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Hierarchy of Stochastic Pure States for Open Quantum System Dynamics

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We derive a hierarchy of stochastic evolution equations for pure states (quantum trajectories) for open quantum system dynamics with non-Markovian structured environments. This *hierarchy of pure states* (HOPS) is generally applicable and provides the exact reduced density operator as an ensemble average over normalized states. The corresponding nonlinear equations are presented. We demonstrate that HOPS provides an efficient theoretical tool and apply it to the spin-boson model, the calculation of absorption spectra of molecular aggregates, and energy transfer in a photosynthetic pigment-protein complex.

The treatment of the dynamics of realistic open quantum systems still poses both conceptual and computational challenges. These arise from non-Markovian behavior due to a structured environment or strong system-environment interaction [1,2]. Severe assumptions, like the weak-coupling or Markov approximation, are often made for practical reasons. However, they fail for many systems of interest. Non-Markovian systems are far more challenging and, for example, may be treated with path integral approaches [3,4] or hierarchical equations of motion [5,6] for the system's reduced density matrix.

In this Letter, we follow a different strategy and derive a hierarchy of stochastic differential equations for pure states in the system Hilbert space (quantum trajectories). From this hierarchy of pure states (HOPS), the exact reduced density operator is obtained as an ensemble average. Quantum trajectories are well established in the Markov case, where single realizations describe continuously measured open quantum systems or serve as models for spontaneous wave function collapse. The generalization to the non-Markovian regime proves challenging and is an active field of research. Non-Markovian quantum state diffusion (NMQSD) derived in its general form in Refs. [7–10] constitutes a theory for non-Markovian quantum trajectories. Other stochastic approaches with various levels of applicability have been suggested [11–13]. NMQSD provides a framework for the still-debated problem of non-Markovian continuous measurement theory [14,15], non-Markovian spontaneous wave function collapse [16], and complex open quantum dynamics. Examples for the latter are energy transfer in photosynthesis [17,18] and absorption of self-assembled dye aggregates [19].

Although the NMQSD approach is formally exact, it is difficult to handle because of the appearance of a functional derivative with respect to a stochastic process. In previous works, we have replaced that functional derivative by an operator ansatz. For a few cases, an exact explicit expression for that operator ansatz is known (see, e.g., [20–23]).

In general, however, to determine the assumed operator (approximately), we dealt with it in the so-called zeroth order functional expansion approximation [17,24–26] that agrees remarkably well with established results for a large number of problems. However, in certain cases this method is known to fail (see, e.g., [17,26]). In Ref. [27], a hierarchical approach is applied to the operator ansatz of the functional derivative.

It is important to realize that, prior to the present work, we were able to obtain a nonlinear NMQSD equation for normalized states only by assuming the replacement ansatz for the functional derivative [10]. The existence of such a nonlinear evolution equation is fundamental for an interpretation in terms of wave function collapse or measurement-conditioned dynamics as well as necessary for an efficient sampling in trajectory-based open system dynamics. The HOPS approach to NMQSD presented in this Letter does not rely on the ansatz and, thus, without further ado provides the nonlinear equations for normalized quantum trajectories. Therefore, fundamental questions concerning non-Markovian quantum trajectories can be addressed from a new angle. Furthermore, HOPS is numerically exact, converges rapidly, and offers a systematic way to check for convergence by increasing the number of equations taken into account. In addition, it offers the advantages of stochastic Schrödinger equations; e.g., one deals with pure states (and not large density matrices) and the calculation of independent realizations can be parallelized trivially.

In the following, we first state the form of the open system problem we are interested in. After a brief review of the general NMQSD approach, we present our new theory for the case of zero temperature and an exponential bath-correlation function. We derive a linear as well as the corresponding nonlinear set of equations. An extension to finite temperature and a more general bath-correlation function is presented afterwards. We demonstrate the power of HOPS by applying it to the spin-boson model, the calculation of absorption spectra of molecular aggregates,

and energy transfer in a photosynthetic pigment-protein complex. We use units where $k_B = \hbar = 1$.

