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Nonperturbative generalized master equation for the spin-boson problem

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A generalized master equation for the spin-boson model is proposed, that does not require a perturbative treatment of the interstate or system-bath couplings. The nonperturbative formulation is based on the assumption of a decoupling of system and bath density operators, and results in a generalized memory function, that reduces in the limit of weak system-bath coupling to the standard result of the perturbative noninteracting-blip approximation. Numerical studies in comparison to exact path-integral calculations demonstrate that the nonperturbative master equation represents a clear improvement to perturbation theory as long as the overall coupling is still small enough to justify the underlying decoupling assumption. Finally, possible generalizations of the method to the description of a dissipative N-level system and the limitations of the decoupling ansatz are discussed in some detail.

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I. INTRODUCTION

The separation of a physical problem into a relevant part (the "system") and an irrelevant part (the "bath") is an ubiquitous strategy in many areas of physics and chemistry. The underlying idea is to treat the relevant dynamics (usually modeled by a one-dimensional reaction coordinate) exactly and approximate the dynamics of the remaining degrees of freedom in terms of a harmonic bath that is bilinearly coupled to the system degree of freedom. If applicable, the system-bath concept therefore allows one to reduce the complexity of a real physical system considerably. The concept furthermore suggests a simple approximation to introduce irreversibility and dissipation into quantum mechanics [1–4]. The basic assumption usually made is that the bath has so many degrees of freedom that the reaction of the system on the bath can be neglected, i.e., the bath stays in thermal equilibrium for all times.

One of the simplest and best studied model problems of quantum-mechanical relaxation dynamics is the dissipative two-level system, often referred to as the spin-boson problem [4–21]. Although each subproblem (i.e., the two-level system and the harmonic bath) is easily solvable, the dissipative two-level system in general can only be solved exactly by numerical path-integral evaluation [6–10]. There exists a variety of approximate formulations of the spin-boson problem, however, which treat either the interstate coupling or the system-bath coupling in a perturbative manner. The first case is often referred to as the golden rule approximation, which in particular has proven to be valuable in the field of chemical physics [11,12]. The latter case is often referred to as the noninteracting-blip approximation (NIBA). The NIBA has been introduced in a path-integral framework by Leggett and co-workers [5] and has been found to be fully equivalent to a second-order perturbative treatment of general relaxation theory [15]. A further simplification arises if only the diagonal elements of the reduced density operator (i.e., the populations) are of interest. In this case a generalized master equation can be derived, which is an integro-differential equation for the populations with a non-Markovian memory kernel [14–17]. During the past decade there has been a large amount of literature, considering, in particular, the numerical implementation [6–11,13], formal extensions [16–19], and semiclassical approximations [20,21] to the spin-boson problem.

In this work we propose a generalized master equation that does not require a perturbative treatment of the interstate or system-bath couplings. The theory is based on a decoupling approximation, that is, we assume that for all times the total density operator can be written as a product of system density operator and bath density operator, i.e., the system degrees of freedom are coupled to the bath degrees of freedom in a self-consistent manner. The nonperturbative formulation results in a generalized memory function, which reduces to the standard NIBA result in the limit of weak system-bath coupling. We present computational results for a spin-boson model with an Ohmic bath, which are compared to exact path-integral calculations. It is demonstrated that the nonperturbative master equation represents a clear improvement of the NIBA as long as the overall coupling is still small enough to justify the underlying decoupling assumption. Finally, we compare the theory to a nonperturbative semiclassical approach [20,21] and discuss the limitations and possible generalizations of the decoupling ansatz in some detail.

II. THEORETICAL FORMULATION

In its simplest version, the spin-boson problem consists of a two-level system (characterized by the electronic coupling Δ) that is linearly coupled to a harmonic bath h_0. To be specific, we will refer to the spin and the boson variables as electronic and nuclear degrees of freedom, respectively. Representing the two-level system by the

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diabatic electronic basis states $|\varphi_1\rangle, |\varphi_2\rangle$, the spin-boson Hamiltonian reads

$$\begin{aligned} H &= \sum_{k=1,2} |\varphi_k\rangle\, h_k \,\langle\varphi_k| + \{|\varphi_1\rangle\, \Delta\, \langle\varphi_2| + \text{H.c.}\}\,, \\ h_k &= h_0 \pm \sum_j C_j x_j, \\ h_0 &= \sum_j \tfrac{1}{2}\omega_j (p_j^2 + x_j^2). \end{aligned} \tag{1}$$

Here the x_j and p_j represent the dimensionless coordinates and momenta of the jth oscillator, ω_j and C_j being the vibrational frequency and the linear coupling constant, respectively. Within the spin-boson model (1) all properties of the bath can be captured by a single function called the spectral density

$$J(\omega) = \frac{\pi}{2} \sum_j C_j^2 \delta(\omega - \omega_j). \tag{2}$$

In the case of an Ohmic bath, the spectral density takes the form

$$J(\omega) = \frac{\pi}{2} \alpha \omega e^{-\omega/\omega_c}, \tag{3}$$

where α is the dimensionless Kondo parameter characterizing the strength of the system-bath coupling and ω_c denotes the cutoff frequency defining the time-scale distribution of the bath dynamics.

