

# Markovian Approximation in the Relaxation of Open Quantum Systems<sup>†</sup>

Y. C. Cheng and R. J. Silbey\*

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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In this paper, we examine the validity of the Markovian approximation and the slippage scheme used to incorporate short time transient memory effects in the Markovian master equations (Redfield equations). We argue that for a bath described by a spectral function,  $J(\omega)$ , that is dense and smoothly spread out over the range  $\omega_d$ , a time scale of  $\tau_b \sim 1/\omega_d$  exists; for times of  $t > \tau_b$ , the Markovian approximation is applicable. In addition, if  $J(\omega)$  decays to zero reasonably fast in both the  $\omega \rightarrow 0$  and  $\omega \rightarrow \infty$  limits, then the bath relaxation time,  $\tau_b$ , is determined by the width of the spectral function and is weakly dependent on the temperature of the bath. On the basis of this criterion of  $\tau_b$ , a scheme to incorporate transient memory effects in the Markovian master equation is suggested. Instead of using slipped initial conditions, we propose a concatenation scheme that uses the second-order perturbation theory for short time dynamics and the Markovian master equation at long times. Application of this concatenation scheme to the spin-boson model shows that it reproduces the reduced dynamics obtained from the non-Markovian master equation for all parameters studied, while the simple slippage scheme breaks down at high temperatures.

## 1. Introduction

Dissipative dynamics of a quantum system embedded in a complex environment has gained much 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.<sup>1,2</sup> However, in contrast to classical dissipative processes, that can be satisfactorily described by classical Langevin or Fokker–Planck equations,<sup>3</sup> 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. 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.<sup>4–6</sup> 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,  $\tau_b$ . This approximation allows us to derive Markovian master equations (Redfield equations) for the reduced dynamics of the quantum system.

However, the applicability of the Markovian approximation has long been criticized in the literature.<sup>7,8</sup> In addition to the assumption for 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 results. Suarez et al. have

shown that the problem of nonpositivity is due to the transient memory effects in a short time scale and can be repaired by a modification of the initial conditions (slippage).<sup>9</sup> Gaspard and Nagaoka adopted the slippage idea and developed a slippage superoperator method that can determine the slippage of initial conditions in a consistent way, but the range of applicability of their slippage superoperator has not been fully tested.<sup>10</sup> 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.<sup>11,12</sup> Therefore, a scheme that can ensure the positivity of the reduced system dynamics in the framework of quantum Markovian equations is desirable.

In this paper, we examine two problems concerning the applicability of the Markovian approximation and propose a simple scheme for applying Markovian master equations that is capable of reproducing results from the non-Markovian master equations over a wide range of parameters. In section 2, we shall briefly review the derivation of the Markovian master equation. In section 3, the physical requirements for the Markovian approximation will be examined in detail and the factors defining the time scale for the non-Markovian dynamics will be clarified. In section 4, we will then formulate a concatenation scheme that avoids using slippage initial conditions and absorbs the transient memory effects in a natural manner. In addition, we show that Gaspard and Nagaoka’s slippage superoperator method is not successful in preserving positivity in all cases. Finally, in section 5, we will examine the concatenation scheme by applying it to study the spin-boson problem.

## 2. The Quantum Master Equation

Consider a system,  $S$ , governed by a system Hamiltonian,  $H_S$ , and coupled to a bath,  $B$ , of harmonic oscillators through

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an interaction linear in the oscillator coordinates ( $\hbar = 1$ ):<sup>3,13</sup>

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

where  $a_{\alpha}^{\dagger}$  and  $a_{\alpha}$  are the creation and annihilation operators of the  $\alpha$ 'th bath mode,  $\omega_{\alpha}$  is the mode frequency,  $S$  is an operator referring to the system degree of freedom only, and  $g_{\alpha}$  is the coupling constant. The dynamics of the total system can be described by a time-dependent density matrix,  $\rho(t)$ , and follows the Liouville equation

$$\dot{\rho}(t) = -i[H, \rho(t)]$$

To obtain the reduced description for the system, we define the following projection operator  $\mathcal{P}$ :

$$\mathcal{P}\rho = \rho_b^{\text{eq}} \text{Tr}_B \rho$$

where

$$\rho_b^{\text{eq}} = \frac{\exp(-\beta H_B)}{\text{Tr}_B \{\exp(-\beta H_B)\}}$$