The open quantum system.—Let us consider a system linearly coupled to a bath of harmonic oscillators. The Hamiltonian is a sum

$$H_{\text{tot}} = H \otimes \mathbb{1} + \mathbb{1} \otimes H_{\text{B}} + H_{\text{int}} \qquad (1)$$

of the system Hamiltonian H, the bath Hamiltonian $H_{\text{B}} = \sum_\lambda \omega_\lambda a_\lambda^\dagger a_\lambda$, and the interaction Hamiltonian

$$H_{\text{int}} = \sum_\lambda (g_\lambda^* L \otimes a_\lambda^\dagger + g_\lambda L^\dagger \otimes a_\lambda). \qquad (2)$$

Here, L is an operator in the system's Hilbert space and $a_\lambda^\dagger$ the creation operator of bath mode λ. The interaction strength between the system and that mode is quantified by the complex number g_λ. Let us emphasize that the form of Eq. (2) does not imply a rotating wave approximation. In many important cases, one has in fact $L = L^\dagger$. It is convenient to encode the frequency dependence of the interaction strength by the so-called spectral density $J(\omega) = \sum_j |g_j|^2 \delta(\omega - \omega_j)$. The latter is related to the bath-correlation function $\alpha(\tau)$ by [2]

$$\alpha(\tau) = \int_0^\infty d\omega \, J(\omega) \left[\coth\left(\frac{\omega}{2T}\right) \cos(\omega\tau) - i\sin(\omega\tau) \right], \qquad (3)$$

where T is the temperature. Note that $\alpha(-\tau) = \alpha^*(\tau)$.

In the following, we are interested only in the dynamics in the system Hilbert space and, in particular, the reduced density matrix obtained by tracing over the bath degrees of freedom.

Non-Markovian quantum state diffusion.—For now, let us consider initial conditions $|\Psi_0\rangle = |\psi_0\rangle \otimes |0\rangle$, where $|0\rangle$ is the vacuum state for all a_λ in the bath Hilbert space (zero temperature). The reduced density matrix is

$$\rho_t = \text{Tr}_{\text{B}}\{|\Psi_t\rangle\langle\Psi_t|\}, \qquad (4)$$

where Tr_{B} denotes the partial trace over the bath degrees of freedom and $|\Psi_t\rangle$ is the solution of the Schrödinger equation $i\partial_t|\Psi_t\rangle = H_{\text{tot}}|\Psi_t\rangle$.

By using a coherent state representation of the bath degrees of freedom, the reduced density matrix can be obtained from an ensemble average over trajectories of (non-normalized) pure states $|\psi_t(z^*)\rangle$ in the system Hilbert space via

$$\rho_t = \mathbb{E}\{|\psi_t(z^*)\rangle\langle\psi_t(z^*)|\}, \qquad (5)$$

where $z = z_t$ is a complex Gaussian stochastic process with mean $\mathbb{E}[z_t] = 0$ and correlations $\mathbb{E}[z_t z_s] = 0$ and $\mathbb{E}[z(t)z^*(s)] = \alpha(t - s)$. The time evolution of the states $|\psi_t(z^*)\rangle$ is determined [9,10] by

$$\partial_t \psi_t = -iH\psi_t + L z_t^* \psi_t - L^\dagger \int_0^t ds \, \alpha(t - s) \frac{\delta\psi_t}{\delta z_s^*} \qquad (6)$$

with initial conditions $\psi_{t=0} = \psi_0$.

While Eq. (5) with (6) determines the reduced density operator exactly, in general, it is unclear how to solve Eq. (6) due to the functional derivative $(\delta\psi_t)/(\delta z_s^*)$.

In previous works, we replaced this expression by an operator acting in the system Hilbert space: $(\delta\psi_t)/(\delta z_s^*) = O(t, s, z^*)\psi_t$. For some special cases, this operator can be determined exactly [10,28]. However, in general, approximation schemes are necessary (e.g., the zeroth order functional expansion approximation [17,25]). Here, we will proceed differently without any approximation.