The time-dependent dynamics of the total density operator $\rho(t)$ of system and bath is described by the Liouville–von Neumann equation ($\hbar \equiv 1$)

$$i\dot{\rho}(t) = [H, \rho(t)]. \tag{4}$$

We assume factorizing initial conditions, i.e., at $t = 0$ the electronic system is in the $|\varphi_1\rangle$ electronic state and the bath is in thermal equilibrium

$$\rho(0) = |\varphi_1\rangle \langle\varphi_1|\, e^{-\beta h_B}/\text{Tr}e^{-\beta h_B}, \tag{5}$$

where β denotes the inverse temperature $1/k_BT$ and $h_B = h_1 - \delta_{\text{neq}} \sum_j C_j x_j$. Depending on the physical situation under consideration, the bath is initially in the equilibrium geometry of the $|\varphi_1\rangle$ electronic state (i.e., $h_B = h_1$, the "tunneling case") or in the equilibrium geometry of the uncoupled bath Hamiltonian H_B (i.e., $h_B = h_0$, the "spectroscopic case"). The latter case results in a nonequilibrium (neq) initial preparation of the system and can be thought of as a photoexcitation of the electron from a neutral electronic state (e.g., $|\varphi_0\rangle$) to the $|\varphi_1\rangle$ state.

We wish to obtain a generalized master equation for time-dependent electronic population

$$P(t) = \text{Tr}_B \{\rho_{11}(t) - \rho_{22}(t)\}\,, \tag{6}$$

where $\rho_{kk'} = \langle\varphi_k|\, \rho\, |\varphi_{k'}\rangle$ are the electronic matrix elements of the total density operator $\rho(t)$. As usual, we insert the formal solution of (4) for the offdiagonal elements $\rho_{kk'}$ into the equation of motion for the diagonal elements ρ_{kk} [3], thus obtaining the integro-differential equation

$$\dot{P}(t) = -(2\Delta)^2 \text{Re} \int_0^t dt' \text{Tr}_B \Big\{ e^{ih_1(t-t')} e^{-ih_2(t-t')} \times [\rho_{11}(t') - \rho_{22}(t')] \Big\}. \tag{7}$$

Equation (7) is still exact. Representing an operator equation with respect to the multidimensional boson field, it is not solvable without some approximation. To solve Eq. (7), we make a decoupling ansatz and assume that for all times the total density operator $\rho(t)$ can be written as a product of system density operator $\rho_S(t)$ and bath density operator $\rho_B(t)$

$$\rho(t) = \rho_S(t) \rho_B(t), \tag{8a}$$

$$\rho_S(t) = \sum_{k,k'=1,2} \chi_k(t)\, |\varphi_k\rangle \langle\varphi_{k'}|\, \chi_{k'}^*(t), \tag{8b}$$

$$\rho_B(t) = \sum_n w_n\, |\Phi_n(t)\rangle \langle\Phi_n(t)|\,. \tag{8c}$$

Here the electronic density operator is represented by two complex numbers χ_1 and χ_2, the squared moduli of which represent the population probability in the electronic state $|\varphi_1\rangle$ and $|\varphi_2\rangle$, respectively. The bath density operator is represented in terms of the multidimensional state vectors $|\Phi_n(t)\rangle$, where $w_n = e^{-\beta\epsilon_n}/\text{Tr}e^{-\beta h_B}$ denote the thermal occupation probabilities of the initial states $|\Phi_n(0)\rangle = |n\rangle$, $|n\rangle$ being the eigenstates of h_B such that $h_B\, |n\rangle = \epsilon_n\, |n\rangle$. Note that by virtue of ansatz (8) the electronic (system) degrees of freedom are coupled to the nuclear (bath) degrees of freedom in a self-consistent manner, i.e., (8) can be considered a time-dependent self-consistent-field (TDSCF) approximation [22]. The ansatz (8) is somewhat different from common TDSCF formulations, however, which assume that the total density operator factorizes in single-mode density operators [23–27], thus introducing a self-consistent coupling between the individual nuclear degrees of freedom.

