

Excitation energy transfer with initial system-bath correlations for coherent initial conditions in a toy donor-acceptor model

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A theory of coherent resonant energy transfer with initial system-bath correlations [Qin *et al.*, *Phys. Rev. A* **99**, 032111 (2019)] is extended for a coherent initial system condition, which is a linear superposition of donor and acceptor excitations, and is more general and actual in many respects. The nonequilibrium bath state, containing initial system-bath correlations, is expanded in powers of coupling strength within the polaron formalism of second-order time-convolutionless quantum master equation. Detailed expressions for both homogeneous and inhomogeneous terms are derived and calculations are performed under the assumption of super-Ohmic spectral densities where the case of common bath modes is also included. Numerical results indicate that, for certain initial system conditions, the nonequilibrium due to the initial system-bath correlations brings about larger amplitude of population oscillation. And the initial system condition is of crucial importance in determining whether the initial system-bath correlations would play a significant role in the transfer dynamics. We identify a sensitive window in which the transfer dynamics is especially vulnerable to the bath such that there exists a greatly obvious difference between the dynamics with and without initial correlations. Besides, the system-bath coupling strength, the evolution time, and the nature of common bath modes are also shown to contribute to these effects. Rate equations based on Förster-Dexter energy transfer theory are derived for comparison.

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I. INTRODUCTION

In natural photosynthesis, light energy is captured and transferred to the reaction center with high efficiency of nearly 100%. This feature inspires widespread interest in revealing the microscopic mechanism of excitation energy transfer (EET) in light-harvesting complexes, which is a vital step for photosynthetic organism [1]. Recently, growing experimental and theoretical explorations indicate that quantum coherence may have a positive effect on the efficient energy transfer despite substantial environment of the protein scaffold and solvent [2–15]. An appropriate and reliable theory that can provide a precise description of excitation energy transfer dynamics is thus in urgent need.

With the development of experimental techniques, the timescales of various reaction processes can now be determined. It is recognized that clear separation of these timescales is really not easy. Conventional approaches of incoherent quantum transfer [16–18] and weak system-bath coupling approximation [19,20] become inaccurate since it is hard to define a perturbation term. This leads to alternative approaches to overcome this difficulty, including several nonperturbative techniques [21–28] as well as sophisticated stochastic description of system-plus-bath dynamics [29]. Although these methods can give exact dynamics numerically, they suffer from being computationally demanding with in-

creasing system size. In this respect, a modified perturbative method named a polaron-transformed second-order master equation has been developed to describe the dynamics in the intermediate or strong coupling regime [30–47]. In terms of a combined electronic-bath basis, this approach assumes the electronic excitation moves collectively with its surrounding bath deformation rather than treats them separately. The electronic system-plus-phonon bath Hamiltonian is transformed into the so-called polaron frame in which electronic couplings are renormalized and fluctuate as a result of interaction with the bath [30–47]. Although based on a perturbative treatment, it can give reliable results to describe the excitation energy transfer dynamics beyond weak system-bath coupling limit, allowing for a consistent exploration of the intermediate regime where many multichromophoric systems operate, serving as a bridge between the Förster-Dexter and Redfield situations, provided that the high-frequency bath modes dominate and the energy scale related to the fluctuations of the electronic coupling in the polaron frame is the smallest in the system [32,34]. Meanwhile, it is quite computationally economic compared with the numerically exact nonperturbative techniques [21–29] and therefore has advantages for studying large systems. In this work, we adopt the polaron quantum master equation (QME) to study the excitation energy transfer dynamics.

As far as we know, one common assumption in describing such open systems as light-harvesting complexes with a master equation amenable to analytic or numerical solutions is referred to as “factorized initial condition,” i.e., the system and its surrounding environment (or bath) are completely

