# Quantifying Early Time Quantum Decoherence Dynamics through Fluctuations

Bing Gu[†] and Ignacio Franco[*,†,‡]

[†]Department of Chemistry and [‡]Department of Physics, University of Rochester, Rochester, New York 14627, United States

ABSTRACT: We introduce a general but simple relation between the timescale for quantum coherence loss and the initial fluctuations of operators that couple a quantum system with a surrounding bath. The relation allows the prediction and measurement of early time decoherence dynamics for any open quantum system, through purity, without reconstructing the system's many-body density matrix. It is applied to predict the decoherence time for basic models—the Holstein chain, spin-boson and Caldeira-Legget models—commonly employed to capture electronic, vibrational, and vibronic dynamics in molecules. Such development also offers a practical platform to test the ability of approximate quantum dynamics methods to capture decoherence. In particular, a class of mixed quantum-classical schemes for molecular dynamics where the bath is treated classically, such as Ehrenfest dynamics, are shown to correctly capture short-time decoherence when the initial conditions are sampled from the Wigner distribution. These advances provide a useful platform to develop decoherence times for molecular processes and to test approximate molecular dynamics methods.
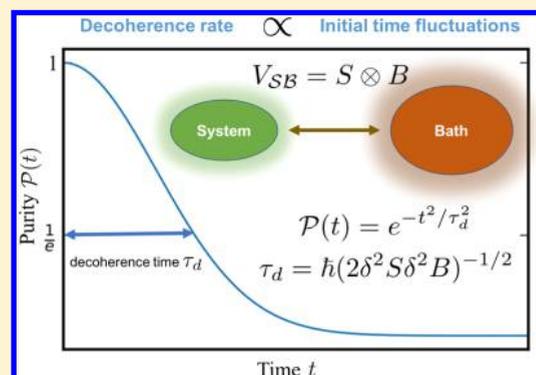
The loss of quantum coherence is a fundamental and ubiquitous process in nature that occurs in any quantum system coupled to an environment, e.g., electrons coupled to vibrations, or vibrations in the presence of solvent. Understanding decoherence is central to our description of a variety of quantum mechanical phenomena that play an important role in understanding molecular processes, including interference, adiabatic and nonadiabatic molecular dynamics, measurement, and the quantum-classical transition.[1−6] During decoherence, a system changes from a pure state $\sigma = |\psi\rangle\langle\psi|$ to a mixed state $\sigma = \sum_i w_i |\psi_i\rangle\langle\psi_i|$ ($\omega_i > 0$). Such a process reduces the ability of a system to fully exhibit its quantum mechanical features.

In spite of its central role in quantum mechanical processes, determining decoherence timescales remains an open challenge because purity and other well-defined basis-independent measures of decoherence[7] are based on the full many-body density matrix of the system $\sigma(t)$, which is an experimentally and theoretically removed quantity.[8,9] Experimental and numerical efforts to monitor decoherence dynamics are thus forced to do so indirectly via other physical observables that reflect off-diagonal elements of $\sigma(t)$ expressed in a given basis, but that are not necessarily indicative of state purity.[2] For instance, in spectroscopic experiments, the decay of laser-induced polarization is often used as a measure of decoherence. The polarization informs about the decay of off-diagonal elements in the system's density matrix expressed in the energy eigenbasis.[10−12] However, as a measure of decoherence, such an approach is limited by the fact that polarization only reflects coherences between states with nonzero transition dipoles. Further, the absence of polarization does not necessarily imply decoherence as, for instance, a pure state prepared in an energy

eigenstate with no net dipole will exhibit zero polarization. Other commonly used observables such as transport, line-shapes, and interference can only offer a basis-dependent perspective on the decoherence dynamics that is not necessarily informative of state purity.[13−16] Ongoing efforts[2,17−19] to understand the role of quantum decoherence in molecules and materials are currently limited by our ability to directly monitor state purity.

In this Letter, we introduce a general theory that relates the short-time purity dynamics to the initial-time fluctuations of operators that couple a system with a surrounding bath. This theory is based on a perturbative expansion of purity that is useful in capturing the initial decoherence dynamics for systems in interaction with non-Markovian baths. The resulting expression permits quantifying short-time decoherence time-scales through experimentally and computationally accessible quantities. It also opens the way to establish rigorous decoherence times for basic chemical processes, and to test the ability of approximate quantum dynamics methods to correctly capture decoherence. The considerations below apply to any system-bath Hamiltonian with an initially pure system.

To proceed, consider a general quantum system ($\mathcal{S}$) coupled to an environment ($\mathcal{B}$), with Hamiltonian $H = H_\mathcal{S} + H_\mathcal{B} + H_{\mathcal{SB}}$ where $H_\mathcal{S}$ describes the system, $H_\mathcal{B}$ the bath, and

$$H_{S\mathcal{B}} = \sum_\alpha S_\alpha \otimes B_\alpha \tag{1}$$

the system−bath interactions. Here S_α (or B_α) is an operator defined in the Hilbert space of $\mathcal{S}$ (or $\mathcal{B}$). The dynamics of the composite system with density matrix ρ is governed by the von Neumann equation $i\hbar\frac{d}{dt}\rho = [H, \rho] = H\rho - \rho H$ and generally leads to entanglement between $\mathcal{S}$ and $\mathcal{B}$, and thus to decoherence.

