Fourth-order quantum master equation and its Markovian bath limit

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Fourth-order quantum master equations (FQMEs) are derived in both time nonlocal and local forms for a general system Hamiltonian, with new detailed expressions for the fourth-order kernel, where the bath correlation functions are explicitly decoupled from the system superoperators. Further simplifications can be made for the model of linearly coupled harmonic oscillator bath. Consideration of the high temperature Ohmic bath limit leads to a general Markovian FQME with compact forms of time independent superoperators. Two examples of this equation are then considered. For the system of a quantum particle in a continuous potential field, the equation reduces to a known form of the quantum Fokker–Planck equation, except for a fourth-order potential renormalization term that can be neglected only in the weak system-bath interaction regime. For a two-level system with off-diagonal coupling to the bath, fourth-order corrections do not alter the relaxation characteristics of the second-order equation and introduce additional coherence terms in the equations for the off-diagonal elements.
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I. INTRODUCTION

Quantum master equations (QMEs)[1–17] offer direct prescriptions on how to evolve an open quantum system, and have provided canonical frameworks for the description of various quantum relaxation processes. Although formally exact equations are available,[3–7] in practical applications[18,19] the usual choices have been second-order equations such as Bloch–Redfield equation[1–4] and its generalizations.[8–14] These retain the necessary ingredients of the dissipative quantum dynamics while being simple enough, and can be related to the microscopic properties of the system, an important asset hardly attainable by axiomatic approaches[15–17] only.

However, the second-order QME (SQME)[1–4,8–14] has a limitation, the assumption of weak system-bath interaction. With the advance of ultrafast spectroscopy and submicroscale experiments, increasing number of studies are being performed for condensed phase systems where the weak system-bath interaction does not necessarily hold. If suitable transformations[20–22] can be found such that the weak interaction regime is recovered, applications of the SQME to such systems after the transformation can be justified. Otherwise, explicit considerations of the higher order terms may be necessary. Recent theoretical studies on the higher order QME[23–26] or its stochastic Schrödinger equation version[27,28] have important implications in this respect.

Due to the perturbative nature, the interaction strength regime where a higher order QME is applicable may not be dramatically larger than that of the SQME. However, model calculations[26–28] demonstrate that higher order corrections can bring substantial improvements in intermediate coupling regimes of physical relevance. In other cases, even new qualitative features can arise.[24] These examples indicate that a systematic extension of the SQME to a higher order is worthwhile and that it may provide a more solid theoretical understanding of open system quantum dynamics.

In the present paper, we derive a general and a detailed form of the fourth-order QME (FQME). The expression for the FQME where the superoperators are given by Liouville operators, without explicit averaging over the bath degrees of freedom, are well known.[5–7,23–28] Our new contribution is to perform the explicit averaging over the bath, based on few necessary assumptions, and to derive general expressions for the kernels of the FQME, where the bath correlation functions are decoupled from the system superoperators. This result leads to the ability to perform routine FQME calculations for various systems and general formal analyses in some limiting situations. Our main focus here is on the latter aspect, in one particular limit. We derive more detailed expressions of the kernels for the model of linearly coupled harmonic oscillator bath and then make a careful examination of the Markovian bath limit.

For the model of linearly coupled harmonic oscillator bath, the path integral formalism[29–32] provides a powerful alternative to the perturbation approaches. Caldeira and Leggett (CL)[30,31] applied the Feynman–Vernon influence functional formalism[33] to a system of a quantum particle in a continuous potential field. In the limit where the bath becomes Markovian, they derived a quantum Fokker–Planck equation[30] which has the correct classical limit. Hereafter, this will be called CL master equation (CLME). Quite interestingly, the CLME can also be derived from the SQME for the same model.[10,11,14] Does this mean that consideration up to the second order is exact for the CL model in the Markovian bath limit? Although various works on the model of harmonic oscillator system seem to advocate this view,[34–36] no rigorous clarification is available for a general system Hamiltonian, as has been recently pointed out.[37] Although a satisfactory answer for this remains a challenge, the more modest goal of examining the CLME at the fourth-order level can be achieved through our Markovian FQME.

A two-level system coupled to the harmonic oscillator bath has been studied numerous times, since it is the simplest nontrivial model mimicking an open discrete quantum system.[32] However, straightforward perturbative studies beyond the second order are rare.[23–26] Important contributions were made by Skinner and co-workers[23,24] who showed that the dephasing time (T_2) can be different from twice the population relaxation time (T_1) even when the system-bath coupling is off-diagonal. More surprisingly, T_2 can be greater than $2T_1$ for a certain complex coupling. These results are obtained for finite bath correlation time. According to their formal expression for the pure dephasing time,[24] however, the second-order result of $T_2=2T_1$ is recovered in the limit where the bath timescale becomes zero. Thus for the model of two-level system off-diagonally coupled to the Markovian bath, the fourth-order corrections should appear only in the coherence terms. Confirmation of this and calculation of the coherence terms can be done quite easily using our general expression for the Markovian FQME.

The paper is organized as follows. In Sec. II, we derive FQMEs for a general system plus bath Hamiltonian. Section III considers the special case of linearly coupled harmonic oscillator bath. In Sec. IV, a Markovian FQME is derived in the high temperature Ohmic bath limit, which is then applied to the above two examples of the system Hamiltonian, the CL model and a two-level system off-diagonally coupled to the bath. Section V summarizes conclusions and the implications of the present work.

II. GENERAL EXPRESSIONS FOR THE FOURTH-ORDER EQUATION

Consider a closed composite of system plus bath with the Hamiltonian given by

$$H=H_s+H_b+H_1=H_0+H_1, \tag{1}$$

where H_s is the system Hamiltonian, H_b the bath Hamiltonian, and H_1 represents the interaction between the system and the bath. For the clarity of presentation, we assume that the interaction is a single product of a system operator S and a bath operator B as follows:

$$H_1=SB. \tag{2}$$

All the following results are, however, general enough to be extended to the cases where the interaction is given by a sum of terms like Eq. (2). Appendix A provides derivations for this general situation, and all the results of the present section can be obtained from those in Appendix A by dropping all the indices.

In the interaction picture defined by the zeroth-order Hamiltonian H_0, the total density operator satisfies the following time dependent quantum Liouville equation:

$$\dot{\rho}(t)=-i\mathcal{L}_1(t)\rho(t)\equiv-\frac{i}{\hbar}[S(t)B(t),\rho(t)], \tag{3}$$

where $S(t)\equiv e^{iH_st/\hbar}Se^{-iH_st/\hbar}$ and $B(t)\equiv e^{iH_bt/\hbar}Be^{-iH_bt/\hbar}$. For notational convenience, we have used the same symbols for the interaction picture operators as those in the Schrödinger picture. Hereafter, *all operators are defined in the interaction picture unless specified otherwise*.

The total density operator at $t=0$ is assumed to be the following product form:

$$\rho(0)=\sigma(0)\rho_b, \tag{4}$$

where $\sigma(0)$ is an arbitrary system density operator and ρ_b is an equilibrium bath density operator commuting with H_b. The bath part of the interaction Hamiltonian satisfies the following condition:

$$\mathrm{Tr}_b\{\rho_bB\}=0, \tag{5}$$

which is always possible for a properly defined system Hamiltonian.

For the conditions as specified above, formally exact quantum master equations with simple structure can be derived. From these formally exact equations, the FQMEs can be obtained by making approximations valid up to the fourth order of the system-bath interaction. There are two well-known distinctive procedures. One uses the projection operator technique,[3,5–10,38,39] which leads to time-nonlocal (TN) equation, and the other employs the generalized cumulant theorem,[5–7,23,40] which leads to time-local (TL) equation. When considered up to the infinite order, these two equations are equivalent.[5–7] Within the perturbative approximations, however, they become different.

A. Time-nonlocal fourth-order quantum master equation (TN-FQME)

The TN equation is often called chronological ordering prescription[6] or time convolution[7] equation. The derivation can be made using the projection operator technique as mentioned above. Although this procedure has been demonstrated many times,[3,5–10,38,39] we provide our own derivation in Appendix A to make the present work self-contained. Equation (A8) is the formally exact TN-QME for the reduced system density operator $\sigma(t)\equiv\mathrm{Tr}_b\{\rho(t)\}$. The TN-FQME can be found by making a second-order approximation for $\exp_{(+)}\{-i\int_\tau^t d\tau'(1-\mathcal{P})\mathcal{L}_1(\tau')\}$. The result is Eq. (A9), which can be equivalently written as

$$\dot{\sigma}(t)\approx-\int_0^t d\tau(\mathcal{K}^{(2)}(t,\tau)-\mathcal{K}^{(4)}(t,\tau))\sigma(\tau), \tag{6}$$

where

$$\mathcal{K}^{(2)}(t,\tau)\equiv\langle\mathcal{L}_1(t)\mathcal{L}_1(\tau)\rangle, \tag{7}$$

$$\mathcal{K}^{(4)}(t,\tau)\equiv\int_\tau^t d\tau_1\int_\tau^{\tau_1}d\tau_2\langle\mathcal{L}_1(t)\mathcal{L}_1(\tau_1)\mathcal{L}_1(\tau_2)\mathcal{L}_1(\tau)\rangle - \langle\mathcal{L}_1(t)\mathcal{L}_1(\tau_1)\rangle\langle\mathcal{L}_1(\tau_2)\mathcal{L}_1(\tau)\rangle, \tag{8}$$

where $\langle\cdots\rangle\equiv\mathrm{Tr}_b\{\cdots\rho_b\}$. When transformed back to the Schrödinger picture, Eq. (6) involves time convolution integrals, the solution of which may be obtained more easily in the Laplace domain. After the bath averaging is taken explicitly, Eq. (7) can be expressed as

$$\mathcal{K}^{(2)}(t,\tau)(\cdot)=\frac{1}{\hbar^2}[S(t),\langle B(t)B(\tau)\rangle S(\tau)(\cdot) - \langle B(\tau)B(t)\rangle(\cdot)S(\tau)], \tag{9}$$