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uncorrelated at the initial moment of the evolution process. This assumption is justified under the conditions of weak system-bath coupling and Markovian bath [48–50]. The weak system-bath coupling condition implies that the system has a negligible impact on the bath statistics and the initial system-bath state would not play a significant role in system dynamics. And if the bath is Markovian, any influence of initial system-bath correlation is quickly lost. It is not the case, nevertheless, for natural light-harvesting complexes. The surrounding solvent and protein scaffold, especially the quantized vibration modes, serve as the environment (bath), and couple strongly to the electronic excitations within photosynthetic chromophores like a “memory” for the system [45, 51–57]. By the way, a separable initial state generally adopted in most previous works corresponds to sudden creation of an excited state in the system originally in the ground electronic state with the bath in thermal equilibrium, by an impulsive excitation at time $t = 0$. This is a good approximation for the case of excitation pulse less than 100 fs, ensured by the Franck-Condon principle. However, for natural photosynthesis, most excitation transfer in light-harvesting complexes is initialized from an excited molecule, rather than direct absorption of a photon [2,3]. In this case, the validity of the assumption of initial uncorrelated state should be under close scrutiny [58–65], and the role of initial system-bath correlations should be reconsidered seriously to assess its influence on the excitation energy transfer dynamics.

In a recent work [66], which will be designated as Paper I hereafter, a theory of coherent resonant energy transfer with initial system-bath correlations was developed. This theory combines the weak coupling expansion of the bath state with the polaron transformation, thus is valid not only in weak system-bath coupling regime. Model calculations in Paper I indicated that the nonequilibrium due to the initial system-bath correlations and the polaron transformation can accelerate or slow down the dynamics depending on different energy situations. Moreover, it was shown that initial correlations cause larger amplitude of population oscillation, which may help to interpret long-lasting quantum phenomenon under natural conditions. In this work, the theory in Paper I is extended for a coherent initial system state that means linear superposition of donor and acceptor excitations since a coherent initial system condition is more general and actual for excitation energy transfer in light-harvesting complexes [32,67].

The remainder of the paper is organized as follows: In Sec. II, a donor-acceptor model for this paper is introduced. Then, the formalism of polaron master equation is sketched, including the Hamiltonian, initial system-plus-bath condition, homogeneous and inhomogeneous terms of the polaron master equation, and the spectral densities adopted for the model. In Sec. III, we focus on the time evolution of the donor population to inspect the influence of nonequilibrium preparation due to the initial system-bath correlations under two different energetic situations and a variety of initial system conditions. The effects of common bath modes are examined in order to assess how the nature of common bath modes impacts the transfer dynamics. Rate equations based on Förster-Dexter energy transfer theory are derived as well for comparison. At last, Sec. IV is devoted to concluding remarks. More details of expressions of inhomogeneous terms and necessary

transformation operations in the polaron master equation are presented in the Appendices.

II. THEORY

Motivated by the possible effects of initial system-bath correlations on EET dynamics, we focus on the case of single excitation in a simple donor-acceptor (D - A) pair [31–34] throughout the paper. First, we introduce the theoretical framework.

A. Hamiltonian and initial condition

Serving as a toy model to investigate the EET dynamics subjected to surrounding bath modes, the model of donor-acceptor pair to be studied in this paper is basically consistent with that in Paper I, except that a more general initial system condition is employed. It consists of single chromophoric energy donor (D) and acceptor (A) together with a phonon bath linearly coupled to the individual chromophore (site). The phonon bath can be regarded as an infinite number of degrees of freedom each described by a quantum harmonic oscillator. Then, the excitation energy transfer between the donor and acceptor is governed by a Frenkel exciton model Hamiltonian expressed as

$$H = H_s^p + H_s^c + H_b + H_{sb}. \quad (1)$$

The first term in Eq. (1) is

$$H_s^p = \sum_{i=D,A} E_i |i\rangle \langle i|, \quad (2)$$

denoting population of the system Hamiltonian. $|D\rangle$ ($|A\rangle$) is designated as the state where only D (A) is excited. E_i ($i = D, A$) is the corresponding energy with respect to $|g\rangle$ where both sites are in the ground electronic state. The second term in Eq. (1) is given by

$$H_s^c = J(|D\rangle \langle A| + |A\rangle \langle D|), \quad (3)$$

with J the resonant electronic coupling between $|D\rangle$ and $|A\rangle$. The third term in Eq. (1) represents the bath Hamiltonian

$$H_b = \sum_k \omega_k b_k^\dagger b_k, \quad (4)$$

where b_k^\dagger (b_k) is the creation (annihilation) operator and ω_k the frequency of the k th phonon mode of surrounding bath. The last term in Eq. (1),

$$H_{sb} = \sum_{i=D,A} \sum_k g_{ki} (b_k^\dagger + b_k) |i\rangle \langle i|, \quad (5)$$

describes the system-bath interaction Hamiltonian with g_{ki} the coupling strength of site i ($i = D, A$) to the k th mode of bath.

