Computable form of the Born-Markov master equation for open multilevel quantum systems

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The Redfield and Lindblad forms of the master equations are obtained under not only the Born and Markov approximations but also the secular approximation. In this paper, we propose a computable form of the master equation for open multilevel quantum systems beyond the secular approximation. The proposed form can retain some dynamical effects that are lost due to use of the secular approximation. Two kinds of open multilevel quantum systems are investigated by using this method, and the results are compared to the ones obtained from the Redfield equation and an exactly numerical path integral approach. It is shown that the results obtained from this computable form match those from the exact numerical path integral approach better than results from the Redfield equation. The normal-diffusion coefficient, momentum-damping coefficient, anomalous-diffusion coefficient, etc. in the master equation are also reevaluated.

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I. INTRODUCTION

Strictly speaking, any quantum system in any dynamical process will unavoidably suffer from interactions with uncontrollable degrees of freedom in surrounding. Therefore, the evolution of a quantum state will be affected by the environment of the system, although the influence is always overlooked in low-temperature conditions. However, when we investigate the evolution of quantum states of condensed systems, especially those of living substances in room-temperature surroundings, the environmental influence may be important and should not be ignored. Thus, understanding the dissipative quantum dynamics of a system embedded in a complex environment is an important topic across various subdisciplines of matter science [1,2]. Some significant progress in this field [3–5] has been achieved in last few years. A few prototypical physical models such as the Caldeira-Leggett model [6] and spin-boson model [1] have been developed and applied to these studies. In most cases the environment is described with a bosonic bath, which is a set of noninteracting harmonic oscillators whose influence on the system is concisely encoded in a spectral density function [2]. The prevalent adoption of a bosonic bath is based on the argument that knowing the linear response of an environment near equilibrium should be sufficient to predict the dissipative dynamics of the open quantum systems [7,8].

The theory and methods of studying open quantum systems have been strongly developed in recent decades [9–12], pushed by technological demand. The basic tool of these studies is the master equation [13], which allows for insight into some physical properties by computing average physical quantities [14–21]. However, it is difficult to obtain and in particular to solve the general master equation of an open quantum system. The Born-Markov master equation, which is derived from the von Neumann–Liouville equation by means of Born and Markov approximations, is a good starting point for the task. To obtain reliable results from the Born-Markov master equation, the investigated system must satisfy the following two conditions: First, the interaction between the system and its environment must be sufficiently weak and the environment large enough in comparison to the size of the system such that the bath state does not change significantly because of the interaction. Second, the timescale of the system dynamics must be larger than the reservoir correlation time. However, even if these conditions are satisfied, with the exception of the two-level system and the harmonic oscillator, it is still difficult to obtain and solve the Born-Markov master equation for open multilevel quantum systems [22].

The dynamics of open multilevel quantum systems can be investigated by using the Redfield equation, which was derived from the Born-Markov master equation by imposing the secular approximation. It has been widely employed and is attractive because its numerical time propagation is simplified and the positivity is guaranteed. Furthermore, when the interaction Hamiltonian between the interest system and its environment can be written as a sum of products of the system and environment operators, the Lindblad equation can be derived from the Redfield equation. Insofar as simplicity and positivity are concerned, the master equations of the Redfield and Lindblad forms have many advantages [23,24]. However, in these methods, the secular approximation which eliminates some relaxation terms results in partial destruction of the reduced dynamics of the open quantum system [25]. Namely, the secular approximation distorts the true dynamics within the Redfield framework.

A direction for solving the quantum dissipative dynamics including non-Markovian effects is formulating the reduced density matrix based on the path integral [2,26]. Makri and co-workers have developed an exact numerical dynamics approach—quasi-adiabatic propagator path integral (QUAPI) method [15,27]. This is an efficient way of including memory effects via tensor products of element memory kernels. A different approach was proposed by Tanimura and co-workers,

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who introduced a hierarchical treatment of non-Markovian dynamics in which the primary density operator is coupled to an auxiliary one, describing the effects of successively higher-order system-bath interaction [16,28]. These two kinds of non-Markovian dynamical methods are extensively used in the investigations of decoherence, disentanglement, energy transformation, and spectral analysis in quantum open systems. Many other methods have also been proposed and used in recent years [29–31]. However, to discover other dynamical schemes for open quantum systems is still expected, because in the existing methods, huge analytical and/or numerical efforts should be made.

In this paper, we propose a scheme to formulate the Born-Markov master equation into a computable form. In the derivation of this form, the Born and Markov approximations are used. However, different from the derivation of the Redfield form, the secular approximation does not need to be used in this scheme. By using this computable form of the master equation, we can compute the evolution of the reduced density matrix of open multilevel quantum systems. As examples, we shall study the dynamics of two models. One is a three-level model, and the other is the Fenna-Matthews-Olson (FMO) complex [32], which is a model extensively used to study photosynthetic pigment protein complex in green sulfur bacteria. It is shown that compared with the traditional Redfield form [33,34], the form of the master equation we propose agrees better with the numerical path integral method [15,27] and requires less computation.

II. THE BORN-MARKOV MASTER EQUATION

A. The general form of Born-Markov master equation

The total system-environment Hamiltonian is set as

$$H = H_s + H_b + H_{sb}. \tag{1}$$

Here, H_s, H_b, and H_{sb} are the Hamiltonians of the system, bath, and the interaction between them. It is convenient to switch to the interaction picture in the derivations of the master equation. Thus, we set

$$H_0 = H_s + H_b, \quad H_I = H_{sb}, \tag{2}$$

where H_0 denotes the total free Hamiltonian, and H_I represents the interaction one. By using the Born approximation, namely,

$$\rho(t) \approx \rho_s(t) \otimes \rho_b, \qquad \forall t \geqslant 0, \tag{3}$$

one has

$$\frac{d\rho_s^{(I)}(t)}{dt} = -\int_0^t dt' \mathrm{Tr}_b[H_I(t), [H_I(t'), \rho_s^{(I)}(t') \otimes \rho_b]]. \tag{4}$$