HOPS.—First, Eq. (6) is written as

$$\partial_t \psi_t = -iH\psi_t + L z_t^* \psi_t - L^\dagger \psi_t^{(1)}, \qquad (7)$$

with the auxiliary pure state

$$\psi_t^{(1)} := \int_0^t ds \, \alpha(t - s) \frac{\delta\psi_t}{\delta z_s^*}. \qquad (8)$$

We now construct a hierarchy of equations by first considering the time derivative of $\psi_t^{(1)}$. Note that one can write $\psi_t^{(1)} = D_t \psi_t$, where [29]

$$D_t = \int_{-\infty}^\infty ds \, \alpha(t - s) \frac{\delta}{\delta z_s^*}. \qquad (9)$$

Then $\dot{\psi}_t^{(1)} = \partial_t(D_t\psi_t) = \dot{D}_t\psi_t + D_t\dot{\psi}_t$. Reversing the argument that led to Eq. (9) allows us to write $\dot{D}_t\psi_t = \int_0^t ds\,\dot{\alpha}(t - s)(\delta\psi_t)/(\delta z_s^*)$.

In order to illustrate the derivation of the hierarchy of equations most clearly, we first consider a bath-correlation function of the form

$$\alpha(\tau) = ge^{-w\tau} \quad (\tau \geq 0) \quad \text{and} \quad \alpha(\tau) = \alpha^*(-\tau) \quad (\tau < 0) \qquad (10)$$

with $w = \gamma + i\Omega$. As shown, for example, in Refs. [30,31], sums of such exponentials are well suited to approximately describe a large class of spectral densities and also finite temperature. For such an exponential correlation function, one has $\dot{D}_t\psi_t = -wD_t\psi_t$ and thus obtains

$$\partial_t \psi_t^{(1)} = -wD_t\psi_t - iHD_t\psi_t + LD_t z_t^* \psi_t - L^\dagger D_t^2 \psi_t \qquad (11)$$

$$= (-iH - w + L z_t^*)\psi_t^{(1)} + \alpha(0)L\psi_t^{(0)} - L^\dagger \psi_t^{(2)}, \qquad (12)$$

with $\psi_t^{(k)} := D_t^k \psi_t$. In the first equality, we used (6) as well as the fact that D_t commutes with all system operators. The second equality follows from the commutator relation

$[D_t, z_s^*] = \alpha(t - s)$. By considering the time derivatives of $\psi_t^{(k)}$, one gets coupled stochastic equations for an infinite hierarchy of pure states (HOPS):

$$\partial_t \psi_t^{(k)} = (-iH - kw + Lz_t^*)\psi_t^{(k)}$$
$$+ k\alpha(0)L\psi_t^{(k-1)} - L^\dagger\psi_t^{(k+1)}, \qquad (13)$$

with $\psi_{t=0}^{(0)} = \psi_0$ and $\psi_{t=0}^{(k)} = 0$ for $k > 0$. Solving the infinite system Eq. (13) is equivalent to solving Eq. (6), with $\psi_t = \psi_t^{(k=0)}$. This is our first important result.

Clearly, our HOPS approach Eq. (13) has a similar structure as hierarchical equations of motions in the density operator formalism [5].

Truncation.—In order to transform Eq. (13) into a practical scheme, we truncate the hierarchy at finite order. In the present work, we use the following "terminator":

$$\psi_t^{(k+1)} \approx \frac{\alpha(0)}{w} L\psi_t^{(k)} \qquad (14)$$

for some suitable k large enough (see Supplemental Material [32]). Such a truncation is motivated by similar considerations as in Ref. [5]. By inserting the terminator into (13), we obtain a closed system of $k + 1$ coupled equations. We remark that the use of this particular terminator is not essential. We have also found a good performance by using $\psi_t^{(k+1)} = 0$ with an appropriate k.

Markov limit.—The terminator (14) ensures the usual Markov limit in zeroth-order HOPS (see Supplemental Material [32]).