and  $\text{Tr}_B$  means ‘‘trace over the bath degrees of freedom’’. The choice of projection operator corresponds to factorized initial conditions for the total system

$$\rho(0) = \sigma(0) \otimes \rho_b^{\text{eq}}$$

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

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

Following the standard projection operator technique and neglecting all terms of higher order than  $\lambda^2$ ,<sup>14</sup> we obtain the differential-integral equation for the reduced density matrix for the system

$$\begin{aligned} \dot{\sigma}(t) &= -i[H_S, \sigma(t)] + i\lambda^2 \int_0^t \Gamma_r(\tau) [S, [S_0(-\tau), \sigma(t)]_+] d\tau - \\ &\quad \lambda^2 \int_0^t \Gamma_i(\tau) [S, [S_0(-\tau), \sigma(t)]] d\tau \quad (1) \end{aligned}$$

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. In this linear coupling model, these memory kernels can be explicitly written as

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

Equation 1 is the quantum master equation that describes the dynamics of the reduced quantum system. To derive this equation, we have assumed that the system–bath coupling is small, so that we can neglect terms of higher order than  $\lambda^2$  and replace the evolution kernel in the integrals by the zeroth-order one. Note that in eq 1 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. Equation

1 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,  $\tau_b$ , then, for long times of  $t \gg \tau_b$ , we can extend the integrations over  $\tau$  to infinity and obtain the Markovian master equation:

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

This step is the Markovian approximation. The resulting Markovian master equation (Redfield equation) has been studied in innumerable papers in the literature. However, to the best of our knowledge, concrete criteria for the applicability of the Markovian approximation are still unclear. In the next two sections, we will study the applicability of the Markovian approximation and provide a simple scheme that absorbs the transient memory effects in a straightforward manner.

### 3. The Markovian Approximation

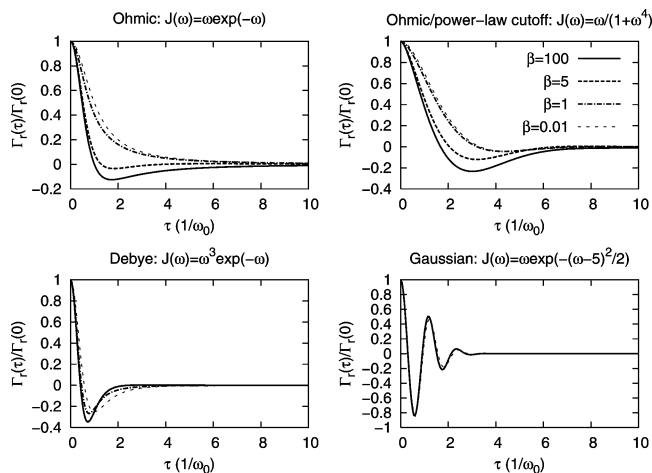
It is convenient to define a spectral strength function for the bath,  $J(\omega) = \sum_{\alpha} g_{\alpha}^2 \delta(\omega_{\alpha} - \omega)$ , and rewrite memory kernels  $\Gamma_r(\tau)$  and  $\Gamma_i(\tau)$  as integrals:

$$\begin{aligned} \Gamma_r(\tau) &= \int_0^{\infty} J(\omega) \cos(\omega \tau) \coth(\beta \omega / 2) d\omega \\ \Gamma_i(\tau) &= \int_0^{\infty} J(\omega) \sin(\omega \tau) d\omega \quad (3) \end{aligned}$$

To avoid infrared and ultraviolet divergences, we assume that  $J(\omega)$  has the form  $\omega^s$ , with  $s \geq 1$  at small  $\omega$ , and decays to zero faster than  $\omega^{-1}$  in the limit of  $\omega \rightarrow \infty$ . In addition, we assume that  $J(\omega)$  does not depend on the temperature. These conditions are reasonable assumptions for many physical problems.<sup>15</sup> Also, note that if the low frequency behavior of  $J(\omega)$  is subohmic (of the form  $\omega^s$  with  $0 < s < 1$  at small  $\omega$ ), 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,  $\tau_b$ , 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  $\tau_b$  defined by the width of the spectral function  $J(\omega)$ . If the width of the spectral function is  $\omega_d$ , then at times  $t \gg 1/\omega_d$  the oscillating integrand cancels out and the integral tends to zero, that is,  $\tau_b \sim 1/\omega_d$ .