Suppose the coupling of the system to its environment is described by the interaction Hamiltonian as

$$H_I = \sum_\alpha S_\alpha \otimes E_\alpha. \tag{5}$$

Here S_α and E_α are the system and environment operators. By using the Markov approximation, one can obtain the equation in Schrödinger picture as [13]

$$\frac{d\rho_s(t)}{dt} = -i[H_s, \rho_s(t)] - \int_0^\infty d\tau \sum_{\alpha\beta} \{W_{\alpha\beta}(\tau) [S_\alpha, S_\beta(-\tau)\rho_s(t)] + W_{\beta\alpha}(-\tau)[\rho_s(t)S_\beta(-\tau), S_\alpha]\}. \tag{6}$$

Here and in the following we set $\hbar = 1$, and

$$W_{\alpha\beta}(\tau) = \mathrm{Tr}_b\{E_\alpha(\tau)E_\beta\rho_b\}. \tag{7}$$

Set

$$B_\alpha = \int_0^\infty d\tau \sum_\beta W_{\alpha\beta}(\tau)S_\beta(-\tau),$$
$$C_\alpha = \int_0^\infty d\tau \sum_\beta W_{\beta\alpha}(-\tau)S_\beta(-\tau), \tag{8}$$

with

$$E_\alpha(\tau) = e^{iH_0\tau}E_\alpha e^{-iH_0\tau},$$
$$S_\alpha(\tau) = e^{iH_0\tau}S_\alpha e^{-iH_0\tau}, \tag{9}$$

and the master equation can be written as

$$\frac{d}{dt}\rho_s(t) = -i[H_s, \rho_s(t)] - \sum_\alpha \{[S_\alpha, B_\alpha\rho_s(t)] + [\rho_s(t)C_\alpha, S_\alpha]\}. \tag{10}$$

We call Eq. (10) the Born-Markov master equation.

B. The Born-Markov master equation for the open two-level system (spin-boson model)

The Born-Markov master equation Eq. (10) is not a general computable form. The computable forms of the Born-Markov master equation for a two-level system and harmonic oscillator have been obtained [35]. In this section, we shall review the derivation of the computable form of the Born-Markov master equation for the spin-boson model. The Hamiltonian of a simplified spin-boson model can be written as

$$H = -\frac{1}{2}\Delta\sigma_x + \sum_k \left(\frac{\hat{p}_k^2}{2m_k} + \frac{1}{2}m_k\omega_k^2\hat{q}_k^2\right) + \sigma_z\sum_k c_k\hat{q}_k. \tag{11}$$

Here, $S_\alpha = \sigma_z$. From Eq. (7), we have

$$W(\tau) = \sum_{jk} c_j c_k \langle \hat{q}_j(\tau)\hat{q}_k\rangle_{\rho_b} \equiv \nu(\tau) - i\mu(\tau), \tag{12}$$

where

$$\nu(\tau) = \frac{1}{2}\sum_k c_k^2\langle\{\hat{q}_k(\tau), \hat{q}_k\}\rangle_{\rho_b} = \int_0^\infty d\omega J(\omega)\coth\left(\frac{\omega}{2k_BT}\right)\cos(\omega\tau),$$
$$\mu(\tau) = \frac{i}{2}\sum_k c_k^2\langle[\hat{q}_k(\tau), \hat{q}_k]\rangle_{\rho_b} = \int_0^\infty d\omega J(\omega)\sin(\omega\tau), \tag{13}$$

with Boltzmann constant k_B, temperature T, and $J(\omega)$ is the spectral density function of the environment. Here $H_s = -\frac{1}{2}\Delta\sigma_x$, and thus we have

$$S(\tau) = e^{iH_s\tau}\sigma_z e^{-iH_s\tau} = \sigma_z\cos(\Delta\tau) + \sigma_y\sin(\Delta\tau), \tag{14}$$

and

$$B = \int_0^\infty d\tau W(\tau)[\sigma_z\cos(\Delta\tau) - \sigma_y\sin(\Delta\tau)],$$
$$C = \int_0^\infty d\tau W^*(\tau)[\sigma_z\cos(\Delta\tau) - \sigma_y\sin(\Delta\tau)]. \tag{15}$$

Setting

$$\xi = \int_0^\infty d\tau W(\tau)\cos(\Delta\tau),\ \zeta = \int_0^\infty d\tau W(\tau)\sin(\Delta\tau), \tag{16}$$

we have $B \equiv \xi\sigma_z - \zeta\sigma_y$ and $C = \xi^*\sigma_z - \zeta^*\sigma_y$. Setting $\xi = \bar{D} - i\bar{k}$ and $\zeta = \bar{f} - i\bar{\gamma}$, with

$$\bar{D} = \int_0^\infty d\tau\nu(\tau)\cos(\Delta\tau),\ \bar{\kappa} = \int_0^\infty d\tau\mu(\tau)\cos(\Delta\tau),$$
$$\bar{f} = \int_0^\infty d\tau\nu(\tau)\sin(\Delta\tau),\ \bar{\gamma} = \int_0^\infty d\tau\mu(\tau)\sin(\Delta\tau), \tag{17}$$

we can finally obtain

$$\frac{d}{dt}\rho_s(t) = -i[H_s, \rho_s(t)] - \bar{D}[\sigma_z, [\sigma_z, \rho_s(t)]] + i\bar{\kappa}[\sigma_z, \{\sigma_z, \rho_s(t)\}] + \bar{f}[\sigma_z, [\sigma_y, \rho_s(t)]] - i\bar{\gamma}[\sigma_z, \{\sigma_y, \rho_s(t)\}]. \tag{18}$$

This is the computable form of the Born-Markov master equation for the simplified spin-boson model. It means that if only the coefficients $\bar{D}, \bar{\kappa}, \bar{f}$, and $\bar{\gamma}$ are determined, the equation can be exactly numerical analyzed. These coefficients are evaluated in detail in the Appendix.

