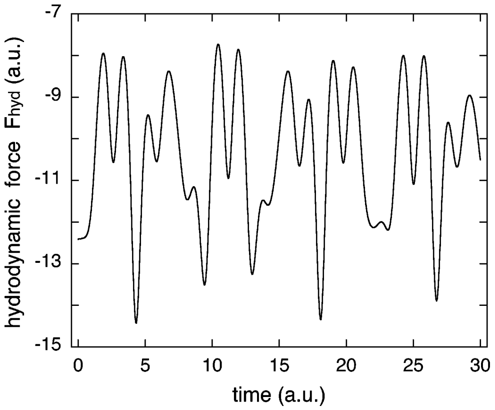

Figure 3. Hydrodynamic force eq 33 as a function of time for a given (q, Q, P) trajectory taken from a hybrid ensemble as illustrated in the preceding figure.

the double-well potential, where each potential well corresponds to a stable conformation of the molecule. A typical example is intramolecular proton transfer such as keto−enol tautomerizations. When the transfer takes place between heavy atoms, a natural setting is provided for a mixed quantum−classical description of the dynamics. In nanotechnology, the ability of certain molecules to isomerize from one physically distinct form to another makes them ideal candidates for molecular switches where the two distinct isomeric forms can act as the “on” and “off” states of the switch. A group of molecules that potentially fits the criterion of an ideal molecular switch are azo compounds.[72,73] These are molecules of the form R−N═N−R that can adopt isomers where the R groups are cis or trans to each other. The isomerization process can proceed by a torsion around the N═N bond, an inversion between the cis−trans isomers, or a combination of both. In most studies, the R groups are large, usually too large to be treated in a completely quantum mechanical framework. However, a mixed quantum−classical approach may be feasible, where the isomerization is treated quantum mechanically and the dynamics of the remainder of the other modes of the molecule is defined in a classical framework.

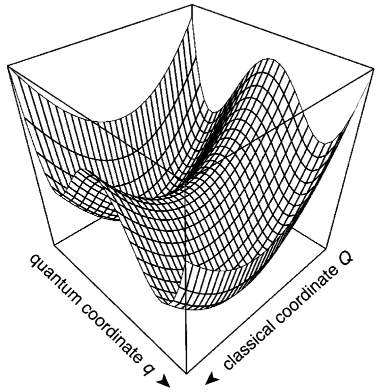

Figure 4. The double-well potential function defined in eq 36 with parameters given in Table 1.

In this section, the dynamics of a quantum subsystem subject to a quartic double-well potential and bilinearly coupled to a classical harmonic oscillator is studied. The potential given by

$$V(q, Q) = V_2q^2 + V_4q^4 + V_5Q^2 + V_6qQ \qquad (36)$$

is illustrated in Figure 4, and the parameters are given in Table 1. The composite system is taken to be in an initial pure state. Since the classical subsystem is harmonic, the mixed quantum−classical approach based on the hybrid Liouville−hydrodynamic representation described in this study is quantum mechanically exact. The system therefore remains in a pure state[82] and is described in terms of its first two moments, $\langle \mathscr{P}^n\rho\rangle$, $n = 0, 1$, and the underlying $\tilde{\rho}$ and $\tilde{p}$ variables of eq 22. However, since no analytical form of the hydrodynamic force is available for this system, the approach of the preceding section cannot be directly applied, and we have to adopt a different, more numerical strategy to evaluate the hydrodynamic quantities. The approach adopted was to carry out the Lagrangian trajectory propagation according eq 14 but extract the hydrodynamic force from the time-dependent wave function.

Generally, numerical approaches to time-dependent quantum mechanics fall into two categories, a grid-based approach or basis set methods. In a grid based approach, the time-dependent Schrödinger equation is generally solved on a fixed Eulerian grid. Extracting the hydrodynamic force eq 15 required for the trajectories of eq 14 from an Eulerian grid would involve interpolating all of the hydrodynamic quantities from the Eulerian grid to the Lagrangian frame on which eq 14 is defined and to do the interpolation at every time step of the propagation. Furthermore, the hydrodynamic force F_{hyd} requires accurate evaluation of spatial derivatives of various hydrodynamic moments. Consequently, any errors introduced in the interpolation technique are magnified in the evaluation of spatial derivatives, and in the context of a long discretized time propagation scheme, these errors are propagated with the trajectories. Certain basis

TABLE 1: Parameters in Atomic Units Associated with the Potential Function Described in Eq 36, the Initial Conditions Specified in Eq 39, and the Masses *m* and *M*

V_2	V_4	V_5	V_6	m
−0.033	0.030	0.010	0.002	2000
β_q	q_e	β_Q	Q_e	M
28	0.8	14	−0.2	20000

set methods, however, avoid the need for interpolation. For bound potentials such as a double well bilinearly coupled to a harmonic oscillator, the wave function $\psi(q, Q, t)$ and, hence, the partial moments $\langle\mathscr{P}^n\rho\rangle_{qQP}$ may be expanded in terms of the eigenstates $\phi(q, Q)$ of the system (see also eq 20)

$$\langle\mathscr{P}^n\rho\rangle_{qQP} = \sum_{j,j'} c_j c_{j'} \exp\left(-\frac{i}{\hbar}[E_j - E_{j'}]t\right)\frac{1}{2\pi\hbar}\int \mathrm{d}R \exp\left(-\frac{iPR}{\hbar}\right)\times \left(\frac{\hbar}{i}\right)^n \frac{\partial^n}{\partial r^n}[\phi_{j'}^*(q - r/2, Q - R/2)\phi_j(q + r/2, Q + R/2)]_{r=0} \quad (37)$$

where E_j are the eigenvalues of the composite system and $c_j = \langle\phi_j|\psi\rangle$. The eigenstates can be expressed in terms of a product harmonic oscillator basis

$$\phi_j(q, Q) = \sum_{m,k} a^j_{m,k}\chi_m(q)\xi_k(Q) \quad (38)$$

and, as detailed in Appendix D, a general equation can then be formulated for the moments expressed in terms of associated Laguerre polynomials for the classical Q, P phase space and derivatives of the Hermite polynomial in the quantum q coordinate. Further details of this approach are provided in Appendix D. Apart from the finite representation of the basis in eqs 37 and 38, the moments and hence F_{hyd} of eq 15 expressed in the form $F_{\text{hyd}} = -1/(m\langle\rho\rangle_{qQP})\partial/\partial q[\langle\mathscr{P}^2\rho\rangle^c_{qQP} - p^2_{qQP}\langle\rho\rangle^c_{qQP}]$ are evaluated exactly for any point in (qQP) space and for all times; hence, there is no need for any interpolation. Furthermore, since F_{hyd} is completely defined, the continuity equation of eq 13 is not propagated explicitly since there is no need to do so in this approach. For the propagation of the trajectories, the equations of motion of eq 14 were numerically integrated using a simple explicit Euler method using a time step of $\Delta t = 0.1$ au.