Nonlinear evolution equation.—For fundamental issues related to continuous measurement or spontaneous collapse, a theory for normalized pure states is much preferred. Moreover, the Monte Carlo determination of the density operator according to Eq. (5) converges much faster if the contributions of individual realizations $\psi_t(z^*)$ are of the same order of magnitude (importance sampling). We therefore transform the linear equation (6) to a nonlinear form with the help of a Girsanov transformation [10] to ensure the correct statistics, and we find the following nonlinear hierarchy [33]:

$$\dot{\tilde{\psi}}_t^{(k)} = (-iH - kw + \tilde{z}_t L)\tilde{\psi}_t^{(k)}$$
$$+ k\alpha(0)L\tilde{\psi}_t^{(k-1)} - (L^\dagger - \langle L^\dagger\rangle_t)\tilde{\psi}_t^{(k+1)}. \qquad (15)$$

Here, $\tilde{z}_t = z_t^* + \int_0^t ds\,\alpha^*(t-s)\langle L^\dagger\rangle_s$, and $\langle\cdot\rangle_s$ denotes the normalized average over $\tilde{\psi}_s^{(0)}$. The terminator is the same as in the linear case, i.e., $\tilde{\psi}^{(k+1)} = [\alpha(0)/w]L\tilde{\psi}^{(k)}$. Finally, the average in Eq. (5) can now be performed over the normalized states $\tilde{\psi}_t \equiv \tilde{\psi}_t^{(k=0)}/|\tilde{\psi}_t^{(k=0)}|$.

Generalizations.—We now generalize the results of the previous section to bath-correlation functions of the form

$$\alpha(\tau) = \sum_{j=1}^{J} g_j e^{-w_j\tau} \quad \text{for } \tau \geq 0 \qquad (16)$$

with $w_j = \gamma_j + i\Omega_j$. As shown, for instance, in Ref. [30], such a representation can be achieved for realistic applications. We then define auxiliary states $\psi_t^{(\mathbf{k})} = \psi_t^{(k_1,\ldots,k_J)}$, where the index k_j refers to the order with which the corresponding mode w_j appears in the hierarchy. One can choose the truncation order independently for each mode. In the examples shown below, we have used the "triangular" condition $|\mathbf{k}| := k_1 + \cdots + k_J \leq \mathcal{K}$. Details about the multimode HOPS equation and the terminator can be found in Ref. [32].

Note that, depending on the situation, different truncation conditions might be more efficient. Furthermore, one can also treat independent environments ($n = 1, 2, \ldots$) with different coupling operators L_n along the same lines as required for the quantum aggregates below.

Finite temperature.—The case $T > 0$ can be mapped to the zero-temperature case by using the *thermofield method* doubling the number of processes required [10,34,35]. Remarkably, a system with a self-adjoint coupling operator (i.e., $L = L^\dagger$) admits a description in terms of the zero-temperature non-Markovian quantum state diffusion equation (6) by introducing a sum process with correlation (3) in combination with a *Padé decomposition* of the hyperbolic cotangent [35,36].

Spin-boson model.—As a first example, we consider the spin-boson model [37], where the system Hamiltonian is $H = -\frac{1}{2}\Delta\sigma_x + \frac{1}{2}\epsilon\sigma_z$ and the coupling to the bath is mediated by $L = \sigma_z$. It is used to demonstrate the convergence of the method with respect to the truncation order of the hierarchy and with respect to the number of realizations. In particular, we show the superior convergence properties of the nonlinear equation. This can be clearly seen in Fig. 1, where the dependence of the solution on the
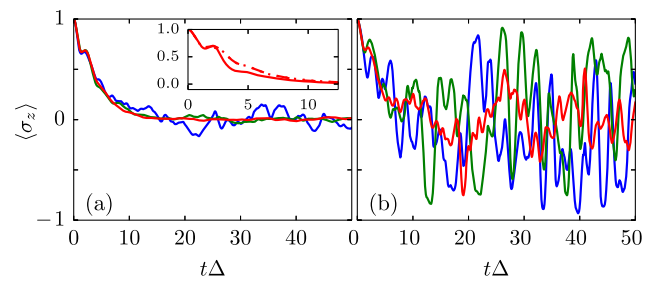

