Quantum Liouville-space trajectories for dissipative systems

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In this paper we present a new quantum-trajectory based treatment of quantum dynamics suitable for dissipative systems. Starting from a de Broglie/Bohm-like representation of the quantum density matrix, we derive and define quantum equations-of-motion for Liouville-space trajectories for a generalized system coupled to a dissipative environment. Our theory includes a vector potential which mixes forward and backwards propagating components and non-local quantum potential which continuously produces coherences in the system. These trajectories are then used to propagate an adaptive Lagrangian grid which carries the density matrix, $\rho(x,y)$, and the action, $A(x,y)$, thereby providing a complete hydrodynamic-like description of the dynamics.

The causal or hydrodynamic trajectory model of quantum mechanics provides a useful glimpse into the dynamics underlying the quantum wavefunction. Starting from the time-dependent Schrödinger equation, one can derive quantum trajectory equations by casting the wavefunction in polar form, $\psi = R \exp(iS/\hbar)$ and subsequently separating $\psi$ into real and imaginary components. The resulting equations are a continuity equation for the quantum density, $\rho = R^2$, and “Newtonian” equations for trajectories. The distinguishing feature of these quantum equations-of-motion is the presence of the non-local quantum potential, $Q$, which both introduces non-local coupling between the trajectories and represents a differential geometric constraint between the extrinsic curvature invariants of a surface generated by $z = C \ln R$ and the action per unit volume of a trajectory element. This prescription introduced independently by de Broglie and Madelung, and later developed by Bohm has been used primarily as an interpretive tool where one first solves the time-dependent Schrödinger equation for the wavefunction, $\psi(x,t)$, and then uses $\bar{\psi}$ as an ancillary field to drive an ensemble of quantum trajectories. Furthermore, there has been a recent surge of activity to use this approach to develop new adaptive-grid based methods for performing quantum dynamical calculations. Such ab initio approaches construct $\psi$ directly from the dynamical information obtained in computing the trajectories. While it is unclear at this time whether such approaches offer considerable computational advantages over more standard finite-basis set or fixed grid approaches, the appeal is that by moving to a particle-based description, computational effort required scales almost linearly with the number of trajectories introduced.

In this letter we derive a causal-trajectory approach for the quantum density matrix under dissipative conditions. So far as we know, this is the first presentation of such an approach and certainly is the first ab initio application. The formal construction presented here is similar in spirit to the Wigner phase-space representation which is widely used for quantum dissipative dynamics in both the quantum and semi-classical regimes; however, our approach does not require the definition of a quantum phase space and retains all of the physical properties associated with the quantum density matrix. Secondly, we describe an ab initio approach for computing the trajectories based upon a finite-element/least squares procedure. This provides a highly efficient and adaptive scheme which can be applied to a wide variety of systems. Moreover, the computational effort scales almost linearly with number of finite-elements/trajectories. In this letter we focus upon the construction of the underlying theory with application towards the relaxation of a tagged oscillator in contact with an environment.

The theory is initiated by writing the density matrix as $\rho(x,y) = \psi(x)\psi^*(y)$. If $\rho$ represents the entire system+bath ensemble, its evolution is given by the Liouville-von Neumann equation, $\dot{\rho} = L\rho$, where $L$ is the full Liouville operator which we decompose into system and bath components: $L = L_s + L_b + L_{sb}$. If we take the bath as an ensemble of harmonic oscillators with masses, $m_n$, and frequencies, $\omega_n$, which is at thermal equilibrium at $t = 0$ coupled to the system coordinate, $x$, via a linear combination $x = \sum_n c_n q_n$, then the response of the bath to this coupling is encoded in the correlation functions $\langle h(\nu(t) + i\eta(t)) \rangle = \langle x(t)x(0) \rangle/\tau$ where $\langle \ldots \rangle_T$ denotes the expectation value taken in the thermal equilibrium state of the bath. The real and imaginary parts of this correlation function are the noise and dissipation kernels. This procedure is starting point of many quantum statistical mechanical treatments and the result is either a master equation for $\dot{\rho}_s$, or a path-integral treatment for propagator. Various forms of the master equation have been presented in the literature by a number of groups including Caldeira and Leggett, Unruh and Zurek, and by Hu and co-workers. Each of these is slightly different...
in final form due to the various approximations made over the course of the derivation. Consequently, each possesses certain regions of validity. Without loss of generality, we will focus our attention here on the Caldeira-Leggett (CL) model whereby the noise and dissipation terms take the form \(v(t) = \frac{\gamma}{\lambda^2} \delta(t)\) and \(\eta(t) = -\gamma \delta(t)\). This model is strictly valid in the high-temperature regime where the thermal excitations in the bath dominate and fluctuations of the vacuum can be ignored. Here, the master equation for the reduced density matrix is given by