As a well-defined basis-independent measure of decoherence, we focus on the purity $\mathcal{P}(t) = \mathrm{Tr}_S\{\sigma^2(t)\} \leq 1$ which measures the nonidempotency of the reduced density matrix of the system of interest $\sigma(t) = \mathrm{Tr}_{\mathcal{B}}\{\rho(t)\}$, where Tr_A denotes a partial trace over the degrees of freedom of $A = \{\mathcal{S}, \mathcal{B}\}$. The quantity $\mathcal{P} = 1$ for pure states, and $\mathcal{P} < 1$ for mixed states. To define a decoherence time, we assume that the system is initially in a pure state. This implies that $\mathcal{P}(0) = 1$ and that the initial system-bath state is not entangled, such that $\rho(0) = \sigma(0) \otimes \rho_{\mathcal{B}}(0)$ where $\rho_{\mathcal{B}}(t)$ is the reduced density matrix for the bath.

To capture the short-time purity dynamics, it is natural to expand the von Neumann equation around initial time $t = 0$ in Schrödinger picture as done in ref 20. That procedure leads to a formal expression for the decoherence time τ_d that, while general, is of limited utility because it depends on the many-body reduced density matrix σ and requires performing operations with the full Hamiltonian H. Below we overcome these limitations and derive a universal and simple formula for τ_d that clearly exposes the basic physics behind the early time decoherence dynamics. To do so, we exploit the general form for $H_{S\mathcal{B}}$ in eq 1 and work in the interaction picture of $H_S + H_{\mathcal{B}}$ to considerably reduce the complexity of the calculation and be able to isolate the full consequences of the short time expansion. In the interaction picture, the von Neumann equation is given by

$$i\hbar\frac{d}{dt}\tilde{\rho}(t) = [\tilde{H}_{S\mathcal{B}}, \tilde{\rho}(t)] \tag{2}$$

where $\tilde{O} = U^\dagger O U$ denotes the operator O in the interaction picture. In turn, $U(t) = U_S(t) \otimes U_{\mathcal{B}}(t)$ is the evolution operator of the noninteracting (i.e., $H_{S\mathcal{B}} = 0$) composite system, where $U_A(t)$ denotes the evolution operator for subcomponent A.

To determine the purity, it suffices to isolate the reduced density matrix for the system in the interaction picture, i.e., $\tilde{\sigma} = \mathrm{Tr}_{\mathcal{B}}\{\tilde{\rho}\}$. This is because the purity in the interaction and Schrödinger picture coincide, i.e., $\mathcal{P} = \mathrm{Tr}_S\{\sigma^2\} = \mathrm{Tr}_S\{\tilde{\sigma}^2\}$. To capture the short-time purity dynamics, we perform a second-order expansion in time of eq 2 around $t = 0$ and then trace over the bath. Specifically, $\tilde{\rho}(t) = \rho(0) + t\frac{d}{dt}\tilde{\rho}(t)\big|_{t=0} + \frac{t^2}{2}\frac{d^2}{dt^2}\tilde{\rho}(t)\big|_{t=0}$, where we have taken into account that at initial time $\tilde{O}(0) = O(0)$. The first-order derivative can be obtained by setting $t = 0$ in eq 2 $\frac{d}{dt}\tilde{\rho}(t)\big|_{t=0} = \frac{1}{i\hbar}[H_{S\mathcal{B}}, \rho(0)]$. The second-order derivative is obtained by differentiating eq 2 with respect to time and setting $t = 0$,

$$\frac{d^2}{dt^2}\tilde{\rho}(t)\Big|_{t=0} = \frac{1}{(i\hbar)^2}[H_{S\mathcal{B}}, [H_{S\mathcal{B}}, \rho(0)]] + \frac{1}{i\hbar}\left[\frac{d}{dt}\tilde{H}_{S\mathcal{B}}(t)\Big|_{t=0}, \rho(0)\right]$$

Inserting these two expressions into $\tilde{\rho}(t)$ and tracing out the bath, one obtains

$$\tilde{\sigma}(t) = \sigma(0) + (-it/\hbar)\sigma^{(1)} + \frac{1}{2}(-it/\hbar)^2\sigma^{(2)} \tag{3}$$

where $\sigma^{(1)} = \mathrm{Tr}_{\mathcal{B}}\{[H_{S\mathcal{B}}, \rho(0)]\}$ and $\sigma^{(2)} = \mathrm{Tr}_{\mathcal{B}}\left\{[H_{S\mathcal{B}}, [H_{S\mathcal{B}}, \rho(0)]] + \left[i\hbar\frac{d}{dt}\tilde{H}_{S\mathcal{B}}(t)\Big|_{t=0}, \rho(0)\right]\right\}$. Such $\tilde{\sigma}(t)$ can be used to calculate the purity at short times

$$\mathcal{P}(t) = 1 + (-it/\hbar)^2\mathrm{Tr}_S\{\sigma(0)\sigma^{(2)} + (\sigma^{(1)})^2\} \tag{4}$$

where we have taken into account $\mathcal{P}(0) = 1$ and that the first-order contribution vanishes as $\mathrm{Tr}_S[\sigma(0)\sigma^{(1)}] = 0$ due to the invariance of the trace under cyclic permutation. Equation 4 recovers the well-known Gaussian decay[20] for the initial purity dynamics $\mathcal{P}(t) = \exp(-t^2/\tau_d^2)$ where

$$\tau_d = \hbar\,\mathrm{Tr}_S[\sigma(0)\sigma^{(2)} + (\sigma^{(1)})^2]^{-1/2} \tag{5}$$

is the decoherence time, that has been observed in spin,[21] electronic[22−24] and vibrational decoherence.[25]