Then, the quantum Liouville equation corresponding to the total Hamiltonian (1) is as follows:

$$\frac{d\rho(t)}{dt} = -i\mathcal{L}\rho(t) = -i(\mathcal{L}_s^p + \mathcal{L}_s^c + \mathcal{L}_b + \mathcal{L}_{sb})\rho(t), \quad (6)$$

where the total Liouville operator \mathcal{L} is defined as $\mathcal{L}(\cdot) = [H, (\cdot)]$ and the spontaneous decay to the ground electronic state $|g\rangle$ is neglected. Similarly, \mathcal{L}_s^p , \mathcal{L}_s^c , \mathcal{L}_b , and \mathcal{L}_{sb} are

Liouville operators corresponding to the Hamiltonians (2)–(5), respectively. $\rho(t)$ is the total density operator for the combined system plus bath at time t . Taking trace of $\rho(t)$ over the bath degrees of freedom, we obtain the reduced density operator for the system written as

$$\sigma(t) = \text{Tr}_b\{\rho(t)\}. \quad (7)$$

It is generally assumed that the system is originally prepared in the ground electronic state, while the bath in the canonical equilibrium [2–15]. The two parts as a whole are in thermal equilibrium. Then, a single excitation is suddenly created by a pulse laser with time duration less than that of bath relaxation as well as the ensuing energy transfer dynamics. Therefore, the bath remains unchanged due to the timescale separation, and the initial condition can be approximated as an uncorrelated state with the following form:

$$\rho(0) = \sigma(0) \otimes \rho_b, \quad (8)$$

in which $\rho_b = e^{-\beta H_b}/Z_b$ is the canonical equilibrium state with $\beta = 1/k_b T$, $Z_b = \text{Tr}_b\{e^{-\beta H_b}\}$. Although it neglects the initial correlations between the single excitation system and the bath, many works adopt this initial condition of direct product form since it is a good approximation for a rapid photoexcitation from the ground state, which is ensured by the Franck-Condon principle. In addition, the short laser pulse is widely employed to excite the pigment molecule in the experiments with light-harvesting complexes [6–8], which also makes this approximation well grounded.

Nevertheless, we can go further in order to give more reliable elucidation of excitation energy transfer dynamics in actual light-harvesting complexes, such as FMO and LH2. It should be noted that most pigment molecules accept excitation energy from the adjacent excited molecules, rather than via absorbing photons directly [2,3]. Such intermolecular excitation process of pigment molecules from ground electronic state essentially equals to the excitation energy transfer between molecules, and spans the same characteristic timescale, which is in turn longer than that of bath relaxation. When the excitation is being transferred into the D - A system we are interested in, it begins to interact with surrounding bath [6–8]. Consequently, if we set a particular instant, at which the excitation energy is totally absorbed into the D - A system, as the initial moment for the excitation energy transfer evolution we focus on, the initial system-bath correlations have been established and then can not be neglected. One may safely assume that the bath modes have already relaxed and become equilibrated with the excited donor-acceptor system before the energy transfer takes place. Consideration of the initial system-bath correlations thus can be justified for this case [58–65]. In addition, for the case of actual photosynthetic energy transfer process, system-bath coupling strength can be comparable to the electronic couplings among pigment molecules, and the surrounding solvent and protein scaffold acts as a “memory” for the system [45,51–57], therefore, from the point of view of quantum open system theory, the initial system-bath correlations should be taken into account in this case. In light of these discussions, it is clearly worthwhile to investigate how EET dynamics is modified by initial system-bath correlations. We assume that at time $t = 0$, the incoming excitation energy from the antenna creates a superposition of

excited D and A :

$$|I\rangle = I_D|D\rangle + I_A|A\rangle, \quad (9)$$

where I_D and I_A are arbitrary complex numbers satisfying $|I_D|^2 + |I_A|^2 = 1$. And the initial condition for this situation is assumed to be of the following form:

$$\rho(0) = \sigma(0) \otimes \frac{\langle I|e^{-\beta H}|I\rangle}{Z}, \quad (10)$$

