Quantum Master Equation Approach for the Relaxation of Quantum Open Systems

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I. INTRODUCTION

Dissipative dynamics of a quantum system embedded in a complex environment has been of great interest in recent years. Because of its important role in physics and chemistry, numerous works have been devoted to theoretical models for open quantum systems[1, 2]. However, in contrast to classical dissipative processes, that can be satisfactorily described by classical Langevin or Fokker-Planck equations [3], a general theory for quantum dissipation is still considered an unsolved issue.

Despite the difficulty of formulating a general theory, adequate results can be obtained in many limiting cases. As a general theoretical framework, the celebrated reduced dynamics description derived from projection operator or cumulant expansion techniques has generated promising results over the past few decades. By partitioning the total system into a "system" part and a "bath" part, one can reformulate the exact quantum Liouville equation and perform a mathematically rigorous expansion in the weak-coupling limit. As a result, time-convolution or time-convolutionless quantum master equations describing the dynamics of the reduced system can be derived by following either a chronological ordering prescription (COP) or partial ordering prescription (POP), respectively [4–6]. These equations are usually non-Markovian and difficult to treat analytically. Therefore, a separation of time scales is usually postulated and the memory effects in the dynamics are then neglected for times greater than the bath relaxation time τ_b. This approximation allows us to derive the popular Markovian master equations (Redfield equations [7]) for the reduced dynamics of the quantum system.

It is instructive to formally derive the Markovian quantum master equation and see how the irreversible dynamics of the reduced system emerges from the reversible dynamics generated by the Hamiltonian of a macroscopic total system. Here, we provide such a derivation and explicitly show the approximations involved in deriving the Markovian quantum master equation.

II. DERIVATION OF A GENERALIZED QUANTUM MASTER EQUATION

We start from the quantum Liouville equation ($\hbar = 1$) that describes the density matrix $\rho(t)$ of a total system with Hamiltonian H

$$\begin{aligned} \dot{\rho}(t) &= -i[H, \rho(t)] \\ &= -i\mathcal{L}\rho(t), \end{aligned} \tag{1}$$

where we have defined the Liouville superoperator as the commutator of the Hamiltonian with an arbitrary operator $\mathcal{O}$, $\mathcal{L}\mathcal{O} = [H, \mathcal{O}]$. In the Laplace space ($t \to s$), the Liouville equation is

$$s\tilde{\rho}(s) = \rho(0) - i\mathcal{L}\tilde{\rho}(s), \tag{2}$$

where $\tilde{\rho}(s)$ is the Laplace transform of $\rho(t)$, and $\rho(0)$ is the initial condition of the total system. Equation (2) provides the formal solution of the Liouville equation in the Laplace space, $\tilde{\rho}(s) = \frac{1}{s+i\mathcal{L}}\rho(0)$. Note that $\frac{1}{s+i\mathcal{L}}$ is a superoperator and should be interpreted as the inverse of $(s + i\mathcal{L})$.

In most physical applications, we are only interested in properties that are determined by states in a subspace of the total Hilbert space. Using a projection operator $\mathcal{P}$, we divide the density matrix of the total system into a relevant part $\rho_1(t) = \mathcal{P}\rho(t)$, and an irrelevant part $\rho_2(t) = (1 - \mathcal{P})\rho(t) \equiv \mathcal{Q}\rho(t)$, so that $\rho(t) = \rho_1(t) + \rho_2(t)$. Note that by definition, projectors $\mathcal{P}$ and $\mathcal{Q}$ must satisfy $\mathcal{P}\mathcal{P}\ldots\mathcal{P} = \mathcal{P}$, $\mathcal{Q}\mathcal{Q}\ldots\mathcal{Q} = \mathcal{Q}$, and $\mathcal{P}\mathcal{Q} = \mathcal{Q}\mathcal{P} = 0$. Applying $\mathcal{P}$ and $\mathcal{Q}$ to both sides of Eq. (2), we obtain two coupled linear equations:

$$\begin{aligned} s\tilde{\rho}_1(s) - \rho_1(0) &= -i\mathcal{P}\mathcal{L}[\tilde{\rho}_1(s) + \tilde{\rho}_2(s)], \\ s\tilde{\rho}_2(s) - \rho_2(0) &= -i\mathcal{Q}\mathcal{L}[\tilde{\rho}_1(s) + \tilde{\rho}_2(s)]. \end{aligned}$$

