
Quantum Hydrodynamics: Mixed States, Dissipation, and a New Hybrid Quantum-Classical Approach

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ABSTRACT: The formulation of quantum hydrodynamics for mixed states provides a complement, in a quantum-statistical context, to its pure-state “Bohmian mechanics” analogue. We summarize our recent work in this area, focusing on two key aspects. We first describe the formulation of a generalized hydrodynamic force, which includes the effects of thermal fluctuations and “quantum fluctuations” and thus determines the time evolution under the influence of dissipation. Second, we introduce a mixed hydrodynamic–Liouville space representation in terms of partial moments, as applied in the context of coupled electronic states and mixed quantum-classical dynamics. © 2004 Wiley Periodicals, Inc. *Int J Quantum Chem* 100: 1153–1162, 2004

Key words: Bohmian mechanics; density matrix; dissipation; mixed quantum-classical dynamics; moment hierarchy; quantum hydrodynamics

“Les équations traditionnelles de la mécanique des fluides sont beaucoup plus proches de la théorie quantique qu’on ne le croit généralement. . . . La procédure consiste à substituer à la transformation de Fourier de la représentation de Wigner un développement en série entière.”

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Yvon, J. Navier-Stokes et Quanta; *J Phys Lett* 1978, 39, L-363.

Introduction

While much recent interest and activity in the field of quantum hydrodynamics has focused on recasting the time evolution of wavefunctions in a fluid-dynamical or “Bohmian” picture [1,

2], we have explored in our recent work [3–10] the connection to hydrodynamic methods in a quantum-statistical context, involving so-called mixed quantum states represented by density operators. This generalizes the hydrodynamic picture to include the description of thermal states, nonequilibrium ensembles, and dissipative processes.

The hydrodynamic description of mixed quantum states has a long history, including early contributions by Moyal [11], Fröhlich [12], Irving and Zwanzig [13], Yvon [14], and, more recently, Lill et al. [15, 16], Frenley [17], Muga et al. [18], and others. As shown by these authors, not only the Schrödinger equation but also the quantum-statistical equations of motion can be written in a hydrodynamic form, by referring to moments of the density matrix or Wigner function. One can derive a hierarchy of coupled moment equations that have the form of the hydrodynamic equations of classical mechanics, that is, coupled equations for the mass density, momentum density, kinetic energy density, etc. Recently, the reconstruction of the density matrix or Wigner function in terms of their moments has become an important topic in quantum optics and molecular physics [19, 20]. Although the connection between mixed-state hydrodynamics and the pure-state hydrodynamics as introduced by Madelung [21], de Broglie [22, 23], and Bohm [24, 25] can be established in a straightforward fashion, this relation has barely been addressed in the literature. One of the lines of enquiry of our recent work therefore concerns the analogy between the wavefunction and mixed-state pictures in the hydrodynamic context.

The quantum-statistical hydrodynamic moments in question can be derived, in an equivalent fashion, from the density operator in the coordinate-space representation, $\rho(x, x')$, or from its phase-space analogue, the Wigner function $\rho_W(q, p)$ [26],

$$\rho_W(q, p) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dr \tilde{\rho}(q, r) \exp(-ipr/\hbar). \quad (1)$$

Here, the coordinate-space density was rewritten as a function $\tilde{\rho}(q, r)$ of the sum and difference coordinates $q = 1/2(x + x')$ and $r = x - x'$. In the hydrodynamic description, the time evolution of the quantum densities $\tilde{\rho}(q, r)$ or $\rho_W(q, p)$ is obtained in terms of the time evolution of a set of moment functions, or moment densities [3, 6, 9, 11, 14–17, 19] obtained from $\rho_W(q, p)$ by integration over momentum only,

$$\langle \mathcal{P}^n \rho \rangle_q = \int_{-\infty}^{\infty} dp p^n \rho_W(q, p) \quad (2)$$

or from $\tilde{\rho}(q, r)$ by differentiation with respect to the difference coordinate r ,

$$\langle \mathcal{P}^n \rho \rangle_q = \left(\frac{\hbar}{i} \right)^n \frac{\partial^n}{\partial r^n} \tilde{\rho}(q, r) \Big|_{r=0}. \quad (3)$$

Given that the phase-space momentum p and the difference coordinate $r = x - x'$ represent conjugate Fourier variables in accordance with Eq. (1), the coordinate-space density plays the role of a moment-generating function, that is, the hydrodynamic moments correspond to the coefficients of the Taylor expansion of $\tilde{\rho}(q, r)$ in the coordinate r , $\tilde{\rho}(q, r) = \sum_n 1/n! \langle \mathcal{P}^n \rho \rangle_q (ir/\hbar)^n$. (This representation is at the root of the observation by Yvon [14], as quoted above.)

The description in terms of moment densities is a reduced description in the following sense. The momentum information contained in the Wigner distribution—or the phase information contained in the $x \neq x'$ elements of the density matrix—is projected onto coordinate space in terms of moments. This is analogous to the derivation of the classical hydrodynamic equations from the classical-statistical kinetic equations, in particular, the Boltzmann equation [27].

