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Nonperturbative time-convolutionless quantum master equation from the path integral approach

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The time-convolutionless quantum master equation is widely used to simulate reduced dynamics of a quantum system coupled to a bath. However, except for several special cases, applications of this equation are based on perturbative calculation of the dissipative tensor, and are limited to the weak system-bath coupling regime. In this paper, we derive an exact time-convolutionless quantum master equation from the path integral approach, which provides a new way to calculate the dissipative tensor nonperturbatively. Application of the new method is demonstrated in the case of an asymmetrical two-level system linearly coupled to a harmonic bath. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3108521]

I. INTRODUCTION

Quantum processes play an important role in many condensed phase phenomena,[1,2] while accurate and efficient methods to simulate quantum dynamics in multidimensional systems remain one of the most important challenges in theoretical chemistry. A popular method to calculate quantum dynamics with many degrees of freedom is to decompose the total system into system and bath parts, where the system part is described explicitly using the reduced density operator (RDO) and the bath part is treated implicitly in the equation of motion of the system RDO.[3–5] Within the reduced system dynamics framework, exact generalized quantum master equations (GQMEs) can be derived using the Nakajima–Zwanzig approach[6–8] and the Hashitsume–Shibata–Takahashi approach,[9,10] which formulate the reduced system dynamics in the time-convolution (TC) and time-convolutionless (TCL) forms. However, in practice, most GQME calculations were based on approximate versions of the exact GQMEs, especially the second order perturbation approximations, due to their simplicity.

In their applications to condensed phase systems, a major problem of the second order quantum master equations is that their validity is not guaranteed because of the strong system-bath coupling usually encountered in such systems. To overcome this problem, fourth order perturbative quantum master equations were derived.[11–15] However, the formulation of these fourth order perturbation expansions is rather cumbersome and their extensions to higher orders are difficult. A different approach is to use the Padé approximation for the perturbation series to infinite order,[16–18] where only the calculations of second and fourth order expansions are needed. This approach works well when the collective bath dynamics is near Markovian, while its applicability in general systems is not very clear. An alternative approach is to explicitly include a collective bath coordinate into the system degrees of freedom, such that the weak coupling approximation could be applied.[4,19] This approach relies on the reduction in coupling strength between the newly defined system and bath parts, and was found to be successful in several problems. Nonperturbative approaches to the GQME method were also investigated. Golosov *et al.*[20,21] derived an approximate memory equation based on the path integral tensor multiplication method. Geva and co-workers[22–24] introduced a method to calculate exact or approximate dissipative kernels in the TC form of GQME using correlation function methods.

In this paper, we will investigate the possibility to nonperturbatively calculate the dissipative tensor in the TCL form of GQME. Comparing to the TC form of GQME, the TCL GQME does not involve the integration over the system history, and has found wide applications in quantum dissipative theory.[5,25,26] Exact TCL quantum master equation exists in the case of a harmonic oscillator coupled bilinearly to a harmonic bath,[5,27,28] and pure dephasing dynamics.[29] However, nonperturbative dissipative tensor for general anharmonic systems has not been calculated before.

We will derive an exact TCL quantum master equation using the path integral method. The path integral approaches have been widely used to calculate condensed phase quantum dynamics, leading to important analytical results[28,30] and efficient numerical algorithms.[31–36] Calculating the time derivatives of the exact path integral expression has also lead to the exact hierarchical equations of motion (HEOM) method involving a infinite number of auxiliary RDOs.[37–42] It is also found out that truncations of the HEOM equations at specific

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level can further provide a convenient formulation of high order perturbative quantum master equations.[15,41] In Refs. 43 and 44, the path integral formalism have been used to show that the HEOM can be terminated at the first tier for a pure dephasing system, and at the second tier for a harmonic system bilinearly coupled to a harmonic bath, which leads to exact TCL GQMEs in such special cases. It should be noted that the argument in Ref. 44 that the second order TCL GQME is exact for all coupling strengths is not correct, as this is only true for pure dephasing cases.[45]

In this paper, we employ a different strategy from the previous studies by explicitly writing the exact time-dependent dissipative tensor in the path integral formula. The applicability of the new method is then demonstrated on a model system.

The remainder of this paper is organized as follows. In Sec. II, we briefly review the TC and TCL forms of the exact quantum master equations, and derive an exact TCL quantum master equation from the path integral approach. A practical way to calculate the exact dissipative tensor is then presented. In Sec. III, we present numerical results for the exact time-dependent dissipative tensor and the reduced system dynamics for an asymmetric spin-boson model. Conclusions are made in Sec. IV.

II. THEORY

A. The TC and TCL quantum master equations

Considering a general total Hamiltonian describing a system coupled to a bath

$$\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_{sb}, \tag{1}$$

where $\hat{H}_s$ is the system Hamiltonian, $\hat{H}_b$ is the bath Hamiltonian, and $\hat{H}_{sb}$ couples the system and bath degrees of freedom. For simplicity, we assume that

$$\hat{H}_{sb} = \hat{F} \otimes \hat{Q}, \tag{2}$$

where $\hat{F}$ is a system operator and $\hat{Q}$ is a bath operator.