which corresponds to Eq. (A11) with all the indices dropped. This expression for the second-order kernel is well-known.[10–12,14] Similarly, Eq. (8) can be expressed as

$$\mathcal{K}^{(4)}(t,\tau)(\cdot)=\frac{1}{\hbar^4}\int_\tau^t d\tau_1\int_\tau^{\tau_1}d\tau_2[S(t),S(\tau_1)F(t,\tau_1,\tau_2,\tau;\cdot) - F^\dagger(t,\tau_1,\tau_2,\tau;\cdot)S(\tau_1)], \tag{10}$$

with

$$\begin{aligned}F(t,\tau_1,\tau_2,\tau;\cdot)=&(\langle B_tB_{\tau_1}B_{\tau_2}B_\tau\rangle-\langle B_tB_{\tau_1}\rangle\langle B_{\tau_2}B_\tau\rangle)S_{\tau_2}S_\tau(\cdot)\\ &-(\langle B_\tau B_tB_{\tau_1}B_{\tau_2}\rangle-\langle B_tB_{\tau_1}\rangle\langle B_\tau B_{\tau_2}\rangle)S_{\tau_2}(\cdot)S_\tau\\ &-(\langle B_{\tau_2}B_tB_{\tau_1}B_\tau\rangle-\langle B_tB_{\tau_1}\rangle\langle B_{\tau_2}B_\tau\rangle)S_\tau(\cdot)S_{\tau_2}\\ &+(\langle B_\tau B_{\tau_2}B_tB_{\tau_1}\rangle-\langle B_tB_{\tau_1}\rangle\langle B_\tau B_{\tau_2}\rangle)(\cdot)S_\tau S_{\tau_2},\end{aligned} \tag{11}$$

where the time arguments were denoted as subscripts. Equations (10) and (11) correspond to Eqs. (A16) and (A17), with all the indices dropped. To our knowledge, this type of general expression for the fourth-order kernel has not been reported before.

Equations (6), (9), (10), and (11) form a closed set of expressions for the TN-FQME. No assumption was made on the system Hamiltonian nor on the system-bath interaction within the form of Eq. (2). As expected, the fourth-order term involves four-time bath correlation functions and triple integrations over time. Solving this in real time domain may be time consuming. When considered in the Laplace domain, the Schrödinger picture version of Eq. (6) can have a relatively simple structure and lend itself to a physically motivated approximation for the remaining infinite order terms. Golosov and Reichman[41] recently demonstrated that this approach enhances the accuracy a great deal when applied to a different type of master equation.

B. Time-local fourth-order quantum master equation (TL-FQME)

The TL equation is often called partial ordering prescription[6] or time convolutionless[27] equation, and can be obtained by employing the generalized cumulant theorem.[40] Alternatively,[7] one can convert the TN equation to the corresponding TL equation by inverting $\sigma(\tau)$ to $\sigma(t)$. At the fourth-order level, this procedure can be performed in a simplified manner shown below.

In Eq. (6), the second-order term can be replaced with the following approximation:

$$\begin{aligned}\mathcal{K}^{(2)}(t,\tau)\sigma(\tau)&=\mathcal{K}^{(2)}(t,\tau)\sigma(t)-\mathcal{K}^{(2)}(t,\tau)(\sigma(t)-\sigma(\tau))\\ &\approx\mathcal{K}^{(2)}(t,\tau)\Big(\sigma(t)-\int_\tau^t d\tau_1\int_0^{\tau_1}d\tau_2 \times\mathcal{K}^{(2)}(\tau_1,\tau_2)\sigma(\tau_2)\Big)\\ &\approx\mathcal{K}^{(2)}(t,\tau)\Big(1-\int_\tau^t d\tau_1\int_0^{\tau_1}d\tau_2 \times\mathcal{K}^{(2)}(\tau_1,\tau_2)\Big)\sigma(t),\end{aligned} \tag{12}$$

where the second equality is obtained by integrating the second order approximation of Eq. (6) from τ to t and the third equality by replacing $\sigma(\tau_2)$ with $\sigma(t)$. These approximations do not affect the accuracy of the equation up to the fourth order because the errors, when multiplied with $\mathcal{K}^{(2)}(t,\tau)\mathcal{K}^{(2)}(\tau_1,\tau_2)$, appear in the fifth and higher order terms. Similarly, the second term in the integrand of Eq. (6) can be approximated as

$$\mathcal{K}^{(4)}(t,\tau)\sigma(\tau)\approx\mathcal{K}^{(4)}(t,\tau)\sigma(t), \tag{13}$$

without degrading the accuracy of the equation up to the fourth order. Employing the approximations given by Eqs. (12) and (13), one can now transform Eq. (6) into the following TL equation:

$$\dot\sigma(t)\approx-(\mathcal{R}^{(2)}(t)-\mathcal{R}^{(4)}(t))\sigma(t), \tag{14}$$

where

$$\mathcal{R}^{(2)}(t)\equiv\int_0^t d\tau\mathcal{K}^{(2)}(t,\tau), \tag{15}$$

$$\mathcal{R}^{(4)}(t)\equiv\int_0^t d\tau\mathcal{K}^{(4)}(t,\tau)-\int_0^t d\tau\int_\tau^t d\tau_1\int_0^{\tau_1}d\tau_2 \times\mathcal{K}^{(2)}(t,\tau)\mathcal{K}^{(2)}(\tau_1,\tau_2). \tag{16}$$

These two relaxation operators involve time integrations of $\mathcal{K}^{(2)}(t,\tau)$ and $\mathcal{K}^{(4)}(t,\tau)$, for which the detailed expressions are given by Eqs. (9) and (10). The TL-FQME, Eq. (14), is suitable for time domain study. Compared to the TL-SQME, solving this equation has an additional cost of calculating the four-time bath correlation functions and triple time integrations. However, if an explicit expression for $\mathcal{R}^{(4)}(t)$ can be found, implementation of the TL-FQME is no more difficult than the TL-SQME. Before ending this section, it is meaningful to check the validity of the derivation presented here by rewriting Eq. (16) in a more familiar form. In the second term, the integration over τ_2 can be divided into the two regions of $0\leqslant\tau_2<\tau$ and $\tau\leqslant\tau_2<\tau_1$. Interchanging τ_2 and τ for the latter case and inserting Eqs. (7) and (8) into the final expression for $\mathcal{R}^{(4)}(t)$, Eq. (16) can be expressed as

$$\begin{aligned}\mathcal{R}^{(4)}(t)=\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\int_0^{\tau_2}d\tau(&\langle\mathcal{L}_1(t)\mathcal{L}_1(\tau_1)\mathcal{L}_1(\tau_2)\mathcal{L}_1(\tau)\rangle\\ &-\langle\mathcal{L}_1(t)\mathcal{L}_1(\tau_1)\rangle\langle\mathcal{L}_1(\tau_2)\mathcal{L}_1(\tau)\rangle\\ &-\langle\mathcal{L}_1(t)\mathcal{L}_1(\tau_2)\rangle\langle\mathcal{L}_1(\tau_1)\mathcal{L}_1(\tau)\rangle\\ &-\langle\mathcal{L}_1(t)\mathcal{L}_1(\tau)\rangle\langle\mathcal{L}_1(\tau_1)\mathcal{L}_1(\tau_2)\rangle).\end{aligned} \tag{17}$$

This is the usual form of the fourth-order kernel found in the literature,[5–7,23–28] and thus demonstrates the validity of the derivation made in the present section.

III. LINEARLY COUPLED HARMONIC OSCILLATOR BATH

For the model of linearly coupled harmonic oscillator bath, the fourth-order terms can be simplified further. Assume the bath Hamiltonian is given by

$$H_b=\sum_n \frac{p_n^2}{2m_n}+\frac{m_n\omega_n^2}{2}x_n^2, \tag{18}$$

and the bath part of the interaction Hamiltonian given by Eq. (2) has the following form:

$$B=-\sum_n c_n x_n . \tag{19}$$

We consider the following canonical density operator:

$$\rho_b=e^{-\beta H_b}/Z_b , \tag{20}$$

where $Z_b=\mathrm{Tr}_b\{e^{-\beta H_b}\}$, as the equilibrium density operator defining the initial condition and the projection operator of Eq. (A3). For these specifications, the two-time bath correlation function is written as

$$\langle B(t)B\rangle=\hbar(\chi(t)-i\varphi(t)), \tag{21}$$

where

$$\chi(t)=\frac{1}{\pi}\int_0^\infty d\omega J(\omega)\coth(\beta\hbar\omega/2)\cos(\omega t), \tag{22}$$

$$\varphi(t)=\frac{1}{\pi}\int_0^\infty d\omega J(\omega)\sin(\omega t), \tag{23}$$

with the spectral density defined as

$$J(\omega)\equiv\frac{\pi}{2}\sum_n \frac{c_n^2}{m_n\omega_n}\delta(\omega-\omega_n). \tag{24}$$

The four-time bath correlation functions appearing in Eq. (11) can be expressed as a sum of products of the two-time correlation functions, with the application of Wick's rule. The resulting expression for the more general case considered in Appendix A is given by Eq. (A18) or (A20). In order to simplify the notation, we denote the commutator and the anticommutator with $S(t)$ as

$$\mathcal{C}(t)(\cdot)\equiv[S(t),\cdot], \tag{25}$$

$$\mathcal{A}(t)(\cdot)\equiv\{S(t),\cdot\}, \tag{26}$$

and define the following superoperator:

$$\mathcal{D}(t,t')\equiv\chi(t-t')\mathcal{C}(t')-i\varphi(t-t')\mathcal{A}(t'). \tag{27}$$

Then the second-order kernel given by Eq. (9) can be compactly written as

$$\mathcal{K}^{(2)}(t,\tau)=\frac{1}{\hbar}\mathcal{C}(t)\mathcal{D}(t,\tau). \tag{28}$$

The detailed form of the fourth-order kernel can be found by inserting Eq. (A20) with all the indices dropped into Eq. (10), which is expressed as

$$\mathcal{K}^{(4)}(t,\tau)=\frac{1}{\hbar^2}\int_\tau^t d\tau_1\int_\tau^{\tau_1}d\tau_2\mathcal{C}(t)\mathcal{C}(\tau_1)\times(\mathcal{D}(t,\tau_2)\mathcal{D}(\tau_1,\tau)+\mathcal{D}(\tau_1,\tau_2)\mathcal{D}(t,\tau)), \tag{29}$$

where the definitions of Eqs. (25)–(27) were used.