The initial density is taken as a 3D Gaussian of the form

$$\langle\rho\rangle_{qQP} = \frac{\sqrt{2\pi\beta_q}}{\pi^2}\exp\left(-2\beta_q(q - q_e)^2 - 2\beta_Q(Q - Q_e)^2 - \frac{P^2}{2\beta_Q}\right) \quad (39)$$

with parameters defined in Table 1 and the initial hydrodynamic momentum is set at zero, $p_{qQP}(t_0) = 0$. The first three hydrodynamic moments are illustrated in Figure 5a−c as a function of time for fixed values of $QP = Q_0P_0$. The moments display complicated dynamics, performing high-frequency intrawell oscillations and transferring density to the adjacent potential well by a tunneling mechanism. In Figure 5a, the transfer of density from the right-hand well to the left-hand well is clearly illustrated. Also displayed in Figure 5a is the widespread formation of nodes in $\langle\rho\rangle_{qQP}$.

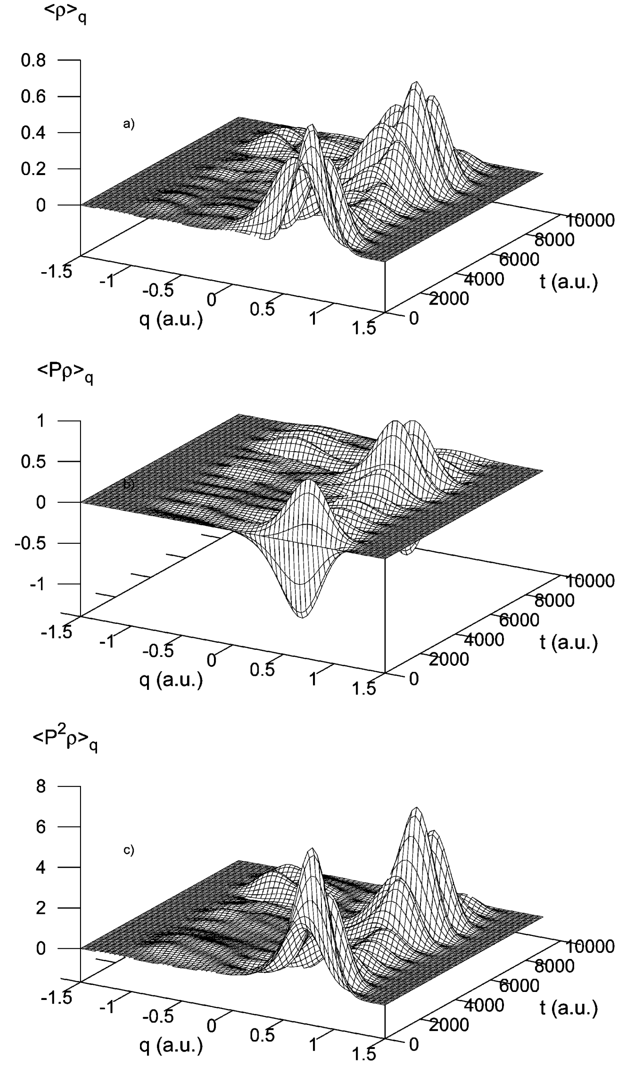

Figure 5. The dynamics of the first three moments, calculated in an Eulerian frame for a range of points in the quantum q coordinate and a single point in the classical phase space ($Q = -0.2$, $P = 0.0$), for the double well bilinearly coupled to a classical harmonic oscillator, eq 36.

It is well-known in Bohmian mechanics that the presence of nodes in the wave function leads to severe computational problems in evaluating the quantum force. Similar problems arise in the hydrodynamic approach adopted here, where the presence of nodes in $\langle\rho\rangle_{qQP}$ leads to singularities in F_{hyd}. The dynamics in a quartic double-well potential is notoriously difficult to solve in a Lagrangian framework,[68,69] and an indication of the nature of the challenge is depicted in Figure 6, which illustrates F_{hyd} along with $\langle\rho\rangle_{qQP}$. The formation of a node at close to $q = -0.6$ au causes F_{hyd} to become singular at the node and to behave erratically around the node. Also illustrated in Figure 5a−c is the variation in the magnitude/norm of the hydrodynamic moments that arises due to the flow of density around elliptical orbits in the classical QP phase space that is characteristic of a harmonic oscillator. Between $t = 4000$ and 6000 au, the amount of density at Q_0P_0 is at a minimum. As the density flows around an elliptical orbit, the amount of density flowing through Q_0P_0 varies in a periodic manner. This is depicted in Figure 7 for two trajectories in the 3D (qQP) space that were evaluated according to eq 14. Both trajectories trace elliptic paths in QP phase space. Furthermore, the trajectory with the initial condition $q_0 = 0.21$ au tunnels to the adjacent potential well, while the other trajectory with initial condition $q_0 = 0.88$ au does not.

The time dependency of F_{hyd} for two trajectories, one that tunnels and one that does not, is depicted in Figure 8. In Figure

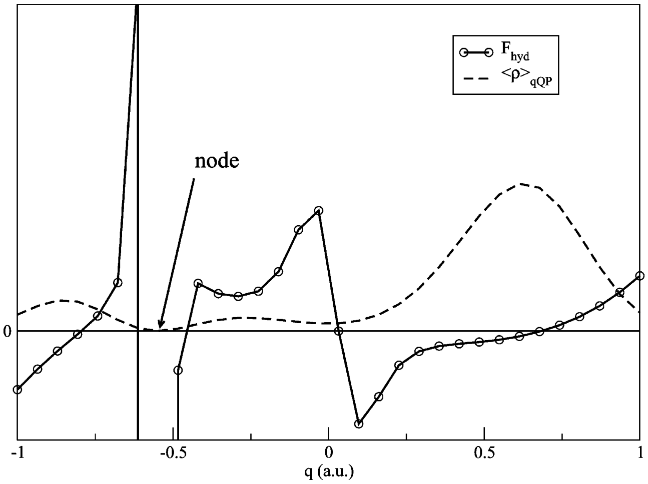

Figure 6. Hydrodynamic force F_{hyd} and the zeroth moment, $\langle\rho\rangle_{qQP}$, computed at fixed $Q = -0.2$, $P = 0.0$, and $t = 4410$ au for the double well bilinearly coupled to a classical harmonic oscillator, eq 36

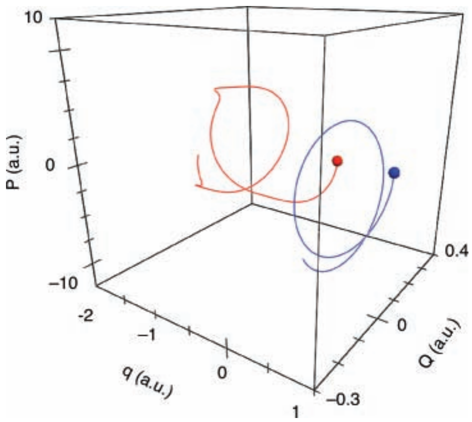

Figure 7. Lagrangian trajectories for two points in 3D (qQP) space with initial conditions that differ only in the quantum q coordinate. The red-colored trajectory tunnels to the adjacent well, but the blue-colored trajectory does not.