C. The computable form of the Born-Markov master equation for open multilevel quantum systems

This computable form Eq. (18) cannot be directly extended to the open multilevel quantum system, because the latter does not have the simple coupling form between the interest system and its bath. In this section, we propose a scheme to formulate the computable form of the Born-Markov master equation for the open multilevel quantum system. This is the core part of this paper. The general Hamiltonian of the open multilevel quantum system can be written as

$$H = H_s + \sum_k\left[\frac{\hat{p}_k^2}{2m_k} + \frac{1}{2}m_k\omega_k^2\hat{q}_k^2 + \sum_\alpha|\alpha\rangle\langle\alpha|c_{k\alpha}\hat{q}_k\right]. \tag{19}$$

where H_s is the system's Hamiltonian, $\hat{q}_k$ and $\hat{p}_k$ are the coordinate and momentum operators, m_k and ω_k the mass and angular frequency of the kth harmonic oscillator of the bath, respectively, and $c_{k\alpha}$ is the coupling coefficient between the αth diagonal mode of the system and the kth harmonic oscillator of the bath. $|\alpha\rangle$ is the αth basis state of the multilevel quantum system. This is actually the Frenkel-exciton Hamiltonian, which is widely used in the study of molecular aggregates in photosynthesis systems and other condensed systems [36–38]. In the study of the master equation, the

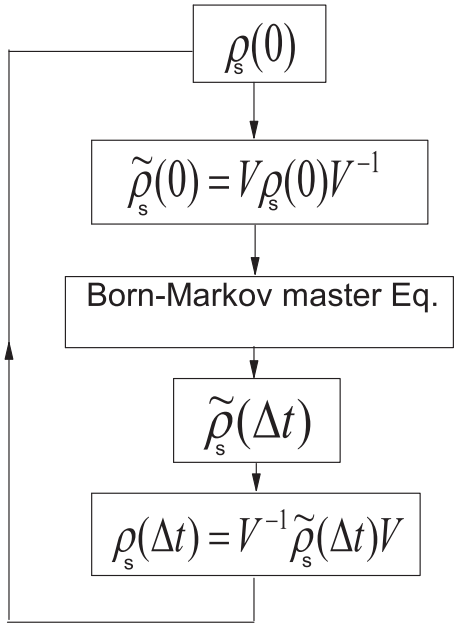

FIG. 1. The strategy sketch for studying the dynamics of nondiagonal Hamiltonian system by means of the Born-Markov master equation of the diagonal Hamiltonian.

Frenkel-exciton Hamiltonian is a general form of an open multilevel quantum system, while Eq. (2) can only be used to describe a two-level system. For convenience, we first derive the computable form of the Born-Markov master equation of an open multilevel quantum system with a diagonalized Hamiltonian $\widetilde{H}_s$. The evolution of reduced density matrix of a nondiagonal Hamiltonian H_s can be obtained through solving the computable form of the diagonal Hamiltonian of the open multilevel quantum system, which can be understood from Fig. 1. Therefore in the following we concentrate on deriving the computable form of the Born-Markov master equation of the diagonal multilevel Hamiltonian model. From Eq. (10) we have

$$\frac{d}{dt}\widetilde{\rho}_s(t) = -i[\widetilde{H}_s, \widetilde{\rho}_s(t)] - \sum_\alpha\{[\widetilde{S}_\alpha, \widetilde{B}_\alpha\widetilde{\rho}_s(t)] + [\widetilde{\rho}_s(t)\widetilde{C}_\alpha, \widetilde{S}_\alpha]\}. \tag{20}$$

Here, $\widetilde{x} = VxV^{-1}$, and V is the transformation matrix from H_s to $\widetilde{H}_s$, namely,

$$\widetilde{H}_s = VH_sV^{-1} = \mathrm{diag}(\lambda_\alpha), \tag{21}$$

where λ_α are the eigenvalues of the $\widetilde{H}_s$, $\widetilde{S}_\alpha = V|\alpha\rangle\langle\alpha|V^{-1}$, and

$$\widetilde{B}_\alpha = \int_0^\infty d\tau\sum_\beta W_{\alpha\beta}(\tau)\widetilde{S}_\beta(-\tau),$$
$$\widetilde{C}_\alpha = \int_0^\infty d\tau\sum_\beta W_{\beta\alpha}(-\tau)\widetilde{S}_\beta(-\tau). \tag{22}$$

When $\alpha \neq \beta$, $W_{\alpha\beta}(\tau) = 0$, and we then denote $W_\alpha(\tau) = W_{\alpha\alpha}(\tau)$. Thus we have

$$\widetilde{B}_\alpha = \int_0^\infty d\tau W_\alpha(\tau)\widetilde{S}_\alpha(-\tau),\ \widetilde{C}_\alpha = \int_0^\infty d\tau W_\alpha(-\tau)\widetilde{S}_\alpha(-\tau).$$

Setting

$$\widetilde{S}_\alpha = \begin{pmatrix} \widetilde{S}_\alpha^{(11)} & \widetilde{S}_\alpha^{(12)} & \widetilde{S}_\alpha^{(13)} & \dots \\ \widetilde{S}_\alpha^{(21)} & \widetilde{S}_\alpha^{(22)} & \widetilde{S}_\alpha^{(23)} & \dots \\ \widetilde{S}_\alpha^{(31)} & \widetilde{S}_\alpha^{(32)} & \widetilde{S}_\alpha^{(33)} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}, \tag{23}$$

we have

$$\begin{aligned}\widetilde{S}_\alpha(-\tau) &= \begin{pmatrix} \widetilde{S}_\alpha^{(11)} & \widetilde{S}_\alpha^{(12)} e^{i\omega_{12}\tau} & \widetilde{S}_\alpha^{(13)} e^{i\omega_{13}\tau} & \dots \\ \widetilde{S}_\alpha^{(21)} e^{i\omega_{21}\tau} & \widetilde{S}_\alpha^{(22)} & \widetilde{S}_\alpha^{(23)} e^{i\omega_{23}\tau} & \dots \\ \widetilde{S}_\alpha^{(31)} e^{i\omega_{31}\tau} & \widetilde{S}_\alpha^{(32)} e^{i\omega_{32}\tau} & \widetilde{S}_\alpha^{(33)} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \\ &\equiv \widetilde{S}_\alpha^{(0)}(-\tau) + \widetilde{S}_\alpha^{(12)}(-\tau) + \dots + \widetilde{S}_\alpha^{(mn)}(-\tau) + \cdots .\end{aligned} \tag{24}$$