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,  $\tau_b$ , 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  $\omega^s$  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 temperatures is determined by the



**Figure 1.** Normalized real part of the bath correlation functions  $[\Gamma_r(\tau)/\Gamma_r(0)]$  for baths with different forms of spectral functions at inverse temperatures  $\beta = 0.01$  (thin dashed line),  $\beta = 1$  (dashed-dotted line),  $\beta = 5$  (dashed line), and  $\beta = 100$  (solid line). The point where  $\Gamma_r(\tau)$  decays to zero is dependent on the form of the spectral function but only weakly dependent on the temperature. In addition, in general, higher temperatures do not correspond to shorter bath relaxation times. The cutoff frequencies are set to 1, so the units of time and  $\beta$  are  $1/\omega_0$ .

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  $\tau_b$  is only weakly dependent on the temperature of the bath and is largely determined by the properties of the spectral function.

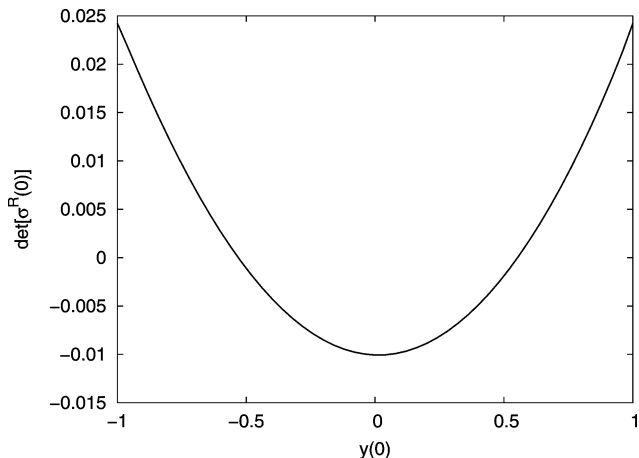
Figure 1 shows the normalized memory kernel  $\Gamma_r(\tau)/\Gamma_r(0)$  for several forms of spectral functions at different temperatures. The time  $\tau_b$  at which  $\Gamma_r(\tau)$  decays to zero depends strongly on the form of the spectral function but only weakly on the temperature. For the Gaussian bath case, the function  $\Gamma_r(\tau)/\Gamma_r(0)$  is almost temperature independent. Note that the widths of the spectral functions used in Figure 1 are set to 1; as a result, all memory kernels shown decay within a time scale of order  $\sim 1$ .

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

#### 4. 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. This has been a major problem for the application of the Markovian master equations. Suarez, Silbey, and Oppenheim 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. In this section, we will present a prescription that quantitatively incorporates the short time memory effects in the Markovian evolution.

The slippage scheme proposed by Suarez, Silbey, and Oppenheim (SSO slippage scheme) aligns the trajectories given by the Markovian evolution and second-order perturbation theory (known to be correct at short times) and then extrapolates the Markovian evolution back to zero time to find a set of



**Figure 2.** Violation of the positivity condition in the slippage superoperator method. We show the determinant of the slipped initial conditions for a spin-boson model with an Ohmic-like bath as a function of  $y(0)$ , where  $y(0)$  defines different nonslipped initial density matrices,  $\rho_s(0) = [I + \sqrt{1-y(0)^2}\sigma_x + y(0)\sigma_y]$ . The results are calculated using eqs 43–47 in ref 10 and an Ohmic-like spectral function,  $J(\omega) = \omega e^{-\omega/\omega_c}$ . The parameters used are  $\Delta = 0.1$ ,  $\lambda = 0.1$ ,  $\omega_c = 1$ , and temperature  $T = 0$ . All notations used here are the same as those defined in ref 10. The negative values of the determinant for  $-0.55 < y(0) < 0.55$  indicate violations of the positivity condition.

slipped initial conditions. Using the slipped initial conditions together with the Markovian master equation correctly produces the long time dynamics of the system and solves the nonpositivity problem. However, the amount of the slippage depends on the particular initial conditions and cannot be predicted quantitatively. This makes the slippage scheme difficult to implement.