\[
\partial_t \rho = \hat{L_s} \rho - \gamma(x-y)(\partial_x \rho - \partial_y \rho) - \frac{\gamma}{2\lambda^2} (x-y)^2 \rho. \tag{1}
\]

Here, \(\hat{L_s}\) denotes the system Liouvillian where the potential energy term has been renormalized due to the interaction with the bath. For a harmonic system, the renormalized oscillator frequency is related to the bare frequency, \(\omega\), by \(\tilde{\omega}^2 = \omega^2 - 2\gamma \omega / \pi\). The last two terms are related to interaction between the system and the bath. The second being responsible for population relaxation and the third for coherence relaxation. Finally \(\lambda = \hbar / \sqrt{2mkT}\) is the thermal de Broglie wavelength and \(\gamma\) is the coupling strength.

To make the connection to a quantum trajectory scheme, we write the density matrix in complex polar form, \(\rho_s(x,y) = \exp(\mathcal{g}(x,y) + iA(x,y)/\hbar)\), and insert this into the master equation for \(\rho_s(x,y)\). In what follows, we shall take \(x\) as the coordinate associated with \(\psi(x)\) and \(y\) as the coordinate associated with the complex conjugate, \(\psi^*(y)\). Our Liouville space is then the two-dimensional configuration space \([x,y]\) with phase-space defined as \([x, p_x, y, p_y]\) where \(p_x = \partial_x A\) and \(p_y = -\partial_y A\). The \(-\) sign in the definition of the canonical momentum in \(y\) reflects the time-reversed dynamics in the \(y\) direction. In a geometric-optical construction, the wavefront for the density matrix is given by contours of constant \(S(x) + S(y) = \text{c}\) with velocities and momenta are both normal to these curves. For non-dissipative dynamics, the Hamilton-Jacobi equation for the action \(A(x,y)\) is separable into forward (in \(x\)) and backward (in \(y\)) propagating components:

\[
\frac{\partial A}{\partial t} = -\frac{1}{2m} (p_x^2 - p_y^2) - \mathcal{V} - \mathcal{Q}, \tag{2}
\]

where \(\mathcal{V} = V(x) - V(y)\) and \(\mathcal{Q} = Q(x) - Q(y)\). The quantum potential, \(Q(x) = -\hbar^2 (\partial_x^2 g + \partial_y^2 \partial_x g) / 2m\), introduces non-local interactions between the trajectories but does not couple motion in \(x\) and \(y\). The resulting equations of motion take the form, \(m \nu \dot{\mu} = \nu\mu\), where upon taking the time derivative yields Bohm’s quantum equations of motion in \(x\) and \(y\): \(m \ddot{\nu} (x,y) = \pm \partial_x (V + Q)\) (– for \(x\) and + for \(y\)). We also have the continuity equation for \(g\): \(2 \dot{\gamma} = -\partial_x \nu^2\).

Taking the CL equation and using the substitution \(\log \rho = g + iA/\hbar\) as before again yields a Hamilton-Jacobi equation for \(A(x,y)\):

\[
\partial_t A + \frac{1}{2m} (p_x^2 - p_y^2) - \gamma(x-y)(p_x - p_y) + \mathcal{V} + \mathcal{Q} = 0.
\]

However, this equation now sports an explicit coupling between the forward and backward propagating paths. This dissipative coupling term involving \(\gamma(x-y)\) can be cast as a vector potential, \(\Gamma = \pm \gamma (x-y)\) where – is for \(x\) and + is for \(y\). Using this we define the components of the material velocities as \(m \ddot{\nu} (x,y) = \pm \partial_x (V + Q)\) which describe the velocities of the particles in the presence of dissipation.