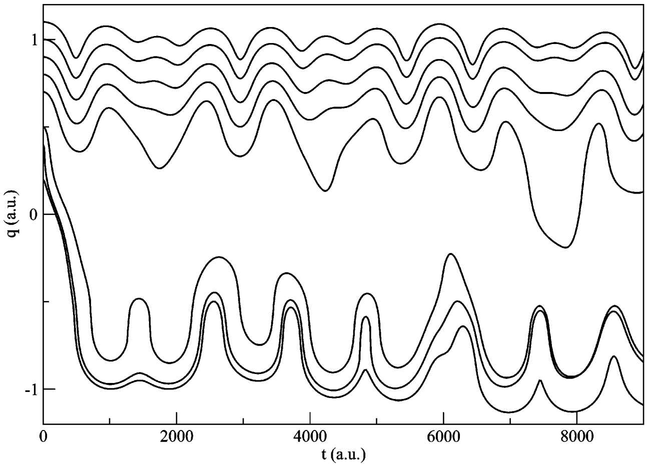

Figure 9. Lagrangian trajectories with initial conditions (in atomic units) $Q_0 = -0.2$, $P_0 = 0.0$, and $0.2 \leq q_0 \leq 1.1$ for the double well bilinearly coupled to a classical harmonic oscillator, eq 36.

9, the temporal evolution of a row of trajectories, again evaluated according to eq 14, are displayed along the quantum q coordinate. As anticipated for a quartic double well, the trajectories trace a complicated path along q as the trajectories undergo high-frequency intrawell oscillations. The three trajectories closest to the barrier tunnel to the adjacent potential well with the first high-frequency oscillation and remain there throughout the propagation.

The propagation scheme outlined above clearly demonstrates the complicated nature of the 3D trajectories in anharmonic potentials such as a double well. A basis set approach is ideally suited for this type of problem, where evaluation of the hydrodynamic force F_{hyd} is computed accurately despite its complicated structure around nodes. In its present form, the propagation bears similarities to the quantum trajectory method of Wyatt[31,56] in that the dynamical (qQP) variables are propagated directly along trajectories that define a Lagrangian frame. However, since F_{hyd} is constructed from information of the underlying wave function, the continuity eq 13 is not directly propagated in this approach. Future schemes of the QCM approach are aimed at evaluating F_{hyd} directly "on the fly" from the time-evolving moments on the Lagrangian frame, in the spirit of a true molecular dynamics-type approach.

Furthermore, these schemes will consider the more general case of mixed states, involving the moment hierarchy eq 7. The

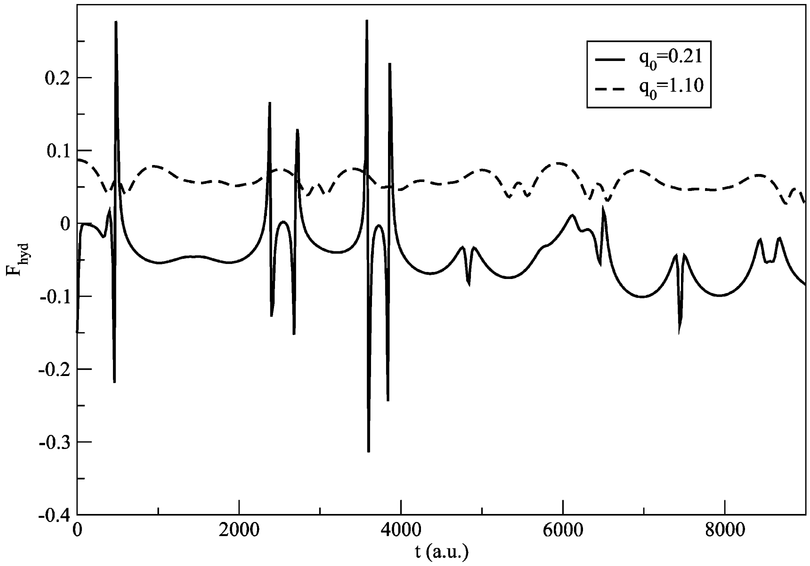

Figure 8. F_{hyd} evaluated along Lagrangian trajectories for two points in 3D (qQP) space with initial conditions that differ only in the quantum q coordinate. The trajectory with $q_0 = 0.21$ au tunnels to the adjacent well; the trajectory with $q_0 = 1.10$ au remains in the right-hand well.

hydrodynamic force $F_{\mathrm{hyd}} = -1/m\langle\rho\rangle_{qQP}^{-1}\partial\sigma_{qQP}/\partial q$ is then not evaluated from an explicit expressions for the variance σ_{qQP} as in eq 24 (or in eq D1 using eq 38), but σ_{qQP} itself obeys a dynamical equation involving the coupling to the higher orders of the hierarchy. In this case, the complications of evaluating third-order derivatives of the local density, as in the conventional Bohmian quantum force, is avoided, however, at the expense of propagating the moment hierarchy up to a certain order. In that case, a central issue is the closure of the hierarchy since, apart from Gaussian densities, no simple closure relations exist. A promising approach under investigation is the use of maximum entropy methods[55] for truncating the moment hierarchy.

V. Conclusions

We have demonstrated the mixed quantum−classical approach of refs 34 and 35, referred to here as the quantum−classical moment (QCM) approach, for harmonic and anharmonic (double-well) oscillator systems coupled to a harmonic classical mode. For these systems, the present dynamical scheme is exact. A natural extension of this study is the inclusion of many classical modes constituting a bath to which the quantum subsystem is coupled, thus allowing for a systematic study of dissipation and decoherence in the hydrodynamic picture. Even though our method is naturally designed for mixed quantum states (density matrices), the present pure-state applications demonstrate its feasibility. The pure-state closure condition of the hydrodynamic hierarchy, that is, exact termination of the hierarchy with the first two partial moments, facilitates the present study; for general mixed states, approximate truncation schemes need to be introduced.

The key concept of the QCM approach is the combination of the quantum hydrodynamic and classical Hamiltonian trajectory pictures in the mixed Lagrangian scheme of eq 14. These trajectory equations of the QCM are distinct from other approaches in several respects. (i) They capture the details of the phase-space correlations between the quantum and classical sectors, thus going far beyond mean-field (Ehrenfest) methods. (ii) No hydrodynamic force is present in the classical subspace (which is described within a Liouvillian setting), but the hydrodynamic force appearing in the quantum sector also depends upon the classical (Q, P) variables. (iii) The trajectory equations do not carry an explicit $\hbar$ dependence; they are, in fact, formally identical with purely classical mixed hydrodynamic−Liouvillian equations. This is in contrast to a mixed quantum−classical representation in terms of phase-space ("Wigner") trajectories, where quantum correction terms appear both in the quantum and classical sectors.[58−61] (iv) The coupled trajectory equations eq 14 are deterministic, contrary to the stochastic trajectory dynamics (that is, surface hopping-type trajectories), which is necessary if the quantum part of the quantum−classical Liouville equation is expressed in a discretized representation.[6,17] (v) Finally, the QCM method is exact if the classical subsystem is harmonic; this is in keeping with the quantum−classical Liouville equation (from which the present method can be derived) but makes it distinct from the MQCB method[21,22] and related approaches.[23] All of these features result from the partial moment construction of eq 1, in conjunction with the classical phase-space limit as described in section II.C. This construction "localizes" the quantum sector at the expense of introducing a hydrodynamic pressure force while preserving the Liouville phase-space picture for the classical sector.