Here and in the following, $n, m = 1, 2, \dots N$ (N is the dimension of the matrix H_s, and $m < n$), and

$$\begin{aligned}&\widetilde{S}_\alpha^{(0)}(\tau) = \mathrm{diag}(\widetilde{S}_\alpha^{(nn)}), \\ &\widetilde{S}_\alpha^{(12)}(\tau) = \widetilde{S}_{\alpha x}^{(12)} \cos(\omega_{12}\tau) + \widetilde{S}_{\alpha y}^{(12)} \sin(\omega_{12}\tau), \\ &\widetilde{S}_\alpha^{(13)}(\tau) = \widetilde{S}_{\alpha x}^{(13)} \cos(\omega_{13}\tau) + \widetilde{S}_{\alpha y}^{(13)} \sin(\omega_{13}\tau), \\ &\quad \dots \quad \dots \quad \dots \\ &\widetilde{S}_\alpha^{(mn)}(\tau) = \widetilde{S}_{\alpha x}^{(mn)} \cos(\omega_{mn}\tau) + \widetilde{S}_{\alpha y}^{(mn)} \sin(\omega_{mn}\tau), \\ &\quad \dots \quad \dots \quad \dots\end{aligned} \tag{25}$$

with $\omega_{mn} = \lambda_n - \lambda_m$, and $\widetilde{S}_{\alpha x}^{(mn)}$ is a matrix with elements $\widetilde{S}_{\alpha x}^{(mn)}(m, n) = \widetilde{S}_\alpha(m, n)$, $\widetilde{S}_{\alpha x}^{(mn)}(n, m) = \widetilde{S}_\alpha(n, m)$, and other elements are zero. Similarly, $\widetilde{S}_{\alpha y}^{(mn)}$ is a matrix with elements $\widetilde{S}_{\alpha y}^{(mn)}(m, n) = -i\widetilde{S}_\alpha(m, n)$, $\widetilde{S}_{\alpha y}^{(mn)}(n, m) = i\widetilde{S}_\alpha(n, m)$, $(m < n)$, and other elements are zero. Thus we have

$$\begin{aligned}\widetilde{B}_\alpha &= \int_0^\infty d\tau W_\alpha(\tau) \sum_\alpha [\widetilde{S}_\alpha^{(0)} + \widetilde{S}_\alpha^{(12)} + \cdots + \widetilde{S}_\alpha^{(mn)} + \cdots], \\ \widetilde{C}_\alpha &= \int_0^\infty d\tau W_\alpha^*(\tau) \sum_\alpha [\widetilde{S}_\alpha^{(0)} + \widetilde{S}_\alpha^{(12)} + \cdots + \widetilde{S}_\alpha^{(mn)} + \cdots].\end{aligned}$$

Setting $\widetilde{S}_{\alpha x}^{(00)} = \widetilde{S}_\alpha^{(0)}$, we have

$$\begin{aligned}\widetilde{B}_\alpha &= \int_0^\infty d\tau [\nu_\alpha(\tau) - i\mu_\alpha(\tau)] \\ &\quad \times \sum_{mn} \left[\widetilde{S}_{\alpha x}^{(mn)} \cos(\omega_{mn}\tau) - \widetilde{S}_{\alpha y}^{(mn)} \sin(\omega_{mn}\tau)\right], \\ \widetilde{C}_\alpha &= \int_0^\infty d\tau [\nu_\alpha(\tau) + i\mu_\alpha(\tau)] \\ &\quad \times \sum_{mn} \left[\widetilde{S}_{\alpha x}^{(mn)} \cos(\omega_{mn}\tau) - \widetilde{S}_{\alpha y}^{(mn)} \sin(\omega_{mn}\tau)\right], \\ &(m = n = 0; \quad m = 1, n = 2; \quad m = 1, n = 3; \dots).\end{aligned} \tag{26}$$

Setting

$$\begin{aligned}\xi_\alpha^{mn} &= \int_0^\infty d\tau [\nu_\alpha(\tau) - i\mu_\alpha(\tau)] \cos(\omega_{mn}\tau), \\ \zeta_\alpha^{mn} &= \int_0^\infty d\tau [\nu_\alpha(\tau) - i\mu_\alpha(\tau)] \sin(\omega_{mn}\tau),\end{aligned} \tag{27}$$

we have

$$\begin{aligned}\widetilde{B}_\alpha &= \sum_{mn} \xi_\alpha^{mn} \widetilde{S}_{\alpha x}^{(mn)} - \zeta_\alpha^{mn} \widetilde{S}_{\alpha y}^{(mn)}, \\ \widetilde{C}_\alpha &= \sum_{mn} \xi_\alpha^{mn*} \widetilde{S}_{\alpha x}^{(mn)} - \zeta_\alpha^{mn*} \widetilde{S}_{\alpha y}^{(mn)}.\end{aligned} \tag{28}$$

Thus it is clear that

$$\begin{aligned}&[\widetilde{S}_\alpha, \widetilde{B}_\alpha \widetilde{\rho}_s(t)] = \xi_\alpha^{mn} [\widetilde{S}_\alpha, \widetilde{S}_{\alpha x}^{(mn)} \widetilde{\rho}_s(t)] - \zeta_\alpha^{mn} [\widetilde{S}_\alpha, \widetilde{S}_{\alpha y}^{(mn)} \widetilde{\rho}_s(t)], \\ &[\widetilde{\rho}_s(t)\widetilde{C}_\alpha, \widetilde{S}_\alpha] = \xi_\alpha^{mn*} [\widetilde{\rho}_s(t) \widetilde{S}_{\alpha x}^{(mn)}, \widetilde{S}_\alpha] - \zeta_\alpha^{mn*} [\widetilde{\rho}_s(t) \widetilde{S}_{\alpha y}^{(mn)}, \widetilde{S}_\alpha].\end{aligned}$$