At this point we find it easier to work in the rotated coordinate frame given by \(\xi = (x+y)/\sqrt{2}\) and \(\eta = (y-x)/\sqrt{2}\). In this frame, the quantum Lagrangian is

\[
\mathcal{L} = -m \dot{\xi} \dot{\eta} + 2m \gamma \eta \dot{\xi} - \mathcal{V} - \mathcal{Q}. \tag{3}
\]

Here the quantum potential is given by

\[
\mathcal{Q} = \frac{\hbar^2}{m} (\partial_\xi \partial_\eta \nu + \partial_\xi \partial_\eta \nu), \tag{4}
\]

and \(\mathcal{V} = V(x) - V(y)\). In this new frame, the canonical momenta are given by \(p_\xi = -\partial \mathcal{L} / \partial \dot{\eta}\) and \(p_\eta = -\partial \mathcal{L} / \partial \dot{\xi}\). This modified relation between the canonical momenta and the Lagrangian is again due to the time-reversed dynamics in \(y\). The resulting material velocities are then

\[
\dot{\eta} = p_\eta / m + 2 \gamma \eta \text{ and } \dot{\xi} = p_\xi / m. \tag{5}
\]

Finally, the continuity equation for \(g\) is given in the rotated frame as

\[
\frac{dg}{dt} = -\frac{1}{2} \left[ \partial_\xi \dot{\xi} + \partial_\eta \dot{\eta} \right] + \gamma - \frac{2\gamma}{\lambda^2} \eta^2. \tag{6}
\]
This equation includes a term proportional to $\eta^2$ which dampens components of the density matrix which are far from the diagonal axis leaving the elements along the $\xi$-axis unchanged. This is the process of decoherence, i.e. the dynamical diagonalization of the density matrix due to the interaction with the environment. \[4\]

We take as an example problem the case of harmonic oscillator embedded in a dissipative bath. Such a system could easily represent a vibrational coordinate of a molecule that has been displaced from its equilibrium position by some action at $t = 0$. Our computational methodology is based upon the moving weighted least-squares (MWLS) method reported by Lopreore and Wyatt and reader is referred to Ref.\[5\] for details of this approach and to Ref.\[6\] for our implementation as applied to quantum wavepacket dynamics. \[15\]

Taking $k$ as the renormalized force constant and $\omega^2 = k/m$, the quantum Lagrangian is

$$L = -m\dot{\xi}\ddot{\eta} + 2m\gamma\dot{\xi}\eta + k\xi\eta - Q.$$ \(7\)

Using the Euler-Lagrange equations, we can derive equations of motion for the Liouville space quantum trajectories:

$$\ddot{\xi} = -\omega^2\xi - \frac{1}{m}Q\eta - 2\gamma\dot{\xi},$$ \(8\)

$$\ddot{\eta} = -\omega^2\eta - \frac{1}{m}Q\xi + 2\gamma\dot{\eta}. $$ \(9\)

Defining the semi-classical limit as $\hbar \to 0$ so that $Q$ vanishes, the equations of motion are trivial to solve. For motion in $\xi$ we have damped harmonic motion which is easy to understand in terms of pure populational relaxation. However, in $\eta$, the trajectories diverge towards $\pm\infty$.

This introduces a small problem in our computational scheme, namely, all of the non-diagonal grid points are swept away as the calculation progresses. To circumvent this, we re-meshed the grid periodically by discarding the off-diagonal trajectories and re-initiating $\rho$, $g$, and $A$ at the new points via least-squares interpolation. We also took advantage of the parity of these functions under $\eta \to -\eta$ by explicitly propagating only the upper triangle of each and selecting polynomial bases which carried the appropriate symmetry. To wit: $g(\xi, \eta) = g(\xi, -\eta)$, $A(\xi, \eta) = -A(\xi, -\eta)$, $Q(\xi, \eta) = -Q(\xi, -\eta)$, $v_\xi(\xi, \eta) = v_\xi(\xi, -\eta)$, $v_\eta(\xi, \eta) = -v_\eta(\xi, -\eta)$. These symmetries were enforced throughout the calculation.