The potential usefulness of a dynamical description in terms of moments resides in the fact that one may selectively probe not the complete information contents of the density operator but relevant information corresponding to the local density, current density, and other low-order moments. The practical advantage essentially relates to adopting the numerical techniques of fluid dynamics—in particular, the propagation of fluid-dynamical trajectories—which present a promising alternative to the conventional quantum dynamical techniques based on grid methods.

Moment Hierarchies and Generalized Hydrodynamic Forces

HYDRODYNAMIC MOMENT HIERARCHY

The dynamical equations for the moments Eq. (2) or, equivalently, Eq. (3) are derived from the Liouville–von Neumann (LvN) equation for the density operator,

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} [\hat{T} + \hat{V}, \hat{\rho}] \quad (4)$$

or, more specifically, the representation of the LvN equation in either coordinate space or the associated Wigner phase space. The moment equations in their general form read [3, 9, 15–17, 19]

$$\begin{aligned} \frac{\partial \langle \mathcal{P}^n \rho \rangle_q}{\partial t} = & -\frac{1}{m} \frac{\partial}{\partial q} \langle \mathcal{P}^{n+1} \rho \rangle_q - n \left(\frac{\partial V}{\partial q} \right) \langle \mathcal{P}^{n-1} \rho \rangle_q \\ & - \sum_{k=1}^{(n-1)/2} \left(\frac{\hbar}{2i} \right)^{2k} \binom{n}{2k+1} \frac{\partial^{2k+1} V}{\partial q^{2k+1}} \langle \mathcal{P}^{n-(2k+1)} \rho \rangle_q. \end{aligned} \quad (5)$$

Notice that the first two terms on the right side are of a “classical” form and actually correspond to those derived from the classical Liouville equation, if we choose to formulate the analogous moment problem for classical distribution functions [9]. To these add explicit contributions in \hbar , of the same structure as the Wigner–Moyal expansion [26] from which they can be derived in a straightforward fashion. In its entirety, the hierarchy of coupled moment equations is equivalent to the LvN equation for the density operator.

In Eq. (5), the kinetic-energy contribution (first term on the right side of the equation) generates a dynamical coupling between the n -th hydrodynamic moment $\langle \mathcal{P}^n \rho \rangle_q$ and the $(n + 1)$ st moment $\langle \mathcal{P}^{n+1} \rho \rangle_q$. The coupling of successive orders implies that the hierarchy does not terminate, unless a given moment can be expressed in terms of the lower-order moments. This is not generally the case, except for particular types of densities, for which the hierarchy closes with a few of the lowest-order members. These include, in particular, pure states (see following section) and general Gaussian mixed-state densities. For the latter, the third moment may be represented as follows in terms of the lower-order moments [3, 6, 9]:

$$\langle \mathcal{P}^3 \rho \rangle_q = \bar{p}^3(q) \langle \rho \rangle_q + 3\bar{p}(q) [\langle \mathcal{P}^2 \rho \rangle_q - \bar{p}^2(q) \langle \rho \rangle_q]. \quad (6)$$

with the momentum field $\bar{p}(q) = \langle \mathcal{P} \rho \rangle_q / \langle \rho \rangle_q$.

The hierarchy of dynamical equations therefore terminates with the second order in this case.

For general densities, the closure of the hydrodynamic hierarchy represents a central difficulty in applying the moment methodology. Quoting from the context of plasma physics, where a similar problem occurs in connection with the Vlasov equation, the corresponding moment equations “must be terminated somewhere by a flash of insight” [28].

More systematically, two types of truncation schemes can be envisaged: (1) global truncation schemes. Considering, for example, Eq. (6) for $\langle \mathcal{P}^3 \rho \rangle_q$, this expression—even though exactly valid only for the Gaussian form—may provide a reasonable first approximation even for the general case. In an improved scheme, a moment of much higher order can be approximated in a similar fashion in terms of lower-order moments [3, 8]; (2) local truncation schemes. Here, a general density is locally approximated, for example, by a Gaussian form, such that Gaussian moments are locally valid [3] (see also similar approaches in a Liouville-space context [29]). This scheme is related to a strategy used in classical hydrodynamics, whereby a Gaussian “Maxwellian” approximation along with a local thermal equilibrium assumption are invoked [27]. For recent developments regarding the moment closure problem, in the context of both classical and quantum kinetic theories, see Refs. [30, 31].

CONNECTION TO PURE-STATE HYDRODYNAMICS

The hydrodynamic description for pure quantum states, or wavefunctions, naturally emerges as a particular case of the moment hierarchy, for the form $\hat{\rho} = |\psi\rangle\langle\psi|$ of the density operator. Although this case is expected to connect with the hydrodynamic theory for wavefunctions as introduced by Madelung, de Broglie and Bohm, the relation has barely been made explicit in the literature. Two apparently distinct lines of research have coexisted over a number of years, pertaining to pure-state hydrodynamics and the Bohmian theory of quantum mechanics [1, 2, 21–25, 32] versus mixed-state hydrodynamics in the quantum-statistical tradition [11–17, 19]. An exception is Ref. [18] by Muga et al. whose work suggests a unified moment development for classical and quantum phase-space distributions.