where $\sigma(0) = |I\rangle\langle I|$ is the initial state for the system. Z is the partition function such that $\text{Tr}_{s,b}\{\rho(0)\} = 1$. One may imagine other different forms by considering structural characteristics of specific pigment molecules. Physically, Eq. (10) can be interpreted as follows: at time $t < 0$, the single excitation system is in equilibrium with the bath at an inverse temperature $1/\beta$. The bath state is modified due to the finite system-bath interaction and the correlations between the system and the bath have been established. Then, one makes a measurement operating only on the system at $t = 0$, such that the system is prepared in the pure state $\sigma(0) = |I\rangle\langle I|$. Based on general principles of quantum measurement theory, the combined system plus bath after the measurement can be described by Eq. (10). The bath now is prepared in a state of $\rho_b(0) = \langle I|e^{-\beta H}|I\rangle/Z$, which contains the system-bath correlations that have been established beforehand. From Eq. (10) we see that, due to the system-bath interaction, the bath state is no longer a thermal equilibrium state ρ_b since in Eq. (8) ρ_b keeps fixed for any initial states of the system $\sigma(0)$, which means the system and the bath are initially uncorrelated. Thus, it is generally recognized that Eq. (10) contains initial system-bath correlations though it resembles Eq. (8) in form. It is not equal to the reduced state of the total equilibrium state $\text{Tr}_s\{e^{-\beta H}\}/Z$ either. As a result, after the system preparation, the bath evolves under the action of the total Hamiltonian H and finally approaches the total system-bath equilibrium state. Inaccurate and even some kind of artificial manipulation as this form of initial condition might be for actual photosynthetic energy transfer processes, it contains initial system-bath correlations that are often neglected in previous works.

By the way, a straightforward extension of the formalism presented here may be multistate generalization. In this case, Eq. (1) represents the model Hamiltonian of N sites coupling to surrounding phonon bath. The initial system state (9) is then generalized to a superposition of these N excited electronic states. A minimal model for multistate system, for example, consists of donor-bridge-acceptor (D - B - A) states coupled to a phonon bath. Clarification of how such initial system-bath correlations manifest may help to understand the mechanism underlying the remarkably efficient EET across entire light-harvesting complexes of 100-nm length scale, which has attracted a rapidly growing interest from different scientific communities by various experimental and theoretical approaches [4–30]. Further works will be committed to this aspect.

It should be made clear that the formalism of polaron transformation does not refer to actual physical formation of polaron. Rather, it is just a unitary transformation used to identify a small term of Hamiltonian beyond weak system-bath coupling regime such that this term can serve as perturbation in deriving a QME even in intermediate and strong

system-bath coupling regime. It was first used to treat charge transfer in organic molecular crystals and then developed to consider population dynamics in EET [37]. It does not separate the exciton and bath, but assumes that the electronic excitation moves collectively with its surrounding bath deformation. With this in mind, we move into the polaron frame following previous works [30–47] through the application of the polaron transformation generated by $G = \sum_{i=D,A} \sum_k \frac{g_{ki}}{\omega_k} (b_k^\dagger - b_k) |i\rangle \langle i|$ to Eq. (6). This results in a quantum Liouville equation for the total density operator $\tilde{\rho}(t)$ in the polaron frame. The next step is to go into the interaction picture and derive a time-convolutionless (TCL) quantum master equation for $\tilde{\sigma}_I(t) = \text{Tr}_b[\tilde{\rho}_I(t)]$ in the following form:

$$\frac{d}{dt} \tilde{\sigma}_I(t) = \text{Tr}_b[\mathcal{K}(t)\tilde{\rho}_I(t)] + \text{Tr}_b[\mathcal{I}(t)\tilde{\rho}_I(0)], \quad (11)$$

where $\tilde{\rho}_I(t)$ denotes the total density operator in the interaction picture. This procedure is the same with Paper I and we sketch the derivations in Appendix A.

B. Homogeneous terms

The first term on the right-hand side of the TCL master equation (11) gives the homogeneous contribution

$$\text{Tr}_b[\mathcal{K}(t)\tilde{\rho}_I(t)] = -\alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\tilde{\sigma}_I(\tau) \otimes \rho_b\}, \quad (12)$$

which gives rise to the standard form of second-order terms in the master equation. If we insert the interaction Hamiltonian (A13) into (11) and use the cyclic invariance of the bath operators within $\text{Tr}_b[\dots]$, the bath correlation functions can be decoupled from the commutators of system operators. These derivations lead to the explicit expressions for the homogeneous term in (11) (here we set $\alpha = 1$) as follows:

$$\begin{aligned} & \text{Tr}_b[\mathcal{K}(t)\tilde{\rho}_I(t)] \\ &= -J^2 e^{S(0,0)} \int_0^t d\tau \{(e^{S(0,\tau-t)} - 1)[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_I(\tau)] \\ &+ (e^{-S(0,\tau-t)} - 1)[\mathcal{T}^\dagger(t), \mathcal{T}(\tau)\tilde{\sigma}_I(\tau)] \\ &+ (e^{-S(0,\tau-t)} - 1)[\mathcal{T}(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(\tau)] \\ &+ (e^{S(0,\tau-t)} - 1)[\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(\tau)]\} + \text{H.c.}, \quad (13) \end{aligned}$$

in which

$$\begin{aligned} S(\lambda, t) &= -\frac{1}{2} \sum_k \left(\frac{\delta g_k}{\omega_k} \right)^2 \left[\coth\left(\frac{\beta\omega_k}{2}\right) (e^{\lambda\omega_k - i\omega_k t} + e^{-\lambda\omega_k + i\omega_k t}) \right. \\ &\quad \left. - (e^{\lambda\omega_k - i\omega_k t} - e^{-\lambda\omega_k + i\omega_k t}) \right]. \quad (14) \end{aligned}$$

The same convention will be used hereafter. Besides, ‘‘H.c.’’ denotes the Hermitian conjugates of all the previous terms.

C. Inhomogeneous terms with initial uncorrelated state

The second term on the right-hand side of Eq. (11) represents inhomogeneous contribution due to the nonequilibrium preparation of initial bath state in the polaron frame, involving

the influence of the initial system-bath correlations

$$\begin{aligned} \text{Tr}_b[\mathcal{I}(t)\tilde{\rho}_I(0)] &= -i\alpha \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\mathcal{Q}\tilde{\rho}_I(0)\} \\ &\quad - \alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_I(0)\}. \quad (15) \end{aligned}$$

The expressions for the inhomogeneous term can be obtained by substituting the initial condition $\tilde{\rho}_I(0)$ into Eq. (15). These are much more complicated than those obtained in Paper I and the details of their derivations are left to the following two subsections.

For the case of initial uncorrelated state (8), the application of polaron transformation leads to

$$\begin{aligned} \tilde{\rho}_{\text{uncor}}(0) &= e^G \sigma(0) \otimes \rho_b e^{-G} \\ &= |D\rangle\langle D| \theta_D^\dagger \rho_b \theta_D |D\rangle\langle D| + I_A I_D^* \theta_A^\dagger \rho_b \theta_D |A\rangle\langle D| \\ &\quad + I_D I_A^* \theta_D^\dagger \rho_b \theta_A |D\rangle\langle A| + |A\rangle\langle A| \theta_A^\dagger \rho_b \theta_A |A\rangle\langle A|, \quad (16) \end{aligned}$$

from which the corresponding reduced system density operator can be obtained by taking trace of Eq. (16) over the bath degrees of freedom as follows:

$$\begin{aligned} \text{Tr}_b\{\tilde{\rho}_{\text{uncor}}(0)\} &= |D\rangle\langle D| + w I_D I_A^* |D\rangle\langle A| \\ &\quad + w I_A I_D^* |A\rangle\langle D| + |A\rangle\langle A|. \quad (17) \end{aligned}$$

The subscript in Eqs. (16) and (17) is for the sake of distinction. With Eq. (17), one can show that

$$\begin{aligned} \mathcal{Q}\tilde{\rho}_{\text{uncor}}(0) &= (1 - \mathcal{P})\tilde{\rho}_{\text{uncor}}(0) \\ &= |D\rangle\langle D| (\theta_D^\dagger \rho_b \theta_D - \rho_b) |D\rangle\langle D| \\ &\quad + I_A I_D^* (\theta_A^\dagger \rho_b \theta_D - w \rho_b) |A\rangle\langle D| \\ &\quad + I_D I_A^* (\theta_D^\dagger \rho_b \theta_A - w \rho_b) |D\rangle\langle A| \\ &\quad + |A\rangle\langle A| (\theta_A^\dagger \rho_b \theta_A - \rho_b) |A\rangle\langle A|. \quad (18) \end{aligned}$$