Time evolution of the total system and bath density matrix $\hat{\rho}_T$ is governed by the Liouville equation,

$$\frac{d}{dt}\hat{\rho}_T = -\frac{i}{\hbar}[\hat{H},\hat{\rho}_T] = -\frac{i}{\hbar}\mathcal{L}\hat{\rho}_T. \tag{3}$$

The reduced system density operator $\hat{\rho}_s(t)$ is defined as the partial trace of $\hat{\rho}_T$ over the bath degrees of freedom, $\hat{\rho}_s(t) = \text{Tr}_b\hat{\rho}_T(t)$. The projection operator formalism by Nakajima and Zwanzig allows us to derive the equation of motion for $\hat{\rho}_s(t)$. A projection operator onto the system subspace is defined as $\mathcal{P} = \hat{\rho}_b^{\text{eq}} \otimes \text{Tr}_b$. Here, as in many previous studies, we have used the equilibrium Boltzman bath density operator $\hat{\rho}_b^{\text{eq}} = e^{-\beta\hat{H}_b}/\text{Tr}\, e^{-\beta\hat{H}_b}$ as the reference operator in defining $\mathcal{P}$. The superoperator $\mathcal{Q}$ is defined as $\mathcal{Q} = 1 - \mathcal{P}$.

The formal exact generalized quantum master equation can be written as[3,7,28,46]

$$\frac{d}{dt}\hat{\rho}_s(t) = -\frac{i}{\hbar}\mathcal{L}_s^{\text{eff}}\hat{\rho}_s(t) - \int_0^t d\tau \mathcal{K}(\tau)\hat{\rho}_s(t-\tau) + \mathcal{I}(t), \tag{4}$$

$$\mathcal{L}_s^{\text{eff}} = \mathcal{L}_s + \text{Tr}_b\mathcal{L}_{sb}\hat{\rho}_b^{\text{eq}}, \tag{5}$$

$$\mathcal{K}(\tau) = \frac{1}{\hbar^2}\text{Tr}_b\mathcal{L}_{sb}e^{-i\mathcal{QL}\tau/\hbar}\mathcal{Q}(\mathcal{L}_b + \mathcal{L}_{sb})\hat{\rho}_b^{\text{eq}}, \tag{6}$$

$$\mathcal{I}(t) = -\frac{i}{\hbar}\text{Tr}_b\mathcal{L}_{sb}e^{-i\mathcal{QL}t/\hbar}\mathcal{Q}\hat{\rho}_T(0), \tag{7}$$

where $\mathcal{K}(t)$ is the dissipative memory kernel, and $\hat{\rho}_T(0)$ is the initial density operator of the total system. Equations (4)–(7) consist of the TC form of the exact GQME.

We will choose a separable initial condition

$$\hat{\rho}_T(0) = \hat{\rho}_s(0) \otimes \hat{\rho}_b^{\text{eq}}, \tag{8}$$

the inhomogeneous term $\mathcal{I}(t)$ [Eq. (7)] then vanishes. Since the equilibrium bath density operator is used in Eq. (8), $\mathcal{L}_b\hat{\rho}_b^{\text{eq}} \otimes \rho_s = 0$, the kernel can be simplified as

$$\mathcal{K}(\tau) = \frac{1}{\hbar^2}\text{Tr}_b\{\mathcal{L}_{sb}e^{-i\mathcal{QL}\tau/\hbar}\mathcal{L}_{sb}\hat{\rho}_b^{\text{eq}}\}. \tag{9}$$

Without losing generality, we also assume that the average of the bath operator $\hat{Q}$, $\langle\hat{Q}\rangle_{\text{eq}}^0 \equiv \text{Tr}(\hat{Q}\hat{\rho}_b^{\text{eq}}) = 0$, such that $\mathcal{L}_s^{\text{eff}} = \mathcal{L}_s$.

The TC form of GQME involves the integration over the history of the system RDO. It has been shown that such explicit dependence on the system history can be removed. Particularly, Hashitsume and co-workers[9,10] derived the following exact quantum master equation

$$\frac{d}{dt}\hat{\rho}_s(t) = -\frac{i}{\hbar}\mathcal{L}_s^{\text{eff}}\hat{\rho}_s(t) - \mathcal{R}(t)\hat{\rho}_s(t) + \tilde{\mathcal{I}}(t), \tag{10}$$

where

$$\mathcal{R}(t)\hat{\rho}_s(t) = \frac{i}{\hbar}\text{Tr}_b\{\mathcal{L}[\theta(t) - 1]\hat{\rho}_b^{\text{eq}}\}, \tag{11}$$

$$\tilde{\mathcal{I}}(t) = -\frac{i}{\hbar}\text{Tr}_b\{\mathcal{L}\theta(t)e^{-i\mathcal{QL}t/\hbar}\mathcal{Q}\hat{\rho}_T(0)\}, \tag{12}$$

and $\theta(t)$ is defined as the inverse of a superoperator

$$\theta(t) = (\mathcal{P} + e^{-i\mathcal{QL}t/\hbar}\mathcal{Q}e^{i\mathcal{L}t/\hbar})^{-1}. \tag{13}$$

If the initial condition (8) is used, $\tilde{I}(t) = 0$. The time derivative of $\hat{\rho}_s(t)$ in Eq. (10) thus depends only on $\hat{\rho}_s(t)$. This is the reason that Eq. (10) is called the TCL form of GQME.