A remarkably simple expression for τ_d results by taking advantage of the form for $H_{S\mathcal{B}}$ in eq 1. Introducing eq 1 into $\sigma^{(1)}$ and $\sigma^{(2)}$ yields

$$\sigma^{(1)} = \sum_\alpha [S_\alpha, \sigma(0)]\langle B_\alpha\rangle$$

$$\sigma^{(2)} = \sum_{\alpha,\beta} ([S_\alpha S_\beta, \sigma(0)]_+ - 2S_\beta\sigma(0)S_\alpha)\langle B_\alpha B_\beta\rangle$$
$$+ \sum_\alpha [[S_\alpha, H_S], \sigma(0)]\langle B_\alpha\rangle + \sum_\alpha [S_\alpha, \sigma(0)]\langle [B_\alpha, H_{\mathcal{B}}]\rangle \tag{6}$$

where $[A, B]_+ = AB + BA$ is the anticommutator. Using eq 6 in eq 5 and simplifying yields the decoherence time

$$\tau_d = \hbar\left(2\sum_{\alpha\beta}\Delta^{\mathcal{B}}_{\alpha\beta} \times \Delta^S_{\alpha\beta}\right)^{-1/2} \tag{7}$$

where $\Delta^S_{\alpha\beta} \equiv \langle S_\alpha S_\beta\rangle - \langle S_\alpha\rangle\langle S_\beta\rangle$ and $\Delta^{\mathcal{B}}_{\alpha\beta} = \langle B_\alpha B_\beta\rangle - \langle B_\alpha\rangle\langle B_\beta\rangle$ are the crossed fluctuations of the system and bath operator that enter into $H_{S\mathcal{B}}$. Surprisingly, the decoherence time only depends on $H_{S\mathcal{B}}$, with no dependence on the system or bath Hamiltonian.

Equation 7 is the first result of this Letter. It applies to any initially pure system provided the system-bath interaction can be written in the form of eq 1 and does not invoke common approximations employed in open quantum system dynamics such as harmonic baths, pure dephasing dynamics and rotating-wave approximations. As such, it generalizes previous efforts to develop decoherence times for specific models[20,26] and pure dephasing dynamics.[1,27] Equation 7 is symmetric with respect to $\mathcal{S} \leftrightarrow \mathcal{B}$ reflecting the inherent system-bath symmetry in the Hamiltonian. However, this does not imply that the decoherence time for system and bath are identical, as in eq 7 we have supposed that only the system is pure. In the particular case where both system and bath are initially pure, then τ_d for system and bath coincide in agreement with the Schmidt theorem.[28]

At a qualitative level, eq 7 demonstrates that the initial system and bath state controls the decoherence by influencing the magnitude of the fluctuations in the operators that enter into $H_{S\mathcal{B}}$. The larger the crossed fluctuations, the faster the decoherence. This essential feature of eq 7 is best appreciated in the specific case where there is only one term contributing to $H_{S\mathcal{B}} = S \otimes B$. In this case, eq 7 simplifies to

$$\tau_d = \hbar (2\delta^2 B \delta^2 S)^{-1/2} \tag{8}$$

that directly signals an inverse relation between decoherence time and the magnitude of initial-time physical fluctuations of the system and bath operators, $\delta^2 B \equiv \langle B^2 \rangle - \langle B \rangle^2$ and $\delta^2 S \equiv \langle S^2 \rangle - \langle S \rangle^2$, that enter into $H_{S\mathcal{B}}$.

Importantly, eq 7 makes the decay of purity at early times an experimentally and computationally accessible quantity. This is because it avoids reconstructing the full many-body density matrix of the system to determine the decoherence dynamics. Instead, it requires measuring $\Delta_{\alpha\beta}^{S}$ and $\Delta_{\alpha\beta}^{\mathcal{B}}$ which are few-body quantities accessible in simulations and experiments. The crossed fluctuations $\Delta_{\alpha\beta}^{S}$ and $\Delta_{\alpha\beta}^{\mathcal{B}}$ are determined at initial time and require no dynamical propagation. Further, $\Delta_{\alpha\beta}^{S}$ (or $\Delta_{\alpha\beta}^{\mathcal{B}}$) depends only on the system (or bath) and, thus, to determine τ_d it is sufficient to analyze properties of the isolated system and bath. Experimentally determining the decoherence time requires identifying the relevant interaction between system and bath, and then measuring the associated fluctuations.

A convenient feature of the analysis is that the effects of independent baths to the decoherence are just additive in τ_d^{-2}. This is because the crossed fluctuations between operators from different baths vanish. Thus, it is straightforward to consider the cumulative effect of competing decoherence sources, e.g., the effect of solvent and vibrations to electronic decoherence in molecules. For a system interacting with multiple baths $k = 1, \cdots, N_{\mathcal{B}}$, the total purity function is given as a product

$$\mathcal{P}(t) = \prod_{k=1}^{N_{\mathcal{B}}} \mathcal{P}^{(k)}(t) = \exp\left(-t^2 \sum_k (\tau_d^{(k)})^{-2}\right) \tag{9}$$

where $\mathcal{P}^{(k)}(t)$ is the purity decay due to bath k with decoherence timescale $\tau_d^{(k)}$.