As we pointed out above, Gaspard and Nagaoka suggested a slippage superoperator that can generate slipped initial conditions in a consistent way.<sup>10</sup> On the basis of the assumption that the dynamics of the Markovian master equation with slipped initial conditions can be approximately equal to that of the direct second-order perturbation theory for intermediate times of  $t \gg \tau_b$ , they integrated the Markovian master equation up to second order in  $\lambda$  and compared the outcome to the result from second-order perturbation theory to obtain the slippage superoperator. Their formal result (eq 25 in ref 10) is rather complicated and difficult to apply to real systems; therefore, they suggested using a short time expansion to compute the simplified slippage superoperator. They also demonstrated that the simplified slippage superoperator indeed solved the nonpositivity problem for a spin-boson system with a Debye-like spectral function and gave excellent results. However, the applicability of their method for more general systems has not been tested. In fact, we find that their slippage superoperator does not always give results that satisfy the positivity condition. For example, if we replace the Debye-like spectral function of the spin-boson system studied in ref 10 with a Ohmic-like spectral function,  $J(\omega) = \omega e^{-\omega/\omega_c}$ , the slippage superoperator gives nonpositive initial conditions in a broad range of parameters. Figure 2 shows the determinant of the slipped initial conditions calculated using eqs 43–47 in ref 10 and the spectral function  $J(\omega) = \omega e^{-\omega/\omega_c}$ . The negative determinant values shown in Figure 2 clearly indicate that the slippage superoperator breaks down for the spin-boson model with an Ohmic-like bath. Therefore, we conclude that the slippage superoperator method in its simplified form (eq 26 in ref 10) does not always give physically admissible slipped initial conditions. The applicability of the

slippage superoperator in its formal form, which does not require the short time expansion, is still untested.

We now turn to an extension of the SSO slippage scheme in order to increase its range of applicability. A natural and simple modification of the SSO slippage scheme is to concatenate the second-order perturbation theory with the Markovian master equation. The idea is to use second-order perturbation theory to propagate the reduced dynamics at short times and switch to using the Markovian master equation at long times. We define a transient time,  $\tau_t$ , at which the Markovian master equations are applied with the initial conditions given by the second-order perturbation theory at time  $\tau_t$ . To this end,  $\tau_t$  must be in the regime where both the second-order perturbation theory and the Markovian master equation are valid, that is, where the memory kernels already decay to zero and the second-order perturbation theory is still correct. As we have mentioned in the previous section, the Markovian master equation is valid after times of  $t > \tau_b \sim 1/\omega_d$ . In addition, for the second-order perturbation theory to be correct, we need the temperature weighted parameter  $J(\omega_0) \coth(\beta\omega_0/2)\tau_t \ll 1$ , where  $\omega_0$  is the averaged frequency for modes that contribute strongly in the spectral function  $J(\omega)$ . Therefore, we obtain the range of  $\tau_t$  for the concatenation scheme to be valid:

$$\frac{1}{\omega_d} \ll \tau_t \ll \frac{1}{J(\omega_0) \coth(\beta\omega_0/2)} \quad (4)$$

For simplicity, we choose  $\tau_t$  as the midpoint between the upper bound and lower bound in the log scale:

$$\tau_t = \sqrt{\frac{\omega_d}{J(\omega_0) \coth(\beta\omega_0/2)}} \quad (5)$$

Note that the expression of  $\tau_t$  in eq 5 is just a convenient choice. Any choice of  $\tau_t$  that satisfies eq 4 is valid. When the second-order perturbation theory and the Markovian master equation are both valid during intermediate times, the resulting dynamics will not be sensitive to the choice of  $\tau_t$  and  $\omega_0$ . Therefore, the requirement of specifying  $\tau_t$  is not a weak point of the concatenation scheme. On the contrary, the choice of  $\tau_t$  and eq 4 provide a measure for the quality of the concatenated dynamics.

There is a fundamental difference between the SSO slippage scheme and the concatenation scheme described here. The slippage scheme implicitly assumes that the Markovian trajectory generated from invalid initial conditions is parallel to the trajectories from slipped initial conditions, while the concatenation scheme assumes that the new initial conditions given by the second-order perturbation at the time  $\tau_t$  correctly absorb the memory effects. In the next section, we will show that at high temperatures the SSO slippage scheme breaks down, while the concatenation scheme still gives a correct description of the long time dynamics.