Inserting Eq. (28) into Eq. (15), one can show that the second-order relaxation operator in the TL equation has the following form:

$$\mathcal{R}^{(2)}(t)=\frac{1}{\hbar}\int_0^t d\tau\mathcal{C}(t)\mathcal{D}(t,\tau). \tag{30}$$

Inserting Eqs. (28) and (29) into Eq. (16), one can show that the fourth-order relaxation operator in the TL equation can be expressed as

$$\begin{aligned}\mathcal{R}^{(4)}(t)=\frac{1}{\hbar^2}\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\int_0^{\tau_2}d\tau_3\mathcal{C}(t)&\\ \times(\mathcal{C}(\tau_1)\mathcal{D}(t,\tau_2)\mathcal{D}(\tau_1,\tau_3)&\\ -\mathcal{D}(t,\tau_2)\mathcal{C}(\tau_1)\mathcal{D}(\tau_1,\tau_3)&\\ +\mathcal{C}(\tau_1)\mathcal{D}(\tau_1,\tau_2)\mathcal{D}(t,\tau_3)&\\ -\mathcal{D}(t,\tau_3)\mathcal{C}(\tau_1)\mathcal{D}(\tau_1,\tau_2)),&\end{aligned} \tag{31}$$

where the same manipulation as deriving Eq. (17) from Eq. (16) has been made but using the explicit forms of $\mathcal{K}^{(2)}(t,\tau)$ and $\mathcal{K}^{(4)}(t,\tau)$ given by Eqs. (28) and (29). A similar structure can be seen in a different fourth-order analysis.[42]

Equations (28) and (29) are the final expressions for the kernels of the TN-FQME, Eq. (6), and Eqs. (30) and (31) are those for the relaxation operators of the TL-FQME given by Eq. (14). The only assumption necessary for these simplifications is the Wick's rule, and no specification for the bath time scale has been made yet. Compared to Eq. (29), Eq. (31) has additional two terms with different ordering and sign. The net contribution of the four terms in Eq. (31) is expected to diminish as the timescale of the bath decreases. Thus the fourth-order correction for the TL-SQME in the Markovian bath limit may have a relatively simple structure.

IV. HIGH TEMPERATURE OHMIC BATH LIMIT

Assume that the spectral density is given by

$$J(\omega)=\eta\omega\Theta(\omega/\omega_c), \tag{32}$$

where $\Theta(x)$ is a cutoff function decaying faster than $1/x$ and ω_c is the cutoff frequency determining the spectral range of the bath, which is assumed to be much larger than the inverse of the system timescale τ_s. In the high temperature limit of $\beta\hbar\omega_c\ll 1$, the real part of the bath correlation function, Eq. (22), can be approximated as

$$\chi(t)\approx\frac{2\eta}{\beta\hbar\pi}\int_0^\infty d\omega\Theta(\omega/\omega_c)\cos(\omega t)\equiv\frac{2\eta}{\beta\hbar}\tilde{\delta}(t). \tag{33}$$

Irrespective of the temperature, the imaginary part, Eq. (23), can be written as

$$\varphi(t) = -\eta\tilde{\delta}'(t). \tag{34}$$

In Eqs. (33) and (34), $\tilde{\delta}(t)$ and $\tilde{\delta}'(t)$ become the Dirac-delta function and its derivative if $\omega_c \to \infty$. Physically, however, ω_c always remain finite, which is also consistent with the high temperature condition stated above. Here we assume that the system-bath time scale ratio $\omega_c \tau_s$ is large enough such that $\tilde{\delta}(t)$ can be approximated as the genuine Dirac-delta function when being integrated with slowly varying system operators.[43] Otherwise, $\tilde{\delta}(t)$ is still a well-defined function localized near $t \sim 1/\omega_c$ and with finite $\tilde{\delta}(0)$ of order ω_c. To be consistent, however, one should disregard terms of order $1/(\omega_c \tau_s)$ or smaller in all other integrations involving $\tilde{\delta}(t)$ and its derivative. Recognition of this fact is important in unambiguous evaluation of the fourth-order kernels as will be shown later. In the following, we assume that $t\omega_c \gg 1$. Thus initial slippage dynamics[44,45] is not a concern here.

The TL-FQME of Eq. (14) is suitable for the consideration of the Markovian bath limit. Inserting Eqs. (27), (33), and (34) into Eq. (30),

$$\mathcal{R}^{(2)}(t) = \frac{1}{\hbar}\int_0^t d\tau \mathcal{C}(t)\left(\frac{2\eta}{\beta\hbar}\tilde{\delta}(t-\tau)\mathcal{C}(\tau) + i\eta\tilde{\delta}'(t-\tau)\mathcal{A}(\tau)\right)$$

$$\approx \frac{\eta}{\beta\hbar^2}\mathcal{C}\mathcal{C} - \frac{i\eta}{\hbar}\tilde{\delta}(0)\mathcal{C}\mathcal{A} + \frac{i\eta}{2\hbar}C\dot{\mathcal{A}}, \tag{35}$$

where all the operators in the last line have the same time argument t, which was omitted, and $\dot{\mathcal{A}} = d\mathcal{A}(t)/dt$. For the calculation of $\mathcal{R}^{(4)}(t)$, we insert Eq. (27) into Eq. (31) and arrange terms as follows:

$$\mathcal{R}^{(4)}(t) = \frac{1}{\hbar^2}\int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \int_0^{\tau_2} d\tau_1 \mathcal{C}(t)(\kappa_1(\tau_1,\tau_2,\tau_3,t) + \kappa_2(\tau_1,\tau_2,\tau_3,t)), \tag{36}$$

where a change of time integrands, $\tau_i \to t - \tau_i$, has been made, and the two kernels κ_1 and κ_2 are given by

$$\begin{aligned}\kappa_1(\tau_1,\tau_2,\tau_3,t) \equiv{}& \chi(\tau_2)\chi(\tau_3-\tau_1)(\mathcal{C}_1\mathcal{C}_2\mathcal{C}_3 - \mathcal{C}_2\mathcal{C}_1\mathcal{C}_3)\\ &- i\varphi(\tau_2)\chi(\tau_3-\tau_1)(\mathcal{C}_1\mathcal{A}_2\mathcal{C}_3 - \mathcal{A}_2\mathcal{C}_1\mathcal{C}_3)\\ &- i\chi(\tau_2)\varphi(\tau_3-\tau_1)(\mathcal{C}_1\mathcal{C}_2\mathcal{A}_3 - \mathcal{C}_2\mathcal{C}_1\mathcal{A}_3)\\ &- \varphi(\tau_2)\varphi(\tau_3-\tau_1)(\mathcal{C}_1\mathcal{A}_2\mathcal{A}_3 - \mathcal{A}_2\mathcal{C}_1\mathcal{A}_3),\end{aligned} \tag{37}$$

and

$$\begin{aligned}\kappa_2(\tau_1,\tau_2,\tau_3,t) \equiv{}& \chi(\tau_2-\tau_1)\chi(\tau_3)(\mathcal{C}_1\mathcal{C}_2\mathcal{C}_3 - \mathcal{C}_3\mathcal{C}_1\mathcal{C}_2) - i\varphi(\tau_2-\tau_1)\chi(\tau_3)(\mathcal{C}_1\mathcal{A}_2\mathcal{C}_3 - \mathcal{C}_3\mathcal{C}_1\mathcal{A}_2)\\ &- i\chi(\tau_2-\tau_1)\varphi(\tau_3)(\mathcal{C}_1\mathcal{C}_2\mathcal{A}_3 - \mathcal{A}_3\mathcal{C}_1\mathcal{C}_2)\\ &- \varphi(\tau_2-\tau_1)\varphi(\tau_3)(\mathcal{C}_1\mathcal{A}_2\mathcal{A}_3 - \mathcal{A}_3\mathcal{C}_1\mathcal{A}_2).\end{aligned} \tag{38}$$

In Eqs. (37) and (38), the subscripts 1, 2, and 3 in the superoperators $\mathcal{C}$ and $\mathcal{A}$ represent the time arguments $t-\tau_1$, $t-\tau_2$, and $t-\tau_3$, and $\chi(t)$ and $\varphi(t)$ are given by Eqs. (33) and (34). Due to the near singular nature of these functions, care should be taken in evaluating the integrations of κ_1 and κ_2. The calculations are detailed in Appendix B.