While the early time Gaussian decay of purity does not necessarily quantify the complete decoherence dynamics of molecular systems, experiments in spin[21] systems, and computations for electronic[22−24] and vibrational[25] decoherence have identified the Gaussian decay to be a dominant event in the decoherence dynamics in condensed phase environments. In an analysis of a pure-dephasing spin-boson problem,[1] the Gaussian decay is seen to dominate for times $t < \Omega^{-1}$, where Ω is the cutoff frequency of the ohmic harmonic bath. In the long time limit, the bath induces an exponential decay of coherence. Thus, the Gaussian decay is expected to be important for non-Markovian baths as is often the case in chemical dynamics.

Equation 7 makes it straightforward to calculate decoherence timescales for *any* system-bath model relevant in chemistry in the short time regime, and to recover expressions that have been developed for specific models. For example, consider first the well-known spin-boson model describing a two-level system coupled to a harmonic bath.[26,29] This model has been widely used to study electronic decoherence in condensed phase environments,[26] and electronic excitations of biomolecules and quantum dots in solvents.[30] The Hamiltonian for this model is

given by $H = \frac{\epsilon_0}{2}\sigma_z + \Delta\sigma_x + \frac{1}{2}q_0\sigma_z \sum_\mu c_\mu x_\mu + H_{\mathcal{B}}$ where ϵ_0 and Δ are system coefficients, q_0 is the system-bath interaction strength, σ_i ($i = x, y, z$) are the spin-$\frac{1}{2}$ Pauli matrices expressed in eigenbasis of σ_z ($\sigma_z | \pm \rangle = \pm | \pm \rangle$) and $\sum_\mu c_\mu x_\mu$ is a collective spatial coordinate of the harmonic bath. The bath Hamiltonian $H_{\mathcal{B}} = \sum_\mu \left(\frac{p_\mu^2}{2m_\mu} + \frac{1}{2}m_\mu\omega_\mu^2 x_\mu^2 \right)$ is composed of a collection of independent oscillators with frequencies $\{\omega_\mu\}$, displacements $\{x_\mu\}$, momenta $\{p_\mu\}$ and associated masses $\{m_\mu\}$. Generally, the dynamics of this model is not pure dephasing in nature as $[H_{S\mathcal{B}}, H_S] \neq 0$. Identifying $B = \sum_\mu c_\mu x_\mu$ and $S = \frac{1}{2}q_0\sigma_z$, $\delta^2 B = \sum_{\mu\nu} \frac{1}{Z_\beta} c_\mu c_\nu \mathrm{Tr}_{\mathcal{B}}[e^{-\beta H_{\mathcal{B}}} x_\mu x_\nu]$ for a bath initially at thermal equilibrium of inverse temperature $\beta = 1/k_B T$ and partition function $Z_\beta = \mathrm{Tr}_{\mathcal{B}}[e^{-\beta H_{\mathcal{B}}}]$, where we have used $\langle x_\mu \rangle = 0$. The above expression can be evaluated by taking into account that[31]

$$\langle x_\mu | e^{-\beta H_\mu} | x_\mu \rangle$$
$$= \left(\frac{m_\mu\omega_\mu}{2\pi\hbar \sinh(\beta\hbar\omega_\mu)} \right)^{1/2} \exp\left(-\frac{m_\mu\omega_\mu x_\mu^2}{\hbar \sinh(\beta\hbar\omega_\mu)} (\cosh(\beta\hbar\omega_\mu) - 1) \right)$$

to yield $\delta^2 B = \sum_\mu \frac{c_\mu^2}{2m_\mu\omega_\mu} \coth(\beta\hbar\omega_\mu/2)$. In the continuous limit, the variance is given by an integral form $\delta^2 B = \int J(\omega) \coth(\beta\hbar\omega/2) \, d\omega$, where $J(\omega) \equiv \sum_\mu \frac{c_\mu^2}{2m_\mu\omega_\mu} \delta(\omega - \omega_\mu)$ is the spectral density. For a general initial state of the system $|\psi\rangle = c_+ |+\rangle + c_- |-\rangle$, $\delta^2 S = q_0^2 |c_+|^2 |c_-|^2$, and

$$\tau_d = \hbar (q_0 |c_+||c_-|)^{-1} \left(2 \int J(\omega) \coth(\beta\hbar\omega/2) d\omega\right)^{-1/2} \tag{10}$$

which is consistent with the results in ref 26 and the basis for an often-used expression for the electronic decoherence time.

As a second example, consider now the Caldeira-Legget model for quantum Brownian motion in which a harmonic oscillator with coordinate X couples with harmonic bath through $H_{S\mathcal{B}} = X \sum_\mu c_\mu x_\mu$. This model is often employed to capture vibrational dynamics of molecules in condensed phase environments.[32,33] In this case, we identify $S = X$ and $B = \sum_\mu c_\mu x_\mu$ is identical to the spin-boson case. Thus,

$$\tau_d = \hbar (2\delta^2 X \int J(\omega) \coth(\beta\hbar\omega/2) d\omega)^{-1/2} \tag{11}$$

in agreement with ref 20.