## 5. The Spin-Boson Model

To illustrate the concatenation scheme, we study the spin-boson model in this section. Consider a nondegenerate two-level system coupled to its environment through the system  $\sigma_x$  operator:

$$H = -\frac{\Delta}{2}\sigma_z + \sum_{\alpha} \omega_{\alpha} a_{\alpha}^{\dagger} a_{\alpha} + \sigma_x \sum_{\alpha} g_{\alpha} (a_{\alpha}^{\dagger} + a_{\alpha}) \quad (6)$$

The model chosen for the bath is a Debye-like bath of

independent harmonic oscillators described by the following spectral function:

$$J(\omega) = \eta(\omega^3/\omega_c^2)e^{-\omega/\omega_c} \quad (7)$$

where  $\eta$  is a dimensionless friction constant of order  $\lambda^2$  and  $\omega_c$  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  $\omega_c$  as 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 eq 1, we can easily obtain the non-Markovian master equations for the spin-boson model in the Bloch representation:

$$\begin{aligned} \dot{x}(t) &= \Delta y(t) \\ \dot{y}(t) &= -[\Delta + 4f(t)]x(t) - 4g(t)y(t) \\ \dot{z}(t) &= -4g(t)z(t) + 4h(t) \end{aligned} \quad (8)$$

where we have defined time-dependent functions

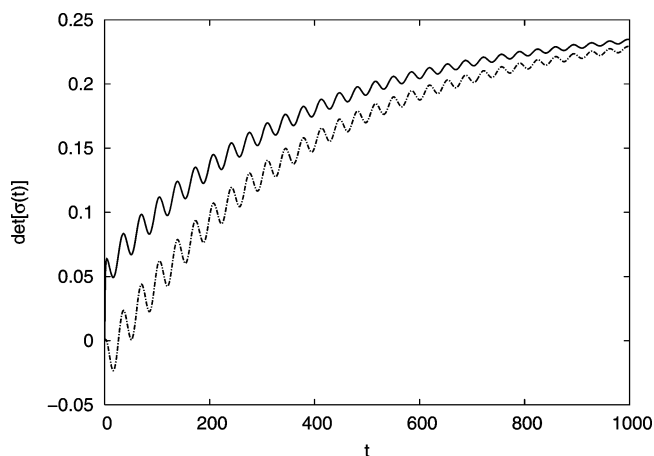
$$\begin{aligned} f(t) &= \int_0^t \Gamma_r(\tau) \sin(\Delta\tau) d\tau \\ g(t) &= \int_0^t \Gamma_r(\tau) \cos(\Delta\tau) d\tau \\ h(t) &= \int_0^t \Gamma_i(\tau) \sin(\Delta\tau) d\tau \end{aligned} \quad (9)$$

The non-Markovian master equations (eqs 8 and 9) cannot be solved analytically; therefore, we propagate the solutions numerically using the fourth-order Runge–Kutta method. On the other hand, the Markovian master equations can be solved analytically, yielding

$$\begin{aligned} x(t) &= \left\{ x(0) \cosh(\nu t) - \frac{\sinh(\nu t)}{\nu} [\Delta y(0) + \gamma x(0)] \right\} e^{-\gamma t} \\ y(t) &= \left\{ y(0) \cosh(\nu t) - \frac{\sinh(\nu t)}{\nu} [\gamma y(0) + \Delta x(0) + 4f(\infty)x \right. \\ &\quad \left. (0)] \right\} e^{-\gamma t} \\ z(t) &= z_{\text{eq}} + [z(0) - z_{\text{eq}}] e^{-2\gamma t} \end{aligned} \quad (10)$$

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

Figure 3 shows the non-Markovian (eq 8) and Markovian (eq 10) evolution of the determinant of the reduced density matrix, with the initial conditions  $x(0) = 0$ ,  $y(0) = \sqrt{3}/2$ , and  $z(0) = 0.5$ . The parameters used are  $\Delta = 0.1$ ,  $\eta = 0.01$ , 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, 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  $\eta$ , because of the thermal population of the phonon 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 nonpositivity problem is the short time memory effects.



**Figure 3.** Non-Markovian (solid line) and Markovian (dashed–dotted line) dynamics of  $\det[\sigma(t)]$ . The Debye-like spectral function from eq 7 is used. The parameters used are  $\Delta = 0.1$ ,  $\eta = 0.01$ , and  $\beta = 0.5$ ; the initial conditions are  $x(0) = 0$ ,  $y(0) = \sqrt{3}/2$ , and  $z(0) = 0.5$ .