Introducing the ansatz (8) into the integro-differential equation (7), we obtain the generalized master equation

$$\dot{P}(t) = -(2\Delta)^2 \text{Re} \int_0^t dt' K(t,t') P(t'), \tag{9}$$

where

$$K(t,t') = \sum_n w_n \,\langle\Phi_n(t')|\, e^{ih_1(t-t')} e^{-ih_2(t-t')}\, |\Phi_n(t')\rangle \tag{10}$$

represents in general a nonstationary and nonlinear memory function, accounting for the electronic population dynamics of the spin-boson problem to all orders of interstate and system-bath couplings.

Before proceeding to the general expression for (10), it is instructive to consider the limiting case of weak system-bath coupling. Assuming $h_B = h_1$, the latter approximation directly gives

$$|\Phi_n(t)\rangle = e^{-ih_1 t}\, |\Phi_n(0)\rangle = e^{-i\epsilon_n t}\, |n\rangle\,, \tag{11}$$

i.e., the resulting memory kernel $K(t,t') \equiv K_0(t-t')$ is equivalent to a product of autocorrelation functions of shifted harmonic oscillators [28]

$$K_0(t-t') = \exp\left\{-Q_2(t-t') - iQ_1(t-t')\right\}, \tag{12}$$

where

$$Q_1(t) = 2\sum_j \frac{C_j^2}{\omega_j^2} \sin\omega_j t, \tag{13}$$

$$Q_2(t) = 2\sum_j \frac{C_j^2}{\omega_j^2} \coth(\tfrac{1}{2}\beta\omega_j)(1-\cos\omega_j t) \tag{14}$$

are recognized as the ubiquitous functions from standard spin-boson theory [5]. Equation (12) coincides exactly with the NIBA result of Leggett *et al.* [5], where it is assumed that the bath density operator stays in thermal equilibrium for all times [i.e., $|\Phi_n(t)\rangle = |\Phi_n(0)\rangle$]. Employing furthermore the Markov approximation, that is, assuming that $\dot{P}(t)$ depends only on its present value $P(t)$, the integro-differential equation (9) simplifies to a rate equation with the golden rule rate $k = (2\Delta)^2 \mathrm{Re}\int_0^\infty K_0(t)dt$. Although usually derived in the limit of weak interstate coupling ($\Delta/\omega_c \ll 1$), the Golden Rule approximation therefore can be considered a limiting case of the NIBA.

To evaluate (10) in a nonperturbative manner, let us consider the equations of motion for the system and bath density operator, respectively, that result from the ansatz (8). As every contribution $\rho_S(t)\,|\Phi_n(t)\rangle\,\langle\Phi_n(t)|$ of $\rho(t)$ corresponds to a pure state of the complete system, the equations of motion for χ_k and Φ_n can directly be taken from the well-known wave-function TDSCF formalism [29], yielding

$$i\dot{\chi}_k(t) = \langle h_k\rangle\,\chi_k(t) + \Delta\chi_{k'}(t) \qquad (k' \neq k), \tag{15}$$

$$\begin{aligned} i\dot{\Phi}_n(\mathbf{x},t) = \Bigg(&h_0 + P(t)\sum_j C_j x_j \\ &+ 2\mathrm{Re}\Delta\chi_1(t)\chi_2^*(t)\Bigg)\Phi_n(\mathbf{x},t). \end{aligned} \tag{16}$$

It is seen that within the TDSCF approximation the electronic (system) equations of motion reduce to a coupled two-level system with explicitly time-dependent coefficients $\langle h_k\rangle = \sum_n w_n \langle\Phi_n(t)|h_k|\Phi_n(t)\rangle$. The nuclear (bath) equation of motion is recognized as the time-dependent Schrödinger equation for a driven harmonic oscillator, which has the formal solution

$$\begin{aligned} |\Phi_n(t)\rangle = \exp_T\Bigg\{-i\int_0^t d\tau\Bigg(&h_0 + P(\tau)\sum_j C_j x_j \\ &+ 2\mathrm{Re}\Delta\chi_1(\tau)\chi_2^*(\tau)\Bigg)\Bigg\}\,|\Phi_n(0)\rangle\,, \end{aligned} \tag{17}$$

where $\exp_T$ denotes the time-ordered exponential.