B. TCL equation from the path integral approach

To perform the path integral calculations, we consider a system coupled linearly to a harmonic bath, where $\hat{H}_b$ and $\hat{H}_{sb}$ are given by

$$\hat{H}_b = \sum_{i=1}^{N}\left(\frac{\hat{p}_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2\hat{q}_i^2\right), \tag{14}$$

$$\hat{H}_{sb} = \hat{F} \otimes \hat{Q} = \hat{F} \otimes \sum_{i=1}^{N} c_i \hat{q}_i, \tag{15}$$

where $\hat{q}_i$, $\hat{p}_i$, m_i, and ω_i are the coordinate, momentum, mass, and frequency of the ith bath mode, respectively; c_i is the coupling coefficient between the system and the ith bath mode. $\hat{Q}$ is defined as a linear combination of bath coordinates. We now define the reduced density matrix using the eigenstates of $\hat{F}$: $\rho_{ab}(t) = \langle \phi_a | \hat{\rho}_s(t) | \phi_b \rangle$, where $\hat{F}|\phi_a\rangle = \phi_a|\phi_a\rangle$ and $\hat{F}|\phi_b\rangle = \phi_b|\phi_b\rangle$. $\rho_{ab}(t)$ can then be calculated using the path integral approach by analytically integrating over the harmonic bath[47,48]

$$\rho_{ab}(t) = \sum_{ef} \int \mathcal{D}\phi^+(t) \int \mathcal{D}\phi^-(t) e^{i/\hbar(S[\phi^+(\tau)]-S[\phi^-(\tau)])} \times e^{-F[\phi^+(\tau),\phi^-(\tau)]} \rho_{ef}(0). \tag{16}$$

Here, $\phi^+(\tau)$ and $\phi^-(\tau)$ define the forward and backward system paths, $\hat{F}|\phi^\pm(\tau)\rangle = \phi^\pm(\tau)|\phi^\pm(\tau)\rangle$, $\phi^+(t) = \phi_a$, $\phi^-(t) = \phi_b$, $\phi^+(0) = \phi_e$, $\phi^-(0) = \phi_f$, $S[\phi^+(\tau)]$, and $S[\phi^-(\tau)]$ are the forward and backward system actions, and $F[\phi^+(\tau),\phi^-(\tau)]$ is the Feynman–Vernon influence functional:

$$F[\phi^+(\tau),\phi^-(\tau)] = \frac{1}{\hbar^2} \int_0^t ds \int_0^s du V_-(s)[\alpha_R(s-u)]V_-(u) + i\alpha_I(s-u)V_+(u)]. \tag{17}$$

In the above Eq. (17), $V^+(\tau) = \phi^+(\tau) + \phi^-(\tau)$, $V^-(\tau) = \phi^+(\tau) - \phi^-(\tau)$, α_R and α_I are the real and imaginary parts of the bath correlation function

$$\alpha_R(t) + i\alpha_I(t) = \frac{1}{Z_b} \mathrm{Tr}[e^{-\beta \hat{H}_b} e^{(i/\hbar)\hat{H}_b t} \hat{Q} e^{-(i/\hbar)\hat{H}_b t} \hat{Q}], \tag{18}$$

with $Z_b = \mathrm{Tr}\, e^{-\beta \hat{H}_b}$.

The harmonic bath is usually characterized by the spectral density $J(\omega)$ defined as

$$J(\omega) = \frac{\pi}{2} \sum_i \frac{c_i^2}{m_i \omega_i} \delta(\omega - \omega_i). \tag{19}$$

$\alpha_R(t)$ and $\alpha_I(t)$ can then be calculated

$$\alpha_R(t) = \frac{\hbar}{\pi} \int_0^\infty d\omega J(\omega) \coth\left(\frac{\hbar\omega\beta}{2}\right) \cos \omega t, \tag{20}$$

$$\alpha_I(t) = -\frac{\hbar}{\pi} \int_0^\infty d\omega J(\omega) \sin \omega t. \tag{21}$$

The equation of motion for $\rho_{ab}(t)$ can be obtained by taking the time derivative of Eq. (16),

$$\frac{\partial \rho_{ab}(t)}{\partial t} = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_s(t)]_{ab} - \frac{1}{\hbar^2} \sum_{cd;ef} \int \tilde{\mathcal{D}}\phi^+(t) \int \tilde{\mathcal{D}}\phi^-(t) \int_0^t \times d\tau V_-(t)[\alpha_R(t-\tau)V_-(\tau) + i\alpha_I(t-\tau)V_+(\tau)] \times e^{(i/\hbar)(S[\phi^+(\tau)]-S[\phi^-(\tau)])} e^{-F[\phi^+(\tau),\phi^-(\tau)]} \rho_{ef}(0). \tag{22}$$