One may in fact argue that the hydrodynamic description is the pertinent way to translate between the Liouville space, or phase-space picture of quantum mechanics, and the usual coordinate-space representation of the wavefunction [33]. The hydrodynamic projection of a pure-state phase-space distribution onto coordinate space directly yields the amplitude and phase information for the wavefunction, in the shape of the first two hydrodynamic moments, that is, the local density and momentum density. This can be seen most explicitly by referring to the polar form of the wavefunc-

tion, $\psi(x) = R(x)\exp(iS(x)/\hbar)$, with the hydrodynamic moments—the probability density and the current density—given as

$$P(q) = \langle \rho \rangle_q = \psi(x)\psi^*(x')|_{x=x'=q} = R^2(q)$$

$$j(q) = \frac{\langle \mathcal{P}\rho \rangle_q}{m} = \left[\frac{\hbar}{2im} \left(\frac{\partial}{\partial x} - \frac{\partial}{\partial x'} \right) \psi(x)\psi^*(x') \right]_{x=x'=q}$$

$$= \frac{1}{m} \frac{\partial S}{\partial q} \langle \rho \rangle_q. \quad (7)$$

By defining the current density in terms of a velocity field, $j(q) = \bar{v}(q)\langle \rho \rangle_q$, one recovers the velocity and momentum as defined in Bohmian mechanics, $\bar{v}(q) = \bar{p}(q)/m = 1/m(\partial S/\partial q)$.

In accordance with the fact that the first two moments entirely determine the wavefunction (apart from a piecewise constant phase factor [34]), the moment hierarchy Eq. (5) is expected to terminate with its first two members. In fact, the second moment is expressible in terms of the zero-th and first moments [3, 35]

$$\langle \mathcal{P}^2 \rho \rangle_q = \bar{p}^2(q)\langle \rho \rangle_q - \frac{\hbar^2}{4} \langle \rho \rangle_q \frac{\partial^2}{\partial q^2} \ln \langle \rho \rangle_q, \quad (8)$$

such that—upon substitution of the expression Eq. (8) into the dynamical equation for the momentum density $\langle \mathcal{P}\rho \rangle_q$ —the equations for the local density and the momentum density indeed form a closed subset [3].

With the definition $\langle \mathcal{P}\rho \rangle_q = \bar{p}(q)\langle \rho \rangle_q$ for the momentum field, the dynamical equations for the first two moments of the hierarchy may be cast in the following form,

$$\frac{\partial}{\partial t} \langle \rho \rangle_q = -\frac{1}{m} \frac{\partial}{\partial q} [\bar{p}(q)\langle \rho \rangle_q]$$

$$\frac{d\bar{p}}{dt} = -\frac{\partial V}{\partial q} + F_{\text{hyd}} \Big|_{\text{pure state}}. \quad (9)$$

Here, the hydrodynamic force derives from the second moment Eq. (8),

$$F_{\text{hyd}} = -\frac{1}{m} \langle \rho \rangle_q^{-1} \frac{\partial}{\partial q} [\langle \mathcal{P}^2 \rho \rangle_q - \bar{p}^2(q)\langle \rho \rangle_q], \quad (10)$$

and can be written in the pure-state case as the gradient of the quantum potential of Bohmian mechanics [2],

$$F_{\text{hyd}} \Big|_{\text{pure state}} = -\frac{\partial Q}{\partial q}, \quad (11)$$

with $Q = -\hbar^2/(2m)\langle \rho \rangle_q^{-1/2} \partial^2/\partial q^2 \langle \rho \rangle_q^{1/2}$. Note that Q depends on the curvature of the local density.

The derivation of the pure-state hydrodynamic equations from the Liouville space perspective of densities and phase-space distributions sheds some light on the physical meaning of the fluid-dynamical quantities involved. In particular, the hydrodynamic momentum $\bar{p}(q) = \partial S/\partial q$ is found to correspond to an average momentum at a given value of position q [3, 9, 33, 36]. If we choose to refer to a hydrodynamic phase space, with fluid-particle or “Bohmian” momenta defined by $p_t = \bar{p}(q, t)|_{q=x_t}$, the time-evolving trajectory ensembles in this phase space will be distinctly different from trajectory ensembles defined in Liouville space. In particular, the Bohmian ensemble is always single-valued in the momentum, with a distribution function of the form $\rho_{\text{hyd}}(q, p) = P(q)\delta(p - \bar{p}(q))$ [2, 9, 36]. Concomitantly, the presence of the hydrodynamic force in the equation of motion for the momentum can be understood to “compensate” for the fact that an average momentum is being considered [9], rather than the momenta of individual Liouville-space (i.e., classical, or Wigner type [29]) trajectories. The classical limit of Bohmian mechanics should therefore be considered from the particular perspective of hydrodynamic ensembles [2].