These equations can be solved to obtain the formal solution for the relevant part of the density matrix in the Laplace space,

$$s\tilde{\rho}_s(s) - \rho_s(0) = -i\mathcal{P}\mathcal{L}\tilde{\rho}_s(s) - i\mathcal{P}\mathcal{L}\frac{1}{s + i\mathcal{Q}\mathcal{L}}\rho_b(0) - \mathcal{P}\mathcal{L}\frac{1}{s + i\mathcal{Q}\mathcal{L}}\mathcal{Q}\mathcal{L}\tilde{\rho}_s(s)]. \tag{3}$$

The inverse Laplace transform of Eq. (3) yields the following differential-integral equation that describes the time evolution of $\rho_1(t)$:

$$\dot{\rho}_1(t) = -i\mathcal{P}\mathcal{L}e^{-i\mathcal{Q}\mathcal{L}t}\rho_2(0) - i\mathcal{P}\mathcal{L}\rho_1(t) - \int_0^t d\tau \mathcal{K}(\tau)\rho_1(t-\tau), \tag{4}$$

where we have defined the memory kernel

$$\mathcal{K}(\tau) = \mathcal{P}\mathcal{L}e^{-i\mathcal{Q}\mathcal{L}\tau}\mathcal{Q}\mathcal{L}. \tag{5}$$

The first term in the right hand side of Eq. (4) explicitly depends on the initial condition of the irrelevant part of the total system $\rho_2(0)$. However, by choosing an initial condition so that $\mathcal{P}\rho(0) = \rho(0)$, we can make $\rho_2(0) = 0$, and the $\rho_2(0)$ term will vanish identically. For example, the projection operator defined in Eq. (**??**) and the product state initial condition defined in Eq. (10) satisfy the this condition. Hence, by selecting a proper combination of projector and initial conditions, Eq. (4) can be simplified to

$$\dot{\rho}_1(t) = -i\mathcal{P}\mathcal{L}\rho_1(t) - \int_0^t d\tau \mathcal{K}(\tau)\rho_1(t-\tau). \tag{6}$$

Equation (6) has a non-Markovian memory kernel, and is in the form of a generalized Fokker-Planck equation. The first term in Eq. (6) represents the unitary evolution governed by the Hamiltonian of the system, and the second term represents the dissipative dynamics of the relevant part of the total system. Note that total system still undergoes unitary evolution [Eq. (1)], it is the reduced system degrees of freedom (after tracing out the environment degrees of freedom) that have to be described by a non-unitary evolution. Clearly, the non-unitary evolution is a result of the separation of the total system into the system part and the bath part.

To derive the dynamics for a reduced system, we separate the total Hamiltonian H into the system part H_S, the bath part H_B, and the system-bath interaction part λH_{SB}. We also require that H_S and H_B operate in two different Hilbert spaces, so that their commutator vanishes, $[H_S, H_B] = 0$. The corresponding Liouville operator can be decomposed accordingly:

$$\mathcal{L} \;=\; \mathcal{L}_S + \mathcal{L}_B + \lambda \mathcal{L}_{SB}. \tag{7}$$

In addition, we also define the projection operators $\mathcal{P}$ and $\mathcal{Q} = 1 - \mathcal{P}$ using

$$\mathcal{P}\rho = \rho_b^{eq} \mathrm{Tr}_B \rho. \tag{8}$$

where

$$\rho_b^{eq} = \frac{\exp(-\beta H_B)}{\mathrm{Tr}_B\{\exp(-\beta H_B)\}}, \tag{9}$$

and Tr_B means “trace over the bath degrees of freedom”. The choice of projection operator corresponds to a factorized initial condition for the total system,

$$\rho(0) = \sigma(0) \otimes \rho_b^{eq}, \tag{10}$$

where $\sigma(0)$ is an arbitrary state for the system. The reduced density matrix for the system is then defined as

$$\sigma(t) = \mathrm{Tr}_B \rho(t).$$

Note that the projector in Eq. (8) not only defines the relevant part of the total system by tracing out the irrelevant part, it also provides a definition for the temperature of the system. Eq. (8) is a convenient choice of projector, but this form is not required. Other projection operators can be chosen [8, 9].