Inserting (17) into (10) and making use of standard reordering techniques for boson operators, it is shown in the Appendix that the generalized memory function (10) can be evaluated as

$$K(t,t') = K_0(t-t')K_{\mathrm{nl}}(t,t')K_{\mathrm{neq}}(t,t'), \tag{18}$$

$$\begin{aligned} K_{\mathrm{nl}}(t,t') = \exp\Bigg\{-2i\sum_j C_j^2/\omega_j \int_0^{t'} d\tau\Big[&\cos\omega_j(t-\tau) \\ &- \cos\omega_j(t'-\tau)\Big]\Big[1-P(\tau)\Big]\Bigg\}, \end{aligned} \tag{19}$$

$$K_{\mathrm{neq}}(t,t') = \exp\left\{i\delta_{\mathrm{neq}}\Big[Q_1(t) - Q_1(t')\Big]\right\}. \tag{20}$$

The generalized memory function $K(t,t')$ is seen to factorize into three terms: the stationary perturbative memory kernel $K_0(t-t')$ given in (12) and the nonstationary functions $K_{\mathrm{nl}}(t,t')$ and $K_{\mathrm{neq}}(t,t')$. The memory function $K_{\mathrm{nl}}(t,t')$ describes the nonlinear response of the system in the case of strong system-bath coupling, i.e., in perturbation theory we have $P(\tau) = 1$ and thus $K_{\mathrm{nl}} = 1$. The function $K_{\mathrm{neq}}(t,t')$ accounts for transient dynamics owing to a nonequilibrium preparation of the system [30], where the parameter δ_{neq} represents the initial coordinate shift of the bath density operator [cf. Eq. (5)].

The generalized memory function (18) represents the central theoretical result of this work. Note that the only approximation needed to derive Eq. (18) has been the decoupling or TDSCF ansatz (8). Although the numerical evaluation of the nonperturbative response is somewhat more involved as in the perturbative case, it is an easy matter to solve the integro-differential equation (9) with (18) using, e.g., a standard Runge-Kutta integration scheme. The straightforward numerical implementation of the method makes it easy to generalize the approach to more complex model systems (see below). This simplicity also appears advantageous in comparison to the somewhat complementary approach of Laird, Budimir, and Skinner [19], who have given explicit expressions for the population and dephasing rates for the spin-boson problem up to fourth order in the system-bath coupling.

Before proceeding with numerical demonstrations and a further discussion of the nonperturbative method, it is interesting to note that the memory function (10) has been evaluated also employing a semiclassical approximation, which can be written as [21]

$$K(t,t') = \sum_n w_n\left\langle\Phi_n(t')\left|\exp_T\left\{2i\sum_j C_j\int_{t'}^t d\tau\hat{x}_j(\tau)\right\}\right|\Phi_n(t')\right\rangle \tag{21}$$

$$\begin{aligned} &\to \int d\mathbf{x}(0)\int d\mathbf{p}(0)\,w(\mathbf{x}(0),\mathbf{p}(0))\exp\left\{2i\sum_j C_j\int_{t'}^t d\tau x_j(\tau)\right\} \\ &= K_0^{\mathrm{cl}}(t-t')K_{\mathrm{nl}}^{\mathrm{cl}}(t,t')K_{\mathrm{neq}}(t,t'), \end{aligned} \tag{22}$$

where

$$K_0^{\mathrm{cl}}(t-t') = \exp\{-Q_2(t-t') - i\epsilon_r(t-t')\}\,, \qquad (23)$$

$$K_{\mathrm{nl}}^{\mathrm{cl}}(t,t') = \exp\left\{2i\sum_j C_j^2 \int_{t'}^{t} dt_2 \times \int_0^{t_2} dt_1 \sin[\omega_j(t_2-t_1)][1-P(t_1)]\right\}, \qquad (24)$$

and $\epsilon_r = 2\sum_j C_j^2/\omega_j^2$ is the reorganization energy. Equation (21) is still identical to (10), where $\hat{x}_j(t)$ represents the Heisenberg position operator (see the Appendix). The semiclassical approximation (22) consists of (i) replacing the position operator $\hat{x}_j(t)$ by the classical trajectory $x_j(t)$ and (ii) replacing the quantum-mechanical trace over the bath by a quasiclassical average over the initial nuclear conditions $\mathbf{x}(0), \mathbf{p}(0)$, which are weighted by the Wigner distribution $w(\mathbf{x}(0), \mathbf{p}(0))$. Compared to the quantum-mechanical expressions (12) and (19), the semiclassical approximation results in different phase factors but in the same damping term $\exp\{-Q_2(t)\}$. The nonlinear function $K_{\mathrm{nl}}^{\mathrm{cl}}(t,t')$ was derived by Vitali and Grigolini [20], who employed a coordinate transformation of the bath modes [sometimes referred to as the (pseudo)polaronic transformation] and neglected a nonclassical driving term of the nuclear motion. Performing a quantum-mechanical average over the boson field $\hat{x}$, however, they obtained a mixed quantum-classical result $K(t,t') = K_0(t-t')K_{\mathrm{nl}}^{\mathrm{cl}}(t,t')$, i.e., the perturbative memory kernel is given by the quantum-mechanical expression (12), while the nonlinear memory function is given by the semiclassical expression (24).