Numerical studies on non-Markovian quantum master equations have indicated that they provide reasonable results in a wide parameter range.<sup>16–19</sup> In this weak-coupling case, the non-Markovian master equation correctly describes the dynamics of the open system at all times.

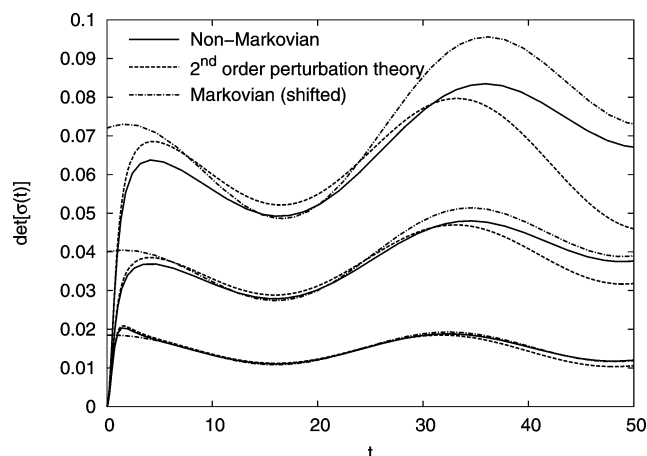
At short times, the second-order perturbation theory can provide correct dynamics. The results are

$$\begin{aligned} x_p(t) &= [\cos(\Delta t) - I_1(t)]x(0) + [\sin(\Delta t) - I_2(t)]y(0) \\ y_p(t) &= [\cos(\Delta t) - I_3(t)]y(0) - [\sin(\Delta t) - I_2(t)]x(0) \\ z_p(t) &= [1 - I_4(t)]z(0) + I_5(t) \end{aligned} \quad (11)$$

where we use subscript p to denote the results obtained from the second-order perturbation theory; the integrals  $I_n(t)$  are

$$\begin{aligned} I_1(t) &= 2 \int_0^t \Gamma_r(\tau) \left\{ (t - \tau) \cos[\Delta(t - \tau)] - \frac{1}{\Delta} \sin[\Delta(t - \tau)] \right\} d\tau \\ I_2(t) &= 2 \int_0^t \Gamma_r(\tau) (t - \tau) \sin[\Delta(t - \tau)] d\tau \\ I_3(t) &= 2 \int_0^t \Gamma_r(\tau) \left\{ (t - \tau) \cos[\Delta(t - \tau)] + \frac{1}{\Delta} \sin[\Delta(t - \tau)] \right\} d\tau \\ I_4(t) &= 4 \int_0^t \Gamma_r(\tau) (t - \tau) \cos(\Delta\tau) d\tau \\ I_5(t) &= 4 \int_0^t \Gamma_i(\tau) (t - \tau) \sin(\Delta\tau) d\tau \end{aligned} \quad (12)$$

Figure 4 compares the short time dynamics obtained from the non-Markovian master equation, second-order perturbation theory (eq 11), and Markovian master equation at three different temperatures. The same parameters and initial conditions as those in Figure 3 are used. To compare the dynamics, the Markovian evolution shown in Figure 4 has been shifted to be aligned with the second-order perturbation result. Notice that the amount of slippage and violation of positivity in the Markovian dynamics increases as the temperature increases, and so does the deviation between the second-order perturbation theory and the non-Markovian master equation. These trends can be explained by the temperature dependence of the phonon-



**Figure 4.** Short time dynamics of  $\det[\sigma(t)]$  at different temperatures (from bottom to top,  $\beta = 10$ ,  $\beta = 1$ , and  $\beta = 0.5$ ). Dynamics obtained from the non-Markovian master equation (solid lines), second-order perturbation theory (dashed lines), and Markovian master equation (dashed–dotted lines) are shown for each temperature. The Debye-like spectral function from eq 7 is used. The parameters used are  $\Delta = 0.1$  and  $\eta = 0.01$ , and the initial conditions are  $x(0) = 0$ ,  $y(0) = \sqrt{3}/2$ , and  $z(0) = 0.5$ .

mode thermal populations. As the temperature increases, the population in the phonon modes increases and the effective system–bath interaction also increases. As a result, the range in which the second-order perturbation theory is applicable reduces when the temperature increases. Also note that at high temperatures the Markovian dynamics is totally off and cannot be aligned with the results calculated from the second-order perturbation theory. This indicates that the Markovian dynamics is not necessarily parallel to the correct dynamics of the reduced system (can be seen clearer in Figure 3), especially at high temperatures. In the high temperature regime, the SSO slipped initial conditions are not well defined and the SSO slippage scheme will be difficult to apply.