With the definition in Eq. (8), the projector $\mathcal{P}$ and the Liouville operators satisfy the equalities $\mathcal{L}_B\mathcal{P} = \mathcal{P}\mathcal{L}_B = 0$, $\mathcal{P}\mathcal{L}_S\mathcal{Q} = \mathcal{Q}\mathcal{L}_S\mathcal{P} = 0$, and $\mathcal{P}\mathcal{L}_{SB}\mathcal{P} = 0$. The last equality is true if the thermal average of H_{SB} over the equilibrium bath states is zero, $\langle H_{SB}\rangle_{eq} = 0$ (where $\langle ... \rangle_{eq}$ denotes $\mathrm{Tr}_B\{...\rho_b^{eq}\}$). Note that for any Hamiltonian with $\langle H_{SB}\rangle_{eq} \neq 0$, we can always absorb the average into H_S and obtain a new interaction term with vanishing average, $H'_{SB} = H_{SB} - \langle H_{SB}\rangle_{eq}$, therefore, the condition to establish the equality $\mathcal{P}\mathcal{L}_{SB}\mathcal{P} = 0$ can always be achieved. For simplicity, we assume $\langle H_{SB}\rangle_{eq} = 0$ hereafter. Plugging Eq. (7) into Eq. (6) and applying the equalities, we obtain the equation of motion for the reduced system after tracing out the irrelevant bath degrees of freedom:

$$\begin{aligned} \dot{\sigma}(t) &= \mathrm{Tr}_B \dot{\rho}_1(t) \\ &= -i\mathcal{L}_s\sigma(t) - \lambda^2 \int_0^t d\tau \mathrm{Tr}_B \left\{ \mathcal{L}_{SB} e^{-i\mathcal{Q}\mathcal{L}\tau} \mathcal{Q}\mathcal{L}_{SB} \rho_b^{eq} \right\} \sigma(t-\tau). \end{aligned} \tag{11}$$

Equation (11) describes the dynamics of the reduced system under the initial condition $\rho(0) = \sigma(0) \otimes \rho_b^{eq}$, and is often called the "generalized master equation" [3] or the "generalized quantum Fokker-Planck equation." Note that Eq. (6) is still exact, provided that the proper projectors and equilibrium bath initial conditions are used. In fact, up to this point we did nothing but reformulating the Liouville equation. Equation (11) is of little use because solving the propagator $e^{-i\mathcal{Q}\mathcal{L}\tau}$ in the memory kernel is as difficult as solving the original Liouville equation, but this equation is a convenient starting point for the derivations of many useful quantum master equations.

To derive a useful quantum master equation, we need to apply two approximations. The first one is to replace the full propagator $e^{-i\mathcal{Q}\mathcal{L}\tau}$ in the memory kernel with the zeroth order propagator $e^{-i\mathcal{Q}(\mathcal{L}_S+\mathcal{L}_B)\tau}$, which effectively neglects terms beyond second order in λ in $\mathcal{K}(\tau)$. This approximation is similar to the Born approximation usually used in the scattering theory. The second one is to replace $\sigma(t-\tau)$ in the integral with $e^{iH_S\tau}\sigma(t)e^{-iH_S\tau}$, which makes the integral time-convolutionless and is effectively the partial ordering prescription (POP) used in the generalized cumulant expansion methods [5, 6]. If the second approximation is not made, then the integral retains the time-convolution $\rho(t-\tau)$ term, which is sometimes called the chronological ordering prescription (COP) [4, 6]. Note that the two approximations both assume weak system-bath interactions, i.e. $\lambda \ll 1$. In the $\lambda \ll 1$ limit, both approximations are valid and we obtain from Eq. (11)

$$\dot{\sigma}(t) = -i[H_S, \sigma(t)] - \lambda^2 \int_0^t d\tau \mathrm{Tr}_B \left\{ [H_{SB}, [H_{SB}(-\tau), \sigma(t) \otimes \rho_b^{eq}]] \right\}. \tag{12}$$