III. COMPUTATIONAL RESULTS AND DISCUSSION

In order to study the capability and accuracy of the different approximations introduced above, we compare these methods to exact path-integral calculations that have been reported recently by Makarov and Makri [9] and Egger and Mak [10]. We consider three examples of increasing challenge and focus primarily on the regime of very low temperature, which is known to represent the most stringent test for a decoupling-type approximation (see below).

Let us first consider the case of low system-bath coupling corresponding to a Kondo parameter $\alpha = 0.09$, where a perturbative method such as the NIBA should be a good approximation. Figure 1 shows the time evolution of the electronic population $P(t)$ for the parameters $\Delta \equiv 1$, $k_BT = 0.2\Delta$, $\omega_c = 2.5\Delta$, and $\delta_{\mathrm{neq}} = 1$. In the regime of low coupling and low temperature, the electronic population undergoes a coherent relaxation, which is to say that $P(t)$ exhibits damped Rabi oscillations. As expected, the NIBA calculation (dashed line) reproduces the exact path-integral results of Ref. [9] (dotted line) rather well. The nonperturbative TDSCF calculation (full line) still represents an improvement to the NIBA results and is virtually quantitative.

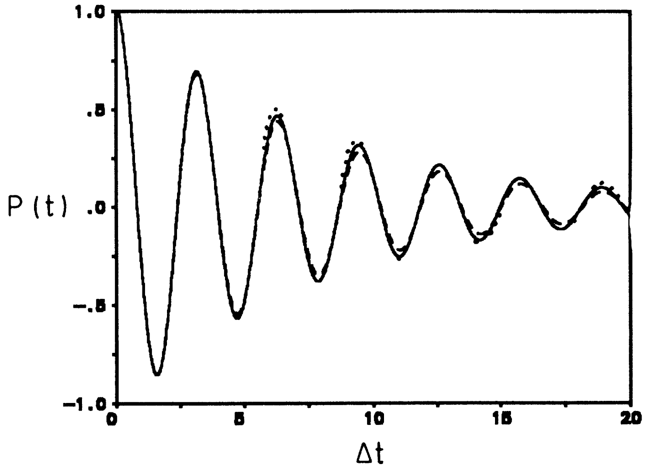

FIG. 1. Electronic population $P(t)$ for weak system-bath coupling $\alpha = 0.09$ and the parameters $\Delta \equiv 1$, $k_BT = 0.2\Delta$, $\omega_c = 2.5\Delta$, and $\delta_{\mathrm{neq}} = 1$. The TDSCF (full line) and NIBA (dashed line) results are compared to exact path-integral calculations (dotted line) of Ref. [9].

Increasing the system-bath coupling to $\alpha = 0.5625$ and keeping the temperature low ($k_BT = 0.1\Delta$), we obtain a strongly damped (weakly coherent) relaxation of the electronic population as shown in Fig. 2. Figure 2(a) again compares the NIBA and TDSCF results to the exact calculation of Ref. [9]. In this medium coupling case there are already considerable differences between the two approximations, the nonperturbative results (full line) being a clear improvement to the perturbative results (dashed line). It is interesting to also compare to the semiclassical approximations introduced above. Figure 2(b) shows the results for the semiclassical approximation [Eq. (22)] and the mixed quantum-classical approximation [Eqs. (12) and (24)] of Vitali and Grigolini [20]. While the semiclassical approximation (full line) reproduces the reference data fairly well, the mixed quantum-classical approximation (dashed line) exhibits a spurious oscillation with the period of the reorganization energy ϵ_r, indicating that this combination of quantum-mechanical perturbative response and semiclassical nonperturbative response may lead to inconsistencies.