In the above Eq. (22), the first term comes from the time derivative of $S[\phi^+] - S[\phi^-]$, which gives the commutator between $\hat{H}_s$ and $\hat{\rho}_s$; the second term comes from the time derivative of the influence functional. The restricted path integration $\tilde{\mathcal{D}}\phi^+(t)$ and $\tilde{\mathcal{D}}\phi^-(t)$ means that the forward and backward path is fixed to ϕ_c and ϕ_d at time $t-\tau$, namely, $\phi^+(t-\tau) \equiv \phi_c$ and $\phi^-(t-\tau) \equiv \phi_d$.

The goal is to derive from Eq. (22) a closed equation for $\rho_{ab}(t)$. In general, this is a difficult task since all the $\phi^\pm(\tau)$'s are correlated in calculating the influence functional and there is no simple way to express the second term in Eq. (22) as a function of $\rho_{ab}(t)$. In special cases such as a harmonic oscillator system, or the pure dephasing case, exact TCL equation can be obtained. It is also possible to derive a set of nonclosed hierarchical equations of motion with an infinite number of auxiliary density operators.[37–42] In this paper, we will adopt a different strategy.

To calculate the second term in Eq. (22), we define

$$K_{ab;cd}(t,\tau) = \sum_{ef} \int \tilde{\mathcal{D}}\phi^+(t) \int \tilde{\mathcal{D}}\phi^-(t) e^{(i/\hbar)(S[\phi^+(\tau)]-S[\phi^-(\tau)])} \times e^{-F[\phi^+(\tau),\phi^-(\tau)]} \rho_{ef}(0). \tag{23}$$

The exact TCL Eq. (22) is now written as

$$\frac{\partial \rho_{ab}(t)}{\partial t} = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_s(t)]_{ab} - \frac{1}{\hbar^2} \sum_{cd} \int_0^t d\tau (\phi_a - \phi_b) \times [\alpha_R(\tau)(\phi_c - \phi_d) + i\alpha_I(\tau)(\phi_c + \phi_d)] K_{ab;cd}(t,\tau). \tag{24}$$

The above Eqs. (23) and (24) are the starting point of our derivation. They can also be used to derive approximate GQMEs. In Appendix A, we show how the TC and TCL second order GQMEs can be derived by applying approximations to the exact path integral result [Eqs. (23) and (24)].

To calculate $K_{ab;cd}(t,\tau)$ nonperturbatively, we inverse $\rho_{ef}(0)$ using the following equation:

$$\rho_{ab}(t) = \sum_{ef} \Phi_{ab;ef}(t) \rho_{ef}(0), \tag{25}$$

where $\Phi(t)$ can be calculated using Eq. (16). The inverse can be calculated as

$$\rho_{ef}(0) = \sum_{mn} \Phi^{-1}_{ef;mn}(t) \rho_{mn}(t). \tag{26}$$

$K_{ab;cd}(t,\tau)$ can now be calculated,

$$
\begin{aligned}
K_{ab;cd}(t,\tau) &= \sum_{ef} \int \tilde{\mathcal{D}}\phi^{+}(t) \int \tilde{\mathcal{D}}\phi^{-}(t) e^{(i/\hbar)(S[\phi^{+}(\tau)]-S[\phi^{-}(\tau)])} e^{-F[\phi^{+}(\tau),\phi^{-}(\tau)]} \rho_{ef}(0) \\
&= \sum_{mn,ef} \int \tilde{\mathcal{D}}\phi^{+}(t) \int \tilde{\mathcal{D}}\phi^{-}(t) e^{(i/\hbar)(S[\phi^{+}(\tau)]-S[\phi^{-}(\tau)])} e^{-F[\phi^{+}(\tau),\phi^{-}(\tau)]} \Phi^{-1}_{ef;mn}(t) \rho_{mn}(t) \\
&= \sum_{mn} M^{mn}_{ab;cd}(t,\tau) \rho_{mn}(t), \qquad (27)
\end{aligned}
$$

where $M^{mn}_{ab;cd}(t,\tau)$ is defined as

$$
\begin{aligned}
M^{mn}_{ab;cd}(t,\tau) = \sum_{ef} \int \tilde{\mathcal{D}}\phi^{+}(t) \int \tilde{\mathcal{D}}\phi^{-}(t) e^{(i/\hbar)(S[\phi^{+}(\tau)]-S[\phi^{-}(\tau)])} \\
\times e^{-F[\phi^{+}(\tau),\phi^{-}(\tau)]} \Phi^{-1}_{ef;mn}(t). \qquad (28)
\end{aligned}
$$