In Eqs. (37) and (38), each difference of the two similar triple products of $\mathcal{C}$ and/or $\mathcal{A}$ within a bracket vanishes if their time arguments become the same. As a result, all terms proportional to $W(0,0,0)$ in Appendix B do not contribute to the integrations of κ_1 and κ_2 in Eq. (36). The only contribution to the integration of κ_1 is made by a term of the type of Eq. (B11). Inserting $W(\tau_1,\tau_2,\tau_3) = \mathcal{C}(t-\tau_1)\mathcal{A}(t-\tau_2)\mathcal{A}(t-\tau_3) - \mathcal{A}(t-\tau_2)\mathcal{C}(t-\tau_1)\mathcal{A}(t-\tau_3)$ into Eq. (B11), one can show that

$$\frac{1}{\eta^2}\int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \int_0^{\tau_2} d\tau_1 \kappa_1(\tau_1,\tau_2,\tau_3,t) = \tfrac{1}{8}(\dot{\mathcal{C}}\mathcal{A}\mathcal{A} - \mathcal{A}\dot{\mathcal{C}}\mathcal{A}) + (\varepsilon' + \tfrac{1}{8})(\mathcal{C}\dot{\mathcal{A}}\mathcal{A} - \dot{\mathcal{A}}\mathcal{C}\mathcal{A}), \tag{39}$$

where the identity of $\mathcal{C}\mathcal{A} = \mathcal{A}\mathcal{C}$ has been used and ε' is defined by Eq. (B13). Similarly, only an identity of the type of Eq. (B14) makes contribution to the integration of κ_2 in Eq. (36). Inserting $W(\tau_1,\tau_2,\tau_3) = \mathcal{C}(t-\tau_1)\mathcal{A}(t-\tau_2)\mathcal{A}(t-\tau_3) - \mathcal{A}(t-\tau_3)\mathcal{C}(t-\tau_1)\mathcal{A}(t-\tau_2)$ into Eq. (B14), one can show that

$$\begin{aligned}\frac{1}{\eta^2}\int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \int_0^{\tau_2} d\tau_1 \kappa_2(\tau_1,\tau_2,\tau_3,t) ={}& (\varepsilon - \tfrac{1}{8})(\dot{\mathcal{C}}\mathcal{A}\mathcal{A} - \mathcal{A}\dot{\mathcal{C}}\mathcal{A}) + (\varepsilon - \varepsilon')(\mathcal{C}\dot{\mathcal{A}}\mathcal{A} - \mathcal{A}\mathcal{C}\dot{\mathcal{A}})\\ &+ (2\varepsilon - \varepsilon' - \tfrac{1}{8})(\mathcal{C}\mathcal{A}\dot{\mathcal{A}} - \dot{\mathcal{A}}\mathcal{C}\mathcal{A}),\end{aligned} \tag{40}$$

where ε is defined by Eq. (B7). Combining Eqs. (39) and (40) into Eq. (36), and recognizing the following identity:

$$\begin{aligned}\mathcal{C}\mathcal{A}\dot{\mathcal{A}} - \dot{\mathcal{A}}\mathcal{C}\mathcal{A} &= (\mathcal{C}\mathcal{A}\dot{\mathcal{A}} - \mathcal{C}\dot{\mathcal{A}}\mathcal{A}) + (\mathcal{C}\dot{\mathcal{A}}\mathcal{A} - \dot{\mathcal{A}}\mathcal{C}\mathcal{A})\\ &= (\mathcal{A}\mathcal{C}\dot{\mathcal{A}} - \mathcal{C}\dot{\mathcal{A}}\mathcal{A}) + (\mathcal{A}\dot{\mathcal{C}}\mathcal{A} - \dot{\mathcal{C}}\mathcal{A}\mathcal{A}),\end{aligned} \tag{41}$$

one can show that the fourth-order relaxation operator, Eq. (36), becomes

$$\begin{aligned}\mathcal{R}^{(4)}(t) \approx{}& -\varepsilon\eta^2\mathcal{C}(\dot{\mathcal{C}}\mathcal{A}\mathcal{A} - \mathcal{A}\dot{\mathcal{C}}\mathcal{A})\\ &- (\varepsilon - \tfrac{1}{8})\eta^2\mathcal{C}(\mathcal{C}\dot{\mathcal{A}}\mathcal{A} - \mathcal{A}\mathcal{C}\dot{\mathcal{A}}).\end{aligned} \tag{42}$$

The two terms in this equation, by explicit manipulations, can be expressed as

$$(\dot{\mathcal{C}}\mathcal{A}\mathcal{A} - \mathcal{A}\dot{\mathcal{C}}\mathcal{A})\sigma = \{[\dot{S},S],\{S,\sigma\}\}, \tag{43}$$

$$(\mathcal{C}\dot{\mathcal{A}}\mathcal{A} - \mathcal{A}\mathcal{C}\dot{\mathcal{A}})\sigma = (\mathcal{C}\dot{\mathcal{A}}\mathcal{A} - \mathcal{C}\mathcal{A}\dot{\mathcal{A}})\sigma = [S,[[\dot{S},S],\sigma]]. \tag{44}$$

Combining Eqs. (35) and (42)–(44) and using the fact that $\mathcal{C}\mathcal{A}(=\mathcal{A}\mathcal{C})$ is equal to the commutation with S^2, one can show that the detailed expression of Eq. (14) for the linearly coupled Markovian harmonic oscillator bath is given by

$$\dot{\sigma} \approx -\frac{\eta}{\beta\hbar^2}[S,[S,\sigma]] + i\tilde{\delta}(0)\frac{\eta}{\hbar}[S^2,\sigma] - \frac{i\eta}{2\hbar}[S,\{\dot{S},\sigma\}] - \varepsilon\frac{\eta^2}{\hbar^2}[S,\{[\dot{S},S],\{S,\sigma\}\}] - (\varepsilon - \tfrac{1}{8})\frac{\eta^2}{\hbar^2}[S,[S,[[\dot{S},S],\sigma]]]. \quad (45)$$

This is the main result, represented in the interaction picture, of the present section. The corresponding equation in the Schrödinger picture can be obtained by adding the inertial term due to H_s. Before doing this, we first introduce a bare system Hamiltonian H_s^0 and assume that

$$H_s = H_s^0 + \tilde{\delta}(0)\eta S^2. \quad (46)$$

The second term $\tilde{\delta}(0)\eta S^2$ in above equation serves as a counter term canceling the second term on the right-hand side of Eq. (45). The resulting FQME *in the Schrödinger picture* thus reads

$$\dot{\sigma} \approx -\frac{i}{\hbar}[H_s^0,\sigma] - \frac{\eta}{\beta\hbar^2}[S,[S,\sigma]] - \frac{i\eta}{2\hbar}[S,\{\dot{S},\sigma\}] - \varepsilon\frac{\eta^2}{\hbar^2}[S,\{[\dot{S},S],\{S,\sigma\}\}] - (\varepsilon - \tfrac{1}{8})\frac{\eta^2}{\hbar^2}[S,[S,[[\dot{S},S],\sigma]]], \quad (47)$$

where all the operators are defined *in the Schrödinger picture*. The same convention will be used hereafter.

Equation (47) is based on the assumption of timescale separation, $\tau_s\omega_c \gg 1$, and it is important to keep in mind that τ_s is the timescale of H_s, not of H_s^0. We denote the timescale of the latter as τ_s^0. If the dynamics due to $\tilde{\delta}(0)\eta S^2$ occurs in a time comparable to τ_s^0, the condition of $\tau_s^0\omega_c \gg 1$ is sufficient to validate Eq. (47). If the dynamics due to $\tilde{\delta}(0)\eta S^2$ is dominantly faster that that due to H_s^0, subtle issues arise. First, the condition of $\tau_s\omega_c \gg 1$ imposes an upper bound on η, the detailed value of which varies with the type of S. Second, the approximation of Eq. (35) need to be revised to maintain consistency with other approximations based on the timescale separation argument. The reason for this is that additional fourth-order term due to the definition of H_s as Eq. (46) appears in $\mathcal{R}^{(2)}(t)$, which cannot be neglected in the regime where $\tilde{\delta}(0)\eta S^2$ dominates the fast dynamics. A detailed account of this aspect will be provided for the CL model considered later.

Another important feature of Eq. (47) is that the fourth-order terms depend on the detailed nature of the cutoff function $\Theta(x)$ through the value of ε. Table I provides the numerical values for some typical choices of the cutoff function. No long time limit of ε exists when $\Theta(x)$ is either step function or exponential. For the former case, the value of ε is still bounded and may be approximated with its time average $1/\pi^2$. However, for the latter case, ε diverges logarithmically with time, the implication of which is that there is no well-defined Markovian FQME for this type of cutoff function. For Gaussian and Drude cutoffs, the long time limit of ε is finite and of order unity. Considering the facts that the fourth-order terms reflect the feedback of the bath in response to system's influence and that the bath timescale cannot be separated with itself, the dependencies of the fourth-order terms on the detailed nature of the high frequency bath components is physically sensible.

TABLE I. Functional types of $\tilde{\delta}(t)$ defined by Eq. (33) and the corresponding values of ε defined by Eq. (B7). The limiting value of $t\to\infty$ in Eq. (B7), if it exists, is shown.

Cutoff function	$\tilde{\delta}(t)$	ε
Step function	$\frac{\sin(\omega_c t)}{\pi t}$	$\frac{2\sin^2(\omega_c t/2)}{\pi^2}$
Exponential	$\frac{\omega_c}{\pi(1+(\omega_c t)^2)}$	$\frac{1}{2\pi^2}\ln(1+(\omega_c t)^2)$
Gaussian	$\frac{\omega_c}{2\sqrt{\pi}}e^{-(\omega_c t)^2/4}$	$\frac{1}{2\pi}$
Drude	$\frac{\omega_c}{2}e^{-\omega_c\lvert t\rvert}$	$\frac{1}{4}$

One may ask when the Markovian FQME becomes independent of the detailed nature of the cutoff function. Summing the two terms proportional to ε in Eq. (47),

$$[S,\{[\dot{S},S],\{S,\sigma\}\}] + [S,[S,[[\dot{S},S],\sigma]]] = [S,\{[\dot{S},S^2],\sigma\}]. \quad (48)$$

This relation implies that, as long as $[\dot{S},S^2]=0$, ε does not enter the fourth-order terms and the Markovian bath limit is uniquely defined. For a two-level system, an infinite number of possibilities exists for which such a condition is satisfied. For the case where the system consists of a quantum particle in a continuous potential field, such a condition is not satisfied in general. However, even in this case, if the net contribution of Eq. (48) is smaller than other terms by an order of $1/(\omega_c\tau_s)$, one should disregard the term in order to maintain consistency with other approximations based on the timescale separation.