As an initial example, we consider the relaxation of a density matrix corresponding to the ground state displaced from equilibrium by a shift in $x$.

$$g(0) = g_0 - \frac{1}{2\sigma_0^2}((\xi - \xi_0)^2 + \eta^2) $$ \(10\)

In the plots shown here, we scaled the time units in terms of the oscillator period $\tau = 2\pi/\omega$ and lengths by the initial width of the gaussian density matrix, $\sigma_0^2 = \hbar/m\omega$.

In the Fig. 1, we show an ensemble of quantum trajectories corresponding to diagonal element of the density matrix (i.e. $\eta = 0$) at $kT = 2.5\hbar\omega$ in the underdamped ($\gamma/\omega = 0.25$) and critically damped ($\gamma/\omega = 1$) regimes. The superimposed dashed line is the semi-classical trajectory obtained by solving Eq.\(8\) in the limit of $\hbar \to 0$. As one expects, the the semi-classical result follows the peak of the gaussian. Furthermore, the diagonal trajectories are not allowed to cross one another. This is a directly analogous to the non-crossing rule for ordinary quantum trajectories. Each diagonal element carries a unique populational trajectory which must remain single-valued. As time progresses the trajectories become stationary corresponding to thermal equilibrium.

In Fig. 2 we show the time evolution of the gaussian coefficients $\sigma_\xi$ and $\sigma_\eta$ for various temperatures and coupling constants. At thermal equilibrium, these quantities should become stationary and can be computed from equilibrium statistical mechanics,

$$\sigma_{\xi,eq}^2 = \sigma_{\xi,0}^2\coth(\hbar\omega\beta/2)$$ \(11\)

$$\sigma_{\eta,eq}^2 = \sigma_{\eta,0}^2\tanh(\hbar\omega\beta/2). $$ \(12\)

For the critically damped case, we see exponential relaxation back to equilibrium. For $\sigma_\xi$, the relaxation is largely independent of temperature and each case reaches the equilibrium value at $t/\tau = 1$. The relaxation of the coherence width, $\sigma_\eta$, shows a strong temperature dependence, relaxing faster at higher temperatures. Moreover, the time-scale for coherence relaxation is considerably shorter than in $\sigma_\xi$. This is due to the fact that the thermal de Broglie wavelength, $\lambda$, sets both a length and

![FIG. 2: Relaxation of $\sigma_\xi$ and $\sigma_\eta$ at various temperatures in the overdamped ($\gamma/\omega = 1.75$), underdamped ($\gamma/\omega = 0.25$), and critically damped ($\gamma/\omega = 1$) regimes.](image)
time-scale for decoherence. As temperature increases, this length decreases and the relaxation rate increases. The underdamped case shows rather interesting dynamics by relaxing through a series of intermediate plateaus. Finally, the overdamped case relaxes slower than the critically damped without the plateaus seen in the underdamped case.

The picture we are lead to is that the dissipative coupling to the environment causes a net flux of trajectory elements (representing population coherence information) towards $\eta \to \pm \infty$ and causes the populations along the $\eta = 0$ axis to relax to some lowest energy configuration. At $T = 0$ this would be the quantum ground state of the system. At finite temperature the system becomes stretched in $\xi$ reflecting a thermal distribution of energy states. Furthermore, the coherence length as set by the de Broglie wavelength, becomes more and more short ranged as $T$ increases causing the system to become localized in $\eta$, effectively diagonalizing the density matrix. In the equations-of-motion, both the quantum potential and the vector potential, $\Gamma$, force particles to stream outwards in $\eta$ away from the diagonal. Consequently, even when the system becomes stationary (i.e. $\dot{g} = 0$) the trajectories themselves remain in constant motion reflecting the continuous influx and efflux of energy between the system and the bath and the continuous streaming of coherence from the system into the bath degrees of freedom. This continual “production” of coherence is ultimately traced to the non-local nature of the quantum potential, $Q$.

We present here a novel extension of the de Broglie/Bohm quantum theory of motion into Liouville space and use this to propagate quantum trajectories for the density matrix of a system in contact with a thermal bath. This approach opens a clear avenue to a number of new semi-classical and quantum-classical approximations for the quantum density matrix. Furthermore, the formalism itself offers an interesting dynamical twist to interpreting decoherence and population relaxation.

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