Decoherence in a Nonequilibrium Environment:
An Analytically Solvable Model

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In this letter, we describe an analytically solvable model of quantum decoherence in a nonequilibrium environment. The model considers the effect of a bath from equilibrium by, for example, an ultrafast excitation of a quantum chromophore. The nonequilibrium response of the environment is represented by a nonstationary random function corresponding to the fluctuating transition frequency between two quantum states coupled to the surroundings. The nonstationary random function is characterized by a Fourier series with the phase of each term starting initially with a definite value across the ensemble but undergoing random diffusion with time. The decay of the off-diagonal density matrix element is shown to depend significantly on the particular pattern of initial phases of the terms in the Fourier series, or equivalently, the initial phases of bath modes coupled to the quantum subsystem. This suggests the possibility of control of quantum decoherence by the detailed properties of an environment that is driven from thermal equilibrium.

Quantum interference and coherence are phenomena that set the dynamics of molecular scale systems in distinct contrast with the behavior of the macroscopic classical world [1]. In chemical physics applications, the creation, evolution, and destruction of quantum coherence plays a central role in a range of physical processes, such as the harvesting and transport of electronic energy in photobiological systems [2–8], the design and interpretation of nonlinear spectroscopies [9], the coherent control of molecular processes [10–12], the manipulation and storage of quantum information [13, 14], and many others [15–17].

Quantum coherence exists and is most pronounced in simple few body systems. Decoherence—irreversible destruction of quantum coherence—is a phenomenon that is associated with complex systems and the resulting interactions between a coherent subsystem and a many-dimensional environment or bath. System-bath interactions can never be eliminated completely, and so decoherence is in principle always at work eroding quantum superpositions to their incoherent statistical limits. In most formal approaches to dissipative quantum dynamics, the assumption is made that the environment is in thermal equilibrium characterized by a Boltzmann distribution at temperature T [19, 20]. This is a reasonable approximation in most contexts, and greatly simplifies the theoretical analysis.

We conjecture, however, that there are situations where nonequilibrium bath effects may be important. For example, light-induced ultrafast coherent electronic processes in chemical or biological systems may occur on time scales that are sufficiently short that initial nonequilibrium states induced in the bath by the excitation may not have a chance to regress to equilibrium. The transient nonequilibrium bath dynamics may undergo nontrivial interplay with the coherent quantum evolution occurring on comparable time scales. On these time scales, the environment has the opportunity to influence the quantum evolution in a manner that is more rich and complex than simply acting to dissipate energy and randomize and destroy quantum phases. Indeed, recent experiments have suggested that the environmental protein dynamics in light harvesting complexes may play an essential role in enhancing quantum energy transport [2–8]. In the proposed picture, bath fluctuations aid quantum energy flow by overcoming localization due to energy site inhomogeneities, while at the same time acting to destroy quantum phase coherence. The details of the process matter.

Previous theoretical investigations of environmental effects on quantum coherent dynamics have taken a description of the environment as a thermal reservoir, usually with Markovian statistical properties [9, 19, 20]. While this is an important limiting case that undoubtedly describes many dissipative quantum processes quite adequately, we believe that nonequilibrium bath effects leading to nonstationary statistics offer a broad and richly expanded range of possible dynamical effects in some cases of ultrafast quantum transport. Life could have exploited these effects in the design of quantum processes by evolution.

In this letter, we investigate the dynamics of quantum decoherence in nonequilibrium environments. We consider a two level quantum system in a nonequilibrium bath, modeled by random perturbations with nonstationary statistics. Our model allows an approximate analytic solution for the time evolution of the off-diagonal density matrix element ρ_{12} of the density operator describing the two level quantum system interacting with the environment. By introducing a simple and specific ansatz for the dependence of the initial oscillator phases on frequency in terms of a single adjustable parameter, we demonstrate that significant modification of the decoherence process can result from variations of this parameter.

Our model consists of a two level quantum system described by density operator $\hat{\rho}(t)$ [9, 19, 20] with energy

gap $E_2(t) - E_1(t) = \hbar\omega(t)$ that fluctuates due to the effect of the environment, where $E_j(t)$ $(j = 1, 2)$ is the instantaneous energy of state j as perturbed by the surroundings. The bath is modeled by a random function of time. This function represents the transition frequency of the two state quantum system $\omega(t)$, and the Fourier components of the time series represent the modes of motion of the bath. In contrast with the usual treatment [9, 19, 20], the statistical properties of this random function are nonstationary, corresponding physically to impulsively excited phonons of the environment with initial phases that are *not* random, but which have a sharp relation at $t = 0$. The distribution of phases then spreads with time over the interval $(0, 2\pi)$ under a diffusion equation. Well-defined initial phases of a phonon bath could result, for instance, by an ultrafast excitation of a quantum system that abruptly changed its size or charge distribution at $t = 0$, leading to systematic and reproducible mode-specific short time bath response.