So we can obtain the computable form of the Born-Markov master equation with a diagonalized Hamiltonian as

$$\begin{aligned}\frac{d\widetilde{\rho}_s(t)}{dt} &= -i[\widetilde{H}_s, \widetilde{\rho}_s(t)] - \sum_\alpha \sum_{mn} \{\bar{D}_\alpha^{mn} [\widetilde{S}_\alpha, [\widetilde{S}_{\alpha x}^{(mn)}, \widetilde{\rho}_s(t)]] \\ &\quad - i\bar{\kappa}_\alpha^{mn} \left[\widetilde{S}_\alpha, \left\{\widetilde{S}_{\alpha x}^{(mn)}, \widetilde{\rho}_s(t)\right\}\right] - \bar{f}_\alpha^{mn} \left[\widetilde{S}_\alpha, \left[\widetilde{S}_{\alpha y}^{(mn)}, \widetilde{\rho}_s(t)\right]\right] \\ &\quad + i\bar{\gamma}_\alpha^{mn} \left[\widetilde{S}_\alpha, \left\{\widetilde{S}_{\alpha y}^{(mn)}, \widetilde{\rho}_s(t)\right\}\right]\},\end{aligned} \tag{29}$$

where $\xi_\alpha^{mn}, \zeta_\alpha^{mn}, \bar{D}_\alpha^{mn}, \bar{\kappa}_\alpha^{mn}, \bar{f}_\alpha^{mn}$, and $\bar{\gamma}_\alpha^{mn}$ are obtained from $\xi, \zeta, \bar{D}, \bar{\kappa}, \bar{f}$, and $\bar{\gamma}$ in Eq. (17) by replacing Δ with ω_{mn}, and using $J_\alpha(\omega)$. In the following calculations, we set $J_\alpha(\omega) = J(\omega)$, namely, we assume different modes of the system are embedded in the same baths. Finally, we can obtain $\rho_s(t) = V^{-1}\widetilde{\rho}_s(t)V$. Equation (29) is the core result of this paper, from which we can obtain the computable form of the Born-Markov master equation for any open multilevel quantum systems.

III. TWO EXAMPLES

In this section we shall investigate the dynamics of an open three-level quantum system model and FMO complex model by using our computable form of the Born-Markov master equation, Eq. (29) in the last section. The results will be compared with those obtained from the Redfield master equation [39] and the numerical path integral approach [15,27].

A. An open three-level quantum system model

In the open two-level quantum system Hamiltonian, the system operator of coupling to a bath can be simply set as σ_z, as Eq. (2), or other Pauli matrices. It is known that when the system has more than two energy levels, we cannot describe the total system in this simple form. However, no matter whether for two-level or more than two-level systems, the total Hamiltonian can be described with the form as in Eq. (19). In this sense, to study the dynamics of open quantum systems by using this method, the three-level model is general. In this section, we investigate an open three-level quantum system model. The system's Hamiltonian is set as

$$H_s = \begin{pmatrix} E_1 & V_{12} & 0 \\ V_{21} & E_2 & V_{23} \\ 0 & V_{32} & E_3 \end{pmatrix}, \tag{30}$$

where we set $E_1 = 0$, $E_2 = -2.67\ \mathrm{cm}^{-1}$, $E_3 = -3.67\ \mathrm{cm}^{-1}$, and $V_{12} = V_{21} = V_{23} = V_{32} = 0.67\ \mathrm{cm}^{-1}$, and the environment is described with the Drude spectral density function

$$J(\omega) = \frac{\eta\omega\Omega}{\omega^2 + \Omega^2}. \tag{31}$$

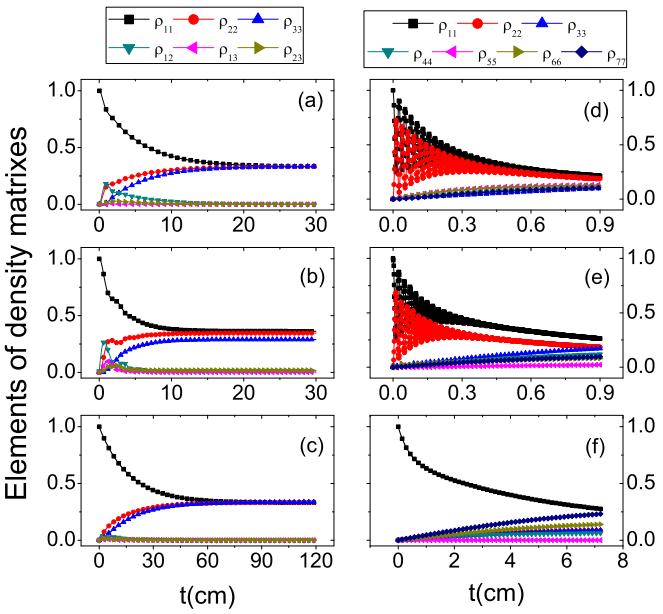

FIG. 2. The evolution of elements of the reduced density matrices for an open three-level quantum system model [left three panels (a), (b), (c)] and the FMO model [right three panels (d), (e), (f)]. The dynamics is respectively described by numerical path integral (a), (d), our form of the Born-Markov master equation, Eq. (29) (b), (e), and the Redfield form of master equation (c), (f). The initial states of the systems are set as $\rho(0) = |1\rangle\langle 1|$, the environmental spectral density functions are set as the Lorentz-Drude form, with $\eta = 0.125$, $\Omega = 100$ cm^{-1} for the three-level model, and $\eta = 12.5$, $\Omega = 1000$ cm^{-1} for the FMO model. The temperature is set as $T = 300$ K. Other model parameters can refer to text.