MIXED STATES: GENERALIZED HYDRODYNAMIC FORCE AND DISSIPATION

For mixed states, the hydrodynamic hierarchy does not terminate with the equations for the local density and momentum density. Still, the dynamical equations Eq. (9) formally carry over to this general case, with a generalized definition of the local density, momentum field, and hydrodynamic force. Furthermore, dissipation, that is, the effects of friction and fluctuations, can be naturally included in this picture. This makes the hydrodynamic description very attractive because it indeed offers a unified framework for pure-state and mixed-state dynamics. Figure 1 illustrates the time evolution of a hydrodynamic trajectory ensemble evolving in a harmonic well while undergoing the effects of dissipation. Similarly to the pure-state case, a generalized hydrodynamic force now guides the trajectory ensemble in such a way that an initial coherent-

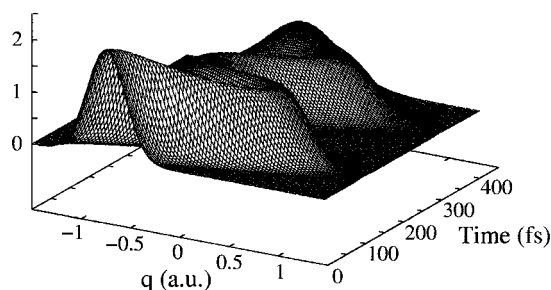
state ensemble spreads and eventually relaxes to the center of the harmonic well [9].

With the form $\rho(x, x') = r(x, x')\exp[is(x, x')/\hbar]$ of a general mixed-state density, the local density is defined as [3]

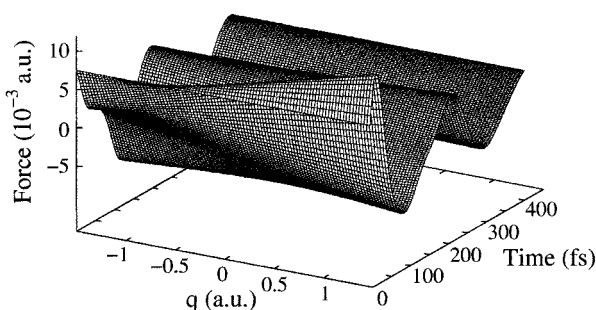
$$\langle \rho \rangle_q = r(x = q, x' = q), \quad (12)$$

the momentum field is given by

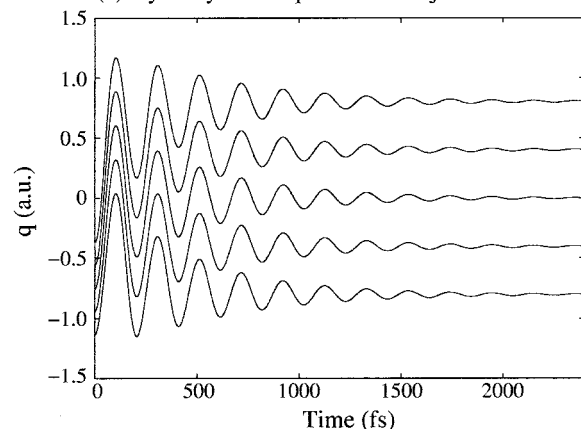
(a) Local Density



(b) Total Force



(c) Hydrodynamic space-time trajectories



$$\bar{p}(q) = \left. \frac{\partial s(x, x')}{\partial x} \right|_{x=x'=q}, \quad (13)$$

and a generalized hydrodynamic force can be defined as [3, 9] (in accordance with Eq. (10), which in fact is not restricted to the pure-state case),

$$F_{\text{hyd}} = -\frac{1}{m} \langle \rho \rangle_q^{-1} \frac{\partial}{\partial q} \tilde{\sigma}_{pp}(q) \quad (14)$$

with $\tilde{\sigma}_{pp}(q)$ the position-dependent variance in the momentum p ,

$$\tilde{\sigma}_{pp}(q) = \langle \mathcal{P}^2 \rho \rangle_q - \bar{p}^2(q) \langle \rho \rangle_q = \langle \mathcal{P}^2 r \rangle_q \quad (15)$$

the spatial variation of which is reflected in F_{hyd} . Notice that $\tilde{\sigma}_{pp}(q)$ is related to the “shape” kinetic energy [2], and essentially plays the role of a hydrodynamic pressure [12, 14, 33]. All quantities reduce to the corresponding pure-state quantities of the preceding section for $r(x, x') = R(x)R(x')$ and $s(x, x') = S(x) - S(x')$. In the general case, the hydrodynamic force carries the coupling to the higher orders of the hydrodynamic hierarchy.