We have applied two strategies of propagation, using either an analytical form of the hydrodynamic force, in the case of coupled harmonic oscillators (section III), or else a basis set expansion approach for calculating F_{hyd} in the case of the double-well system (section IV). Both approaches are not fully general and use explicit information on the underlying wave function. Work in progress addresses a general propagation scheme for the moment hierarchy of eqs 7 and 8. The crucial issue to be addressed here is the construction of approximate truncation schemes for the moment hierarchy. In particular, we plan to use maximum entropy methods[55] that have been explored in previous work in a classical hydrodynamics context.

The quantum statistical moment theory, which our approach is based upon, is unique in that it establishes a direct connection between the Liouville phase-space picture and the hydrodynamic, "Bohmian" picture of quantum dynamics. The QCM method presented here exemplifies a class of hybrid methods which combine the different representations in a rigorous framework. Other hybrid constructions include, for example, the hydrodynamic formulation for coupled electronic states[46,70] and the recently developed mixed quantum−classical scheme of ref 71, which combines an exact, discretized Liouvillian representation for the quantum subspace with a classical hydrodynamic limit for a solvent distribution function. We expect these schemes to provide flexible time-domain statistical mechanics methods at the quantum−classical boundary.

Acknowledgment. We thank Bob Wyatt and Klaus Møller for many stimulating discussions. Financial support was granted by the Centre National de la Recherche Scientifique, the European Social Fund and Gaia Technologies plc.

Appendix A: Wigner Phase Space

In classical mechanics, the state of a system is defined by a point in phase space that simultaneously defines the coordinate, $q(t)$, and momentum, $p(t)$, of the system which evolves along a phase trajectory. Phase-space analysis forms an essential part of classical statistical mechanics, where average values of observables are calculated from a phase-space probability density, $\rho_{\mathrm{cl}}(q, p, t)$. In quantum mechanics, however, the uncertainty principle forbids the simultaneous definition of the position q and momentum p variables in a joint probability function, $\rho(q, p, t)$. Despite this apparent violation, if the product of the root-mean-square half-widths of the marginal distributions[75]

$$\rho(q, t) = \int_{-\infty}^{\infty} \rho(q, p, t)\mathrm{d}p \tag{A1}$$

$$\rho(p, t) = \int_{-\infty}^{\infty} \rho(q, p, t)\mathrm{d}q \tag{A2}$$

are not less than $\hbar/2$, then the uncertainty principle may be satisfied.

A number of methods exist for the quantum phase-space evolution of $\rho(q, p, t)$.[76] The choice of which distribution function to use depends on the physical problem at hand and the physical property that needs extracting from the system. For example, due to its smooth coarse-grained structure, the positive definite Husimi distribution function is popular for the quantum dynamical study of classically chaotic systems;[77,78] in quantum optics, the Glauber−Sudarshan distribution function is widely used due to its suitability for evaluating expectation values of normally ordered operators. Wigner[79] was the first to develop a phase-space distribution function that incorporated quantum effects. The Wigner phase-space distribution, given by

$$\rho_W(q, p) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \mathrm{d}r\rho\left(q + \frac{r}{2}, q - \frac{r}{2}\right) \exp\left(-\frac{ipr}{\hbar}\right) \tag{A3}$$

is defined by its relation to the positional-dependent density operator $\rho(x, x')$, expressed in terms of the sum and difference coordinates, $q = 1/2(x + x')$ and $r = x - x'$. The Wigner distribution should not be considered as a probability distribution since it typically takes on both positive and negative values. Instead, the Wigner distribution should be considered more of a quasi-probability distribution. Despite this, the Wigner distribution has the desirable properties that eqs A1 and A2 yield the quantum mechanical position and momentum probability distributions, that is, the diagonal of the density matrix, $\langle q|\rho|q\rangle$ and $\langle p|\rho|p\rangle$, respectively. Furthermore, the equation of motion for the Wigner distribution, given by

$$\begin{aligned}\frac{\partial\rho_W}{\partial t} &= \{H, \rho_W\}_{qp} + \sum_{\substack{k=3\\ \text{odd}}}^{n} \frac{1}{k!}\left(\frac{\hbar}{2i}\right)^{k-1} \frac{\partial^k V}{\partial q^k}\frac{\partial^k \rho_W}{\partial p^k}\\ &= -\frac{p}{m}\frac{\partial\rho_W}{\partial q} + \frac{\partial V}{\partial q}\frac{\partial\rho_W}{\partial p} - \frac{\hbar^2}{24}\frac{\partial^3 V}{\partial q^3}\frac{\partial^3\rho_W}{\partial p^3} + O(\hbar^4)\end{aligned} \tag{A4}$$

has a simplified form when compared to other distribution functions. Equation A4 comprises a classical Poisson-bracket part, $\{H, \rho_W\}_{qp} = 1/2(H\Lambda_{qp}\rho_W - \rho_W\Lambda_{qp}H)$, with

$$\Lambda_{qp} = \frac{\overleftarrow{\partial}}{\partial q}\cdot\frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial p}\cdot\frac{\overrightarrow{\partial}}{\partial q} \tag{A5}$$

along with a series of explicitly $\hbar$-dependent "quantum correction terms".

Appendix B: Quantum Hydrodynamic Trajectory Picture

In the hydrodynamic description, the quantum densities $\rho(x, x')$ and $\rho_W(q, p)$ are characterized by a set of moment functions, or moment densities, obtained from $\rho_W(q, p)$ by integration over momentum only[37−46]

$$\langle\mathscr{P}^n\rho\rangle_q = \int_{-\infty}^{\infty} \mathrm{d}pp^n\rho_W(q, p) \tag{B1}$$

or else from $\rho(x, x')$ by differentiation with respect to the difference coordinate $r = x - x'$, $\langle\mathscr{P}^n\rho\rangle_q = (\hbar/i)^n(\partial^n/\partial r^n)\rho(q - r/2, q + r/2)|_{r=0}$, where the sum and difference coordinates q and r are defined as they were in Appendix A.

The equations of motion for the hydrodynamic moments follow from the dynamical equation of the Wigner function, eq A4, yielding an infinite hierarchy of coupled moment equations.[37−46] The first two of these equations read

$$\frac{\partial\langle\rho\rangle_q}{\partial t} = -\frac{1}{m}\frac{\partial}{\partial q}\langle\mathscr{P}\rho\rangle q \tag{B2}$$

$$\frac{\partial\langle\mathscr{P}\rho\rangle_q}{\partial t} = -\frac{1}{m}\frac{\partial}{\partial q}\langle\mathscr{P}^2\rho\rangle_q - \frac{\partial V}{\partial q}\langle\rho\rangle_q \tag{B3}$$

and correspond to the continuity equation for the local density $\langle\rho\rangle_q$ and the dynamical equation for the momentum density $\langle\mathscr{P}\rho\rangle_q$. Importantly, these equations do not carry any explicit $\hbar$ dependence, that is, by the moment construction eq B1, the quantum correction terms of eq A4 have been eliminated at the lowest orders. (Quantum correction terms do appear from the third order onward.)