By putting Eq. (27) into Eq. (24)

$$
\frac{\partial \rho_{ab}(t)}{\partial t} = -\frac{i}{\hbar}[\hat{H}_s,\hat{\rho}_s(t)]_{ab} - \sum_{mn} \mathcal{R}_{ab;mn}(t) \rho_{mn}(t,\tau). \qquad (29)
$$

The dissipative tensor $\mathcal{R}_{ab;mn}(t)$ is defined as

$$
\begin{aligned}
\mathcal{R}_{ab;mn}(t) = \frac{1}{\hbar^2} \sum_{cd} \int_0^t d\tau (\phi_a - \phi_b)[\alpha_R(\tau)(\phi_c - \phi_d) \\
+ i\alpha_I(\tau)(\phi_c + \phi_d)] M^{mn}_{ab;cd}(t,\tau). \qquad (30)
\end{aligned}
$$

C. Numerical method to calculate $\mathcal{R}(t)$

Clearly, the above Eqs. (28)–(30) is only useful in case (a) the dissipative tensor $\mathcal{R}(t)$ converges to a fixed value after a short period of time τ_0, otherwise, calculating $\Phi(t)$ at long time requires that we already know the exact dynamics; (b) $\Phi(t)$ and $K_{ab;cd}(t,\tau)$ can be calculated using exact or approximate methods until $\mathcal{R}(t)$ converges to a fixed value. The first condition usually holds when the bath correlation function decays much faster than the system dynamics. The second condition is also not a trivial problem, since many numerical path integral algorithms only work for a short period of time, and the accuracy of most approximate methods deteriorate at long times. We will assume that the above two conditions are satisfied, and proceed with the numerical calculation of $\mathcal{R}(t)$.

To calculate $\mathcal{R}(t)$, we need to obtain $\Phi(t)$ and $K_{ab;cd}(t,\tau)$ first. The path integral expressions Eqs. (16) and (23) are first discretized, using methods such as the quasiadiabatic path integral method by Makri and co-workers.[33–36] $\Phi(t)$ can be calculated in the usually way by setting $\hat{\rho}_s(0)$ to different initial conditions. $\Phi^{-1}(t)$ is then obtained by inversion of $\Phi(t)$. Calculation of the $K_{ab;cd}(t,\tau)$ term using the path integral method is illustrated Fig. 1, namely, we need to fix the system coordinates both at the end points (at time 0 and t), and the middle points (at time $t-\tau$) when summing over all the paths. Each path is indexed with six labels, such that all paths with the same end points and middle points are summed together. This is a rather general approach that could be applied to both direct summation (for short time) and Monte Carlo calculations (for longer time) of the discretized path integral expression.

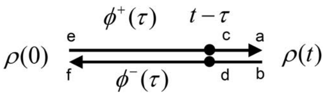

FIG. 1. The path integral scheme to calculate $K_{ab,cd}(t,\tau)$.

III. RESULTS

In this section, we apply the above derived equations to calculate the exact dissipative tensor in an asymmetric spin-boson model. The system Hamiltonian can be written as

$$
\hat{H}_s = \hbar\Delta\hat{\sigma}_x + \hbar\epsilon\hat{\sigma}_z, \qquad (31)
$$

where $\hat{\sigma}_x$ and $\hat{\sigma}_z$ are the Pauli matrices. The system is assumed to couple with the harmonic bath via the operator $\hat{F}=\hat{\sigma}_z$.

Numerical results reported below were obtained for $\hbar\Delta=\hbar\epsilon=1$, $\hbar\Delta\beta=5$. We also assume an Ohmic spectral density $J(\omega)$ with exponential cutoff

$$
J(\omega) = \frac{\pi}{2}\xi\omega e^{-\omega/\omega_c}, \qquad (32)
$$

with the parameters $\xi=0.1$ and $\omega_c=7.5\Delta$.

We first compare the exact dissipative tensor to the weak coupling (WC) result using Eq. (A10) in Appendix A. The dissipative tensor for the spin-boson model is represented by a 4×4 complex-valued matrix. From Eqs. (30) and (A10), the matrix elements of both the exact and approximate dissipative tensors $\mathcal{R}_{ab,mn}(t)$ are zero when $a=b$. They also have the following symmetry relationships: $\mathcal{R}_{12;11}(t)=\mathcal{R}_{21;11}(t)^*$, $\mathcal{R}_{12;12}(t)=\mathcal{R}_{21;21}(t)^*$, $\mathcal{R}_{12;21}(t)=\mathcal{R}_{21;12}(t)^*$, and $\mathcal{R}_{12;22}(t)=\mathcal{R}_{21;22}(t)^*$. Therefore, there are only four independent matrix elements, which will be chosen as $\mathcal{R}_{12;11}(t)$, $\mathcal{R}_{12;12}(t)$, $\mathcal{R}_{12;21}(t)$, and $\mathcal{R}_{12;22}(t)$. The real and imaginary parts of the above four matrix elements are shown in Figs. 2 and 3, respectively. We can see that the real part of $\mathcal{R}_{12;21}(t)$, and the imaginary parts of $\mathcal{R}_{12;12}(t)$ and $\mathcal{R}_{12;21}(t)$ are not well converged in the time interval studied. However, their values are rather small and will not lead to large errors in the dynamics.