As a last example, Fig. 3 shows a case of very strong system-bath coupling ($\alpha = 2$), which has been studied recently by Egger and Mak [10]. The parameters are $\delta_{\mathrm{neq}} = 0$, $\omega_c \equiv 1$, $\Delta/\omega_c = 0.8$ [Fig. 3(a)] and $\Delta/\omega_c = 0.6$ [Fig. 3(b)]. While in the case of high temperature [(a) $k_BT = 4\omega_c$] both the NIBA and TDSCF approximations qualitatively match the exact results, the approximative methods are seen to fail badly in the case of low temperature [(b) $k_BT = 0.4\omega_c$]. (The same holds for the semiclassical approximations mentioned above, which give in both cases results similar to the TDSCF approximation.) The low-temperature results clearly show that in the regime of very strong system-bath interaction the ubiquitous assumption of a decoupling of system and bath is not appropriate. In cases where this underlying assumption breaks down completely, perturbative (including the popular golden rule estimates) as well as nonperturbative methods therefore become meaningless after a rather short propagation time. The breakdown of the decoupling assumption has been found also for model systems, where the overall system-bath coupling α is not continuously distributed over many weakly coupled bath modes, but has been put into a few (≥ 3) strongly coupled vibrational degrees of freedom [31].

One way to go beyond the limitations of the ansatz (8) is to employ a semiclassical mean-field approximation [32–34], which does not require a decoupling approximation (see also the discussion in [21]). It has been shown recently that the simple classical-path methodology describes surprisingly accurately the ultrafast electronic and vibrational relaxation dynamics occurring in the spin-boson problem [21] and in internal conversion [33] and simple photoisomerization processes [34]. Another way, which has quite recently attracted a great deal of attention [8,13,16–18], is to incorporate all strong couplings and interactions into the system density operator such that the residual coupling to the bath remains weak enough to allow for an approximate treatment. In other words, the electronic two-level system is replaced by a vibronic N-level system, representing an electronic two-state system with a (usually one-dimensional) strongly coupled system coordinate, the dynamics of which is accounted for without any approximation.

From the structure of the ansatz (8) it is clear that it is straightforward to generalize the nonperturbative treatment from a two-level system to an N-level system. It should be noted, however, that the nonperturbative approach does not easily generalize to the case of a biased two-level system, i.e., to an unsymmetric double-well problem. Because the ansatz of the vibrational wave function does not depend on the electronic state $|\varphi_k\rangle$ ($k = 1, 2$), the forward rate $k_{2\leftarrow 1}$ is necessarily equal to the backward rate $k_{1\leftarrow 2}$, which is clearly wrong for an unsymmetrical spin-boson problem. This shortcoming can be remedied, in principle, by introducing a multiconfiguration TDSCF ansatz [25–27] such that the bath den-

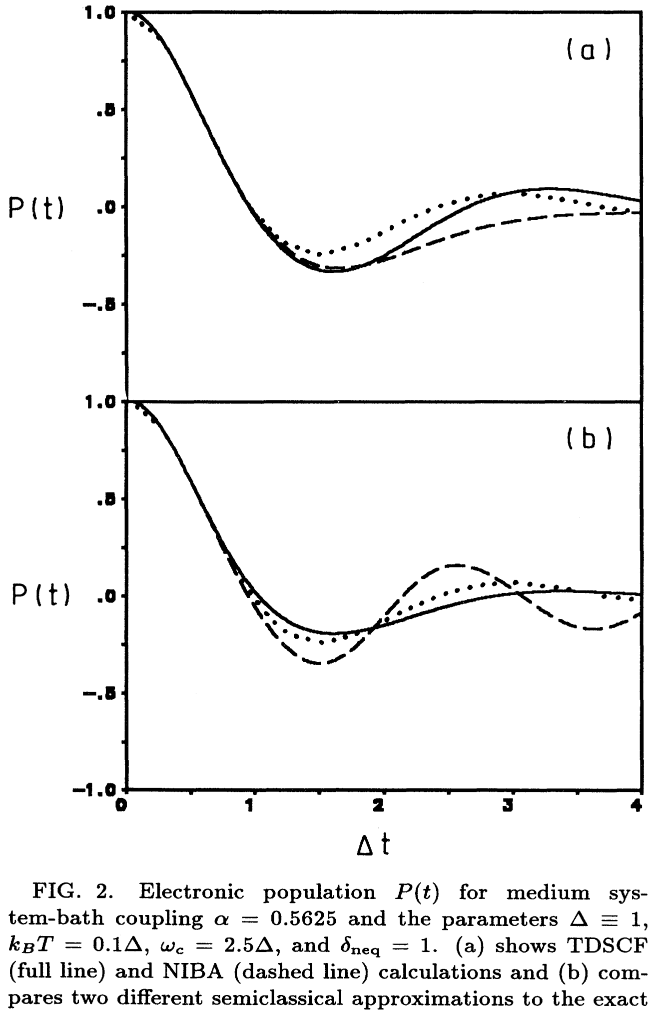

FIG. 2. Electronic population $P(t)$ for medium system-bath coupling $\alpha = 0.5625$ and the parameters $\Delta \equiv 1$, $k_BT = 0.1\Delta$, $\omega_c = 2.5\Delta$, and $\delta_{\rm neq} = 1$. (a) shows TDSCF (full line) and NIBA (dashed line) calculations and (b) compares two different semiclassical approximations to the exact path-integral calculations (dotted line) of [9].