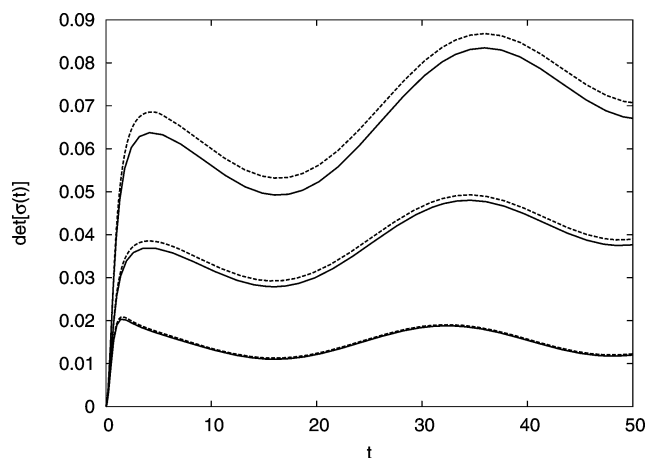
We also applied the concatenation scheme to this problem. The temperature-dependent transient time,  $\tau_t$ , can be estimated from the cutoff frequency,  $\omega_c$ , yielding

$$\tau_t \approx \sqrt{\frac{\omega_c}{J(\omega_c) \coth(\beta\omega_c/2)}}$$

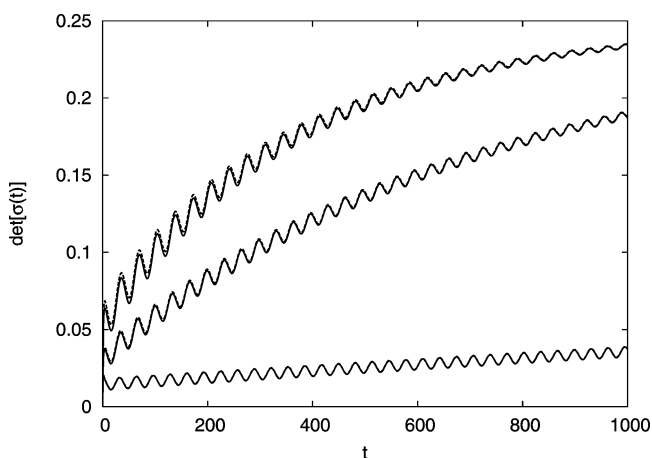
For  $t < \tau_t$ , the second-order perturbation theory (eq 11) is used. For  $t > \tau_t$ , the second-order perturbation theory is used to compute the initial conditions at  $t = \tau_t$  for the Markovian dynamics. Using eqs 10–12, we obtain the concatenation result for  $t > \tau_t$  explicitly:

$$\begin{aligned} x(t) &= \left\{ x_p(\tau_t) \cosh[\nu(t - \tau_t)] - \frac{\sinh[\nu(t - \tau_t)]}{\nu} [\Delta y_p(\tau_t) + \gamma x_p(\tau_t)] \right\} e^{-\gamma(t - \tau_t)} \\ y(t) &= \left\{ y_p(\tau_t) \cosh[\nu(t - \tau_t)] - \frac{\sinh[\nu(t - \tau_t)]}{\nu} [\gamma y_p(\tau_t) + \Delta x_p(\tau_t) + 4f(\infty) x_p(\tau_t)] \right\} e^{-\gamma(t - \tau_t)} \\ z(t) &= z_{\text{eq}} + [z_p(\tau_t) - z_{\text{eq}}] e^{-2\gamma(t - \tau_t)} \end{aligned} \quad (13)$$

Note that there are no adjustable parameters in this scheme. In comparison with eq 10, we can see that simple slipped initial conditions in the Markovian master equation cannot reproduce the concatenation result in eq 13. This indicates the fundamental



**Figure 5.** Short time dynamics of  $\det[\sigma(t)]$  at different temperatures (from bottom to top,  $\beta = 10$ ,  $\beta = 1$ , and  $\beta = 0.5$ ). Dynamics obtained from the non-Markovian master equation (solid lines) and the concatenation scheme (dashed lines) are shown for each temperatures. The Debye-like spectral function from eq 7 is used. The parameters used are  $\Delta = 0.1$  and  $\eta = 0.01$ , and the initial conditions are  $x(0) = 0$ ,  $y(0) = \sqrt{3}/2$ , and  $z(0) = 0.5$ .