To explicitly evaluate the trace over the bath degrees of freedoms, we consider a generic product form for H_{SB}:

$$H_{SB} = \sum_{n,\alpha} S_n \otimes B_\alpha,$$

where S_n are an system operators, and B_α are bath operators, so that $[S_n, B_\alpha] = 0$. Substitution of H_{SB} in Eq. (12) yields

$$\dot{\sigma}(t) = -i[H_S, \sigma(t)]$$

$$-\frac{1}{2}\lambda^2\int_0^t d\tau \sum_{n,n',\alpha,\alpha'} \{[\langle B_{\alpha'}(-\tau)B_\alpha\rangle_{eq} + \langle B_\alpha B_{\alpha'}(-\tau)\rangle_{eq}]\,[S_n,[e^{-iH_S\tau}S_{n'}e^{iH_S\tau},\sigma(t)]]$$
$$-\,[\langle B_{\alpha'}(-\tau)B_\alpha\rangle_{eq} - \langle B_\alpha B_{\alpha'}(-\tau)\rangle_{eq}]\,[S_n,[e^{-iH_S\tau}S_{n'}e^{iH_S\tau},\sigma(t)]_+]\}\,. \tag{13}$$

where $[...]_+$ denotes the anticommutator.

Finally, we define bath correlation functions

$$C_{\alpha'\alpha}(\tau) = \langle B_{\alpha'}(\tau)B_\alpha\rangle_{eq} = \Gamma_r^{\alpha'\alpha}(\tau) + i\Gamma_i^{\alpha'\alpha}(\tau), \tag{14}$$

where $\Gamma_r^{\alpha'\alpha}(\tau)$and $\Gamma_i^{\alpha'\alpha}(\tau)$ are real functions representing the real part and the imaginary part of the correlation functions, respectively. Using the definitions in Eq. (14) and the symmetry properties of quantum correlation functions,

$$\langle B_\alpha B_{\alpha'}(\tau)\rangle_{eq} \;=\; \langle B_{\alpha'}(\tau)B_\alpha\rangle_{eq}^* = \Gamma_r^{\alpha'\alpha}(\tau) - i\Gamma_i^{\alpha'\alpha}(\tau),$$

we obtain

$$\dot{\sigma}(t) \;=\; -i[H_S,\sigma(t)] - \lambda^2\int_0^t d\tau \sum_{n,n',\alpha,\alpha'} \Big\{\Gamma_r^{\alpha'\alpha}(-\tau)[S_n,[e^{-iH_S\tau}S_{n'}e^{iH_S\tau},\sigma(t)]]$$
$$-i\Gamma_i^{\alpha'\alpha}(-\tau)[S_n,[e^{-iH_S\tau}S_{n'}e^{iH_S\tau},\sigma(t)]_+]\Big\}\,, \tag{15}$$

which is a non-Markovian quantum master equation. This is an equation for $\sigma(t)$ along, and the influence of the bath on the system is formulated through the bath correlation functions. The bath correlation functions, which are equilibrium properties of the bath, determine the non-equilibrium dynamics of the system. Note that no fast bath relaxation time has been assumed yet; the only assumptions made in deriving Eq. (16) are the equilibrium bath at the initial time and the weak system-bath interaction.