A. Caldeira–Leggett model

For the CL model,[30,31] the system Hamiltonian is given by

$$H_s = \frac{p^2}{2m} + V(q) + \sum_n \frac{c_n^2}{2m_n\omega_n^2}q^2 \equiv H_s^0 + \eta\tilde{\delta}(0)q^2. \quad (49)$$

The system part in the interaction Hamiltonian of Eq. (2) is the following position operator:

$$S = q. \quad (50)$$

The bath Hamiltonian H_b is given by Eq. (18), and the bath operator B in the interaction Hamiltonian is given by Eq. (19). For the choice of Eq. (50),

$$\dot{S} = \dot{q} = \frac{p}{m}, \quad (51)$$

$$[\dot{S},S] = -\frac{i\hbar}{m}. \quad (52)$$

Due to the relation of Eq. (52), the last term in Eq. (47) vanishes for the present model. Inserting Eqs. (50)–(52) into Eq. (47), our FQME for the CL model in the Markovian bath limit becomes

$$\dot{\sigma} \approx -\frac{i}{\hbar}\left[H_s^0 - \frac{\varepsilon\eta^2}{m}q^2, \sigma\right] - \frac{\eta}{\beta\hbar^2}[q,[q,\sigma]] - \frac{i\eta}{2\hbar m}[q,\{p,\sigma\}]. \tag{53}$$

This has the same form as the CLME[30] except that there is an additional potential renormalization term of fourth order. Table I lists the values of ε for different cutoff functions of the spectral density.

Since terms of order $1/(\omega_c\tau_s)$ have been disregarded based on the assumption of timescale separation, $\omega_c\tau_s \gg 1$, the fourth-order potential renormalization term in Eq. (53) may not be meaningful if

$$\eta^2 \lesssim \frac{m^2}{\tau_s^3\omega_c}, \tag{54}$$

which makes the additional potential renormalization term also of order $1/(\omega_c\tau_s)$. It is important to examine the relevance of this inequality to the assumption of timescale separation. The analysis varies with the degree of system-bath coupling. In the weak coupling regime of $\eta \sim m/(\tau_s^{02}\omega_c)$, the second term of Eq. (49) has a comparable timescale as H_s^0. Thus $\eta^2 \sim m^2/(\tau_s^{04}\omega_c^2) \sim m^2/(\tau_s^4\omega_c^2)$. For this case, the condition of $\omega_c\tau_s \gg 1$ always guarantees Eq. (54). If the system-bath coupling becomes stronger such that $\eta \gg m/(\tau_s^{02}\omega_c)$, the second term in Eq. (49) sets the fast timescale of H_s. Thus $\tau_s \sim \sqrt{m/(\eta\omega_c)}$, which is equivalent to $\eta^2 \sim m^2/(\tau_s^4\omega_c^2)$. For this case, the condition of $\omega_c\tau_s \gg 1$ sets an upper bound on the value of η and also guarantees the condition of Eq. (54). Therefore, it is concluded that the assumption of timescale separation always makes the new fourth-order term in Eq. (53) of order $1/(\omega_c\tau_s)$ or smaller. This implies that a more careful analysis is necessary before including the term in the final expression.

In the weak system-bath coupling limit of $\eta \sim m/(\tau_s^{02}\omega_c)$, the fourth-order term is smaller than H_s^0 by an order of $1/(\omega_c\tau_s)$ and can be disregarded. If $\eta \gg m/(\tau_s^{02}\omega_c)$, the fourth-order term can be comparable to or larger than H_s^0. Thus one need more careful examination of the overall derivation. An account on this aspect has been made in the paragraph below Eq. (47). Due to the definition of H_s as given by Eq. (49), $\mathcal{R}^{(2)}(t)\sigma(t)$ in fact has an additional fourth-order term. Expansion of $\mathcal{A}(\tau)$ in Eq. (35) up to the second order of τ leads to[46]

$$\mathcal{R}^{(2)}(t) \approx \frac{\eta}{\beta\hbar^2}\mathcal{C}\mathcal{C} - \frac{i\eta}{\hbar}\tilde{\delta}(0)\mathcal{C}\mathcal{A} + \frac{i\eta}{2\hbar}\mathcal{C}\dot{\mathcal{A}} - \frac{i\eta\varepsilon}{2\hbar\tilde{\delta}(0)}\mathcal{C}\ddot{\mathcal{A}}, \tag{55}$$

where ε is as defined by Eq. (B7). In this expression, the last term applied to σ can be approximated as

$$-\frac{i\eta\varepsilon}{\hbar\tilde{\delta}(0)}\mathcal{C}\ddot{\mathcal{A}}\sigma = -\frac{i\eta\varepsilon}{\hbar\tilde{\delta}(0)}[q,\{\ddot{q},\sigma\}] \approx \frac{2i\varepsilon\eta^2}{m\hbar}[q,\{q,\sigma\}], \tag{56}$$

using $\ddot{q} \approx -2\eta\tilde{\delta}(0)q/m$ which is valid for $\eta \gg m/(\tau_s^{02}\omega_c)$. One should keep in mind that we have temporarily adopted the interaction picture in Eqs. (55) and (56). Going back to the Schrödinger picture and adding the additional term given by Eq. (56) to Eq. (53), the Markovian FQME in the regime of $m/(\tau_s^{02}\omega_c) \ll \eta \ll m\omega_c$ becomes

$$\dot{\sigma} \approx -\frac{i}{\hbar}\left[H_s^0 + \frac{\varepsilon\eta^2}{m}q^2, \sigma\right] - \frac{\eta}{\beta\hbar^2}[q,[q,\sigma]] - \frac{i\eta}{2\hbar m}[q,\{p,\sigma\}]. \tag{57}$$

This expression still differs from the CLME by an additional quadratic potential renormalization term. Physically, the new term tends to localize the system in the region where the system-bath interaction is minimal.

B. Two-level system

Assume the system consists of two levels, $|1\rangle$ and $|0\rangle$, and the system Hamiltonian is given by

$$H_s = \hbar\omega_s|1\rangle\langle 1|, \tag{58}$$

where the energy of $|0\rangle$ state was assumed to be zero. The system part of the interaction Hamiltonian is assumed to be

$$S = e^{-i\phi}|1\rangle\langle 0| + e^{i\phi}|0\rangle\langle 1|, \tag{59}$$

where ϕ is an arbitrary phase factor. Due the assumption that there are only two states, $|0\rangle$ and $|1\rangle$, the square of S satisfies

$$S^2 = 1. \tag{60}$$

This property makes the term given by Eq. (48) vanish and the Markovian FQME for the present model uniquely defined. By the same reason, the difference between H_s and H_s^0 as given by Eq. (46) simply becomes a constant and can be disregarded. For above choices of H_s and S,

$$\dot{S} = i\omega_s e^{-i\phi}|1\rangle\langle 0| - i\omega_s e^{i\phi}|0\rangle\langle 1|, \tag{61}$$

$$[\dot{S},S] = 2i\omega_s(|1\rangle\langle 1| - |0\rangle\langle 0|). \tag{62}$$

The detailed calculations of the terms in the FQME for the present model are made in Appendix C, utilizing the Pauli matrices. The results are shown in Eqs. (C10)–(C12). When transformed to the state representation of the present section, these can be equivalently written as

$$\begin{aligned}\dot{\sigma}_{11} &= -\frac{2\eta}{\beta\hbar^2}(\sigma_{11} - \sigma_{00}) - \frac{\eta\omega_s}{\hbar} \\ &= -\frac{2\eta}{\beta\hbar^2}\left(1 + \frac{\beta\hbar\omega_s}{2}\right)\sigma_{11} + \frac{2\eta}{\beta\hbar^2}\left(1 - \frac{\beta\hbar\omega_s}{2}\right)\sigma_{00} \\ &= -\dot{\sigma}_{00},\end{aligned} \tag{63}$$

$$\dot{\sigma}_{10} = -i\omega_s\left(1-\frac{\eta^2}{\hbar^2}\right)\sigma_{10} - \frac{2\eta}{\beta\hbar^2}\sigma_{10} + \left(\frac{2\eta}{\beta\hbar^2} + i\frac{\omega_s\eta^2}{\hbar^2}\right)e^{-2i\phi}\sigma_{01}, \tag{64}$$

$$\dot{\sigma}_{01} = i\omega_s\left(1-\frac{\eta^2}{\hbar^2}\right)\sigma_{01} - \frac{2\eta}{\beta\hbar^2}\sigma_{01} + \left(\frac{2\eta}{\beta\hbar^2} - i\frac{\omega_s\eta^2}{\hbar^2}\right)e^{2i\phi}\sigma_{10}, \tag{65}$$

where $\sigma_{ij}=\langle i|\sigma|j\rangle$. Here the dimension of η is different from that for the CL model because of the difference in the system operator S. Equation (63) satisfies the detailed balance condition with respect to H_s up to the first order of β. The fourth-order corrections do not enter the equations for the diagonal elements and do not change the apparent relaxation terms in the equations for the off-diagonal elements. As long as the condition of Appendix A in Ref. 23 is satisfied, the fourth-order corrections do not affect the dephasing rate. Thus the qualitative aspect of the SQME, $T_2=2T_1$, remains the same for the FQME. This result is also consistent with the work of Laird and Skinner,[24] where the pure dephasing rate becomes zero in the limit where the bath response time becomes zero. Equations (64) and (65) show that part of the fourth-order corrections can be included as the effective system Hamiltonian. However, this correction is not reflected in the equation for the diagonal elements, Eq. (63). In fact, inclusion of these terms amounts to a sixth-order correction. Thus Eqs. (63)–(65) are consistent up to the fourth order, but it is important to note that the equilibrium populations resulting from these equations are valid only up to the second order of the system-bath interaction.