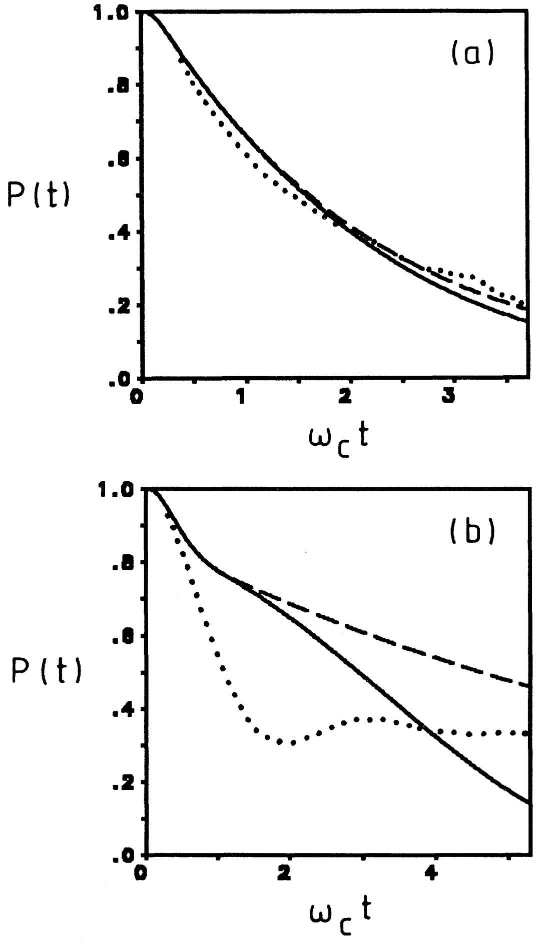

FIG. 3. Comparison of the electronic populations $P(t)$ as obtained by exact quantum Monte Carlo simulations [10] (dotted line) and TDSCF (full line) and NIBA (dashed line) calculations in the case of very strong system-bath coupling $\alpha = 2$. (a) shows an example with high temperature ($k_BT = 4\omega_c$) and (b) shows an example with low temperature ($k_BT = 0.4\omega_c$).

sity operator by construction depends on the electronic state $|\varphi_k\rangle$. In perturbation theory this leads, similarly to the case of the NIBA, to the vibrational wave function $\left|\Phi_n^{(k)}(t)\right\rangle = e^{-ih_k t}\left|\Phi_n^{(k)}(0)\right\rangle$. Unfortunately, for the multiconfiguration case we have not succeeded in finding an easily computable nonperturbative memory function.

IV. CONCLUSIONS

We have given a generalized master equation description for the spin-boson problem, which allows for a nonperturbative treatment of the interstate and system-bath couplings. The theory is based on a decoupling (or TDSCF) ansatz for the total density operator $\rho(t)$, which assumes that for all times $\rho(t)$ can be written as a product of the system density operator and the bath density operator. Within this approximation we have derived a generalized memory function, which reduces to the standard NIBA result in the limit of weak system-bath coupling. In a comparison to exact path-integral calculations in the regime of small to rather strong system-bath coupling, it has been shown that the nonperturbative approach represents a clear improvement to the perturbative NIBA approach as long as the overall coupling is still small enough to justify the underlying decoupling assumption. We have also compared the theoretical and computational results to recently developed semiclassical approximations [20,21]. It has been found that for the sake of consistency it is necessary to describe both perturbative and nonperturbative response either classically or quantum mechanically, but not in a mixed representation. Finally, it has been discussed that, similarly to standard perturbative relaxation theory, it is straightforward within the nonperturbative formulation to generalize from a two-level description to an N-level description. This strategy allows one to incorporate all strong couplings and interactions into the system density operator such that the residual coupling to the bath remains weak enough to allow for an approximate treatment.