Here we set $\eta = 0.125$, $\Omega = 100.0$ cm^{-1}, and suppose the environmental temperature is 300 K. Setting the initial state as $\rho(0) = |1\rangle\langle 1|$, we solve the reduced dynamics of the open three-level system by using our method, the Redfield equation, and the QUAPI. The evolution of the elements of the reduced density matrix is plotted in Figs. 2(a)– 2(c).

The numerical path integral method [15,27] is considered as the exact numerical method because the memory effects of the environment within $\Delta k_{\max}\Delta t$ are included, where Δt is the time step in the calculation program. This means that the strength of nonlocal interaction arising from dissipative environments is omitted beyond a certain value of $\Delta k_{\max}$. Here we set $\Delta k_{\max} = 3$. It can be seen from Fig. 2 that the dynamics predicted from the QUAPI and our method are similar, but the Redfield equation predicts a much longer relaxation time and decoherence time than the other two approaches. This distortion must result from the fact that some degeneracy terms which do not meet the criteria of secular approximation have been discarded in the derivations of the Redfield equation [39].

B. FMO model

In this section, we investigate the dynamics of FMO [32]. The FMO is a photosynthetic pigment-protein complex model whose characteristics of energy transfer and optical spectra have been extensively investigated by using various dynamical methods [40–47]. In the model, the seven pigments of one FMO subunit were independently treated as seven two-level systems with electronically coupled excited states. The effects of vibrations and protein environment were taken into account by the couplings of the electronic degrees of freedom to the phonon bath. The elements of the Hamiltonian are listed in the Table I. Here, the diagonal elements are the values of the site energies ϵ_m (cm^{-1}), and the off-diagonal elements denote the coupling strengths Δ_{mn} (cm^{-1}).

TABLE I. The values of the site energies ϵ_m (cm^{-1}), the coupling strengths Δ_{mn}(cm^{-1}) of the FMO.

	BChl1	BChl2	BChl3	BChl4	BChl5	BChl6	BChl7
BChl1	12400	–106	8	–5	6	–8	–4
BChl2	–106	12540	28	6	2	13	1
BChl3	8	28	12120	–62	–1	–9	17
BChl4	–5	6	–62	12295	–70	–19	–57
BChl5	6	2	–1	–70	12440	40	–2
BChl6	–8	13	–9	–19	40	12480	32
BChl7	–4	1	17	–57	–2	32	12380

The environment is also described with the Drude spectral density function, and we set $\eta = 12.5$, $\Omega = 1000.0$ cm^{-1}, and suppose the environmental temperature is 300 K. The evolution of the elements of reduced density matrix for the FMO model obtained from our method, the Redfield equation, and the QUAPI is plotted in Figs. 2(d)– 2(f). Here we assume that the system is initially populated in the Bchl1. The results obtained from the numerical path integral and our method show that partial populations quickly move to site 2 (Bchl2) from site 1 (Bchl1) in the beginning of the evolution, then they evolve with strong oscillations, and they finally decay to their equilibrium states. But some of these characteristics have not been shown in the results obtained from the Redfield equation. The evolution of the populations in sites of the FMO obtained from our method is similar to that obtained by other groups [48] and by other methods, such as density-functional theory and time-dependent density-functional theory [47]. This means that our computable form of the Born-Markov master equation is reliable for investigating the dynamics of the open multilevel quantum systems.

We see from Fig. 2(f) that the relaxation time predicted from the Redfield equation is much longer than that from the QUAPI and our form of the Born-Markov master equation. The reason is similar to the three-level model discussed in last section, namely, some relaxation terms which do not satisfy the secular approximation are omitted in the Redfield equation. Thus when the quantum system under investigation is quite complicated or when some experimental results, such as optical spectra, are investigated, application of the Redfield form of the Born-Markov master equation may lose some information because of the use of the secular approximation.

IV. DISCUSSION AND CONCLUSIONS

In this paper we introduce a computable form of the Born-Markov master equation without the aid of secular approximation. It is shown that the equation can be used to investigate the dynamics of open multilevel quantum systems and some

dynamical characteristics lost in the Redfield equation are well kept. By using the computable form, we investigate a simple open three-level quantum system model and the FMO complex model, and the results have been compared with the ones obtained from the Redfield equation and QUAPI. The different results imply that the secular approximation imposed in the Redfield and Lindblad forms of the master equations actually weakens the decay of the state and distorts the reduced dynamics of the open quantum system. Compared with the Redfield form, our computable form of the master equation agrees better with the QUAPI method. It retains some effects that are lost due to use of the secular approximation in the Redfield and Lindblad forms of the Born-Markov master equation.

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APPENDIX: ON THE FOUR INTEGRALS IN Eq. (17)

(1) On the coefficient $\bar{D}$, and $\bar{\gamma}$. According to the double Fourier transform [35], we have

$$\bar{D} = \int_0^\infty d\omega \int_0^\infty d\tau J(\omega) \coth\left(\frac{\omega}{2k_BT}\right)\cos(\omega\tau)\cos\Delta\tau = \frac{\pi}{2}J(\Delta)\coth\left(\frac{\Delta}{2k_BT}\right) \tag{A1}$$

and

$$\bar{\gamma} = \int_0^\infty d\omega \int_0^\infty d\tau J(\omega)\sin(\omega\tau)\sin\Delta\tau = \frac{\pi}{2}J(\Delta). \tag{A2}$$

(2) On the coefficient $\bar{\kappa}$. We set the environmental spectral density function in Lorentz-Drude form, as in Eq. (31). It is an odd function of ω, so we have

$$\bar{\kappa} = \frac{1}{2}\int_0^\infty d\tau \int_{-\infty}^\infty d\omega J(\omega)\sin(\omega\tau)\cos(\Delta\tau). \tag{A3}$$

Referring to Fig. 3, we consider a contour integral in a complex plane, namely,

$$I_1 = \oint F_1(z)dz, \tag{A4}$$

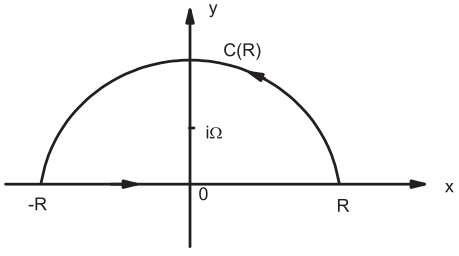

FIG. 3. The computing strategy of contour integral Eq. (A4).