For the present model, the fourth-order corrections do not alter the apparent relaxation characteristics of the SQME. However, this seems not a generic nature of the FQME but rather due to the simplicity of the model considered here. For example, for the more general case of $S=\cos\theta(|1\rangle\langle 1|-|0\rangle\langle 0|)+\sin\theta(e^{-i\phi}|1\rangle\langle 0|+e^{i\phi}|0\rangle\langle 1|)$, by going through a procedure similar to that in Appendix C, one can easily show that the fourth-order corrections alter the apparent dephasing rate. In addition, if one considers multiple system-bath couplings and includes the effects of finite bath response time explicitly, more dramatic effects similar to that observed by Laird and Skinner may appear. For this purpose, one needs to examine the general expression given in Appendix A for a specific model and also take all terms of order $1/(\omega_c\tau_s)$ into consideration. The corresponding expansions become more complicated in this case, and a detailed presentation will be provided in a separate paper.

V. CONCLUDING REMARKS

Based on the simple identity of Eq. (A10), which results from the cyclic symmetry of the trace operation in the bath subspace, we have derived a new expression for the fourth-order kernel, Eq. (10), which completes the general and detailed forms of the TN-FQME and TL-FQME. For the model of linearly coupled harmonic oscillator bath, these equations can be simplified further. The TN-FQME for this model is specified by Eqs. (6), (28), and (29), and the TL-FQME by Eqs. (14), (30), and (31). No assumption was made on the form of the system Hamiltonian and on the type of the system operator entering the interaction Hamiltonian of Eq. (2), and the derived expressions may facilitate the applicability of the FQME for a broad range of systems.

Analytic considerations were made on the high temperature Ohmic bath limit of the TL-FQME, which led to a simple Markovian FQME with time independent superoperators. Due to the fact that the bath timescale, however small it may be, cannot be separated with itself, the resulting equation has a subtle dependence on the nature of the cutoff function of the bath spectral density. This shows that there is no unique Markovian bath limit of the FQME in general, except for the case where the term given in Eq. (48) is zero or negligible.

The Markovian FQME was applied to the CL model, i.e., a one-dimensional quantum particle in a continuous potential field with bilinear coupling to the harmonic oscillator bath. The resulting equation has the same form as the CLME, except that there is an additional fourth-order potential renormalization term, which depends on the type of the cutoff function. In the weak system-bath interaction regime of $\eta \sim m/(\tau_s^{02}\omega_c)$, this term can be neglected according to the timescale analysis. However, for moderately large system-bath interaction, the final expression for the consistent fourth-order equation has an additional potential renormalization. Recently, a quantum Smoluchowski equation for the CL model has been derived,[47,48] which shows that the CLME[30] and other variants[49,50] ensuring the positivity do not become the desired form for strong damping unless the classical limit is taken first. The relevance of this to our present result is not clear at this point, but both of them indicate the approximate nature of the CLME from two different perspectives.

The Markovian FQME was also applied to the model of a two-level system with an off-diagonal coupling[23–26] to the harmonic oscillator bath. We have confirmed that the fourth-order corrections in the Markovian bath limit do not exist in the relaxation terms nor in the dephasing terms, and have derived explicit forms of the fourth-order corrections in the coherence terms. However, this feature is limited to the specific type of the off-diagonal coupling considered. As mentioned in Sec. IV B, for the more general case where there are both diagonal and off-diagonal components in the system operator of the interaction Hamiltonian, the fourth-order corrections also alter the dephasing rate.

We have limited our analysis of the TL-FQME only to the high temperature Ohmic bath limit and considered two simple well-known model systems. Although we have identified corrections important in the intermediate system-bath coupling regime, these do not affect the main relaxation characteristics of the SQME, which partly explain the good performance of a SQME for a similar model and condition.[51] However, in the low temperature regime and/or for more realistic models with multiple system-bath interactions and finite bath response time, the interplay between the coherence and delayed responses can render the FQME to exhibit

a qualitatively different feature. The general result provided in Secs. II and III will form an important starting point for the examination of these cases and for a clear understanding of possible new phenomena.

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APPENDIX A: DERIVATION OF THE TIME-NONLOCAL (TN) EQUATION AND THE FOURTH-ORDER APPROXIMATION

In the present section, we consider a general model of the interaction Hamiltonian given by

$$H_1(t)=S_j(t)B_j(t), \tag{A1}$$

where the Einstein convention was used for the summation and $S_j(t)$ and $B_j(t)$ are, respectively, system and bath operators in the interaction picture defined by $H_0=H_s+H_b$. *All other operators appearing in the present section are defined in the same interaction picture*. Since H_s and H_b commute with each other, $S_j(t)=e^{iH_st/\hbar}S_je^{-iH_st/\hbar}$ and $B_j(t)=e^{iH_bt/\hbar}B_je^{-iH_bt/\hbar}$. The bath operators in Eq. (A1) satisfy the following condition:

$$\mathrm{Tr}_b\{\rho_bB_j\}=0, \tag{A2}$$

where ρ_b is an equilibrium bath density operator commuting with H_b.

Although the TN equation based on the projection operator technique has been derived many times previously, we provide another derivation here to make the present work self-contained. For this purpose, define the following projection operator:

$$\mathcal{P}(\cdot)\equiv\rho_b\,\mathrm{Tr}_b\{\cdot\}. \tag{A3}$$

Due the condition of Eq. (A2) and the fact that ρ_b commutes with H_b, this projection operator satisfies the following important property:

$$\mathcal{P}\mathcal{L}_1(t)\mathcal{P}=0. \tag{A4}$$

Application of $\mathcal{P}$ to Eq. (3) and the use of Eq. (A4) leads to

$$\mathcal{P}\dot{\rho}(t)=-i\mathcal{P}\mathcal{L}_1(t)\mathcal{Q}\rho(t), \tag{A5}$$

where $\mathcal{Q}=1-\mathcal{P}$. On the other hand, application of $\mathcal{Q}$ to Eq. (3) with the use of Eq. (A4) leads to

$$\mathcal{Q}\dot{\rho}(t)=-i\mathcal{L}_1(t)\mathcal{P}\rho(t)-i\mathcal{Q}\mathcal{L}_1(t)\mathcal{Q}\rho(t). \tag{A6}$$

The formal solution of Eq. (A6) is

$$\mathcal{Q}\rho(t)=-i\int_0^t d\tau e_{(+)}^{-i\int_\tau^t d\tau' Q\mathcal{L}_1(\tau')}\mathcal{L}_1(\tau)\mathcal{P}\rho(\tau), \tag{A7}$$

where the fact that $\mathcal{Q}\rho(0)=0$, which results from Eq. (4), has been used, and $e_{(+)}$ is the time ordered exponential with chronological ordering. Inserting Eq. (A7) into Eq. (A5) and then taking trace over the bath, one can obtain the following quantum master equation:

$$\dot{\sigma}(t)=-\int_0^t d\tau\langle\mathcal{L}_1(t)e_{(+)}^{-i\int_\tau^t d\tau'(1-\mathcal{P})\mathcal{L}_1(\tau')}\mathcal{L}_1(\tau)\rangle\sigma(\tau), \tag{A8}$$

where $\sigma(t)=\mathrm{Tr}_b\{\rho(t)\}$ and $\langle\cdots\rangle\equiv\mathrm{Tr}_b\{\cdots\rho_b\}$.

Equation (A8) is exact, but an explicit evaluation of the time ordered exponential operator is difficult in general. For this reason, perturbative approximations are usually made. When the second-order approximation is made for the time ordered exponential operator, one obtains the following fourth-order equation:

$$\begin{aligned}\dot{\sigma}(t)\approx&-\int_0^t d\tau\langle\mathcal{L}_1(t)\mathcal{L}_1(\tau)\rangle\sigma(\tau)\\&+\int_0^t d\tau\int_\tau^t d\tau_1\int_\tau^{\tau_1}d\tau_2\langle\mathcal{L}_1(t)\mathcal{L}_1(\tau_1)\\&\times(1-\mathcal{P})\mathcal{L}_1(\tau_2)\mathcal{L}_1(\tau)\rangle\sigma(\tau),\end{aligned} \tag{A9}$$

which is equivalent to Eqs. (6)–(8).

Equation (A9) is not, however, practically meaningful unless the bath averaging can be done explicitly. For the type of the interaction Hamiltonian given by Eq. (A1), this task can be simplified with the use of the following identity:

$$\begin{aligned}\mathrm{Tr}_b\{[S_jB_j,[S_kB_k,\mathcal{O}]]\}=&[S_j,S_k\,\mathrm{Tr}_b\{B_jB_k\mathcal{O}\}\\&-\mathrm{Tr}_b\{B_kB_j\mathcal{O}\}S_k],\end{aligned} \tag{A10}$$

where $\mathcal{O}$ is an arbitrary operator defined in the composite Hilbert space of the system and the bath. The second-order kernel in Eq. (A9) can be obtained by using $\mathcal{O}_2=\sigma(\tau)\rho_b$ in Eq. (A10), which results in

$$\begin{aligned}\langle\mathcal{L}_1(t)\mathcal{L}_1(\tau)\rangle\sigma(\tau)=\frac{1}{\hbar^2}[S_j(t),&\langle B_j(t)B_k(\tau)\rangle S_k(\tau)\sigma(\tau)\\&-\langle B_k(\tau)B_j(t)\rangle\sigma(\tau)S_k(\tau)].\end{aligned} \tag{A11}$$

The fourth-order kernel in Eq. (A9) can be obtained by inserting

$$\mathcal{O}_4=(\mathcal{L}_1(\tau_2)\mathcal{L}_1(\tau)-\langle\mathcal{L}_1(\tau_2)\mathcal{L}_1(\tau)\rangle)\rho_b\sigma(\tau) \tag{A12}$$

into Eq. (A10).