As a third model, we now focus on the Holstein Hamiltonian for molecular crystals.[34] This is a basic model for vibronic interactions in molecules and solids.[35,36] A decoherence timescale due to electron-vibrational interactions has not been developed for this model. The Hamiltonian consists of an electronic tight-binding chain, where each site μ in the chain couples to an independent harmonic oscillator of identical mass M and frequency ω_0. The system−bath interaction in this case is $H_{S\mathcal{B}} = -g\sqrt{2M\omega_0} \sum_\mu n_\mu x_\mu$, where x_μ is the μth oscillator displacement, g is the electron−phonon coupling strength, and $n_\mu = a_\mu^\dagger a_\mu$ (where $a_\mu^\dagger$ creates an electron in site μ) is the Fermionic number operator in the site basis. Due to the additive properties of the decoherence time for independent baths, it suffices to consider the interaction with a single harmonic mode μ and then add over each of these contributions. For a thermal bath this yields

$$\tau_{\mathrm{d}}^{-2} = 2g^2 \coth(\beta\hbar\omega_0/2) \sum_\mu (\langle n_\mu^2 \rangle - \langle n_\mu^2 \rangle) \tag{12}$$

which characterizes the temperature dependence of the decoherence on this many-body molecular system. Equation 12 indicates that for temperatures $T < \hbar\omega_0/2k_{\mathrm{B}}$ the decoherence is independent of temperature and determined by zero-point fluctuations of the bath. For $T > \hbar\omega_0/2k_{\mathrm{B}}$ temperature-dependent effects arise because the excited states of the bath are thermally occupied and lead to additional sources of decoherence. In fact, the decoherence time decreases monotonically with increasing T because of the increased fluctuations of the x_μ in the harmonic bath. At $T \gg \hbar\omega_0/2k_{\mathrm{B}}$, the decoherence time decreases like $\tau_{\mathrm{d}} \sim 1/\sqrt{T}$. Further, eq 12 reveals that electronic states for which there is larger fluctuation in the site occupation numbers will exhibit faster decoherence. Interestingly, it also determines the dependence of the decoherence with chain length. If the fluctuations of the site occupations are comparable among sites, $\tau_{\mathrm{d}} \sim 1/\sqrt{N}$, where N is the number of sites. This decrease in the decoherence time with system size N is a consequence of the product properties of the purity.

This analysis can also be used to test the accuracy of approximate quantum dynamics methods to capture system-bath entanglement. This is useful because, for realistic system-bath problems, exact reference full quantum solutions are often not available to validate approximate methods. An alternative, in this context, is to perform a short-time analysis of the approximate equations of motion and then compare with the exact result in eq 7. This strategy can be used when the equations of motion of the approximate method directly follows $\sigma(t)$.

As a specific case of significant practical importance, consider quantum molecular dynamic simulations in the condensed phase. A commonly used approach is mixed quantum-classical methods[37,38] where the dynamics of the bath is treated classically by propagating an ensemble of trajectories, while the system is described using quantum mechanics. An important, and currently open, question is whether this class of simulations capture decoherence correctly.

As a third contribution of this Letter, below we demonstrate that a class of quantum-classical schemes, that includes Ehrenfest dynamics, can offer the correct short-time decoherence dynamics. This is so provided that the initial classical distribution for the quantum-classical trajectories satisfies the same crossed fluctuations as the true quantum state that it seeks to represent, and that the system couples to the bath through functions of position or momentum only.

To see this, consider a generic quantum-classical method where the full quantum dynamics is represented by an ensemble of quantum-classical trajectories. The classical dynamics of the kth trajectory for the bath is deterministic and given by Newton's equations of motion $\dot{\mathbf{R}}^{(k)} = \mathbf{M}^{-1}\mathbf{P}^{(k)}$, $\dot{\mathbf{P}} = -\nabla V(\mathbf{R}^{(k)})$, where $\mathbf{R}^{(k)}$ is a vector of the positions of all particles in the bath with conjugate momentum $\mathbf{P}^{(k)}$, $V(\mathbf{R}^{(k)})$ is some effective potential, and $\mathbf{M}$ is a diagonal matrix with the masses in the diagonal. In turn, the quantum system responds instantaneously to the classical motion and satisfies $i\hbar\dot{\sigma}^{(k)}(t) = [H(\mathbf{R}^{(k)}(t)), \sigma^{(k)}(t)]$, where $H(\mathbf{R}^{(k)}(t)) = H_S + H_{\mathrm{SB}}(\mathbf{R}^{(k)}(t))$. The reduced density matrix for the system is obtained by averaging over trajectories, $\overline{\sigma}(t) = \sum_k \sigma^{(k)}(t)/N_{\mathrm{traj}}$, where N_{traj} is the total number of trajectories. Because the system is

supposed to be pure at initial time, the initial density matrix for all trajectories coincide, i.e., $\sigma^{(k)}(0) = \sigma(0)$.