FIG. 1 (color online). Dynamics of the spin-boson model. (a) Nonlinear equation, (b) linear equation. In both cases, $\Delta = 1$, $\epsilon = 0$, and the parameters of the spectral density are given by $g = 2$ and $w = 0.5 + 2i$. The blue, green, and red lines represent 100, 1000, and 10 000 realizations, respectively. The order of the hierarchy is $\mathcal{K} = 8$. The inset in (a) shows the convergence (for 10 000 realizations) with respect to the order of the hierarchy. The dotted, dashed, and solid line are orders one, two, and four, respectively.
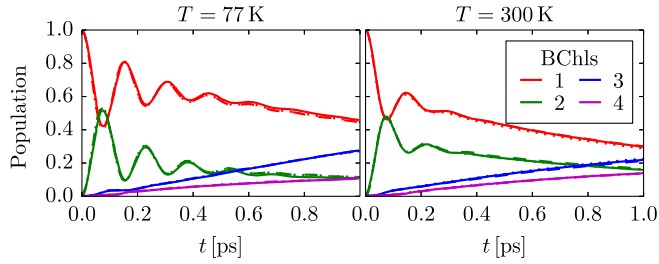
FIG. 2 (color online). Transfer of electronic excitation energy within the FMO complex. The parameters are taken from Refs. [39,40] and can be found in Supplemental Material [32]. Solid line, result of Ref. [39]; dotted line, HOPS first order; dashed line, HOPS second order.

FIG. 3 (color online). Absorption of a linear chain of $N = 7$ monomers with parallel transition dipoles for different values of the interaction V. The inset shows the spectral density used. The reorganization energy $E_r = \int_0^\infty dw J(w)/w$ is chosen as the unit of energy. The temperature is $T = 0.2$. Colors indicate different orders of the hierarchy (blue, $\mathcal{K} = 5$; green, $\mathcal{K} = 6$; red, $\mathcal{K} = 7$).

number of trajectories is shown for the nonlinear [Fig. 1(a)] and the linear equation [Fig. 1(b)]. While the nonlinear solution already converges for 1000 trajectories (and even for 100 trajectories is close to the converged solution), the linear equation shows large fluctuations even for 10 000 trajectories. Previous work [38] indicates that there is no significant difference between the linear and nonlinear variant in the weak coupling (Redfield) regime. However, in the strong coupling regime considered here, the nonlinear version shows far superior convergence properties. The inset displays how the solution of the nonlinear equation converges with respect to the order of the hierarchy: We observe converged results already at $\mathcal{K} = 4$. The convergence is discussed in more detail in Ref. [32].

The quantum aggregate.—As an example, for a more challenging setting we consider a generic system described by a Hamiltonian $H = \sum_n \epsilon_n |n\rangle\langle n| + \sum_{nm} V_{nm} |n\rangle\langle m|$, where $|n\rangle$ denotes a basis of the (small) Hilbert space of the system. In application to molecular aggregates, $|n\rangle$ denotes a localized electronic excitation at "site" n of the system. Each excitation couples to its own bath, that is, $H_{\text{int}} = \sum_n \sum_\lambda (g_{n\lambda}^* L_n \otimes a_{n\lambda}^\dagger + g_{n\lambda} L_n^\dagger \otimes a_{n\lambda})$ and $L_n = |n\rangle\langle n|$.

As an important application, we consider transfer of electronic excitation within the photosynthetic Fenna-Matthews-Olson (FMO) complex. To demonstrate the fast convergence of HOPS, we compare with the numerical hierarchical equation of motion calculations of Ref. [39]. As can be seen in Fig. 2, already the first order of HOPS agrees almost perfectly with the result of Ref. [39] obtained in the (density matrix) hierarchical equations of motion (HEOM) approach. The HEOM computations have also been confirmed by using numerical exact path integral methods [41]. Details about the parameters used and the convergence properties of HOPS can be found in Ref. [32].