Equations B2 and B3 form a closed set if the second moment, $\langle\mathscr{P}^2\rho\rangle_q$, can be expressed in terms of the zeroth-order and first-order moments, as is indeed the case for pure states, or wave functions, $\rho(x, x') = \psi(x)\psi^*(x')$.[44,52] The above equations then constitute the equations of Bohmian mechanics in the Eulerian frame.

In the associated Lagrangian ("moving with the flow") picture, one introduces fluid−particle trajectories $\dot{q} = \upsilon_q$ with the velocity field $\upsilon_q = p_q/m = (1/m)\langle\mathscr{P}\rho\rangle_q/\langle\rho\rangle_q$; this relation defines the hydrodynamic momentum p_q. With the total or "material" time derivative, $\mathrm{d}/\mathrm{d}t = \partial/\partial t + \upsilon_q\partial/\partial q$, the Lagrangian equations of Bohmian mechanics are obtained as follows

$$\frac{\mathrm{d}\langle\rho\rangle_q}{\mathrm{d}t} = -\frac{\langle\rho\rangle_q}{m}\frac{\partial p_q}{\partial q} \tag{B4}$$

$$\frac{\mathrm{d}p_q}{\mathrm{d}t} = -\frac{\partial V}{\partial q} + F_{\mathrm{hyd}} \tag{B5}$$

where the hydrodynamic force F_{hyd} is given as[42,44−46]

$$F_{\mathrm{hyd}} = -\frac{1}{m}\langle\rho\rangle_q^{-1}\frac{\partial\sigma_q}{\partial q} \tag{B6}$$

that is, F_{hyd} is proportional to the spatial derivative of the generalized variance $\sigma_q = \langle\mathscr{P}^2\rho\rangle_q - p_q^2\langle\rho\rangle_q$. While eqs B4−B6 hold for general mixed states, the pure-state case yields the relation $F_{\mathrm{hyd}} = -\partial V_{\mathrm{qu}}/\partial q$ for the quantum force as the gradient of the quantum potential of Bohmian mechanics, $V_{\mathrm{qu}} = -(\hbar^2/2m)\langle\rho\rangle_q^{-1/2}\partial^2/\partial q^2\langle\rho\rangle_q^{1/2}$.[42,44−46]

With the definition of the fluid−particle momentum and eq B5 for the momentum evolution in the Lagrangian frame

$$\begin{aligned}\frac{\mathrm{d}q}{\mathrm{d}t} &= \frac{p_q}{m}\\ \frac{\mathrm{d}p_q}{\mathrm{d}t} &= -\frac{\partial V}{\partial q} + F_{\mathrm{hyd}}\end{aligned} \tag{B7}$$

a hydrodynamic phase-space picture can be constructed. The distribution functions in this hydrodynamic phase space take the form[36,45]

$$\rho_{\mathrm{hyd}}(q, p) = \langle\rho\rangle_q\delta(p - p_q) \tag{B8}$$

that is, they are single-valued in the momentum, with $p = p_q$ as a function of q. Information on the momentum-space width of the underlying Wigner phase-space distribution (along with all other higher-order moments) is thus not directly available in this alternative phase-space picture. However, the higher-order moments indirectly determine the time evolution in the hydrodynamic phase space, via the force F_{hyd}.

Appendix C: Comparison of the Hydrodynamic versus Liouvillian Trajectory Pictures

Both the Wigner phase-space picture (Appendix A) and the hydrodynamic picture (Appendix B) belong to the representations of quantum mechanics which allow for a connection to a classical-like trajectory evolution.[83] These representations are associated with two distinct types of trajectory dynamics, that is, a Hamiltonian-like Liouville phase-space dynamics versus a fluid dynamical, Lagrangian-type dynamics. In this Appendix, we compare these trajectory pictures in order to motivate the partial moment construction of eq 1 and associated trajectory

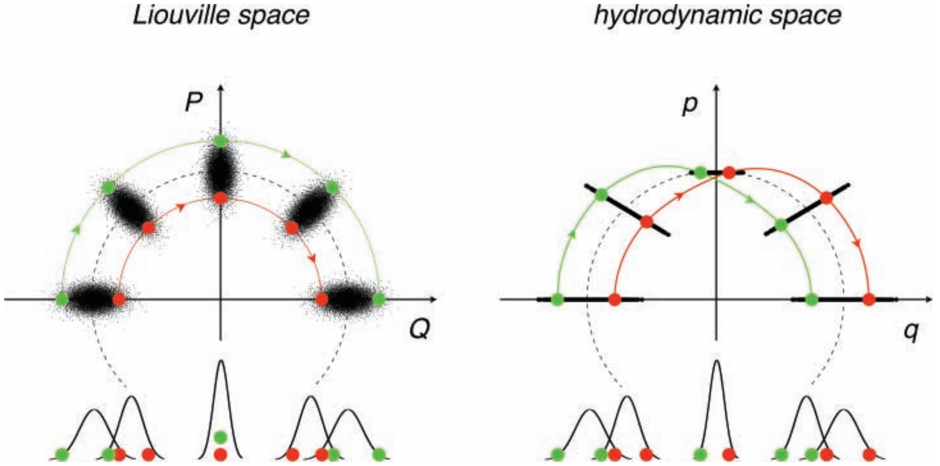

Figure 10. Time evolution of a Gaussian wavepacket for a harmonic potential. The left panel depicts the Liouville phase-space representation, and the right panel depicts the hydrodynamics phase-space representation. Below the phase-space plots are the corresponding reduced positional-dependent densities. In the Liouville representation, the Wigner density is represented by an elliptical distribution of points, and in the hydrodynamic representation, the density is defined by a line in phase space. Also shown in the figure are the trajectories of two (green and red) points located at the edges of the Gaussian. A key observation is that trajectories never cross in Liouville phase space but will cross in the reduced position representation. The opposite is observed in the hydrodynamic representation; trajectories can cross in phase space but never in the reduced position representation.

representation eq 14, which combine the quantum hydrodynamic representation with the classical Liouville-space representation.

We first address the trajectory picture associated with the Wigner function, to be compared with the quantum hydrodynamic trajectory equation eq B7. Given the dynamical equation for the Wigner function, eq A4, a trajectory representation can be obtained by postulating a phase-space continuity equation[60] by analogy to the classical Liouville equation, that is

$$\frac{\partial \rho_W}{\partial t} = -\nabla_{qp}\cdot\mathbf{j}_{qp} \tag{C1}$$

with the phase-space current $\mathbf{j}_{qp} = (\dot{q}\rho_W, \dot{p}\rho_W)$. Comparison with eq A4 leads to the following trajectory picture[60]

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{p}{m}$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{\partial V}{\partial q} + \frac{\hbar^2}{24}\frac{\partial^3 V}{\partial q^3}\frac{1}{\rho_W}\frac{\partial^2 \rho_W}{\partial p^2} + O(\hbar^4) \tag{C2}$$

The quantum correction terms can be interpreted as a different type of quantum force, distinct from the hydrodynamic force of eq B6. Importantly, eq C2 reduces to the classical Hamilton's equations for harmonic potentials since the quantum correction terms involve third-order and higher potential derivatives. The momentum variable of eq C2 is a phase-space momentum, by contrast to the hydrodynamic momentum variable of eq B7, which corresponds to an average over phase-space momenta.