To calculate the reduced system dynamics, we assume that the initial state is $\hat{\rho}_s(0)=|1\rangle\langle 1|$. The population on state $|1\rangle$ from the nonperturbative and second order TCL form of GQME is shown as a function of time in Fig. 4. During the calculation, the dissipative tensors for $\Delta t>2.4$ are assumed

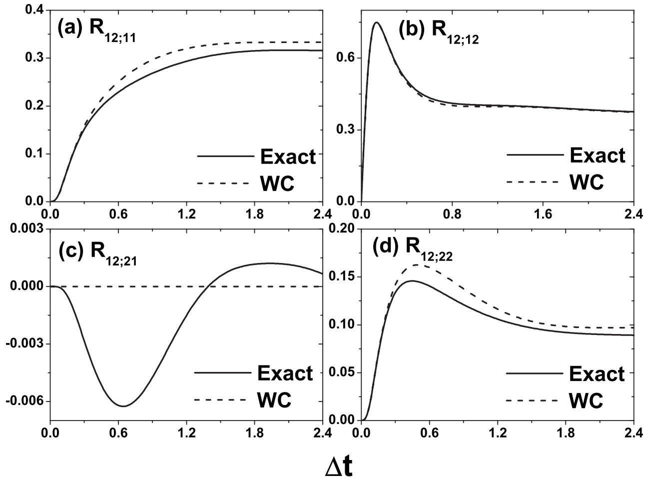

FIG. 2. The real part of (a) $\mathcal{R}_{12;11}(t)$, (b) $\mathcal{R}_{12;12}(t)$, (c) $\mathcal{R}_{12;21}(t)$, and (d) $\mathcal{R}_{12;22}(t)$ for the nonperturbative TCL form of GQME [Eq. (30)] (solid line). Also shown are the corresponding predictions in the second order perturbation approximation [Eq. (A10)] (dashed line, WC indicates the weak coupling approximation).

to be constant using the values of $\mathcal{R}(t=2.4/\Delta)$. For comparison, the numerically exact result from the tensor multiplication method by Makri and co-workers[33–36] is also presented. We can see that the result of nonperturbative TCL GQME is essentially the same as the tensor multiplication result. The second order TCL GQME also performs better than its TC counterpart shown in Ref. 22.

IV. CONCLUSION

We have demonstrated that it is possible to calculate the exact dissipative tensor in the TCL GQMEs nonperturbatively in a general anharmonic system. Efficient application of the new method requires that the bath correlation decays in a short period of time such that the dissipative tensor converges quickly. In this sense, the nonperturbative GQME method presented in this study employs similar ideas as used in the path integral tensor multiplication method[33–36] and the nonperturbative TC quantum master equation method,[22–24] by trying to calculate long time dynamics using accurate short time information. They should be applied to similar kind of problems, and may both have problems in the case of slow baths.

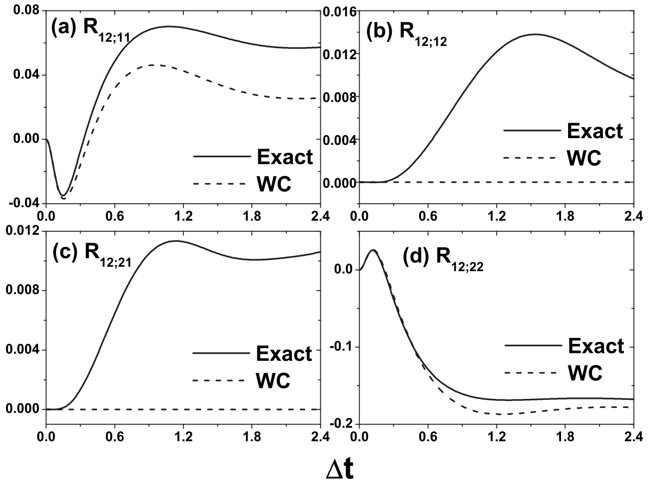

FIG. 3. Same as Fig. 2, for the imaginary parts of (a) $\mathcal{R}_{12;11}(t)$, (b) $\mathcal{R}_{12;12}(t)$, (c) $\mathcal{R}_{12;21}(t)$, and (d) $\mathcal{R}_{12;22}(t)$.