**Figure 6.** Dynamics of  $\det[\sigma(t)]$  at a longer time period at three different temperatures (from bottom to top,  $\beta = 10$ ,  $\beta = 1$ , and  $\beta = 0.5$ ). Dynamics obtained from the non-Markovian master equation (solid lines) and the concatenation scheme (dashed lines) are shown for each temperatures. Damping of the oscillations at high temperatures can be clearly seen. The Debye-like spectral function from eq 7 is used. The parameters used are  $\Delta = 0.1$  and  $\eta = 0.01$ , and the initial conditions are  $x(0) = 0$ ,  $y(0) = \sqrt{3}/2$ , and  $z(0) = 0.5$ .

difference between the SSO slippage scheme and the concatenation scheme proposed here. Figure 5 shows the short time dynamics obtained from the concatenation scheme together with the dynamics from the non-Markovian master equation. The same dynamics at a longer time period is shown in Figure 6. Compared to the Markovian dynamics shown in Figure 3, the simple concatenation scheme gives dramatic improvement. Clearly, the concatenation scheme adequately reproduces the correct dynamics at both short and long times. At high temperatures, small deviations from the non-Markovian results exist at short times. The deviations can be ascribed to the errors in the second-order perturbation theory and do not change the long time dynamics. In fact, Figure 6 shows that the concatenation scheme gives results that are in excellent agreement with the non-Markovian master equation even at high temperatures.

We have also applied the concatenation scheme to a similar spin-boson model with an Ohmic-like spectral function,  $J(\omega) = \omega e^{-\omega/\omega_c}$ . In this case, the concatenation scheme produces

results that satisfy the positivity condition at all times for all of the parameters and initial condition ranges examined. Given the simplicity and the clear background of the concatenation scheme, we expect that it is generally applicable in systems with weak system–bath couplings.

## 6. Conclusion

We have examined the validity of the Markovian approximation based on a generic model with system–bath interaction linear in the oscillator coordinates. We argued that if the spectral function  $J(\omega)$  of the bath is fairly dense and smoothly spread out, then a time scale of  $\tau_b$  exists for bath relaxations. For times of  $t > \tau_b$ , the memory kernels tends to zero and the Markovian approximation is applicable. In addition, if  $J(\omega)$  decays to zero reasonably fast in both the  $\omega \rightarrow 0$  and  $\omega \rightarrow \infty$  limits, the bath relaxation time,  $\tau_b$ , is determined by the width of the spectral function,  $\tau_b \sim 1/\omega_d$ , and is only weakly dependent on the temperature of the bath. We emphasize that in this context the width of the spectral function should be determined by the physical conditions of the system and cannot be chosen arbitrarily by an imposed cutoff frequency. Although all of our discussions are based on the linear form of the coupling, we believe that the random phase argument is generic and can be applied to other forms of interactions.

Moreover, we have proposed a concatenation scheme that absorbs the transient memory effects in a natural manner and fixes the nonpositivity problem. The concatenation scheme applies second-order perturbation theory at short times and uses Markovian master equations for long time dynamics; therefore, it in fact describes both the short time and long time dynamics. Applications of the concatenation scheme on the spin-boson problem show excellent agreement with the results obtained from the non-Markovian master equation at all temperature ranges studied. Our results indicate that, with proper adjustments, the Markovian master equations are applicable in the weak-coupling limit. Although we have only studied the concatenation scheme on the simple spin-boson model, we expect it can be easily applied to multilevel systems. It will be interesting to study the performance of the concatenation scheme on more complicated multilevel problems. Because of its simplicity, the concatenation scheme can provide an efficient way to apply multilevel Markovian master equations, while avoiding the nonpositivity problem.

All our results 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 eqs 1 and 2. However, 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.

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## References and Notes

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