However, the construction eq C2 is not unique (see, for example, ref 76 for an alternative construction of "Wigner trajectories"). Furthermore, the quantum trajectories of eq C2 do not fulfill Liouville's theorem, that is, the density is not conserved along a given time-evolving trajectory, $\mathrm{d}\rho_W/\mathrm{d}t\big|_{q=q_t} \neq 0$.[61] These difficulties, along with the fact that the series of quantum correction terms is difficult to compute, suggest that other quantum trajectory pictures are preferable in practice.

Figure 10 illustrates the two alternative phase-space pictures, Liouvillian versus hydrodynamic, for a harmonic oscillator. Importantly, the hydrodynamic phase-space picture according to eqs B7 and B8 entails an additional force even for the harmonic case. Also illustrated are the corresponding positional space pictures. The initial densities are squeezed Gaussians displaced from the potential minimum and with zero initial momentum. Because the potential function is harmonic, the densities maintain a Gaussian form throughout the propagation. Furthermore, the densities trace out elliptical orbits in phase space, reaching a maximum mean momentum at $q = 0$ and the maximum amplitude of oscillation at $p = 0$, as expected of a harmonic oscillator. The Wigner density is represented by an elliptical distribution of points in phase space, and the hydrodynamic form is represented by a line as defined in eq B8. The figure also depicts the trajectories of two position/phase-space points located at the edges of the Gaussian. For the Wigner/Liouville representation, the trajectories never cross in phase space as they evolve along elliptical paths. However, in the position representation, the trajectories always cross at $q = 0$. In contrast, the hydrodynamic trajectories never cross in position space and are prevented from doing so by the hydrodynamic force defined in eq B6. Trajectory crossing in position space would imply a wave function that is double valued, something completely forbidden in quantum mechanics. In phase space, however, the hydrodynamic trajectories must cross somewhere along the elliptic orbit.

Appendix D: Hydrodynamic Force for the Double-Well Problem

The hydrodynamic force is given by

$$\begin{aligned} F_{\mathrm{hyd}} &= -\frac{1}{m\langle\rho\rangle_{qQP}}\frac{\partial}{\partial q}\sigma_{qQP} \\ &= -\frac{1}{m\langle\rho\rangle_{qQP}}\Bigg[\frac{\partial}{\partial q}\langle\mathscr{P}^2\rho\rangle_{qQP} - \\ &\Bigg(2\langle\rho\rangle_{qQP}\langle\mathscr{P}\rho\rangle_{qQP}\frac{\partial}{\partial q}\langle\mathscr{P}\rho\rangle_{qQP} - \langle\mathscr{P}\rho\rangle_{qQP}^2\frac{\partial}{\partial q}\langle\rho\rangle_{qQP}\Bigg)\langle\rho\rangle_{qQP}^{-2}\Bigg] \end{aligned} \tag{D1}$$

For bound potentials such as a double well bilinearly coupled to a harmonic oscillator, the wave function $\psi(q, Q, t)$ and, hence, the pure state partial moments $\langle\mathscr{P}^n\rho\rangle_{qQP}$ may be expanded in terms of the eigenstates $\phi(q, Q)$ of the system

$$\langle \mathscr{P}^n \rho \rangle_{qQP} = \sum_{j,j'} c_j c_{j'} \exp\left(-\frac{i}{\hbar}[E_j - E_{j'}]t\right) \frac{1}{2\pi\hbar} \int \mathrm{d}R \exp\left(-\frac{iPR}{\hbar}\right) \times \left(\frac{\hbar}{i}\right)^n \frac{\partial^n}{\partial r^n} [\phi^*_{j'}(q - r/2, Q - R/2)\phi_j(q + r/2, Q + R/2)]_{r=0} \tag{D2}$$

where E_j are the eigenvalues of the composite system and $c_j = \langle \phi_j | \psi \rangle$. The eigenstates can be expressed in terms of a product harmonic oscillator basis

$$\phi_j(q, Q) = \sum_{m,k} a^j_{m,k} \chi_m(q) \xi_k(Q) = \sum_{m,k} a^j_{m,k} N_m \exp\left(-\frac{\gamma q^2}{2}\right) \times H_m(\sqrt{\gamma} q) N_k \exp\left(-\frac{\delta Q^2}{2}\right) H_k(\sqrt{\delta} Q) \tag{D3}$$

where

$$N_m = \left[\sqrt{\frac{\gamma}{\pi}} \frac{1}{2^m m!}\right]^{1/2} \quad N_k = \left[\sqrt{\frac{\delta}{\pi}} \frac{1}{2^k k!}\right]^{1/2} \tag{D4}$$

and $H_k(v)$ is the kth order Hermite polynomial. (Note that the integer m is to be distinguished from the symbol used for the mass in the preceding sections.) Continuing

$$\langle \mathscr{P}^n \rho \rangle_{qQP} = \frac{1}{2\pi\hbar} \sum_{j,j'} c_j c_{j'} \exp\left(-\frac{i}{\hbar}[E_j - E_{j'}]t\right) \sum_{\substack{m,k \\ m',k'}} a^j_{m,k}\, a^{j'}_{m',k'}{}' N_k N_{k'} \times \left(\frac{\hbar}{i}\right)^n \frac{\partial^n}{\partial r^n} [\chi_m(q + r/2)\chi_{m'}(q - r/2)]_{r=0} \times \int \mathrm{d}R \exp\left(-\frac{\delta}{2}(Q + R/2)^2\right) H_k(\sqrt{\delta}[Q + R/2]) \times \exp\left(-\frac{\delta}{2}(Q - R/2)^2\right) H_{k'}(\sqrt{\delta}[Q - R/2]) \exp\left(-\frac{iPR}{\hbar}\right) \tag{D5}$$

Setting

$$u = \frac{\sqrt{\delta}}{2} R + \frac{iP}{\sqrt{\delta}\hbar} \tag{D6}$$

and using the relation $H_k(-v) = (-1)^k H_k(v)$ gives

$$\langle \mathscr{P}^n \rho \rangle_{qQP} = \frac{1}{2\pi\hbar} \sum_{j,j'} c_j c_{j'} \exp\left(-\frac{i}{\hbar}[E_j - E_{j'}]t\right) \sum_{m,k} \sum_{m',k'} a^j_{m,k}\, a^{j'}_{m',k'}{}' N_k N_{k'} \times \left(\frac{\hbar}{i}\right)^n \frac{\partial^n}{\partial r^n} [\chi_m(q + r/2)\chi_{m'}(q - r/2)]_{r=0} \exp\left(-\delta Q^2 - \frac{P^2}{\hbar^2 \delta}\right) (-1)^{k'} \frac{2}{\sqrt{\delta}} \times \int \mathrm{d}u \exp(-u^2) H_k(u + z) H_{k'}(u + y) \tag{D7}$$

where

$$y = -\sqrt{\delta} Q - \frac{iP}{\sqrt{\delta}\hbar} \quad z = \sqrt{\delta} Q - \frac{iP}{\sqrt{\delta}\hbar}$$