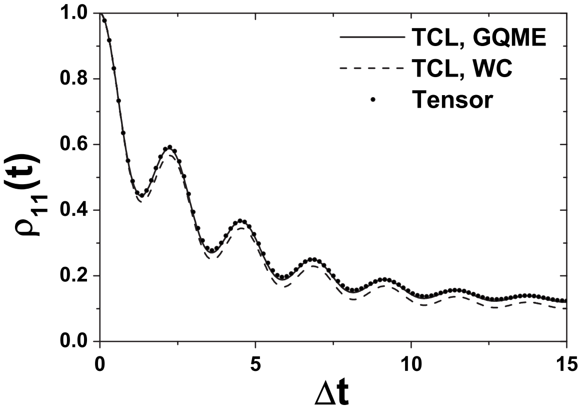

FIG. 4. The population dynamics of $\rho_{11}(t)$ for an asymmetrical two-level system coupled to a bath. The solid line is the result of the nonperturbative GQME in the TCL form [Eq. (29)]; the filled circles are the numerical exact result obtained via the tensor multiplication method by Makri and coworkers; the dashed line is the prediction from the second order GQME in the TCL form [Eq. (A9)] (weak coupling approximation).

On the other hand, the three methods provide different ways to incorporate the bath effects on the reduced system dynamics. The tensor multiplication approach uses a truncated tensor to describe the coupled system-bath states, and multiplication with the influence functional terms to do the time propagation. The TC and TCL GQMEs use reduced density operators to describe the system degrees of freedom, and use the dissipative kernel and tensor to incorporate bath effects on system dynamics. The computational costs of the nonperturbative TC and TCL GQMEs can also be compared. If N is the size of system basis, the TCL quantum master equation approach scales as N^4 after the dissipative tensor is obtained. This is improved over the nonperturbative TC quantum master equation approach, due to the fact that it is no more necessary to perform the integration over the system history. Calculation of the dissipative tensor scales as N^6, which may or may not be more efficient than calculating the dissipative kernel in the nonperturbative TC approach, depending on the particular problem investigated. The current formulation of the nonperturbative TCL approach could also serve as a starting point for further approximations. Such possibilities are currently investigated.

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APPENDIX A: DERIVATION OF THE SECOND ORDER QUANTUM MASTER EQUATIONS

We will derive the second order quantum master equations by applying proper approximations to Eq. (23). If we neglect the system-bath interaction during the time interval from $t-\tau$ to t, by replacing the total system propagator $e^{-(i/\hbar)\hat{H}\tau}$ with $e^{-(i/\hbar)(\hat{H}_s+\hat{H}_b)\tau}$ when calculating $K_{ab;cd}(t,\tau)$ [Eq. (23)],

$$K_{ab;cd}(t,\tau) \approx \langle a|e^{-(i/\hbar)\hat{H}_s\tau}|c\rangle\langle d|e^{(i/\hbar)\hat{H}_s\tau}|b\rangle\rho_{cd}(t-\tau). \tag{A1}$$

Then from Eq. (24), the dynamics of $\hat{\rho}_s(t)$ reduces to

$$\begin{aligned}\frac{\partial\rho_{ab}(t)}{\partial t} &= -\frac{i}{\hbar}[\hat{H}_s,\hat{\rho}_s(t)]_{ab} - \frac{1}{\hbar^2}\sum_{cd}\int_0^t d\tau(\phi_a-\phi_b)\\ &\quad\times[\alpha_R(\tau)(\phi_c-\phi_d)+i\alpha_I(\tau)(\phi_c+\phi_d)]\\ &\quad\times\langle a|e^{-(i/\hbar)\hat{H}_s\tau}|c\rangle\langle d|e^{(i/\hbar)\hat{H}_s\tau}|b\rangle\rho_{cd}(t-\tau)\\ &= -\frac{i}{\hbar}[\hat{H}_s,\hat{\rho}_s(t)]_{ab} - \frac{1}{\hbar^2}\sum_{cd}\int_0^t \mathcal{K}_{wc}^{ab;cd}(\tau)\rho_{cd}(t-\tau),\end{aligned} \tag{A2}$$

where the second order dissipative kernel $\mathcal{K}_{wc}^{ab;cd}$ is defined as

$$\begin{aligned}\mathcal{K}_{wc}^{ab;cd}(\tau) &= (\phi_a-\phi_b)[\alpha_R(\tau)(\phi_c-\phi_d)+i\alpha_I(\tau)(\phi_c+\phi_d)]\\ &\quad\times\langle a|e^{-(i/\hbar)\hat{H}_s\tau}|c\rangle\langle d|e^{(i/\hbar)\hat{H}_s\tau}|b\rangle.\end{aligned} \tag{A3}$$

The above Eqs. (A2) and (A3) consist of the second order TC quantum master equation.