An initial coherence between the two states $\langle 1|\hat{\rho}(t)|2\rangle = \rho_{12}(t)$ will decay due to the environment according to the expression [9, 19, 20]

$$\rho_{12}(t) = \left\langle e^{-i\int_o^t \delta\omega(s)ds} \right\rangle e^{-i\omega_o t} \equiv F(t)e^{-i\omega_o t}, \quad (1)$$

where $\omega(t) = \omega_o + \delta\omega(t)$ and $\langle\ldots\rangle$ represents a nonequilibrium average over the nonstationary random bath. The term ω_o represents the average frequency difference, while the average of the fluctuating term $\delta\omega(t)$ is zero. This defines the function $F(t)$, which we will use in our analysis.

The time-dependent frequency is written in the form $\omega(t) = \omega_o + \delta\omega(t)$, where

$$\delta\omega(t) = \sum_{k=1}^{\infty} c_k \cos(\omega_k t + \theta_k(t)). \quad (2)$$

The Fourier components c_k are positive constants related to the spectral density of the environment and the coupling of the bath modes to the quantum system. In this model the randomness enters only through the *non-stationary* distribution of random phases $\theta_k(t)$. These phases are given by

$$\theta_k(t) = \theta_k(0) + x_k(t). \quad (3)$$

The random function $x_k(t)$ is described by a time-dependent probability distribution $P_k(x_k, t)$ that obeys a diffusion equation

$$\frac{\partial P_k(x,t)}{\partial t} = D_k \frac{\partial^2 P_k(x,t)}{\partial x^2}, \quad (4)$$

where D_k is the diffusion constant. The initial state consists of a distribution localized at $x = 0$: $P_k(x, 0) = \delta(x)$. The quantity x is an angle, so $P(x + 2\pi, t) = P(x, t)$ is

a periodic function of x with period 2π. A 2π-periodic δ function can be written in Fourier series form as

$$\delta(x) = \frac{1}{2\pi} + \frac{1}{\pi}\sum_{n=1}^{\infty}\cos(nx). \quad (5)$$

The time-dependent probability distribution for component k that solves Eq. (4) with this initial condition is

$$P_k(x,t) = \frac{1}{2\pi} + \frac{1}{\pi}\sum_{n=1}^{\infty} e^{-n^2 D_k t}\cos(nx_k). \quad (6)$$

Physically, the phase of each component of the random force is *not* random at $t = 0$, when an impulsive excitation creates a quantum coherence in the system, but decays to a uniform $1/2\pi$ distribution under diffusive evolution with diffusion constant D_k. The bath is thus not initially at equilibrium.

In Fig. 1 we show for illustration an example of a nonstationary random function described by the phase diffusion model in Eq.(2). An ensemble of 500 realizations of the random time series is generated, and the minimum and maximum resulting functions span the shaded region. The width of this region is initially zero but grows with time, illustrating the diffusive loss of initial phase memory. Representative evolution of the probability distribution $P(x, t)$ is shown in Fig. 2.
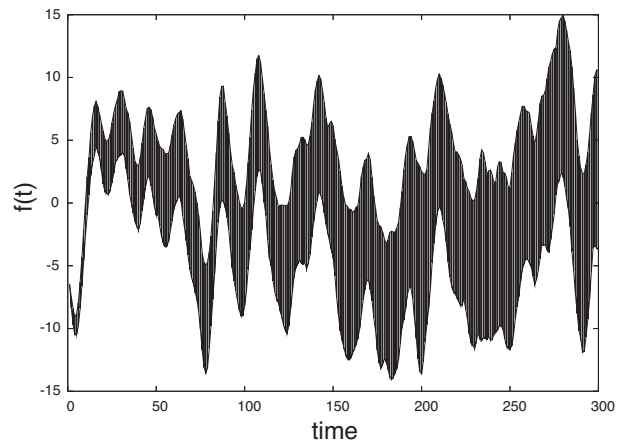

FIG. 1. Illustrative example of a nonstationary random function described by the phase diffusion model in Eq.(2). An ensemble of 500 realizations of the random time series is generated, and the minimum and maximum resulting functions span the shaded region. The width of this region is initially zero but grows with time, illustrating the diffusive loss of initial phase memory.