III. MARKOVIAN QUANTUM MASTER EQUATION AND SPECTRAL DENSITY

Next, we fit the quantum master equation into a physical content. Consider a system S governed by the system Hamiltonian H_S and coupled to a bath B of harmonic oscillators through an interaction linear in the oscillator coordinates [3, 10]:

$$\begin{aligned} H &= H_S + H_B + \lambda H_{SB} \\ &= H_S + \textstyle\sum_\alpha \omega_\alpha a_\alpha^\dagger a_\alpha + \lambda S \cdot \textstyle\sum_\alpha g_\alpha (a_\alpha^\dagger + a_\alpha), \end{aligned}$$

where $a_\alpha^\dagger$ and a_α are the creation and annihilation operators of the α-th bath mode, ω_α is the mode frequency, S is an operator referring to the system degrees of freedom only, and g_α is the coupling constant. The differential-integral equation governing the time-evolution of the reduced density matrix for the system reads

$$\begin{aligned} \dot{\sigma}(t) &= -i[H_S, \sigma(t)] + i\lambda^2 \int_0^t \Gamma_i(\tau) \cdot [S, [S_0(-\tau), \sigma(t)]_+] d\tau \\ &\quad -\lambda^2 \int_0^t \Gamma_r(\tau) \cdot [S, [S_0(-\tau), \sigma(t)]] d\tau, \end{aligned} \tag{16}$$

where $[...]_+$ denotes the anticommutator, $S_0(\tau) = e^{iH_S\tau} S e^{-iH_S\tau}$, and memory kernels $\Gamma_r(\tau)$ and $\Gamma_i(\tau)$ are the real part and imaginary part of the bath correlation function, respectively (see details in Appendix II). In this linear coupling model, these memory kernels can be explicitly written as

$$\begin{aligned} \Gamma_r(\tau) &= \textstyle\sum_\alpha g_\alpha^2 \cos(\omega_\alpha \tau) \cdot \coth(\beta\omega_\alpha/2), \\ \Gamma_i(\tau) &= \textstyle\sum_\alpha g_\alpha^2 \sin(\omega_\alpha \tau). \end{aligned}$$

Equation (16) is the quantum master equation that describes the dynamics of the reduced quantum system. Note that in Eq. (16) we have adopted the POP approximation and derive the time-convolutionless form of the master equation by replacing $\sigma(t-\tau)$ with $e^{iH_S\tau}\sigma(t)e^{-iH_S\tau}$; in the weak-coupling limit, the COP and POP approximations are equivalent. A formal derivation of Eq. (16) using the projection operator technique is given in the previous section.

Equation (16) is not yet a Markovian master equation because the integrals still refer to the initial time. If the bath correlation functions $\Gamma_r(\tau)$ and $\Gamma_i(\tau)$ decay to zero within a finite bath relaxation time τ_b, then for long times $t \gg \tau_b$, we can extend the integrations over τ to infinity and obtain the Markovian master equation:

$$\begin{aligned} \dot{\sigma}(t) &= -i[H_S, \sigma(t)] + i\lambda^2 \int_0^\infty \Gamma_i(\tau) \cdot [S, [S_0(-\tau), \sigma(t)]_+] d\tau \\ &\quad -\lambda^2 \int_0^\infty \Gamma_r(\tau) \cdot [S, [S_0(-\tau), \sigma(t)]] d\tau. \end{aligned} \tag{17}$$

This step is the Markovian approximation. The resulting Markovian master equation (Redfield equation) has been studied in innumerable papers in the literature.

How do we evaluate the applicability of the Markovian approximation? Clearly, it depends on the time scales that the bath correlation functions decays. It is convenient to define a spectral strength function for the bath, $J(\omega) = \sum_\alpha g_\alpha^2 \delta(\omega_\alpha - \omega)$, and rewrite memory kernels $\Gamma_r(\tau)$ and $\Gamma_i(\tau)$ as integrals:

$$\begin{aligned} \Gamma_r(\tau) &= \int_0^\infty J(\omega)\cos(\omega\tau)\cdot\coth(\beta\omega/2)d\omega, \\ \Gamma_i(\tau) &= \int_0^\infty J(\omega)\sin(\omega\tau)d\omega. \end{aligned} \tag{18}$$