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APPENDIX

In this appendix we sketch the derivation of the general expression for the memory function Eq. (18). The basic idea is to change to the interaction representation that yields a product of exponential functions of the form $\exp\{c_1(t)b + c_2(t)b^\dagger\}$, which is readily evaluated using the Baker-Hausdorff theorem. For the sake of notational convenience, we will refer to a single nuclear coordinate x (instead of $\sum_j x_j$). Let us first consider the case $h_B = h_1$ and rewrite the vibrational wave function (17) as

$$\begin{aligned}
|\Phi_n(t)\rangle &= \exp_T\left\{-i\int_0^t d\tau\{h_1 - [1-P(\tau)]Cx + 2\mathrm{Re}\Delta\chi_1(\tau)\chi_2^*(\tau)\}\right\}|n\rangle\,, \\
&= e^{-ih_1t}\exp_T\left\{iC\int_0^t d\tau[1-P(\tau)]x(\tau)\right\}|n\rangle\exp\left\{-2i\mathrm{Re}\Delta\int_0^t d\tau\chi_1(\tau)\chi_2^*(\tau)\right\}, \qquad \text{(A1)} \\
&= e^{-ih_1t}\exp\left\{iC\int_0^t d\tau[1-P(\tau)]x(\tau)\right\}|n\rangle\, e^{-iF(t)}, \qquad \text{(A2)}
\end{aligned}$$

where $\exp_T$ denotes the time-ordered exponential and $x(t) = e^{ih_1t}xe^{-ih_1t} = 1/\sqrt{2}(e^{-i\omega t}b + e^{i\omega t}b^\dagger)$ represents the Heisenberg position operator. In (A1) we have changed to the interaction representation [35] and have used the fact that $\chi_1\chi_2^*$ is a c-number term. In (A2) the Magnus formula for the harmonic oscillator has been employed [36]. The real-valued function $F(t)$ containing the $\chi_1\chi_2^*$ term and the commutator term of the Magnus formula is not of further interest, as it is canceled out in (10) by the complex conjugated term $e^{iF(t)}$ stemming from $\langle\Phi_n(t)|$. Defining $\gamma(t) = iC/\sqrt{2}\int_0^t d\tau e^{-i\omega\tau}[1-P(\tau)]$, we thus obtain for the vibrational wave function

$$|\Phi_n(t)\rangle = e^{-ih_1t}\exp\{\gamma(t)b - \gamma^*(t)b^\dagger\}\,|n\rangle\, e^{-iF(t)}. \qquad \text{(A3)}$$

The remaining propagator terms $e^{\mp ih_k t}$ of (10) are transformed into the interaction representation by introducing the unitary transformation [28]

$$U^\dagger(t) = \exp\left\{\alpha(t)b - \alpha^*(t)b^\dagger\right\} \qquad \text{(A4)}$$

with $\alpha(t) = \sqrt{2}C/\omega\, e^{-i\omega t}$, which satisfies the relation $e^{-ih_2t} = e^{-ih_1t}U^\dagger(t)U(0)$. The insertion of (A3) and (A4) in (10) yields

$$\begin{aligned} K(t,t') &= \sum_n w_n \, \langle n| \exp\{-\gamma(t')b + \gamma^*(t')b^\dagger\} \exp\left\{\alpha(t)b - \alpha^*(t)b^\dagger\right\} \\ &\qquad \times \exp\left\{-\alpha(t')b + \alpha^*(t')b^\dagger\right\} \exp\{\gamma(t')b - \gamma^*(t')b^\dagger\} \, |n\rangle \\ &= \sum_n w_n \left\langle n \left| \exp\left\{ \Big[\alpha(t) - \alpha(t')\Big] b - \Big[\alpha(t) - \alpha(t')\Big]^* b^\dagger \right\} \right| n \right\rangle \\ &\qquad \times \exp\left\{i\mathrm{Im}\alpha(t)\alpha^*(t')\right\} \exp\left\{-2i\mathrm{Im}\gamma^*(t')[\alpha(t) - \alpha(t')]\right\}, \end{aligned} \tag{A5}$$

where in the second equation the Baker-Hausdorff theorem $e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]}$ has been employed. Performing the thermal average [36], the first two exponentials result in the perturbative memory kernel $K_0(t-t')$ of Eq. (12), while the last exponential directly gives $K_{\mathrm{nl}}(t,t')$ of Eq. (19).

In the case of a nonstationary initial condition (i.e., $h_B = h_1 - \delta_{\mathrm{neq}} C x$), we make the replacement $|n\rangle \to U^\dagger |n\rangle$, where $U = \exp\left\{\delta_{\mathrm{neq}} C/\sqrt{2}\omega \, (b - b^\dagger)\right\}$ represents the coordinate transformation from h_B to h_1. An analysis entirely analogous to the above directly leads to the nonequilibrium function $K_{\mathrm{neq}}(t,t')$.

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