By substituting Eq. (18) into (15), we get the expressions for the inhomogeneous contribution with the initial uncorrelated state (8) or (16) as follows:

$$\begin{aligned} & -i\alpha \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\mathcal{Q}\tilde{\rho}(0)\} \\ & - \alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}(0)\} \\ &= -i\alpha J \sum_{l=1}^4 C_l(t) [\mathcal{T}(\tau), \tilde{\sigma}_I(0)] \\ & - \alpha^2 J^2 \int_0^t d\tau \left\{ \sum_{l=1}^4 \mathcal{F}_{(l),I}(t, \tau) [\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_I(0)] \right. \\ & + \mathcal{F}_{(2),I}(t, \tau) [\mathcal{T}^\dagger(t), \mathcal{T}(\tau)\tilde{\sigma}_I(0)] \\ & + \mathcal{F}_{(3),I}(t, \tau) [\mathcal{T}(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(0)] \\ & \left. + \mathcal{F}_{(4),I}(t, \tau) [\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(0)] \right\} + \text{H.c.} \quad (19) \end{aligned}$$

$C_l(t)$ and $\mathcal{F}_{(n),I}(t, \tau)$ are the bath correlation functions due to the nonequilibrium preparation of initial bath state in the polaron frame. More specifically, from Eqs. (16)–(18), we see it is a result of the polaron transformation applied to

thermal equilibrium state ρ_b and the following projection operator formalism, different from that induced by initial system-bath correlations in laboratory frame. The effects of this transformation-induced nonequilibrium preparation on the exciton dynamics is the focus issue of many previous literatures on the polaron theory [30–32,34]. Instead, we will shed light on the role of the nonequilibrium due to the initial system-bath correlations in Sec. III. Detail expressions of these bath correlation functions are presented in Appendix C.

D. Inhomogeneous terms with initial correlated state

Similarly, the initial system-bath correlated density operator [Eq. (10)] after the application of polaron transformation becomes

$$\tilde{\rho}(0) = e^G \rho(0) e^{-G} = |I'\rangle\langle I'| \otimes \frac{e^{-\beta\tilde{H}}}{Z} \otimes |I'\rangle\langle I'|, \quad (20)$$

with

$$|I'\rangle = I_D |D\rangle B^{1/2} + I_A |A\rangle B^{\dagger 1/2}. \quad (21)$$

For the next, we ought to substitute this initial condition into Eq. (15) and work out $\mathcal{Q}\tilde{\rho}_I(0)$. Observing the form of polaron-transformed initial state $\tilde{\rho}(0)$ in Eq. (20), nevertheless, we see that this calculation can not be exactly performed in a straightforward way as shown in Eq. (18), due to the initial correlations stemming from the finite system-bath interaction Hamiltonian contained in $e^{-\beta\tilde{H}}$. As a consequence, appropriate approximations have to be made. Following the approach that has been adopted to deriving Eqs. (11) and (15), we expand Eq. (20) in powers of coupling strength designated by α . For this purpose, the well-known Kubo identity should be employed

$$e^{\beta(X+Y)} = e^{\beta X} \left(1 + \int_0^\beta d\lambda e^{-\lambda X} Y e^{\lambda(X+Y)} \right), \quad (22)$$

in which X and Y are two arbitrary operators. For the case of our model, these two operators are, respectively, $X = -(\tilde{H}_{0,s} + H_b)$ and $Y = -\tilde{H}_1$. It is obvious that, to the first order in system-bath coupling strength, $e^{-\beta\tilde{H}}$ can be performed a perturbative expansion after simple replacement in the following way:

$$e^{-\beta\tilde{H}} \approx e^{-\beta(\tilde{H}_{0,s} + H_b)} \left(1 - \int_0^\beta d\lambda e^{\lambda(\tilde{H}_{0,s} + H_b)} \alpha \tilde{H}_1 e^{-\lambda(\tilde{H}_{0,s} + H_b)} \right). \quad (23)$$