To proceed, we now perform a short time analysis of the equations of motion in the interaction picture of H_S. To second-order in time,

$$\tilde{\sigma}^{(k)}(t) = \sigma(0) - \frac{it}{\hbar}[H_{S\mathcal{B}}^{(k)}, \sigma(0)]$$
$$- \frac{t^2}{2\hbar^2}\left(\left[i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\tilde{H}_{S\mathcal{B}}^{(k)}\Big|_{t=0}, \sigma(0)\right] + [H_{S\mathcal{B}}^{(k)}, [H_{S\mathcal{B}}^{(k)}, \sigma(0)]]\right)$$

We consider interaction forms in which the bath couples to the system through its coordinates, i.e., $H_{S\mathcal{B}} = \sum_\alpha f_\alpha(\mathbf{R})S_\alpha$ where S_α is a system operator and $f_\alpha(\mathbf{R})$ is a general function of the bath position coordinates. Taking the ensemble average over trajectories and using

$$\frac{\mathrm{d}}{\mathrm{d}t}\tilde{H}_{S\mathcal{B}}\Bigg|_{t=0}$$
$$= \sum_\alpha (\dot{\mathbf{R}}(0)\cdot\nabla f_\alpha[\mathbf{R}(0)]S_\alpha + (1/i\hbar)f_\alpha[\mathbf{R}(0)][S_\alpha, H_S])$$

we get an equation for the ensemble-averaged reduced density matrix analogous to eq 3, $\overline{\tilde{\sigma}} = \sigma_0 + (-it/\hbar)\sigma_{\mathrm{cl}}^{(1)} + \frac{1}{2}(-it/\hbar)^2\sigma_{\mathrm{cl}}^{(2)}$. Here

$$\sigma_{\mathrm{cl}}^{(1)} = \sum_\alpha \overline{f_\alpha}[S_\alpha, \sigma(0)],$$

$$\sigma_{\mathrm{cl}}^{(2)} = \sum_{\alpha,\beta} \overline{f_\alpha f_\beta}\,([S_\alpha S_\beta, \sigma(0)]_+ - 2S_\alpha\sigma(0)S_\beta)$$
$$+ \sum_\alpha (i\hbar\overline{\dot{\mathbf{R}}\cdot\nabla f_\alpha}[S_\alpha, \sigma(0)] + \overline{f_\alpha}[[S_\alpha, H_S], \sigma(0)]) \tag{13}$$

where the bar denotes an ensemble average over a classical distribution of initial conditions $\rho_{\mathcal{B}}^c(\mathbf{R}, \mathbf{P})$.

The purity can be calculated in a fashion analogous to eqs 4–7, to give

$$\tau_{\mathrm{d,MQC}} = \hbar(2\sum_{\alpha\beta} \Delta_{\alpha\beta}^{\mathcal{S}}\Delta_{\alpha\beta}^{\mathcal{B}_{\mathrm{cl}}})^{-1/2} \tag{14}$$

where $\Delta_{\alpha\beta}^{\mathcal{B}_{\mathrm{cl}}} \equiv \overline{f_\alpha(\mathbf{R})f_\beta(\mathbf{R})} - \overline{f_\alpha(\mathbf{R})}\,\overline{f_\beta(\mathbf{R})}$. Comparing eq 7 with eq 14, it becomes evident that the mixed quantum-classical scheme offers the correct short-time purity dynamics provided that the initial classical distribution has crossed fluctuations identical to the quantum ones, i.e., when $\Delta_{\alpha\beta}^{\mathcal{B}_{\mathrm{cl}}} = \Delta_{\alpha\beta}^{\mathcal{B}}$. For example, if $\rho_{\mathcal{B}}^c(\mathbf{R}, \mathbf{P})$ is chosen to be the Wigner distribution $\tau_{\mathrm{d, MQC}} = \tau_{\mathrm{d}}$. More generally, any initial classical distribution whose marginals correctly capture the quantum probability distribution in $\mathbf{R}$, i.e., distributions such that $\int d\mathbf{P}\rho_{\mathcal{B}}^c(\mathbf{R}, \mathbf{P}) = \langle\mathbf{R}|\rho_\mathcal{B}|\mathbf{R}\rangle$, like the one employed in Bohmian dynamics,[39,40] will suffice. This remarkable result is valid for *any* type of bath and system–bath interactions of the form $H_{\mathrm{SB}} = \sum_n f_n(\mathbf{R})S_n$, including anharmonic baths and nonlinear system-bath couplings.

System-bath couplings through positions are adequate to describe electrostatic system–bath interactions, such as those of a molecule in the condensed phase. By symmetry, the quantum-classical scheme will also offer the correct purity dynamics for $H_{S\mathcal{B}} = \sum_\alpha f_\alpha(\mathbf{P})S_\alpha$ provided that the distribution of classical

initial conditions mimics the correct momentum distribution of the quantum state of the bath. These two cases cover system-bath couplings encountered in problems of chemical interest. For even more general system-bath couplings of the form $H_{SB} = \sum_\alpha f_\alpha(\mathbf{R}, \mathbf{P}) S_\alpha$ the mixed quantum-classical scheme will recover the decoherence dynamics if the distribution of initial conditions correctly captures all the crossed fluctuations between the $\{f_\alpha(\mathbf{R}, \mathbf{P})\}$. This condition is not usually satisfied by the Wigner distribution because the classical distribution function cannot reflect the commutation relation between position and momentum operators.