In the example of Figure 1, dissipation has been included by deriving the moment equations corresponding to the master equation introduced by Caldeira and Leggett [37]. The latter essentially corresponds to a Langevin-type description and captures the effects of friction and fluctuations in a simple Markovian picture. The dynamical equations for the local density and hydrodynamic momentum

FIGURE 1. Time evolution of an initial coherent-state density in a harmonic potential, subject to Caldeira–Leggett type dissipation (from Ref. [9]). The hydrodynamic trajectories mimic the broadening and evolution toward thermal equilibrium of the density. In the absence of dissipation, the width of the coherent-state density would remain unchanged, with the family of hydrodynamic trajectories experiencing the same force and moving uniformly, parallel to the center path. The trajectory dynamics is induced by the force $F_{\text{total}} = -(\partial V/\partial q) - \gamma \bar{p} + F_{\text{hyd}}$, with $F_{\text{hyd}} = D/(m\sigma_{qq}^2)(q - \langle q \rangle)$. Here, σ_{qq} is the coordinate-space variance of the Gaussian density, and D is the determinant of the matrix of variances. (D provides a measure of the mixed-state character of the time-evolving Gaussian density, and increases from its initial pure-state value $D = (\hbar/2)^2$.) The pronounced initial rise in F_{total} is due to the fluctuation-induced increase in the variances.

represent a straightforward extension to Eqs. (9), with the generalized definition of the hydrodynamic quantities as given above [9]

$$\begin{aligned} \frac{\partial}{\partial t} \langle \rho \rangle_q &= -\frac{1}{m} \frac{\partial}{\partial q} [\bar{p}(q) \langle \rho \rangle_q] \\ \frac{d\bar{p}}{dt} &= -\frac{\partial V}{\partial q} - \gamma \bar{p} + F_{\text{hyd}}. \end{aligned} \quad (16)$$

Notice again that Eqs. (16) are not self-contained and implicitly contain the coupling to the higher-order moments of the hierarchy via F_{hyd} . Dissipation appears in the equations (1) via the frictional term $-\gamma \bar{p}$, and (2) via the effect of thermal fluctuations that contribute to the hydrodynamic force.

This in fact suggests the following picture: the hydrodynamic force reflects the combined effects of thermal fluctuations and “quantum fluctuations,” which together give rise to the momentum-space width of the Wigner phase-space distribution. To illustrate this, consider the second hydrodynamic moment for the thermal equilibrium state of the harmonic oscillator, which is essentially of “quantum” origin at low temperatures,

$$\langle \mathcal{P}^2 \rho \rangle_q \Big|_{kT \ll \hbar\omega} = \frac{1}{2} m \hbar \omega \langle \rho \rangle_q \quad (17)$$

and essentially of thermal origin at high temperatures,

$$\langle \mathcal{P}^2 \rho \rangle_q \Big|_{kT \gg \hbar\omega} = mkT \langle \rho \rangle_q. \quad (18)$$

The quantum-statistical moment description naturally comprises these limits and the intermediate case. Incidentally, notice that the hydrodynamic force resulting from both Eq. (17) and Eq. (18) is temperature-independent, $F_{\text{hyd}} = m\omega^2 q$ and exactly compensates for the effect of the external force on the oscillator. Hydrodynamics thus predicts stationary trajectory solutions for both the quantum ground state and the high-temperature thermal equilibrium state! This highlights the close connection between quantum hydrodynamics and the analogous hydrodynamic description of purely classical distribution functions. In the classical-statistical limit, we may in fact replace the quantum hydrodynamic moments with their classical-statistical counterparts [9, 18].

Partial Moments: A Hybrid Hydrodynamic-Liouvillian Description

In this section, we address the formulation of hybrid methods that combine the hydrodynamic and Liouville-space representations. For a system involving a number of degrees of freedom, possibly of different physical nature, it may in fact be useful to define hydrodynamic moments with respect to chosen degrees of freedom only. This applies, in particular, to coupled electronic surfaces (with moments defined with respect to the nuclear coordinates only) or to systems including different types of nuclear degrees of freedom, some of which we may wish to describe in a Liouville-space setting while a moment description is chosen for others.

To this purpose, the construction of partial moments is a suitable avenue. We outline here a description in terms of partial moments for two different situations: first, nuclear dynamics on coupled electronic surfaces [4] and second, a mixed hydrodynamic-Liouville space dynamics in different nuclear degrees of freedom [10]. For clarity, we refer in a parallel fashion to the coordinate-space representation of the nuclear density operator and to its Wigner-space analogue.