Using ref 74, the integral in eq D7 has the solution

$$\int \mathrm{d}u \exp(-u^2) H_k(u + z) H_{k'}(u + y) = \sqrt{\pi} 2^k k'! z^{k-k'} L_k^{k-k'}(-2yz) \; k' \le k \tag{D8}$$

where $L_k^{k-k'}(-2yz)$ is the associated Laguerre polynomial. For ease of notation, the terms with no q dependency are collected into Ω in the following

$$\begin{aligned} \langle \mathscr{P}^n \rho \rangle_{qQP} &= \frac{1}{\pi\hbar} \sum_{j,j'} c_j c_{j'} \exp\left(-\frac{i}{\hbar}[E_j - E_{j'}]t\right) \sum_{m,k} \sum_{m',k'} a^j_{m,k}\, a^{j'}_{m',k'} N_k N_{k'} \times \sqrt{\frac{\pi}{\delta}} \exp\left(-\delta Q^2 - \frac{P^2}{\delta\hbar^2}\right) 2^k (-1)^{k'} k'! z^{k-k'} L_k^{k-k'}(-2yz) \times \left(\frac{\hbar}{i}\right)^n \frac{\partial^n}{\partial r^n} [\chi_m(q + r/2)\chi_{m'}(q - r/2)]_{r=0} \\ &= \Omega \left(\frac{\hbar}{i}\right)^n \frac{\partial^n}{\partial r^n} [\chi_m(q + r/2)\chi_{m'}(q - r/2)]_{r=0} \end{aligned} \tag{D9}$$

For the first two moments, we have

$$\langle \rho \rangle_{qQP} = \Omega N_m N_{m'} \exp(-\gamma q^2) H_m(\sqrt{\gamma} q) H_{m'}(\sqrt{\gamma} q) \tag{D10}$$

$$\begin{aligned} \langle \mathscr{P} \rho \rangle_{qQP} &= \frac{\hbar}{2i} \Omega \left[\chi_{m'}(q) \frac{\partial}{\partial q} \chi_m(q) - \chi_m(q) \frac{\partial}{\partial q} \chi_{m'}(q)\right] \\ &= \frac{\hbar}{2i} \Omega N_m N_{m'} \sqrt{\gamma} \exp(-\gamma q^2) \{H_{m'}[2mH_{m-1} - \sqrt{\gamma} q H_m] - H_m[2m' H_{m'-1} - \sqrt{\gamma} q H_{m'}]\} \end{aligned} \tag{D11}$$

For the moment derivatives

$$\frac{\partial}{\partial q} \langle \rho \rangle_{qQP} = \Omega N_m N_{m'} \sqrt{\gamma} \exp(-\gamma q^2) \{H_{m'}(2mH_{m-1} - \sqrt{\gamma} q H_m) + H_m(2m' H_{m'-1} - \sqrt{\gamma} q H_{m'})\} \tag{D12}$$

$$\frac{\partial}{\partial q} \langle \mathscr{P} \rho \rangle_{qQP} = \frac{2\hbar}{i} \Omega N_m N_{m'} \gamma \exp(-\gamma q^2) \{m(m - 1) H_{m-2} H_{m'} - \sqrt{\gamma} q m H_{m-1} H_{m'} - m'(m' - 1) H_{m'-2} H_m + \sqrt{\gamma} q m' H_{m'-1} H_m\} \tag{D13}$$

$$\begin{aligned} \frac{\partial}{\partial q} \langle \mathscr{P}^2 \rho \rangle_{qQP} = &-\hbar^2 \Omega N_m N_{m'} \gamma^{3/2} \exp(-\gamma q^2) \{2m(m - 1)(m - 2) H_{m-3} H_{m'} - 2\sqrt{\gamma} q m(m - 1) H_{m-2} H_{m'} - m H_{m-1} H_{m'} - m' H_m H_{m'-1} + \\ &\sqrt{\gamma} q H_m H_{m'} - 2mm'(m' - 1) H_{m-1} H_{m'-2} - 2mm'(m - 1) H_{m-2} H_{m'-1} + 4\sqrt{\gamma} mm' q H_{m-1} H_{m'-1} + \\ &2m'(m' - 1)(m' - 2) H_m H_{m'-3} - 2\sqrt{\gamma} q m'(m' - 1) H_m H_{m'-2}\} \end{aligned} \tag{D14}$$

References and Notes

(1) Kimble, M., Castleman, W., Jr., Eds., *Femtochemistry: Fundamental Ultrafast Processes in Chemistry, Physics, and Biology: Pt. 7*; Elsevier: Amsterdam, The Netherlands, 2006.

(2) Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press: New York, 1999.

(3) Beck, M. H.; Jäckle, A.; Worth, G. A.; Meyer, H. D. *Phys. Rep.* **2000**, *324*, 1.

(4) Tannor, D. J.; Garashchuk, S. *Annu. Rev. Phys. Chem.* **2000**, *51*, 553.

(5) Kay, K. G. *Annu. Rev. Phys. Chem.* **2005**, *56*, 255.

(6) Kapral, R. *Annu. Rev. Phys. Chem.* **2006**, *57*, 129.

(7) Ciccotti, G.; Coker, D.; Kapral, R. In *Quantum Dynamics of Complex Molecular Systems*; Micha, D. A., Burghardt, I., Eds.; Springer: New York, 2006.

(8) Makri, N. *Annu. Rev. Phys. Chem.* **1999**, *50*, 167.

(9) Billing, G. D. *Int. Rev. Phys. Chem.* **1994**, *183*, 335.

(10) Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061.

(11) Tully, J. C. *Faraday Discuss. Chem. Soc.* **1998**, *110*, 407.

(12) Prezhdo, O. V.; Kisil, V. V. *Phys. Rev. A* **1997**, *56*, 162.

(13) Aleksandrov, I. V.; *Z. Naturforsch.* **1981**, *36*, 902.

(14) Boucher, W.; Traschen, J. *Phys. Rev. D* **1988**, *37*, 3522.

(15) Martens, C. C.; Fang, J. Y. *J. Chem. Phys.* **1996**, *106*, 4918.

(16) Roman, E.; Martens, C. C. *J. Chem. Phys.* **2004**, *121*, 11572.

(17) Kapral, R.; Ciccotti, G. *J. Chem. Phys.* **1999**, *110*, 8919.

(18) Nielsen, S.; Kapral, R.; Ciccotti, G. *J. Chem. Phys.* **2001**, *115*, 5805.

(19) Horenko, I.; Weiser, M.; Schmidt, B.; Schütte, C. *J. Chem. Phys.* **2004**, *120*, 8913.

(20) Micha, D. A.; Thorndyke, B. *Adv. Quantum Chem.* **2004**, *47*, 293.

(21) Gindensperger, E.; Meier, C.; Beswick, J. A. *J. Chem. Phys.* **2000**, *113*, 9369.

(22) Gindensperger, E.; Meier, C.; Beswick, J. A. *J. Chem. Phys.* **2002**, *116*, 8.

(23) Prezhdo, O. V.; Brooksby, C. *Phys. Rev. Lett.* **2001**, *86*, 3215.

(24) Kohen, D.; Stillinger, F. H.; Tully, J. C. *J. Chem. Phys.* **1998**, *109*, 4713.

(25) Domcke, W.; Stock, G. *Adv. Chem. Phys.* **1997**, *100*, 1.