Next, we consider absorption of a linear aggregate: Linear absorption can be calculated from the *linear* non-Markovian quantum state diffusion by using only the single trajectory $\psi_t(z^* = 0)$; i.e., no averaging over different realizations of the stochastic processes is needed [26,35]. We will now show that within our pure state hierarchy fast
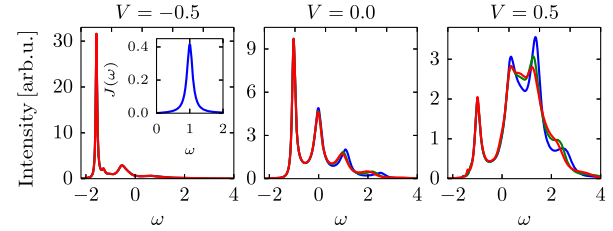
convergence of the optical spectra can be achieved. To this end, we employ the same model system as in Ref. [26], namely, parallel transition dipoles and identical monomers. In that case, the absorption strength for light with frequency ν can be calculated as [26]

$$A(\nu) = \text{Re} \int_0^\infty dt \, e^{i\nu t} M(t), \qquad (17)$$

where M is the correlation function

$$M(t) = \mu^2 \langle \psi_0(z^*) | \psi_t(z^*) \rangle |_{z^*=0}. \qquad (18)$$

Here, μ denotes the magnitude of the monomer's transition dipoles. We have compared our HOPS calculations with numerically exact pseudomode calculations [26]. For all cases considered, we found perfect agreement with the results of Ref. [26] (not shown here). In Ref. [26], only very short aggregates with $N = 2$ and $N = 3$ (ignoring temperature) were considered due to the huge numerical effort of the pseudomode approach. With HOPS, we are now able to study longer chains at finite temperature numerically exact. As an example, in Fig. 3, the absorption spectrum of a chain of seven monomers is shown for the case of negative (left) and positive (right) interaction V together with the case of noninteracting monomers (middle). We have chosen a spiky spectral density [shown in the inset in panel (a)] and set the reorganization energy $E_r = \int_0^\infty dw J(w)/w$ as the unit of energy. For the shown parameters $|V| = 0.5$ and $T = 0.2$, we are in the complicated case where all quantities are of the same order of magnitude and non-Markovian effects become clearly visible. Note that the spectra converge faster at lower energies, so that already for small orders of the hierarchy one has a good description of the important low energy part of the spectrum.

Conclusions and outlook.—The examples above demonstrate that our HOPS is very suitable to treat the dynamics of realistic open quantum systems covering strong coupling as well as highly non-Markovian regimes. HOPS allows for the determination of normalized quantum trajectories as required for a continuous measurement or collapse interpretation. Based on a pure state representation, HOPS is

numerically efficient and converges fast towards the exact results. While previous applications of non-Markovian quantum state diffusion rested on either analytically solvable models or approximation schemes, HOPS provides a numerically exact solution with a systematic control over potential errors. Note that our formalism is not based on the unraveling of a given master equation such as, e.g., non-Markovian quantum jumps [42,43]. We obtain the reduced density operator directly from a closed system-environment model. Since time-dependent Hamiltonians can be included within the HOPS approach, one can treat, e.g., the interaction with an electromagnetic field as in femtosecond or 2D spectroscopy. Moreover, our quantum-trajectory-based formulation might help to shed light on quantum variants of fluctuation theorems [44,45]. We strongly believe that HOPS represents a fruitful approach to the study of dynamics of open quantum systems.

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[29] The bounded integral domain $[0, t]$ in (6) arises due to the initial condition $|\Psi_0\rangle = |\psi_0\rangle \otimes |\mathbf{0}\rangle$, which translates to $(\delta\psi_{t=0})/(\delta z_s^*) = 0$ for $s \in \mathbb{R}$. Hence, $|\psi_t\rangle$ must be independent of the noise z_s^* for $s > t$ and $s < 0$.

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[32] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.113.150403 for details on the terminator, the Markov limit of HOPS, the multiple mode equations, and the convergence properties. The parameters used in the FMO calculation can be found there as well.

[33] Note that our definition of $\tilde\psi$ in Eq. (10) in Ref. [10] involves normalization. Here, in contrast, the notation $\tilde\psi$ refers to the unnormalized, yet Girsanov-transformed state, such that its evolution equation has to be related to (B11) in Ref. [10]. Nevertheless, a closed equation for normalized trajectories in our hierarchy can be derived as well.

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