COUPLED ELECTRONIC SURFACES

To describe nonadiabatic nuclear dynamics on coupled Born–Oppenheimer surfaces, the density operator is expressed in a matrix representation in the basis of electronic states $|k\rangle$, $\hat{\rho}(x, x') = \sum_{kl} \rho_{kl}(x, x') |k\rangle\langle l|$. The diagonal elements $k = l$ correspond to electronic populations while the off-diagonal elements $k \neq l$ correspond to electronic coherences [38,39]. We now introduce partial moments with respect to the nuclear degrees of freedom only, defined as follows for each component density,

$$\begin{aligned} \langle \mathcal{P}^n \rho \rangle_{qkl} &= \left(\frac{\hbar}{2i} \right)^n \left(\frac{\partial}{\partial x} - \frac{\partial}{\partial x'} \right)^n \rho_{kl}(x, x') \Big|_{x=x'=q} \\ &= \int dp p^n \rho_W^{kl}(q, p), \end{aligned} \quad (19)$$

with $\rho_W^{kl}(q, p)$ the Wigner representation of the element $\rho_{kl}(x, x')$.

The three-index moments of Eq. (19) are hybrid quantities that can be considered as density matrix elements (k, l) for the electronic N -level system, parameterized in q or, alternatively, as a family of hydrodynamic moments in q carrying indices for electronic populations $k = l$ and electronic coherences $k \neq l$, respectively.

We consider specifically the case of an electronic two-state system, as detailed in Ref. [4]. The equa-

$$\begin{aligned} \partial \langle \mathcal{P}^n \rho \rangle_{q12} / \partial t = & \left. \begin{aligned} & -1/m \partial / \partial q \langle \mathcal{P}^{n+1} \rho \rangle_{q12} \\ & -n \partial / \partial q ([V_1(q) + V_2(q)]/2) \langle \mathcal{P}^{n-1} \rho \rangle_{q12} \\ & -(n/2) (\partial V_{12} / \partial q) [\langle \mathcal{P}^{n-1} \rho \rangle_{q11} + \langle \mathcal{P}^{n-1} \rho \rangle_{q22}] + \dots \end{aligned} \right] \text{“hydrodynamic part”} \\ & \left. \begin{aligned} & -i/\hbar [V_1(q) - V_2(q)] \langle \mathcal{P}^n \rho \rangle_{q12} \\ & -i/\hbar V_{12}(q) [\langle \mathcal{P}^n \rho \rangle_{q11} - \langle \mathcal{P}^n \rho \rangle_{q22}] \end{aligned} \right] \text{“Liouvillian part”} \quad (20) \end{aligned}$$

Due to the presence of the coupling potential V_{12} , the basic picture of the dynamics involves the coupling between electronic populations and coherences, illustrated in Figure 2. As shown in Ref. [4], this description of the dynamics coincides with the results obtained by Wyatt, Lopreore, and Parlant for the pure-state case [40].

COUPLED BOHMIAN AND CLASSICAL PHASE-SPACE VARIABLES: A NOVEL HYBRID QUANTUM-CLASSICAL APPROACH

Consider next the case of two nuclear degrees of freedom, x and X , and the associated coordinate space density $\rho(x, x', X, X')$. As in Eq. (19), we construct partial hydrodynamic moments with respect to x only,

$$\begin{aligned} \langle \mathcal{P}^n \rho \rangle_{qXX'} &= \left(\frac{\hbar}{2i} \right)^n \left(\frac{\partial}{\partial x} - \frac{\partial}{\partial x'} \right)^n \rho(x, x', X, X') \Big|_{x=x'} \\ &= \int dp p^n \rho_W(q, p, X, X') \quad (21) \end{aligned}$$

or, alternatively,

$$\langle \mathcal{P}^n \rho \rangle_{qQP} = \int dp p^n \rho_W(q, p, Q, P), \quad (22)$$

where the moments $\{\langle \mathcal{P}^n \rho \rangle_{qQP}\}$ represent the Wigner transform of the moments $\{\langle \mathcal{P}^n \rho \rangle_{qXX'}\}$ with

tions of motion for the partial moments Eq. (19) are composed of (1) a hydrodynamic part, involving the average potential $1/2[V_1(q) + V_2(q)]$ along with a contribution in the coupling potential $V_{12}(q)$, and (2) a Liouville-space part reflecting the structure of the LvN equation for the electronic two-level system, with a parametric dependence on q :

respect to the Liouville-space variables, $(X, X') \rightarrow (Q, P)$.

The Wigner transformed representation Eq. (22) is particularly appropriate in view of introducing classical approximants $\{\langle \mathcal{P}^n \rho \rangle_{qQP}^c\}$. These may be thought to be derived from a mixed quantum-classical phase-space distribution, resulting from a classical phase-space limit in the (Q, P) subspace [41,