Then, the initial condition (20) in the polaron frame can be expanded as

$$\tilde{\rho}(0) \approx \frac{1}{Z} |I'\rangle\langle I'| \otimes [e^{-\beta(\tilde{H}_{0,s} + H_b)} - \alpha e^{-\beta H_b} E_0(\beta)] \otimes |I'\rangle\langle I'|, \quad (24)$$

where $E_0(\beta)$ represents the first-order modification to the bath state as a result of the initial system-bath correlations with the following expression:

$$E_0(\beta) = \int_0^\beta d\lambda (e^{\lambda H_b} J \tilde{B} e^{-\lambda H_b} e^{-\beta\tilde{H}_{0,s}} e^{\lambda\tilde{H}_{0,s}} |D\rangle\langle A| e^{-\lambda\tilde{H}_{0,s}} + e^{\lambda H_b} J \tilde{B}^\dagger e^{-\lambda H_b} e^{-\beta\tilde{H}_{0,s}} e^{\lambda\tilde{H}_{0,s}} |A\rangle\langle D| e^{-\lambda\tilde{H}_{0,s}}). \quad (25)$$

Before calculating $\mathcal{Q}\tilde{\rho}_I(0)$, we should get the explicit expression for the partition function Z first. Since it guarantees the normalization condition $\text{Tr}_{s,b}[\rho(0)] = 1$, taking trace of Eq. (24) over both the system and the bath degrees of freedom, one can obtain Z in the following form:

$$Z = \text{Tr}_{s,b}[\tilde{\rho}(0)] = Z' Z_b \quad (26)$$

to the first order in system-bath coupling strength, where $Z_b = \text{Tr}_b\{e^{-\beta H_b}\}$, and

$$\begin{aligned} Z' = & |I_D|^2 |I_D|^2 \langle D| e^{-\beta\tilde{H}_{0,s}} |D\rangle + |I_A|^2 |I_A|^2 \langle A| e^{-\beta\tilde{H}_{0,s}} |A\rangle + |I_D|^2 |I_A|^2 \langle D| e^{-\beta\tilde{H}_{0,s}} |D\rangle + |I_D|^2 |I_A|^2 \langle A| e^{-\beta\tilde{H}_{0,s}} |A\rangle \\ & + w |I_D|^2 I_D I_D^* \left[\langle D| e^{-\beta\tilde{H}_{0,s}} |A\rangle - wJ \int_0^\beta d\lambda (e^{-S(\lambda,0)} - 1) [(dax + day)DD - dazDA] + (e^{S(\lambda,0)} - 1)(adyDD - adzDA) \right] \\ & + w |I_A|^2 I_D I_A^* \left[\langle A| e^{-\beta\tilde{H}_{0,s}} |D\rangle - wJ \int_0^\beta d\lambda (e^{S(\lambda,0)} - 1)(dazAD - dayAA) + (e^{-S(\lambda,0)} - 1)[(adx - ady)AA + adzAD] \right] \\ & + w |I_D|^2 I_D I_A^* \left[\langle A| e^{-\beta\tilde{H}_{0,s}} |D\rangle - wJ \int_0^\beta d\lambda (e^{S(\lambda,0)} - 1)(dazAD - dayAA) + (e^{-S(\lambda,0)} - 1)[(adx - ady)AA + adzAD] \right] \\ & + w |I_A|^2 I_D I_D^* \left[\langle D| e^{-\beta\tilde{H}_{0,s}} |A\rangle - wJ \int_0^\beta d\lambda (e^{-S(\lambda,0)} - 1) [(dax + day)DD - dazDA] + (e^{S(\lambda,0)} - 1)(adyDD - adzDA) \right]. \end{aligned} \quad (27)$$

In Eq. (27), α is set to be 1, and four inner products, according to Eq. (A8), are given by

$$\langle D| e^{-\beta\tilde{H}_{0,s}} |D\rangle = \cosh\left(\frac{\beta\Delta\varepsilon}{2}\right) - \frac{\tilde{E}_D - \tilde{E}_A}{\Delta\varepsilon} \sinh\left(\frac{\beta\Delta\varepsilon}{2}\right), \quad (28)$$

$$\langle D| e^{-\beta\tilde{H}_{0,s}} |A\rangle = -\frac{2Jw}{\Delta\varepsilon} \sinh\left(\frac{\beta\Delta\varepsilon}{2}\right), \quad (29)$$

$$\langle A| e^{-\beta\tilde{H}_{0,s}} |D\rangle = -\frac{2Jw}{\Delta\varepsilon} \sinh\left(\frac{\beta\Delta\varepsilon}{2}\right), \quad (30)$$

$$\langle A|e^{-\beta\tilde{H}_{0,s}}|A\rangle = \cosh\left(\frac{\beta\Delta\varepsilon}{2}\right) + \frac{\tilde{E}_D - \tilde{E}_A}{\Delta\varepsilon} \sinh\left(\frac{\beta\Delta\varepsilon}{2}\right), \quad (31)$$

where

$$\Delta\varepsilon = \sqrt{\left(\frac{\tilde{E}_D - \tilde{E}_A}{2}\right)^2 + J^2w^2}. \quad (32)$$