The expression for $\mathcal{O}_4$ in the Hilbert space is

$$\begin{aligned}\mathcal{O}_4=&(B_lB_m\rho_b-\langle B_lB_m\rangle\rho_b)S_lS_m\sigma\\&-(B_l\rho_bB_m-\langle B_mB_l\rangle\rho_b)S_l\sigma S_m\\&-(B_m\rho_bB_l-\langle B_lB_m\rangle\rho_b)S_m\sigma S_l\\&+(\rho_bB_mB_l-\langle B_mB_l\rangle\rho_b)\sigma S_mS_l.\end{aligned} \tag{A13}$$

The first trace on the right-hand side of Eq. (A10), with $\mathcal{O}_4$ inserted, becomes

$$\begin{aligned}\mathrm{Tr}_b\{B_jB_k\mathcal{O}_4\}=&(\langle B_jB_kB_lB_m\rangle-\langle B_jB_k\rangle\langle B_lB_m\rangle)S_lS_m\sigma\\&-(\langle B_mB_jB_kB_l\rangle-\langle B_jB_k\rangle\langle B_mB_l\rangle)S_l\sigma S_m\\&-(\langle B_lB_jB_kB_m\rangle-\langle B_jB_k\rangle\langle B_lB_m\rangle)S_m\sigma S_l\\&+(\langle B_mB_lB_jB_k\rangle-\langle B_jB_k\rangle\\&\times\langle B_mB_l\rangle)\sigma S_mS_l.\end{aligned} \tag{A14}$$

By direct manipulation, one can prove that

$$\mathrm{Tr}_b\{B_kB_j\mathcal{O}_4\}=(\mathrm{Tr}_b\{B_jB_k\mathcal{O}_4\})^\dagger. \tag{A15}$$

As a result, the fourth-order term in Eq. (A9) can be written as

$$\begin{aligned}&\langle\mathcal{L}_1(t)\mathcal{L}_1(\tau_1)(1-\mathcal{P})\mathcal{L}_1(\tau_2)\mathcal{L}_1(\tau)\rangle\sigma(\tau)\\&\quad=\frac{1}{\hbar^4}[S_j(t),S_k(\tau_1)F_{jk}(t,\tau_1,\tau_2,\tau;\sigma(\tau))\\&\qquad-F_{jk}^\dagger(t,\tau_1,\tau_2,\tau;\sigma(\tau))S_k(\tau_1)],\end{aligned} \tag{A16}$$

where

$$\begin{aligned}&F_{jk}(t,\tau_1,\tau_2,\tau;\sigma(\tau))\\&\quad=(\langle B_jB_kB_lB_m\rangle-\langle B_jB_k\rangle\langle B_lB_m\rangle)S_lS_m\sigma(\tau)\\&\qquad-(\langle B_mB_jB_kB_l\rangle-\langle B_jB_k\rangle\langle B_mB_l\rangle)S_l\sigma(\tau)S_m\\&\qquad-(\langle B_lB_jB_kB_m\rangle-\langle B_jB_k\rangle\langle B_lB_m\rangle)S_m\sigma(\tau)S_l\\&\qquad+(\langle B_mB_lB_jB_k\rangle-\langle B_jB_k\rangle\langle B_mB_l\rangle)\sigma(\tau)S_mS_l,\end{aligned} \tag{A17}$$

where the time arguments of the operators with subscripts j, k, l, and m are, respectively, t, τ_1, τ_2, and τ. Hereafter, the same convention will be used.

For the model of the harmonic oscillator bath linearly coupled to the system, Eq. (A17) can be simplified, with the use of Wick's rule, as follows:

$$\begin{aligned}&F_{jk}(t,\tau_1,\tau_2,\tau;\sigma(\tau))\\&\quad=(\langle B_jB_l\rangle\langle B_kB_m\rangle+\langle B_kB_l\rangle\langle B_jB_m\rangle)S_lS_m\sigma(\tau)\\&\qquad-(\langle B_jB_l\rangle\langle B_mB_k\rangle+\langle B_kB_l\rangle\langle B_mB_j\rangle)S_l\sigma(\tau)S_m\\&\qquad-(\langle B_lB_j\rangle\langle B_kB_m\rangle+\langle B_lB_k\rangle\langle B_jB_m\rangle)S_m\sigma(\tau)S_l\\&\qquad+(\langle B_lB_j\rangle\langle B_mB_k\rangle+\langle B_lB_k\rangle\langle B_mB_j\rangle)\sigma(\tau)S_mS_l.\end{aligned} \tag{A18}$$

If one introduces the following notation for the bath correlation functions:

$$\langle B_j(t)B_k\rangle=\hbar(\chi_{jk}(t)-i\varphi_{jk}(t)), \tag{A19}$$

Eq. (A18) can be rewritten as

$$\begin{aligned}&F_{jk}(t,\tau_1,\tau_2,\tau;\sigma(\tau))\\&\quad=\hbar^2(\chi_{jl}\chi_{km}+\chi_{kl}\chi_{jm})[S_l,[S_m,\sigma(\tau)]]\\&\qquad-\hbar^2(\varphi_{jl}\varphi_{km}+\varphi_{kl}\varphi_{jm})\{S_l,\{S_m,\sigma(\tau)\}\}\\&\qquad-i\hbar^2(\chi_{jl}\varphi_{km}+\chi_{kl}\varphi_{jm})[S_l,\{S_m,\sigma(\tau)\}]\\&\qquad-i\hbar^2(\varphi_{jl}\chi_{km}+\varphi_{kl}\chi_{jm})\{S_l,[S_m,\sigma(\tau)]\},\end{aligned} \tag{A20}$$

where functions with indices jl have time argument $t-\tau_2$, those with km have $\tau_1-\tau$, those with kl have $\tau_1-\tau_2$, and those with jm have $t-\tau$. Either from Eq. (A18) or Eq. (A20), one can prove that $F_{jk}^\dagger=F_{jk}$ for the model of the harmonic oscillator bath.

APPENDIX B: INTEGRALS OF THE FOURTH-ORDER TERMS IN THE MARKOVIAN BATH LIMIT

Consider an arbitrary time dependent system operator $W(\tau_1,\tau_2,\tau_3)$ as a function of τ_1, τ_2, and τ_3, which is defined in the interaction picture of the system Hamiltonian. The terms in Eq. (36) involve the following two types of integrals:

$$\int_0^t d\tau_3\int_0^{\tau_3}d\tau_2\int_0^{\tau_2}d\tau_1 g(\tau_2)h(\tau_3-\tau_1)W(\tau_1,\tau_2,\tau_3), \tag{B1}$$

$$\int_0^t d\tau_3\int_0^{\tau_3}d\tau_2\int_0^{\tau_2}d\tau_1 g(\tau_3)h(\tau_2-\tau_1)W(\tau_1,\tau_2,\tau_3), \tag{B2}$$

where $g(t)$ and $h(t)$ are either $\tilde{\delta}(t)$ or $\tilde{\delta}'(t)$, respectively. In the following, we abbreviate $\tilde{\delta}(t)$ as $\delta(t)$.

For the case where both $g(t)=h(t)=\delta(t)$, Eq. (B1) becomes

$$\begin{aligned}&\int_0^t d\tau_3\int_0^{\tau_3}d\tau_2\int_0^{\tau_2}d\tau_1\delta(\tau_2)\delta(\tau_3-\tau_1)W(\tau_1,\tau_2,\tau_3)\\&\quad=\int_0^t d\tau_2\int_0^{\tau_2}d\tau_1\int_{\tau_2}^t d\tau_3\delta(\tau_2)\delta(\tau_3-\tau_1)W(\tau_1,\tau_2,\tau_3)\\&\quad=\int_0^t d\tau_2\delta(\tau_2)\int_0^{\tau_2}d\tau_1\int_{\tau_2-\tau_1}^{t-\tau_1}d\tau_3\delta(\tau_3)W(\tau_1,\tau_2,\tau_3+\tau_1)\\&\quad=0,\end{aligned} \tag{B3}$$

and Eq. (B2) becomes

$$\begin{aligned}&\int_0^t d\tau_3\int_0^{\tau_3}d\tau_2\int_0^{\tau_2}d\tau_1\delta(\tau_2-\tau_1)\delta(\tau_3)W(\tau_1,\tau_2,\tau_3)\\&\quad=\int_0^t d\tau_3\delta(\tau_3)\int_0^{\tau_3}d\tau_2\int_0^{\tau_2}d\tau_1\delta(\tau_1)W(\tau_2-\tau_1,\tau_2,\tau_3)\\&\quad=0.\end{aligned} \tag{B4}$$

In the final equalities of both Eqs. (B3) and (B4), $\delta(\tau)$ was regarded as the genuine Dirac-delta function. That is, terms of order $1/(\omega_c\tau_s)$ or smaller were neglected. The same approximation will be used throughout this section.

For the case where $g(t)=\delta'(t)$ and $h(t)=\delta(t)$, Eq. (B1) becomes

$$\begin{aligned}&\int_0^t d\tau_3\int_0^{\tau_3}d\tau_2\delta'(\tau_2)\int_0^{\tau_2}d\tau_1\delta(\tau_3-\tau_1)W(\tau_1,\tau_2,\tau_3)\\&\quad=\int_0^t d\tau_3\delta(\tau_3)\int_0^{\tau_3}d\tau_1\delta(\tau_1)W(\tau_3-\tau_1,\tau_3,\tau_3)\\&\qquad-\int_0^t d\tau_3\int_0^{\tau_3}d\tau_2\delta(\tau_2)\delta(\tau_3-\tau_2)W(\tau_2,\tau_2,\tau_3)\\&\quad=-\tfrac{1}{8}W(0,0,0),\end{aligned} \tag{B5}$$

where the second equality was obtained by making a partial integration over τ_2 and recognizing that the boundary term corresponding to $\tau_2=0$ is zero and that the term containing the derivative of W with respect to τ_2 can be disregarded because it is of order $1/(\omega_c\tau_s)$. Similarly, Eq. (B2) for the choice of $g(t)=\delta'(t)$ and $h(t)=\delta(t)$ becomes

$$\int_0^t d\tau_3 \delta(\tau_3) \int_0^{\tau_3} d\tau_2 \int_0^{\tau_2} d\tau_1 \delta'(\tau_2-\tau_1) W(\tau_1,\tau_2,\tau_3)$$
$$= -\delta(0) \int_0^t d\tau_3 \delta(\tau_3) \int_0^{\tau_3} d\tau_2 W(\tau_2,\tau_2,\tau_3)$$
$$+ \int_0^t d\tau_3 \delta(\tau_3) \int_0^{\tau_3} d\tau_2 \delta(\tau_2) W(0,\tau_2,\tau_3)$$
$$= -(\varepsilon - \tfrac{1}{8}) W(0,0,0), \tag{B6}$$

where the second equality was obtained by making a partial integration over τ_1 and disregarding the term containing the derivative of W, and

$$\varepsilon = \int_0^t d\tau_3 \delta(\tau_3) \delta(0) \tau_3. \tag{B7}$$

As can be seen from Table I this quantity is of order unity or larger and cannot be neglected.