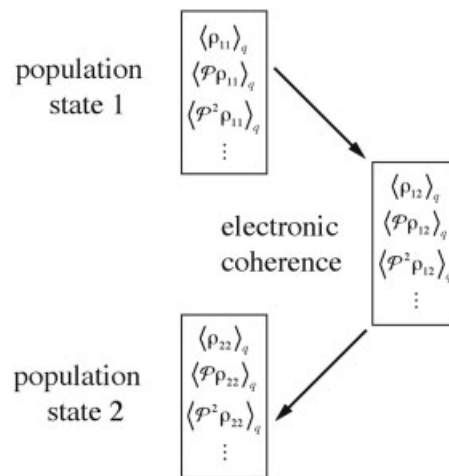
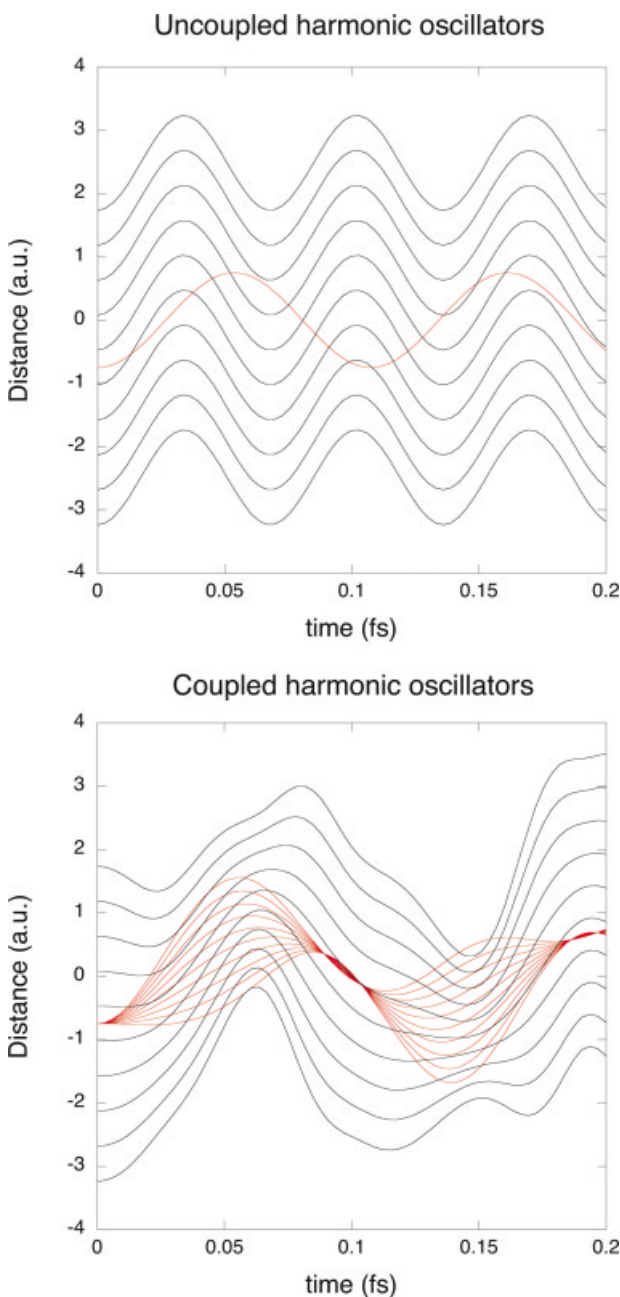


FIGURE 2. Schematic illustrating the hydrodynamic picture of nonadiabatic dynamics, according to Ref. [4]. Families of hydrodynamic moments are associated with electronic populations and coherences, respectively. In accordance with the usual Liouville-space description [39, 40], population transfer is mediated by the electronic coherences, with a time-dependent transition flux density $\Gamma_{12}(q, t) = 2/\hbar V_{12}(q) \text{Im} \langle \rho_{12} \rangle_q$. Notice that an overall continuity equation holds, $\partial / \partial t [\langle \rho_{11} \rangle_q + \langle \rho_{22} \rangle_q] = -1/m \partial / \partial q [\langle \mathcal{P} \rho_{11} \rangle_q + \langle \mathcal{P} \rho_{22} \rangle_q]$.

42]. Following this route, we have derived in Ref. [10] mixed quantum-classical equations of motion,

$$\begin{aligned} \partial \langle \mathcal{P}^n \rho \rangle_{qQP}^c / \partial t \approx & \left. \begin{aligned} & -1/m \partial / \partial q \langle \mathcal{P}^{n+1} \rho \rangle_{qQP}^c \\ & -n (\partial (V_q(q) + V_{\text{int}}(q, Q)) / \partial q) \langle \mathcal{P}^{n-1} \rho \rangle_{qQP}^c + \dots \end{aligned} \right] \text{“hydrodynamic part”} \\ & \left. \begin{aligned} & -P/M \partial / \partial Q \langle \mathcal{P}^n \rho \rangle_{qQP}^c \\ & + \partial / \partial Q (V_Q(Q) + V_{\text{int}}(q, Q)) \partial / \partial P \langle \mathcal{P}^n \rho \rangle_{qQP}^c \end{aligned} \right] \text{“Liouvillian part”}. \quad (23) \end{aligned}$$

for a Hamiltonian of the form $\hat{H} = \hat{H}_q(\hat{q}, \hat{p}) + \hat{H}_{\text{int}}(\hat{q}, \hat{Q}) + \hat{H}_Q(\hat{Q}, \hat{P})$,



As in Eq. (20), the equations of motion for the partial moments comprise a hydrodynamic part and a Liouvillian part; the latter now takes the form of the classical Liouville equation.