To avoid infrared and ultraviolet divergences in $\Gamma_r(\tau)$ and $\Gamma_i(\tau)$, we assume that $J(\omega)$ has the form ω^s with $s \geq 0$ at small ω, and decays to zero faster than ω^{-1} in the limit of $\omega \to \infty$. In addition, we assume that $J(\omega)$ does not depend on the temperature. These conditions are reasonable assumptions for many physical problems.[11] Also note that if the low frequency behavior of $J(\omega)$ is subohmic (of the form ω^s with $0 < s < 1$ at small ω), the memory kernel $\Gamma_r(\tau)$ would never decay to zero within a finite time scale. In this case, the low frequency modes of the bath dominate the dissipative processes, and Markovian dynamics is inapplicable.

At long times, the integrand in $\Gamma_i(\tau)$ is rapidly oscillating due to the $\sin(\omega\tau)$ term. Therefore, if the spectral function $J(\omega)$ can be treated as a continuous and fairly smooth function, then a time scale τ_b exists due to the cancellation of the rapidly oscillating integrand at large t. This means that the number of bath degrees of freedom must be large, the distribution of bath frequencies has to be dense and spread out, and the coupling strength must vary uniformly with frequency. For $J(\omega)$ with these properties, $\Gamma_i(\tau)$ decays to zero within a τ_b defined by the width of the spectral function $J(\omega)$. If the width of the spectral function is ω_d, then at times $t \gg 1/\omega_d$ the oscillating integrand cancels out and the integral tends to zero, i.e. $\tau_b \sim 1/\omega_d$.

The real part seems more difficult because of the temperature dependence, but we found the temperature has only a minor effect on the bath relaxation time τ_b, provided our assumptions on the properties of the bath are correct. Notice that $\coth(\beta\omega/2)$ is a smooth function that peaks at $\omega \approx 0$, and behaves like $2/\beta\omega$ in a range from $\omega = 0$ to $\omega = 2/\beta$. At low temperatures, this range is small and has little effect on the shape of the integrand because of the ω^s factor in the spectral function. At high temperatures, this range can be broad, and the hyperbolic cotangent function can be replaced with $2/\beta\omega$. Therefore, the bath relaxation time at high temperature is determined by the width of the function $J(\omega)/\beta\omega$. Since we assume the spectral function decays to zero faster than $1/\omega$, the extra $1/\omega$ frequency dependence has little effect on the width of the function. We argue that τ_b is only weakly dependent on the temperature of the bath, and is largely determined by the properties of the spectral function.

To summarize, if the spectral function $J(\omega)$ is fairly dense and smooth, and decays to zero reasonably fast in both $\omega \to 0$ and $\omega \to \infty$ limit, then a time-scale $\tau_b \sim 1/\omega_d$ exists. For times $t > \tau_b$, the memory kernels tends to zero and the Markovian approximation is applicable. In addition, for the present model, the bath relaxation time τ_b is solely determined by the properties of the spectral function, and is only weakly dependent on the temperature of the bath.

IV. SPIN-BOSON MODEL AND THE VIOLATION OF POSITIVITY

It is well known that the Markovian master equations derived from the projection operator or cumulant expansion techniques destroy the general positivity of the reduced dynamics [12]. This has been a major problem for the application of the Markovian master equations. Suarez, Silbey, and Oppenheim [13] have argued that the Markovian master equation is in fact correct, and the source of the inconsistency is due to transient memory effects in a short time scale.