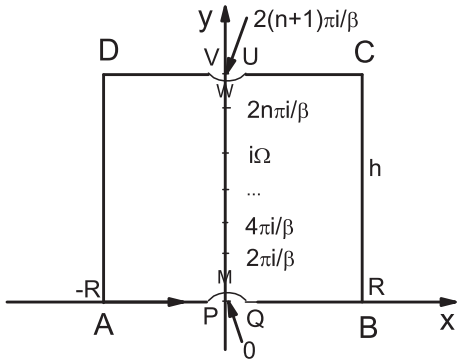

FIG. 4. The computing strategy of contour integral Eq. (A10).

where $z = x + iy$, and

$$F_1(z) = \frac{J(z)e^{i\tau z}}{2}. \tag{A5}$$

$F_1(z)$ has two simple poles $z = \Omega i$ and $z = -\Omega i$, and their residues are [49]

$$\underset{z=\pm i\Omega}{Res}\, F_1(z) = \frac{z\eta\Omega e^{i\tau z}}{2(z^2+\Omega^2)'}|_{z=\pm\Omega i} = \frac{\eta\Omega e^{\mp\tau\Omega}}{4}. \tag{A6}$$

According to Jordan's lemma we have

$$\lim_{R\to\infty}\int_{c(R)} F_1(z)dz = 0,$$

and according to the residue theorem we have

$$I_1 = \int_{-\infty}^\infty \frac{\eta\Omega x e^{i\tau x}}{2(x^2+\Omega^2)}dx = \frac{i\eta\Omega\pi e^{\mp\tau\Omega}}{2}. \tag{A7}$$

Replacing x with ω, we have

$$\bar{\kappa} = \int_0^\infty \mathrm{Im}(I_1)\cos(\Delta\tau)d\tau = \frac{\eta\Omega\pi}{4}\int_0^\infty e^{-\Omega\tau}\cos(\Delta\tau)d\tau = \frac{\eta\pi\Omega^2}{2(\Omega^2+\Delta^2)}, \tag{A8}$$

where $\int_0^\infty e^{-a\tau}\cos(b\tau)d\tau = a/(a^2+b^2)$ is used.

(3) On the coefficient $\bar{f}$. In Ref. [35], it is supposed that when $\Gamma \gg \Omega$ and $k_BT \gg \Omega$, the coefficient $\bar{f}$ can be explicitly evaluated to give the result $\bar{f} = 2\gamma_0 k_BT/\Gamma$. Here, the constant γ_0 describes the effective coupling strength between the system and its environment, and Γ is the cut-off frequency of the bath. It is clear that this is a result of high-temperature approximation. In the following, we evaluate the constant of $\bar{f}$ by using another method. In this method we do not limit the range of the corresponding parameters. The integral can be written as

$$\bar{f} = \frac{1}{2}\int_0^\infty d\tau \int_{-\infty}^\infty d\omega J(\omega)\coth\left(\frac{\beta\omega}{2}\right)\cos(\omega\tau)\sin(\Delta\tau), \tag{A9}$$

where $\beta = 1/(k_BT)$. Referring to Fig. 4, we consider a contour integral in a complex plane as

$$I_2 = \oint F_2(z)dz, \tag{A10}$$

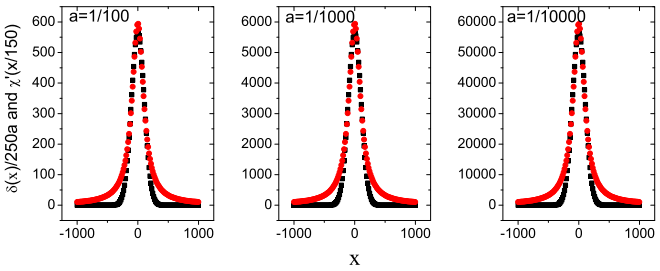

FIG. 5. $\frac{1}{250a}\chi'(x)$ (red circle dots) and $\delta(\frac{x}{150})$ (black square points).

where

$$F_2(z) = \frac{1}{2}J(z)\coth\left(\frac{\beta z}{2}\right)\exp(iz\tau). \tag{A11}$$

It is clear that $F_2(z)$ has the following simple poles: $z = i\Omega$, $-i\Omega$ and $z = 0, \pm\frac{2\pi i}{\beta}, \pm\frac{4\pi i}{\beta}, \pm\frac{6\pi i}{\beta}, \cdots$. The contour integral can be written as

$$\oint F_2(z)dz = \left[\int_{AP} + \int_{P\widehat{M}Q} + \int_{QB} + \int_{BC} + \int_{CU} + \int_{U\widehat{W}V} + \int_{VD} + \int_{DA}\right]F_2(z)dz. \tag{A12}$$

At first we investigate the integrals $\int_{P\widehat{M}Q}F_2(z)dz$ and $\int_{U\widehat{W}V}F_2(z)dz$. According to Jordan's lemma we have $\int_{P\widehat{M}Q}F_2(z)dz = 0$ and $\int_{U\widehat{W}V}F_2(z)dz = 0$.

