HYDRODYNAMIC METHODS FOR ULTRAFAST QUANTUM DYNAMICS, QUANTUM TRANSPORT, AND DISSIPATION

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Quantum hydrodynamics ("Bohmian mechanics") [1] has recently been introduced in molecular physics as a new type of quantum-dynamical simulation technique [2], rather than in its previous role as a purely interpretative tool. Quantum dynamical methods in the molecular domain have gained increasing significance over the last decade, due to the advent of time-resolved spectroscopies which monitor elementary molecular events in "real time", at the femtosecond and picosecond scale [3]. Relevant processes include vibrational dynamics in the electronic ground and excited states, reactive dynamics involving bond-breaking and bond-making, and non-adiabatic processes associated with radiationless transitions between different electronic states. Molecular quantum dynamics is intrinsically multidimensional in most relevant situations: optically excited modes rapidly couple to their local environment in a polyatomic molecule or solute-solvent complex. Modern quantum dynamical methodology therefore either attempts to address the complex, multidimensional nature of the dynamics directly, or else adopts reduced-dimensionality models. The latter lead, for example, to master equations describing dissipative processes. (Note, however, that many commonly made assumptions like the separation of system vs. bath time scales do not generally hold for the interaction between a molecular quantum subsystem and its environment.) Furthermore, one seeks to reduce the information required as a function of time within the subspace of relevant modes. For example, the description of energy and population transfer processes does not necessarily require complete knowledge of the wavefunction or density operator. Hydrodynamic quantities provide a reduced description in this sense. This latter aspect is most relevant when approaching the mesoscopic domain, where the microscopic mechanisms of electronic coupling and mode-mode coupling translate to transport phenomena at a supramolecular level.

Since exact methods of quantum wavepacket propagation encounter an exponential scaling limit which generally does not allow one to go beyond 5 or 6 degrees of freedom, a considerable variety of approximate techniques have been suggested. These include mean-field methods, multiconfigurational mean-field methods which can effectively be made exact, semiclassical methods, and various kinds of mixed quantum-classical methods. While most of these techniques relate to pure states (represented by wavefunctions), the systematic dynamical treatment of mixed states (represented by density operators) including dissipation, has started to grow into a standard approach over the recent years. Against this background, the "Bohmian" or hydrodynamic approach to quantum dynamics has recently attracted much interest as an alternative to the conventional propagation schemes. Due to its proximity to the classical trajectory picture, the scaling problems inherent in many of the above quantum dynamical methods can be in part avoided. Further, new approximate and quantum-classical schemes naturally evolve from the hydrodynamic viewpoint.

While the usual perspective on Bohmian mechanics focuses on the description of wavefunctions, or pure quantum states, we have recently explored the connection to mixed-state quantum hydrodynamics, suitable for non-equilibrium dynamics and dissipative processes [4–7]. The hydrodynamic description of mixed quantum states actually has a long history, including early contributions by Moyal [8], Fröhlich, Zwanzig, Yvon, and others. As shown by these authors, not only the Schrödinger equation, but also the quantum-*statistical* equations of motion can be recast in a hydrodynamic form. Formally, the hydrodynamic formulation can be derived from the density matrix $\rho(x, x')$ or, equivalently, the Wigner function $\rho_W(q, p)$ [4–7], and corresponds to a local-in-space formulation in terms of moments $\langle \mathcal{P}^n \rho \rangle_q = \int dp \, p^n \rho_W(q, p)$. Specifically, the zeroth moment corresponds to the local density $P(q) = \langle \rho \rangle_q$, the first-order moment relates to the current density $j(q) = \langle \mathcal{P} \rho \rangle_q / m$, and the second-order moment corresponds to the kinetic-energy density $T(q) = \langle \mathcal{P}^2 \rho \rangle_q / 2m$. In general, these first few moments carry the information relevant to spectroscopic observation. The dynamical equations for the moments $\langle \mathcal{P}^n \rho \rangle_q$ represent an infinite hierarchy, analogous to the hierarchy of classical hydrodynamic equations. In their entirety, the coupled moment equations are equivalent to the Liouville-von-Neumann equation for the density operator. Hence, the density matrix or Wigner function can be reconstructed from the time-evolving moments. This latter aspect has recently become an important topic in quantum optics and molecular physics [6], and is closely connected to the question of reconstructing the wavefunction from the pure-state hydrodynamic quantities [1,2]. However, while the connection between mixed-state hydrodynamics and the pure-state hydrodynamics as introduced by Madelung, de Broglie and Bohm [1] can be established in a straightforward fashion, this relation has barely been addressed in the literature (an exception is, e.g., Ref. [11]).

In this lecture, we will specifically address the following issues: (i) The derivation, from the general mixed-state formulation, of pure-state hydrodynamics as familiar from the Bohmian picture [7,11]. The moment hierarchy now truncates with the two lowest-order members – i.e., the local density and the current density – which fully characterize the wavefunction. (ii) The formulation of the general mixed-state problem, including dissipation, in terms of a generalized quantum force [7,9]. In a quantum-statistical perspective, the latter carries the effects of both thermal fluctuations and "quantum fluctuations". As a paradigm system, we refer to a harmonic oscillator undergoing dissipation as described by the Caldeira-Leggett master equation [12,13]. The mechanism of dissipation in the hydrodynamic picture is discussed. We further address the possibility of a dynamical transition, induced by dissipation, to a classical-statistical regime characterized by purely *classical* moments [9]. Importantly, a hydrodynamic force, now of purely classical origin, persists in this description. (iii) The extension of the hydrodynamic formulation to non-adiabatic dynamics [8]. This opens up a systematic avenue to molecular quantum dynamics in excited electronic states. We propose a general formulation that, by describing the coupling between electronic populations and coherences, properly takes into account coherent effects in the dynamics. For the particular case of pure states, the coupled-state equations by Wyatt et al. [14] are recovered.

In a recent development [15,16] which highlights the distinction between the dynamical descriptions in Liouville phase space vs. hydrodynamic phase space, we have suggested a new mixed quantum-classical dynamical scheme associated with *partial* moments. Here, a hydrodynamic description is chosen for the quantum subsystem while the classical subsystem is treated in a Liouville-space framework. The method in its general form again applies to mixed quantum states, the dynamics of which is then characterized by a family of partial moments $\langle \mathcal{P}^n \rho \rangle_{qQP} = \int dp\; p^n \rho_W(q,p,Q,P)$, with (q,p) referring to the quantum, hydrodynamic degree of freedom and (Q,P) referring to the classical degree of freedom. For pure quantum states, the moment hierarchy again terminates with the zeroth and first order, by analogy with the case of a single "Bohmian" degree of freedom. Equations of motion are obtained for classical Liouville-space trajectories coupled to hydrodynamic quantum trajectories that are subject to a modified quantum force [16]. This approach provides a new and consistent picture of quantum-classical coupling.

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