Further note that the dynamics of the classical bath could be on any potential energy surface, and that this choice will not affect the estimate of the initial decoherence time. In light of this, it follows that eq 14 also applies to stochastic dynamics for the bath space because only the initial conditions, and not the equation of motion for the trajectories, is required to obtain it. As a particular case of these general observations, we conclude that the commonly used Ehrenfest approach[41] offers a correct short time decoherence dynamics when the trajectories are initially sampled through Wigner distribution.[42]

In conclusion, we have developed a method to theoretically quantify or experimentally measure early time decoherence dynamics that does not require knowledge of the full many-body density matrix of the system, making decoherence timescales accessible to both theory and experiments. The method applies to any system–bath problem, and is particularly useful in cases where the initial Gaussian purity decay dominates the decoherence dynamics, as expected for molecular systems in condensed phase environments. Specifically, we isolated a general relation eq 7 between the Gaussian short-time purity dynamics $\mathcal{P}(t) = e^{-t^2/\tau_d^2}$ and the crossed fluctuations of the components of the system–bath interaction which are (experimentally and numerically accessible) few-body quantities. This relation provides a convenient platform to determine decoherence times for any system–bath interaction as demonstrated using the Holstein, spin-boson and Caldeira–Legget models. A particularly important feature of eq 7 is that, in the short-time, purity decay due to competing decoherence processes is multiplicative or, equivalently, τ_d^{-2} is additive. This structure allows dealing with multiple baths in a simple way in which each of their effects can be considered separately, and then combined at the purity level.

Computationally, eq 7 provides means to determine decoherence times without propagating system–bath dynamics, or invoking approximations such as the rotating wave, pure dephasing or harmonic bath approximation. It also constitutes a useful testbed for approximate description of system–bath quantum dynamics. In particular, we demonstrated that a class of mixed quantum-classical schemes for molecular dynamics, that includes Ehrenfest dynamics, correctly capture the decoherence time when the initial conditions for the trajectories are sampled from the Wigner distribution of the quantum state. These developments provide a well-defined theoretical platform to quantify decoherence using approximate methods for quantum dynamics.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ignacio.franco@rochester.edu.

ORCID

Ignacio Franco: 0000-0002-0802-8185

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Breuer, H.-P.; Petruccione, F. *The theory of open quantum systems*; Oxford University Press: Oxford, U.K., 2002.

(2) Scholes, G. D.; et al. Using coherence to enhance function in chemical and biophysical systems. *Nature* 2017, 543, 647−656.

(3) Zurek, W. H. Decoherence, einselection, and the quantum origins of the classical. *Rev. Mod. Phys.* 2003, 75, 715.

(4) Amico, L.; Fazio, R.; Osterloh, A.; Vedral, V. Entanglement in many-body systems. *Rev. Mod. Phys.* 2008, 80, 517.

(5) Schlosshauer, M. A. *Decoherence and the quantum-to-classical transition*; Springer: Berlin Heidelberg, 2007.

(6) Joos, E.; Zeh, H. D.; Kiefer, C.; Giulini, D. J.; Kupsch, J.; Stamatescu, I.-O. *Decoherence and the appearance of a classical world in quantum theory*; Springer: Berlin Heidelberg, 2013.

(7) Rényi, A. On measures of entropy and information. *Proceedings of the fourth Berkeley symposium on mathematical statistics and probability*; University of California Press: Berkeley, CA, 1961; pp 547−561.

(8) Franco, I.; Appel, H. Reduced purities as measures of decoherence in many-electron systems. *J. Chem. Phys.* 2013, 139, 094109.

(9) Kar, A.; Franco, I. Quantifying fermionic decoherence in many-body systems. *J. Chem. Phys.* 2017, 146, 214107.

(10) Engel, G. S.; Calhoun, T. R.; Read, E. L.; Ahn, T.-K.; Mancal, T.; Cheng, Y.-C.; Blankenship, R. E.; Fleming, G. R. Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems. *Nature* 2007, 446, 782−786.

(11) Collini, E.; Wong, C. Y.; Wilk, K. E.; Curmi, P. M. G.; Brumer, P.; Scholes, G. D. Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature. *Nature* 2010, 463, 644−647.

(12) Zewail, A. H. Optical molecular dephasing: principles of and probings by coherent laser spectroscopy. *Acc. Chem. Res.* 1980, 13, 360−368.

(13) Wang, Y.-T.; Tang, J.-S.; Wei, Z.-Y.; Yu, S.; Ke, Z.-J.; Xu, X.-Y.; Li, C.-F.; Guo, G.-C. Directly Measuring the Degree of Quantum Coherence using Interference Fringes. *Phys. Rev. Lett.* 2017, 118, 020403.

(14) Kubo, R. *Advances in Chemical Physics*; John Wiley & Sons, Inc.: New York, 2007; pp 101−127.

(15) Allen, L.; Eberly, J. *Optical Resonance and Two-level Atoms*; Dover: Mineola, NY, 1975.

(16) Ballmann, S.; Härtle, R.; Coto, P. B.; Elbing, M.; Mayor, M.; Bryce, M. R.; Thoss, M.; Weber, H. B. Experimental Evidence for Quantum Interference and Vibrationally Induced Decoherence in Single-Molecule Junctions. *Phys. Rev. Lett.* 2012, 109, 056801.

(17) Gong, J.; Brumer, P. When is Quantum Decoherence Dynamics Classical? *Phys. Rev. Lett.* 2003, 90, 50402.