Consider a nondegenerate two-level system coupled to its environment through the system σ_x operator:

$$H = -\frac{\Delta}{2}\sigma_z + \sum_\alpha \omega_\alpha a_\alpha^\dagger a_\alpha + \sigma_x \cdot \sum_\alpha g_\alpha (a_\alpha^\dagger + a_\alpha). \tag{19}$$

The model chosen for the bath is a Debye-like bath of independent harmonic oscillators described by the following spectral function:

$$J(\omega) = \eta(\omega^3/\omega_c^2)e^{-\omega/\omega_c}, \tag{20}$$

where η is a dimensionless friction constant of order λ^2, and ω_c is an appropriate cutoff frequency for the bath (for example, the Debye frequency of the crystal). Hereafter we will set $\omega_c = 1$, effectively using ω_c as the the unit for energy and $1/\omega_c$ as the unit for time. It is convenient to adopt the Bloch representation and describe the density matrix for the two-level system using a Bloch vector:

$$\sigma(t) = \frac{1}{2}[I + x(t) \cdot \sigma_x + y(t) \cdot \sigma_y + z(t) \cdot \sigma_z].$$

Using equations (16)-(18), we can easily obtain the non-Markovian master equations for the spin-boson model in the Bloch representation:

$$\begin{aligned} \dot{x}(t) &= \Delta y(t), \\ \dot{y}(t) &= -[\Delta + 4f(t)]x(t) - 4g(t)y(t), \\ \dot{z}(t) &= -4g(t)z(t) + 4h(t), \end{aligned} \tag{21}$$

where we have defined the following time-dependent functions

$$\begin{aligned} f(t) &= \textstyle\int_0^t \Gamma_r(\tau)\sin(\Delta\tau)d\tau, \\ g(t) &= \textstyle\int_0^t \Gamma_r(\tau)\cos(\Delta\tau)d\tau, \\ h(t) &= \textstyle\int_0^t \Gamma_i(\tau)\sin(\Delta\tau)d\tau. \end{aligned} \tag{22}$$

The non-Markovian master equations Eq. (21) - Eq. (22) can not be solved analytically, therefore we propagate the solutions numerically using a 4-*th* order Runge-Kutta method. On the other hand, the Markovian master equations can be solved analytically, yielding

$$\begin{aligned} x(t) &= \left\{x(0)\cosh(\nu t) - \tfrac{\sinh(\nu t)}{\nu}\left[\Delta y(0) + \gamma x(0)\right]\right\} e^{-\gamma t}, \\ y(t) &= \left\{y(0)\cosh(\nu t) - \tfrac{\sinh(\nu t)}{\nu}\left[\gamma y(0) + \Delta x(0) + 4f(\infty)x(0)\right]\right\} e^{-\gamma t}, \\ z(t) &= z_{eq} + \left[z(0) - z_{eq}\right] e^{-2\gamma t}, \end{aligned} \tag{23}$$

where we have used $\gamma = 2g(\infty)$, $z_{eq} = h(\infty)/g(\infty)$, and $\nu = \sqrt{\gamma^2 - \Delta^2 - 4\Delta f(\infty)}$.

Figure 1 shows the non-Markovian [Eq. (21)] and Markovian [Eq. (23)] evolution of the determinant of the reduced density matrix, with initial condition $x(0) = 0$, $y(0) = \sqrt{3}/2$, and $z(0) = 0.5$ chosen to show the violation of positive in the Markovian dynamics. The parameters used are $\Delta = 0.1$ and $\eta = 0.01$, and $\beta = 0.5$. We observe that although the Markovian evolution reaches correct thermal equilibrium at long times, it is negative during a short time period at the beginning, indicating at least one of the two eigenvalues are outside the [0,1] range. Note that at this high temperature regime, the amount by which the positivity is broken can be greater than η, because of the thermal population of the phonon