Upon introducing a hydrodynamic momentum field \bar{p}_{qQP} via the first moment, $\langle \mathcal{P} \rho \rangle_{qQP}^c = \bar{p}_{qQP} \langle \rho \rangle_{qQP}^c$, a picture is obtained by which interleaved hydrodynamic ($q, p = \bar{p}_{qQP}$) and classical-mechanical (Q, P) variables are propagated according to the equations of motion [10]

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

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

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

$$\dot{P} = - \frac{\partial}{\partial Q} (V_Q(Q) + V_{\text{int}}(q, Q)). \quad (24)$$

Here, the classical variables (Q, P) exhibit a local coupling to the quantum subspace, via the interaction potential $V_{\text{int}}(q, Q)$, whereas the quantum hy-

FIGURE 3. Coupling between quantum hydrodynamic and classical Liouville-space variables according to Eq. (24), for a system of bilinearly coupled harmonic oscillators [10]. For an initial ensemble $\rho(q, p, Q, P; t = 0) = P(q)\delta(p - p_0)\delta(Q - Q_0)\delta(P - P_0)$, chosen to be δ -function like in the classical variables (Q, P) for purposes of illustration, the figure shows the time evolution of the mixed hydrodynamic-Liouvillian ensemble (a) in the absence of coupling between the oscillators (upper panel), (b) in the presence of a bilinear coupling (lower panel). In the latter case, the hydrodynamic (q, p) projection of the ensemble (black lines) is deformed due to the coupling to the classical Liouvillian (Q, P) variables, whereas the classical projection of the ensemble (red lines) splits up due to the q -dependent interaction.

hydrodynamic variables evolve under the combined effect of the interaction potential and an additional quantum force $F_{\text{hyd}}(q, Q, P)$. The latter depends on the quantum hydrodynamic variable q and on the classical phase space variables (Q, P) and is a generalization of the conventional hydrodynamic force of Eqs. (11) and (14),

$$F_{\text{hyd}}(q, Q, P) = -\frac{1}{m} [\langle \rho \rangle_{qQP}^c]^{-1} \frac{\partial}{\partial q} \times [\langle \mathcal{P}^2 \rho \rangle_{qQP}^c - \bar{p}_{qQP}^2 \langle \rho \rangle_{qQP}^c]. \quad (25)$$

The time-evolving trajectory ensemble conforms to a hybrid hydrodynamic-Liouvillian distribution function, $\rho_{\text{hybrid}}(q, p, Q, P) = \langle \rho \rangle_{qQP} \delta(p - \bar{p}_{qQP})$. This distribution preserves the features of a Liouville-space distribution in the classical subspace but is singular in the quantum subspace, assigning a given value of the hydrodynamic momentum $p = \bar{p}_{qQP}$ to each combination of variables (q, Q, P) (cf. discussion of “Connection to Pure-State Hydrodynamics”). Figure 3 illustrates the coupling between the quantum hydrodynamic and classical variables.

Equations (23)–(25) define a consistent quantum-classical coupling scheme. Because the classical phase-space approximation is exact for harmonic potentials in the (Q, P) subspace [41, 42] the current approach gives an exact description of the vibrationally nonadiabatic dynamics in a system of bilinearly coupled harmonic oscillators [10]. For this particular example, other mixed quantum-classical methods—notably the mean-field and surface-hopping methods—do not yield satisfactory results [43]. Furthermore, the mixed quantum-classical hydrodynamic approach of Ref. [44], which neglects the hydrodynamic force in the classical sector, is inaccurate. This is in line with the observations described in the section “Mixed States: Generalized Hydrodynamic Force and Dissipation.” Indeed, a classical hydrodynamic force would be required for a consistent hydrodynamic description in the classical subspace. By contrast, the partial moment approach described here translates to a Liouvillian classical-limit trajectory description in the (Q, P) subspace.

Outlook

We expect the mixed-state hydrodynamic methods as outlined here to provide a useful and promising complement to pure-state fluid-dynamical

methods. The mixed-state techniques are very flexible in introducing thermal effects, nonequilibrium dynamics, the classical-statistical limit, nonadiabatic effects, and mixed hydrodynamic-Liouville space approaches. Our future applications will address systematic solutions to the truncation problem [8, 31] and the connection to related statistical mechanical techniques [45].

The hybrid quantum-classical moment approach described in “Mixed States” is closely related to the mixed quantum-classical phase-space distribution techniques introduced in Refs. [41, 42]. Thus, the moment equations Eq. (23) can be derived from a mixed quantum-classical phase space description via the definition of partial moments in Eq. (22). Because “quantum corrections” appear in a different fashion in the two representations—and “quantum trajectories” can be defined both in the hydrodynamic and Wigner phase-space settings [28, 46]—various questions arise regarding the relation between the hydrodynamic and phase-space representations. These issues will be at the center of our future efforts.

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