(26) Meier, C. *Phys. Rev. Lett.* **2004**, *93*, 173003.

(27) Bohm, D. *Phys. Rev.* **1952**, *85*, 166.

(28) Bohm, D. *Phys. Rev.* **1952**, *85*, 180.

(29) Bell, J. S. *Speakable and Unspeakable in Quantum Mechanics*; Cambridge University Press: Cambridge, U.K., 1989.

(30) Holland, P. R. *The Quantum Theory of Motion*; Cambridge University Press: New York, 1993.

(31) Wyatt, R. E. *Quantum Dynamics with Trajectories: Introduction to Quantum Hydrodynamics*; Springer: Heidelberg, Germany, 2005.

(32) Salcedo, L. L. *Phys. Rev. Lett.* **2003**, *90*, 118901.

(33) Prezdho, O.; Brooksby, C. *Phys. Rev. Lett.* **2003**, *90*, 118902.

(34) Burghardt, I.; Parlant, G. *J. Chem. Phys.* **2004**, *120*, 3055.

(35) Burghardt, I. *J. Chem. Phys.* **2005**, *122*, 094103.

(36) Burghardt, I.; Møller, K. B.; Hughes, K. H. In *Quantum Dynamics of Complex Molecular Systems*; Micha, D. A., Burghardt, I., Eds.; Springer: New York, 2006.

(37) Moyal, J. E. *Proc. Cambridge Philos. Soc.* **1949**, *45*, 99.

(38) Fröhlich, H. *Physica* **1967**, *37*, 215.

(39) Yvon, J. *J. Phys. Lett.* **1978**, *39*, 363.

(40) Lill, J. V.; Haftel, M. I.; Herling, G. H. *Phys. Rev. A* **1989**, *39*, 5832.

(41) Frensley, W. R. *Rev. Mod. Phys.* **1990**, *62*, 745.

(42) Muga, J. G.; Sala, R.; Snider, R. F. *Phys. Scr.* **1993**, *47*, 732.

(43) Johansen, L. M. *Phys. Rev. Lett.* **1998**, *80*, 5461.

(44) Burghardt, I.; Cederbaum, L. S. *J. Chem. Phys.* **2001**, *115*, 10303.

(45) Burghardt, I.; Møller, K. B. *J. Chem. Phys.* **2002**, *117*, 7409.

(46) Burghardt, I.; Møller, K. B.; Parlant, G.; Cederbaum, L. S.; Bittner, E. R. *Int. J. Quantum Chem.* **2004**, *100*, 1153.

(47) Hillery, M.; O'Connell, R. F.; Scully, M. O.; Wigner, E. P. *Phys. Rep.* **1984**, *106*, 121.

(48) Schleich, W. P. *Quantum Optics in Phase Space*; Wiley-VCH: Berlin, Germany, 2001.

(49) Takabayasi, T. *Prog. Theor. Phys.* **1954**, *11*, 341.

(50) de Broglie, L. *Compt. Rend.* **1926**, *183*, 447.

(51) de Broglie, L. *Non-linear Wave Mechanics*; Elsevier: Amsterdam, The Netherlands, 1960.

(52) Iafrate, G. J.; Grubin, H. L.; Ferry, D. K. *J. Phys. (Paris), Colloq.* **1981**, *42*, 307, C7, Suppl. 10.

(53) Levermore, C. D. *J. Stat. Phys.* **1996**, *83*, 1021.

(54) Degond, P.; Ringhofer, C. *J. Stat. Phys.* **2003**, *112*, 587.

(55) Trovato, M.; Falsaperla, P. *Phys. Rev. B* **1998**, *57*, 4456.

(56) Wyatt, R. E. *Chem. Phys. Lett.* **1999**, *313*, 189.

(57) Farlow, S. J. *Partial Differential Equations for Scientists and Engineers*; Dover: New York, 1982.

(58) Lee, H. W.; Scully, M. O. *J. Chem. Phys.* **1982**, *77*, 4604.

(59) Lee, H. W. *Phys. Rep.* **1995**, *259*, 147.

(60) Donoso, A.; Martens, C. C. *Phys. Rev. Lett.* **2001**, *87*, 223202.

(61) Daligault, J. *Phys. Rev. A* **2003**, *68*, 010501.

(62) Pulvirenti, M. *J. Math. Phys.* **2006**, *47*, 052103.

(63) Springborg, M. *Physica A* **2003**, *126*, 259.

(64) Lee, S.-Y.; Heller, E. J. *J. Chem. Phys.* **1982**, *76*, 3035.

(65) Møller, K. B.; Burghardt, I. In *Dynamics of Open Quantum Systems*; Hughes, K. H., Ed.; 2006; CCP6.

(66) Møller, K. B.; Parlant, G.; Burghardt, I. In preparation.

(67) Press, W. H.; Flannery, B P.; Teukolsky, S. A.; Vetterling, W. *Numerical Recipes in FORTRAN 77: The Art of Scientific Computing: Fortran Numerical Recipes*; 1992; Vol. 1.

(68) Hughes, K. H.; Wyatt, R. E. *Chem. Phys. Lett.* **2002**, *366*, 336.

(69) Bittner, E. R. *J. Chem. Phys.* **2000**, *112*, 9703.

(70) Burghardt, I.; Cederbaum, L. S. *J. Chem. Phys.* **2001**, *115*, 10312.

(71) Burghardt, I.; Bagchi, B. *Mol. Phys.* **2006**, *329*, 343.

(72) Satzger, H.; Spörlein, S.; Root, C.; Wachteveitl, J.; Zinth, W.; Gilch, P. *Chem. Phys. Lett.* **2002**, *372*, 216.

(73) Chang, C.; Lu, Y.; Wang, T.; Diau, E. W. *J. Am. Chem. Soc.* **2004**, *126*, 10109.

(74) Gradshteyn, I. S.; Ryzhik, I. M.; Jeffrey, A. *Table of Integrals, Series and Products*; Academic Press: San Diego, CA, 2000.

(75) Schleich, W. P. *Quantun Optics in Phase Space*; Wiley-VCH: Berlin, Germany, 2001.

(76) Lee, H. W. *Phys. Rep.* **1995**, *259*, 147.

(77) Lin, W. A.; Ballentine, L. E. *Phys. Rev. Lett.* **1990**, *65*, 2927.

(78) Shin, J. Y.; Lee, H. W. *Phys. Rev. E* **1994**, *50*, 902.

(79) Wigner, E. *Physica (Utrecht)* **1940**, *7*, 749.

(80) Here, $q(t)$ represents the quantum coordinate and $Q(t)$ represents the classical trajectory

(81) Note that q and Q are used throughout as coordinate indices for wave functions and densities alike. In the context of the Wigner transform, q denotes the sum variable, that is, $q = 1/2(x + x')$, while r denotes the difference variable, $r = x - x'$ when derived from a density operator $\rho(x, x') = \psi(x)\psi(x')$.

(82) Note that for anharmonic classical subsystems, the composite system would evolve to a mixed state due to the classical approximation taken in eq 7; see section II.E.

(83) Other classical-like representations include, for example, coherent-state-based representations; however, in this case, the basic physical entity remains an extended, nonlocal object, that is, a minimum-uncertainty wavepacket.