We now evaluate the time evolution of the off-diagonal density matrix element. The nonequilibrium averaged coherence is given by

$$\rho_{12}(t) = \left\langle e^{-i\int_0^t \omega(s)ds} \right\rangle = \prod_k \left\langle e^{-i\int_0^t \delta\omega_k(s)ds} \right\rangle e^{-i\omega_o t}. \quad (7)$$
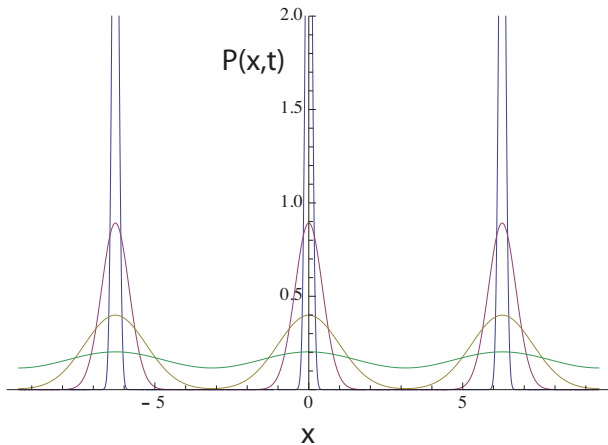
FIG. 2. Evolving probability distribution $P(x,t)$ for the variation of the oscillator phase $\theta(t) = \theta(0) + x(t)$ given by Eq. (6) for $D = 0.1$, at times $t = 0.05, 1, 5,$ and 20.

We consider a typical factor $f_k(t) = \exp(-\int_o^t \delta\omega_k(s)ds)$. Performing the time integral gives

$$\int_0^t \delta\omega_k(s)\,ds \simeq z_k\left[\sin(\omega_k t + \theta_k(0) + x_k(t)) - \sin(\theta_k(0))\right], \tag{8}$$

where $c_k/\omega_k \equiv z_k$. This is an approximate expression, due to the dependence of the integrand on the *random* function $x_k(t)$; we adopt it here for simplicity. Alternatively, we could take Eq. (8) as the *definition* of our nonstationary stochastic time series representing the evolution of the phase.

We now evaluate the average of $\exp(-iz_k\sin(\omega_k t + \theta_k(0) + x_k))$ over the probability distribution $P_k(x_k, t)$:

$$f_k(t) = \left\langle e^{-iz_k \sin(\omega_k t + \theta_k(0) + x_k)}\right\rangle e^{iz_k \sin(\theta_k(0))}, \tag{9}$$

which gives

$$f_k(t) = e^{iz_k \sin(\theta_k(0))}$$
$$\times \sum_{n=-\infty}^{\infty} (-1)^n J_n(z_k) e^{in(\omega_k t + \theta_k(0))} e^{-n^2 D_k t}, \tag{10}$$

where $J_n(z)$ is a Bessel function of order n and argument z. As $t \to 0$ we see that $f_k(0) = 1$, as it should. For $t \to \infty$ we find that $f_k(t) \to J_0(z_k)e^{iz_k \sin(\theta_k(0))}$. This is a number whose absolute value is less than unity, so the product of factors $\prod_{k=1}^{\infty} f_k(\infty) \to 0$ as the number of factors goes to infinity, as expected for a correlation function.

By performing a Taylor series expansion of $f_k(t)$ in powers of z_k and keeping only the most slowly decaying terms, a simple but accurate approximation can be derived:

$$f_k(t) \simeq \exp(iu_k(t) - v_k(t)). \tag{11}$$

Here,

$$u_k(t) = -z_k(e^{-D_k t}\sin(\omega_k t + \theta_k(0)) - \sin(\theta_k(0))) \tag{12}$$

and

$$v_k(t) = \frac{z_k^2}{4}\left(1 - 2e^{-2D_k t} + W_k(t)\cos[2(\omega_k t + \theta_k(0))]\right), \tag{13}$$

where

$$W_k(t) = e^{-2D_k t} - e^{-4D_k t}. \tag{14}$$

We note that the more rapidly decaying term with time dependence of e^{-4Dt} must be retained to give $|f_k(0)| = 1$.

The modulus function $|F(t)|$ is given by

$$|F(t)| = \left|\prod_k f_k(t)\right| \simeq e^{-\beta(t)}, \tag{15}$$

where

$$\beta(t) = \frac{1}{4}\int_0^{\infty} d\omega g(\omega)z(\omega)^2 \tag{16}$$
$$\times \left(1 - 2e^{-2D(\omega)t} + W(\omega, t)\cos[2(\omega t + \theta(\omega))]\right).$$

Here, $g(\omega)$ is the spectral density of the environment, and a continuum limit $\sum_k \ldots \to \int_0^{\infty} g(\omega)\ldots d\omega$ has been taken.