To derive the second order TCL quantum master equation, we apply the Born approximation by applying the same approximation as in Eq. (A1) to calculate Eq. (16)

$$\rho_{ab}(t) \approx \sum_{cd}\langle a|e^{-(i/\hbar)\hat{H}_s\tau}|c\rangle\langle d|e^{(i/\hbar)\hat{H}_s\tau}|b\rangle\rho_{cd}(t-\tau), \tag{A4}$$

which can be inverted

$$\rho_{cd}(t-\tau) = \sum_{ef}\langle c|e^{(i/\hbar)\hat{H}_s\tau}|e\rangle\langle f|e^{-(i/\hbar)\hat{H}_s\tau}|d\rangle\rho_{ef}(t). \tag{A5}$$

Equation (A2) is then written as

$$\begin{aligned}\frac{\partial\rho_{ab}(t)}{\partial t} &= -\frac{i}{\hbar}[\hat{H}_s,\hat{\rho}_s(t)]_{ab} - \frac{1}{\hbar^2}\sum_{cd;ef}\int_0^t d\tau(\phi_a-\phi_b)\\ &\quad\times[\alpha_R(\tau)(\phi_c-\phi_d)+i\alpha_I(\tau)(\phi_c+\phi_d)]\\ &\quad\times\langle a|e^{-(i/\hbar)\hat{H}_s\tau}|c\rangle\langle d|e^{(i/\hbar)\hat{H}_s\tau}|b\rangle\langle c|e^{(i/\hbar)\hat{H}_s\tau}|e\rangle\\ &\quad\times\langle f|e^{-(i/\hbar)\hat{H}_s\tau}|d\rangle\rho_{ef}(t).\end{aligned} \tag{A6}$$

By noticing that

$$\begin{aligned}&\sum_{cd;ef}(\phi_a-\phi_b)\phi_c\langle a|e^{-(i/\hbar)\hat{H}_s\tau}|c\rangle\langle d|e^{(i/\hbar)\hat{H}_s\tau}|b\rangle\langle c|e^{(i/\hbar)\hat{H}_s\tau}|e\rangle\langle f|e^{-(i/\hbar)\hat{H}_s\tau}|d\rangle\rho_{ef}(t)\\ &\quad=\sum_{c,e}(\phi_a-\phi_b)\phi_c\langle a|e^{-(i/\hbar)\hat{H}_s\tau}|c\rangle\langle c|e^{(i/\hbar)\hat{H}_s\tau}|e\rangle\rho_{eb}(t)\\ &\quad=\sum_{e}(\phi_a-\phi_b)\langle a|e^{-(i/\hbar)\hat{H}_s\tau}\hat{F}e^{(i/\hbar)\hat{H}_s\tau}|e\rangle\rho_{eb}(t),\end{aligned} \tag{A7}$$

and

$$\begin{aligned}&\sum_{cd;ef}(\phi_a-\phi_b)\phi_d\langle a|e^{-(i/\hbar)\hat{H}_s\tau}|c\rangle\langle d|e^{(i/\hbar)\hat{H}_s\tau}|b\rangle\langle c|e^{(i/\hbar)\hat{H}_s\tau}|e\rangle\langle f|e^{-(i/\hbar)\hat{H}_s\tau}|d\rangle\rho_{ef}(t)\\ &\quad=\sum_{d,f}(\phi_a-\phi_b)\phi_d\langle d|e^{(i/\hbar)\hat{H}_s\tau}|b\rangle\langle f|e^{-(i/\hbar)\hat{H}_s\tau}|d\rangle\rho_{af}(t)\\ &\quad=\sum_{f}(\phi_a-\phi_b)\langle f|e^{-(i/\hbar)\hat{H}_s\tau}\hat{F}e^{(i/\hbar)\hat{H}_s\tau}|b\rangle\rho_{af}(t),\end{aligned} \tag{A8}$$

Equation (A6) can then be written as

$$\frac{\partial\rho_{ab}(t)}{\partial t} = -\frac{i}{\hbar}[\hat{H}_s,\hat{\rho}_s(t)]_{ab} - \frac{1}{\hbar^2}\sum_{cd}\mathcal{R}_{wc}^{ab;cd}(t)\rho_{cd}(t), \tag{A9}$$

where

$$\begin{aligned}\mathcal{R}_{wc}^{ab;cd}(t) &= \int_0^t d\tau(\phi_a-\phi_b)[\alpha_R(\tau)+i\alpha_I(\tau)]\\ &\qquad\times\langle a|e^{-(i/\hbar)\hat{H}_s\tau}\hat{F}e^{(i/\hbar)\hat{H}_s\tau}|c\rangle\delta_{bd} + \int_0^t d\tau(\phi_b-\phi_a)\\ &\qquad\times[\alpha_R(\tau)-i\alpha_I(\tau)]\langle d|e^{-(i/\hbar)\hat{H}_s\tau}\hat{F}e^{(i/\hbar)\hat{H}_s\tau}|b\rangle\delta_{ac}.\end{aligned} \tag{A10}$$

Equations (A9) and (A10) consist of the TCL second order quantum master equation, and they are used to obtain the perturbative TCL quantum master equation results shown in Figs. 2–4. As in the above derivation of Eqs. (A9) and (A10), the second order TCL quantum master equation is usually regarded as a further approximation to its TC counterpart by applying the Born approximation [Eqs. (A4) and (A5)]. However, we can see from the above derivation that Eqs. (A1) and (A4) involve the same approximation, so generally we cannot tell which one of the second order quantum master equations is more accurate. In fact, the TCL equation may become superior in particular problems due to the cancellation of errors when applying Eqs. (A1) and (A5) simultaneously.

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