Second, we consider the integrals $[\int_{AP} + \int_{QB}]F_2(z)dz$. In the complex plane, we have

$$\left[\int_{AP} + \int_{QB}\right]F_2(z)dz = \int_{-R}^{R} dxJ(x)\coth\left(\frac{\beta x}{2}\right)\exp(ix\tau).$$

Third, we investigate the integrals $[\int_{CU} + \int_{VD}]F_2(z)dz$. Fixing $h = 2(n+1)\pi/\beta$ (see Fig. 4) and setting $J(ih + x)e^{-h\tau} \simeq \chi(x)J(x)$, we have

$$\left[\int_{CU} + \int_{VD}\right]F_2(z)dz = -\int_{-R}^{R} dx\chi(x)J(x)\coth\left(\frac{\beta x}{2}\right)e^{ix\tau},$$

where $\chi(x) = \chi'(x) + i\chi''(x)$, and

$$\chi'(x) = \mathrm{Re}\left(\frac{e^{-h\tau}J(ih+x)}{J(x)}\right),$$

$$\chi''(x) = \mathrm{Im}\left(\frac{e^{-h\tau}J(ih+x)}{J(x)}\right) \to 0.$$

Using the Dirac δ function,

$$\delta(x) = \lim_{a\to 0^+}\frac{1}{a\sqrt{\pi}}e^{-x^2/a^2}, \tag{A13}$$

we can numerically find out

$$\frac{1}{250a}\chi'(x) \simeq \delta\left(\frac{x}{150}\right), \tag{A14}$$

which can be seen from Fig. 5. Thus we have

$$\chi'(x) \simeq 150 \times 250\delta(x). \tag{A15}$$

Within the dynamical timescale of such quantum systems, $\tau < 1$ ps, then $e^{-h\tau} \to 1$. Therefore, by using L'Hôpital's rule, we have

$$\left[\int_{CU} + \int_{VD}\right]F_2(z)dz \simeq \frac{7500\eta}{\beta} \to 0. \tag{A16}$$

Finally, we investigate the integrals $\int_{BC}F_2(z)dz$ and $\int_{DA}F_2(z)dz$. From Fig. 4 we have

$$\int_{BC}F_2(z)dz = \int_B^C dyf_1(y), \quad \int_{DA}F_2(z)dz = \int_D^A dyf_2(y),$$

where

$$f_{1,2}(y) = J(iy \pm R)\coth\left(\frac{\beta(iy \pm R)}{2}\right)\exp[(iy \pm R)i\tau].$$

It is clear that $\lim_{R\to\infty}|f_{1,2}(y)| = 0$, so we have

$$I_2 = \int_{-R}^{R} dxJ(x)\coth\left(\frac{\beta x}{2}\right)\exp(ix\tau). \tag{A17}$$

In the following we calculate the residues in the contour integral shown in Fig. 4.

If $\Omega < 2\pi/\beta$, namely, $T > \frac{\Omega}{2\pi k_B}$, we can choose a circle of integral, one in which there is only one pole, $z_0 = i\Omega$. So we have

$$\operatorname*{Res}_{z=i\Omega}F_2(z) = (z - i\Omega)\frac{1}{2}J(z)\coth\left(\frac{\beta z}{2}\right)e^{iz\tau}|_{z=i\Omega} = \frac{\eta\Omega}{4}\mathrm{ctan}\left(\frac{\beta\Omega}{2}\right)e^{-\Omega\tau}, \tag{A18}$$

$$I_2 = 2\pi i\operatorname*{Res}_{z=i\Omega}F_2(z) = \frac{i\pi\eta\Omega}{2}\mathrm{ctan}\left(\frac{\beta\Omega}{2}\right)e^{-\Omega\tau},$$

where the integral formula $\int_0^\infty e^{-a\tau}\sin(b\tau)d\tau = b/(b^2 + a^2)$ is used. So, according to the residue theorem, we have

$$\bar{f} = \int_0^\infty \mathrm{Re}(I_2)\sin(\Delta\tau)d\tau = 0.$$

If $2\pi/\beta < \Omega < 4\pi/\beta$, namely, $\frac{\Omega}{4\pi k_B} < T < \frac{\Omega}{2\pi k_B}$, we can choose a circle of integral, one in which there are two simple poles, $z_0 = i\Omega$ and $z_1 = 2\pi i/\beta$. We have

$$\operatorname*{Res}_{z=2\pi i/\beta}F_2(z) = J(z)\frac{(e^{\beta z}+1)e^{iz\tau}}{2(e^{\beta z}-1)'}|_{z=\frac{2\pi i}{\beta}} = \frac{i\eta\Omega\bar{\omega}e^{-\bar{\omega}\tau}}{\beta(\Omega^2 - \bar{\omega}^2)}$$

and

$$I_2 = 2\pi i\operatorname*{Res}_{z=2\pi i/\beta}F_2(z) = \frac{-2\pi\eta\Omega\bar{\omega}e^{-\bar{\omega}\tau}}{\beta(\Omega^2 - \bar{\omega}^2)}.$$

So we have

$$\bar{f} = \int_0^\infty \mathrm{Re}(I_2)\sin(\Delta\tau)d\tau = \frac{2\pi\eta\Omega\bar{\omega}\Delta}{(\bar{\omega}^2 - \Omega^2)(\bar{\omega}^2 + \Delta^2)}, \tag{A19}$$

where $\bar{\omega} = 2\pi/\beta$.

If $2n\pi/\beta < \Omega < 2(n+1)\pi/\beta$, namely, $\frac{\Omega}{2(n+1)k_B} < T < \frac{\Omega}{2nk_B}$, there are simple poles $z_0 = i\Omega$, and $z_1 = 2\pi i/\beta, z_2 = 4\pi i/\beta, \ldots, z_n = 2n\pi i/\beta$ in the circle of integral. Similarly, we have

$$\bar{f} = \sum_n \frac{2\pi\eta\Omega\bar{\omega}_n\Delta}{\left(\bar{\omega}_n^2 - \Omega^2\right)\left(\bar{\omega}_n^2 + \Delta^2\right)}, \tag{A20}$$

where $\bar{\omega}_n = 2n\pi/\beta$, and n is the number of poles except for $i\Omega$ in the contour integral, shown in Fig. 4.

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