We now investigate the dependence of the coherence dynamics and decoherence on the detailed nature of the initial bath excitation. To explore the general question of sensitivity of dephasing to these initial phases in a concrete example, we consider one simple model. We make a simple Gaussian approximation to the product of density of states and squared coupling, and take

$$g(\omega)z(\omega)^2 = \frac{A}{\sqrt{2\pi}\omega_c}e^{-\omega^2/2\omega_c^2}, \tag{17}$$

where $A = N_{\text{eff}}z_{\text{eff}}^2$; here N_{eff} is the effective number of bath modes, z_{eff} is the effective coupling, and ω_c is a measure of the frequency range of the bath modes. We also take $D(\omega) = D$, a constant independent of ω. The key quantity to consider in terms of the effect of the initial phases of the bath modes is the function $\theta(\omega)$. There are of course a wide range of possible forms this can take. We adopt a very simple one parameter linear dependence of $\theta(\omega)$ on ω, and take

$$\theta(\omega) = -\lambda\omega. \tag{18}$$

Within this narrow set of possible phase relations, we explore the ability to control dephasing by varying the *single parameter* λ.

Evaluating the integral for $\beta(t)$ for this model yields

$$\beta(t; \lambda) = \frac{1}{8}N_{\text{eff}}z_{\text{eff}}^2$$
$$\times \left[1 - e^{-2Dt}\left(1 - e^{-2\omega_c^2(t-\lambda)^2}\right)\right.$$
$$\left. - e^{-4Dt}e^{-2\omega_c^2(t-\lambda)^2}\right] \tag{19}$$

This result demonstrates an element of controllability of the coherence $\rho_{12}(t)$, whose modulus $|F(t)| = \exp(-\beta(t;\lambda))$. The modulus drops from its initial value of unity toward its asymptotic value $|F(t \to \infty)| = \exp\left(-\frac{1}{8}N_{\text{eff}} z_{\text{eff}}^2\right)$ at the intermediate time $t = \lambda$, but then *rephases* back to the slowly decaying envelope $\exp\left(-\frac{1}{8}N_{\text{eff}} z_{\text{eff}}^2 \left[1 - e^{-2Dt}\right]\right)$. As λ becomes large and positive, or assumes negative values, the decay approaches the envelope function without the nonmonotomic "dip". This behavior is illustrated in Fig. 3.
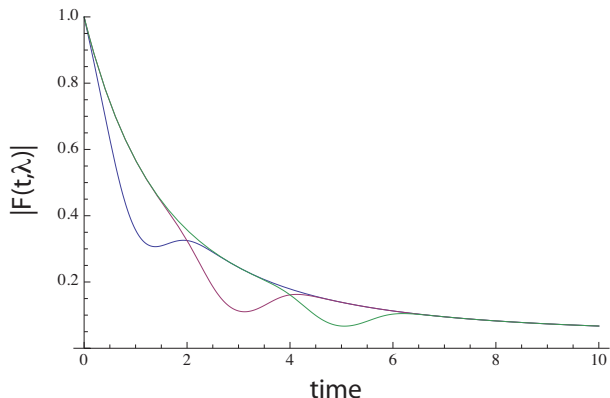

FIG. 3. Comparison of $|F(t;\lambda)|$ *vs.* t for $\lambda = 1$ (blue), $\lambda = 3$ (red) and $\lambda = 5$ (green). The parameters are $N_{\text{eff}} = 100$, $z_{\text{eff}} = 0.5$, $D = 0.1$, and $\omega_c = 1$. Note the dip around $t = \lambda$, showing nonmonotonic decay of the coherence controllable by varying λ.

The simple relation $\theta(\omega) = -\lambda\omega$ is an idealized and minimalistic model allowing the nature of the relative oscillator phases to be varied systematically. Much more rich and variable relations can be contemplated, which in turn will undoubtedly allow more elaborate control of the decoherence dynamics. This will be explored in future work.

In conclusion, we have shown that the decoherence behavior of a two state quantum system interacting with an initially *nonequilibrium* bath can be controlled by manipulating the nature of the relative initial phases of the bath modes. In this work, we have treated a simple model of a special case for illustration. The general phenomenon of environmental modes prepared initially with a well-defined initial phase by optical excitation of a system chromophore seems to be a situation in many-body ultrafast dynamics that has received little attention. By engineering these initial phases, the character, and in particular, the dephasing, of subsequent quantum dynamics can potentially be controlled, in a manner reminiscent of a coherent control experiment using shaped pulses [10–12]. Here, however, the control field is derived not from a shaped laser pulse but rather from the well-defined phase relations between the modes of the many-body bath. In living systems, ultrafast quantum dephasing in a nonequilibrium environment provides another possible handle on biophysical processes that could be exploited by natural selection, and it is of interest to explore whether the signature of this optimization can be found in the quantum dynamics of, for example, biological light harvesting systems.

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