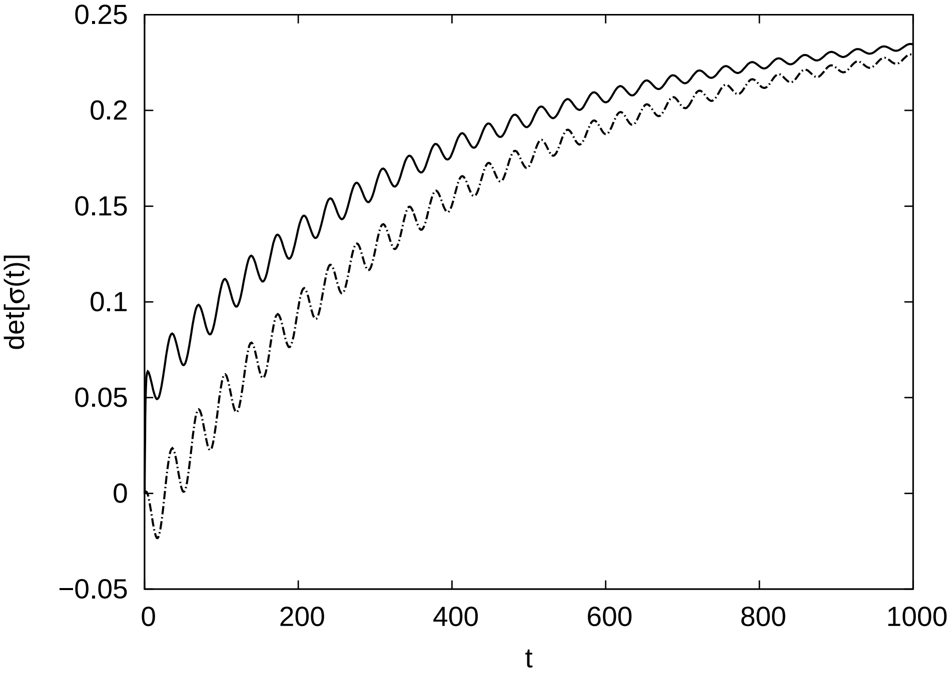

FIG. 1: Non-Markovian (solid line) and Markovian (dashed-dotted line) dynamics of det$[\sigma(t)]$. The Debye-like spectral function in Eq. (20) is used. The parameters used are $\Delta = 0.1$ and $\eta = 0.01$, and $\beta = 0.5$; the initial condition is $x(0) = 0$, $y(0) = \sqrt{3}/2$, and $z(0) = 0.5$.

modes. In contrast to the Markovian evolution, the non-Markovian evolution preserves the positivity of the reduced dynamics at all times. This result confirms that the source of the non-positivity problem is the short time memory effects. Numerical studies on non-Markovian quantum master equations have indicated that they provide reasonable results in a wide parameter range.[14–17] In this weak-coupling case, the non-Markovian master equation correctly describes the dynamics of the open system at all times.

V. REMARKS

The applicability of the Markovian approximation has long been criticized in the literature [18, 19]. In addition to the assumption of the short bath relaxation time, it is well known that the Markovian master equations do not always preserve the positivity of the reduced density matrix of the system, thus resulting in physically inconsistent outcomes. Suarez *et al.* have shown that the problem of non-positivity is due to the transient memory effects in a short time scale, and can be repaired by a modification of the initial conditions (slippage)

[12, 13]. Despite these stringent conditions and obvious inconsistencies, Markovian master equations have been applied successfully to a broad range of physical and chemical problems. Although non-Markovian approaches have grown in interest recently, Markovian approaches are favored due to their simplicity and computational efficiency [20, 21].

All the results shown here are based on the assumption that the system-bath interactions are weak and neglecting higher order terms in the memory kernels is valid. This weak-coupling condition seems to be a stringent limitation for quantum master equations. Recently there have been great interests in developing a formally exact theoretical framework that avoids such weak-coupling approximation [22–24], however, these hierarchical approaches are often limited to specific forms of bath spectral density. Note that in many physical scenarios, the system is strongly coupled to only a few bath modes. Therefore, the system-bath boundary can be redefined to include strongly coupled modes into the system, and the weak coupling approximation can still be adequate. In addition, sometimes a similarity transformation that transforms the total Hamiltonian and recovers the weak-coupling regime can be found [25, 26]. In these systems, the similarity transformation creates a new set of "dressed" states that are only weakly coupled to the bath, thus the weak-coupling approximation is still applicable. The unified theory for exciton transportation presented in Ref. [27], where the Merrifield transformation is applied to the Holstein model to generate partially-dressed polaron states, is a demonstration of such an approach.

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