(18) Izmaylov, A. F.; Franco, I. Entanglement in the BornOppenheimer Approximation. *J. Chem. Theory Comput.* 2017, 13, 20−28.

(19) Kar, A.; Chen, L.; Franco, I. Understanding the Fundamental Connection Between Electronic Correlation and Decoherence. *J. Phys. Chem. Lett.* 2016, 7, 1616−1621.

(20) Kim, J. I.; Nemes, M. C.; de Toledo Piza, A. F. R.; Borges, H. E. Perturbative Expansion for Loss. *Phys. Rev. Lett.* 1996, 77, 207−210.

(21) de Lange, G.; Wang, Z. H.; Ristè, D.; Dobrovitski, V. V.; Hanson, R. Universal Dynamical Decoupling of a Single Solid-State Spin from a Spin Bath. *Science* 2010, 330, 60−63.

(22) Franco, I.; Brumer, P. Electronic coherence dynamics in trans-polyacetylene oligomers. *J. Chem. Phys.* 2012, 136, 144501.

(23) Vacher, M.; Bearpark, M. J.; Robb, M. A.; Malhado, J. a. P. Electron Dynamics upon Ionization of Polyatomic Molecules:

Coupling to Quantum Nuclear Motion and Decoherence. *Phys. Rev. Lett.* **2017**, *118*, 083001.

(24) Arnold, C.; Vendrell, O.; Santra, R. Electronic decoherence following photoionization: Full quantum-dynamical treatment of the influence of nuclear motion. *Phys. Rev. A: At., Mol., Opt. Phys.* **2017**, *95*, 033425.

(25) Joutsuka, T.; Thompson, W. H.; Laage, D. Vibrational Quantum Decoherence in Liquid Water. *J. Phys. Chem. Lett.* **2016**, *7*, 616−621.

(26) Prezhdo, O. V.; Rossky, P. J. Relationship between Quantum Decoherence Times and Solvation Dynamics in Condensed Phase Chemical Systems. *Phys. Rev. Lett.* **1998**, *81*, 5294−5297.

(27) Akimov, A. V.; Prezhdo, O. V. Persistent electronic coherence despite rapid loss of electron-nuclear correlation. *J. Phys. Chem. Lett.* **2013**, *4*, 3857−3864.

(28) Ekert, A.; Knight, P. L. Entangled quantum systems and the Schmidt decomposition. *Am. J. Phys.* **1995**, *63*, 415−423.

(29) Leggett, A. J.; Chakravarty, S.; Dorsey, A. T.; Fisher, M. P. A.; Garg, A.; Zwerger, W. Dynamics of the dissipative two-state system. *Rev. Mod. Phys.* **1987**, *59*, 1−85.

(30) Gilmore, J.; McKenzie, R. H. Spin boson models for quantum decoherence of electronic excitations of biomolecules and quantum dots in a solvent. *J. Phys.: Condens. Matter* **2005**, *17*, 1735.

(31) Feynman, R. P.; Hibbs, A. R. *Quantum Mechanics and Path Integrals*; McGraw-Hill: New York, 1965.

(32) Caldeira, A.; Leggett, A. Quantum tunnelling in a dissipative system. *Ann. Phys.* **1983**, *149*, 374−456.

(33) Gottwald, F.; Ivanov, S. D.; Kühn, O. Applicability of the Caldeira-Leggett Model to Vibrational Spectroscopy in Solution. *J. Phys. Chem. Lett.* **2015**, *6*, 2722−2727.

(34) Holstein, T. Studies of polaron motion. *Ann. Phys.* **1959**, *8*, 325−342.

(35) West, B. A.; Womick, J. M.; McNeil, L. E.; Tan, K. J.; Moran, A. M. Influence of Vibronic Coupling on Band Structure and Exciton Self-Trapping in alpha-Perylene. *J. Phys. Chem. B* **2011**, *115*, 5157−5167.

(36) Chen, L.; Zhao, Y.; Tanimura, Y. Dynamics of a One-Dimensional Holstein Polaron with the Hierarchical Equations of Motion Approach. *J. Phys. Chem. Lett.* **2015**, *6*, 3110−3115.

(37) Kapral, R.; Ciccotti, G. Mixed quantum-classical dynamics. *J. Chem. Phys.* **1999**, *110*, 8919−8929.

(38) Tully, J. C. Molecular dynamics with electronic transitions. *J. Chem. Phys.* **1990**, *93*, 1061−1071.

(39) Gu, B.; Franco, I. Partial hydrodynamic representation of quantum molecular dynamics. *J. Chem. Phys.* **2017**, *146*, 194104.

(40) Gu, B.; Hinde, R. J.; Rassolov, V. A.; Garashchuk, S. Estimation of the Ground State Energy of an Atomic Solid by Employing Quantum Trajectory Dynamics with Friction. *J. Chem. Theory Comput.* **2015**, *11*, 2891−2899.

(41) Li, X.; Tully, J. C.; Schlegel, H. B.; Frisch, M. J. Ab initio Ehrenfest dynamics. *J. Chem. Phys.* **2005**, *123*, 084106.

(42) Hillery, M.; O'Connell, R.; Scully, M.; Wigner, E. Distribution functions in physics: Fundamentals. *Phys. Rep.* **1984**, *106*, 121−167.