For the case where $g(t)=\delta(t)$ and $h(t)=\delta'(t)$, Eq. (B1) becomes

$$\int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \delta(\tau_2) \int_0^{\tau_2} d\tau_1 \delta'(\tau_3-\tau_1) W(\tau_1,\tau_2,\tau_3)$$
$$= -\int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \delta(\tau_2)\delta(\tau_3-\tau_2) W(\tau_2,\tau_2,\tau_3)$$
$$+ \int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \delta(\tau_2)\delta(\tau_3) W(0,\tau_2,\tau_3)$$
$$= -\tfrac{1}{8} W(0,0,0), \tag{B8}$$

where the second equality was obtained by a partial integration over τ_1 and disregarding the term containing the derivative of W. On the other hand, Eq. (B2) becomes

$$\int_0^t d\tau_1 \int_{\tau_1}^t d\tau_2 \delta(\tau_2-\tau_1) \int_{\tau_2}^t d\tau_3 \delta'(\tau_3) W(\tau_1,\tau_2,\tau_3)$$
$$= -\int_0^t d\tau_1 \int_{\tau_1}^t d\tau_2 \delta(\tau_2-\tau_1)\delta(\tau_2) W(\tau_1,\tau_2,\tau_2)$$
$$= -\int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \delta(\tau_1)\delta(\tau_2) W(\tau_2-\tau_1,\tau_2,\tau_2)$$
$$= -\tfrac{1}{8} W(0,0,0). \tag{B9}$$

Finally, for the case where $g(t)=h(t)=\delta'(t)$, Eq. (B1) becomes

$$\int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \int_0^{\tau_2} d\tau_1 \delta'(\tau_2)\delta'(\tau_3-\tau_1) W(\tau_1,\tau_2,\tau_3)$$
$$= \int_0^t d\tau_2 \delta(\tau_2)\delta(0) W(\tau_2,\tau_2,\tau_2) + \int_0^t d\tau_3 \delta(\tau_3)\delta(\tau_3) W(0,\tau_3,\tau_3) - \int_0^t d\tau_3 \delta(\tau_3)\delta(0) W(\tau_3,\tau_3,\tau_3)$$
$$+ \int_0^t d\tau_3 \int_0^{\tau_3} d\tau_1 \delta(\tau_3)\delta(\tau_1) W_1'(\tau_3-\tau_1,\tau_3,\tau_3) + \int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \delta(\tau_2)\delta(\tau_3-\tau_2) W_3'(\tau_2,\tau_2,\tau_3)$$
$$+ \int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \delta(\tau_2)\delta(\tau_3-\tau_2) W_2'(\tau_2,\tau_2,\tau_3) - \int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \delta(\tau_2)\delta(\tau_3) W_2'(0,\tau_2,\tau_3), \tag{B10}$$

where partial integrations over τ_2 and then over the remaining variable have been made and W_i' denotes partial derivative with respect to the ith argument of W. In evaluating the first three terms of this equation, expansions up to the first derivatives of W should be made to retain finite terms of order unity. Then, Eq. (B10) reduces to

$$\int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \int_0^{\tau_2} d\tau_1 \delta'(\tau_2)\delta'(\tau_3-\tau_1) W(\tau_1,\tau_2,\tau_3)$$
$$= \delta_0 W(0,0,0) + \tfrac{1}{8} W_1'(0,0,0) + (\varepsilon' + \tfrac{1}{8}) W_2'(0,0,0)$$
$$+ (\varepsilon' + \tfrac{1}{4}) W_3'(0,0,0), \tag{B11}$$

where

$$\delta_0 = \int_0^t d\tau_3 \delta(\tau_3)\delta(\tau_3), \tag{B12}$$

$$\varepsilon' = \int_0^t d\tau_3 \delta(\tau_3)\delta(\tau_3)\tau_3, \tag{B13}$$

where δ_0 is of order $\delta(0)$ while ε' is of order unity. Similarly, Eq. (B2) for the case of $g(t)=h(t)=\delta'(t)$ becomes

$$\int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \int_0^{\tau_2} d\tau_1 \delta'(\tau_2-\tau_1)\delta'(\tau_3) W(\tau_1,\tau_2,\tau_3)$$

$$= \delta(0)\int_0^t d\tau_2 \delta(\tau_2) W(\tau_2,\tau_2,\tau_2)$$

$$- \int_0^t d\tau_2 \delta(\tau_2)\delta(\tau_2) W(0,\tau_2,\tau_2)$$

$$+ \delta(0)\int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \delta(\tau_3) W_3'(\tau_2,\tau_2,\tau_3)$$

$$- \int_0^t d\tau_3 \int_0^{\tau_3} d\tau_2 \delta(\tau_3)\delta(\tau_2) W_3'(0,\tau_2,\tau_3)$$

$$- \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \delta(\tau_2)\delta(\tau_2-\tau_1) W_1'(\tau_1,\tau_2,\tau_2)$$

$$= \left(\frac{\delta(0)}{2} - \delta_0\right) W(0,0,0) + (\varepsilon - \tfrac{1}{8}) W_1'(0,0,0)$$

$$+ (\varepsilon-\varepsilon') W_2'(0,0,0) + (2\varepsilon - \varepsilon' - \tfrac{1}{8}) W_3'(0,0,0). \tag{B14}$$

APPENDIX C: DERIVATION OF THE FOURTH-ORDER MASTER EQUATION FOR THE TWO-LEVEL SYSTEM

In order to derive the final expression for the Markovian FQME for the model of Sec. IV B, we employ the Pauli matrices, σ_x, σ_y, and σ_z. The system Hamiltonian of Eq. (58) can be written as

$$H_s = \frac{\hbar\omega_s}{2}(\sigma_z + 1), \tag{C1}$$

and the interaction Hamiltonian of Eq. (59) can be written as

$$S = \cos\phi\,\sigma_x + \sin\phi\,\sigma_y. \tag{C2}$$

Equations (61)–(62) can be equivalently written as

$$\dot{S} = \omega_s(-\cos\phi\,\sigma_y + \sin\phi\,\sigma_x), \tag{C3}$$

$$[\dot{S},S] = 2i\omega_s\sigma_z. \tag{C4}$$

The general form of the reduced system density operator can be written as

$$\sigma = \tfrac{1}{2}(1 + c_x\sigma_x + c_y\sigma_y + c_z\sigma_z). \tag{C5}$$

Due to the condition of Eq. (60), for the present model, the fourth-order equation of Eq. (47) reduces to

$$\dot{\sigma} = -\frac{i}{\hbar}[H_s,\sigma] - \frac{\eta}{\beta\hbar^2}[S,[S,\sigma]] - i\frac{\eta}{2\hbar}[S,\{\dot{S},\sigma\}]$$

$$+ \frac{\eta^2}{8\hbar^2}[S,[S,[[\dot{S},S],\sigma]]]. \tag{C6}$$

The terms in this expression can be calculated utilizing the properties of the Pauli matrices and the results are as follows:

$$[S,[S,\sigma]] = 2c_z\sigma_z + 2(\cos^2\phi\, c_y - \sin\phi\,\cos\phi\, c_x)\sigma_y$$

$$- 2(\sin\phi\cos\phi\, c_y - \sin^2\phi\, c_x)\sigma_x$$

$$= 2c_z\sigma_z + c_y\sigma_y + c_x\sigma_x + (\cos 2\phi\, c_y$$

$$- \sin 2\phi\, c_x)\sigma_y - (\sin 2\phi\, c_y + \cos 2\phi\, c_x)\sigma_x, \tag{C7}$$

$$[S,\{\dot{S},\sigma\}] = -2i\omega_s\sigma_z, \tag{C8}$$

$$[S,[S,[[\dot{S},S],\sigma]]] = -4\omega_s(2\cos^2\phi\, c_x + \sin 2\phi\, c_y)\sigma_y$$

$$+ 4\omega_s(\sin 2\phi\, c_x + 2\sin^2\phi\, c_y)\sigma_x. \tag{C9}$$

Inserting Eqs. (C7)–(C9) into Eq. (C6), one can show that the three real coefficients defined by Eq. (C5) satisfy the following coupled differential equations:

$$\dot{c}_x = -\omega_s c_y - \frac{2\eta}{\beta\hbar^2}((1-\cos 2\phi)c_x - 2\sin 2\phi\, c_y)$$

$$+ \frac{\omega_s\eta^2}{\hbar^2}((1-\cos 2\phi)c_y + \sin 2\phi\, c_x), \tag{C10}$$

$$\dot{c}_y = \omega_s c_x - \frac{2\eta}{\beta\hbar^2}((1+\cos 2\phi)c_y - \sin 2\phi\, c_x)$$

$$- \frac{\omega_s\eta^2}{\hbar^2}(2(1+\cos 2\phi)c_x + \sin 2\phi\, c_y), \tag{C11}$$

$$\dot{c}_z = -\frac{4\eta}{\beta\hbar^2}c_z - \frac{2\eta\omega_s}{\hbar}. \tag{C12}$$

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