Besides, the identities

$$e^{\lambda\tilde{H}_{0,s}}|D\rangle\langle A|e^{-\lambda\tilde{H}_{0,s}} = dax|D\rangle\langle A| + day(|D\rangle\langle A| - |A\rangle\langle D|) + daz(|D\rangle\langle D| - |A\rangle\langle A|) \quad (33)$$

and

$$e^{\lambda\tilde{H}_{0,s}}|A\rangle\langle D|e^{-\lambda\tilde{H}_{0,s}} = adx|A\rangle\langle D| + ady(|D\rangle\langle A| - |A\rangle\langle D|) + adz(|D\rangle\langle D| - |A\rangle\langle A|) \quad (34)$$

can be derived, in which the coefficients are of the following forms:

$$dax = \frac{(\tilde{E}_D - \tilde{E}_A)^2}{\Delta\varepsilon^2} \cosh(\lambda\Delta\varepsilon) + \frac{4J^2w^2}{\Delta\varepsilon^2} + \frac{\tilde{E}_D - \tilde{E}_A}{\Delta\varepsilon} \sinh(\lambda\Delta\varepsilon), \quad (35)$$

$$day = \frac{2J^2w^2}{\Delta\varepsilon^2} [\cosh(\lambda\Delta\varepsilon) - 1], \quad (36)$$

$$daz = \frac{Jw(\tilde{E}_D - \tilde{E}_A)}{\Delta\varepsilon^2} [1 - \cosh(\lambda\Delta\varepsilon)] - \frac{Jw}{\Delta\varepsilon} \sinh(\lambda\Delta\varepsilon), \quad (37)$$

and

$$adx = \frac{(\tilde{E}_D - \tilde{E}_A)^2}{\Delta\varepsilon^2} \cosh(\lambda\Delta\varepsilon) + \frac{4J^2w^2}{\Delta\varepsilon^2} - \frac{\tilde{E}_D - \tilde{E}_A}{\Delta\varepsilon} \sinh(\lambda\Delta\varepsilon), \quad (38)$$

$$ady = \frac{2J^2w^2}{\Delta\varepsilon^2} [1 - \cosh(\lambda\Delta\varepsilon)], \quad (39)$$

$$adz = \frac{Jw(\tilde{E}_D - \tilde{E}_A)}{\Delta\varepsilon^2} [1 - \cosh(\lambda\Delta\varepsilon)] + \frac{Jw}{\Delta\varepsilon} \sinh(\lambda\Delta\varepsilon). \quad (40)$$

Thus, the partition function Z is determined.

Now, the explicit expressions for $\mathcal{Q}\tilde{\rho}_t(0)$ can be calculated explicitly. Substituting (21) into (24) gives rise to further expansion of the initial condition in the polaron frame, which is rather complicated since it can be decomposed into 16 terms:

$$\tilde{\rho}(0) = \sum_{n=1}^{16} \tilde{\rho}_n(0). \quad (41)$$

The expressions for these 16 terms are given in Appendix D. Here, we take only two terms for example to elaborate the derivation process. Detail expressions for the other terms are presented in Appendix E. Taking trace of Eq. (24) over ρ_b , one can obtain the initial condition for the reduced system density

operator also consisting of 16 terms as follows:

$$\text{Tr}_b\{\tilde{\rho}(0)\} = \tilde{\sigma}(0) = \sum_{n=1}^{16} \tilde{\sigma}_n(0), \quad (42)$$

where

$$\tilde{\sigma}_3(0) = \frac{1}{Z'} |I_D|^2 I_D I_A^* |D\rangle\langle A| \times [\langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle w - \alpha \langle\langle D|E_0(\beta)|D\rangle B\rangle] \quad (43)$$

and

$$\tilde{\sigma}_{13}(0) = \frac{1}{Z'} |I_D|^2 I_A I_D^* |A\rangle\langle D| \times [\langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle w - \alpha \langle\langle D|E_0(\beta)|D\rangle B^\dagger\rangle] \quad (44)$$

are the two terms selected as paradigms as mentioned above. It corresponds to $\tilde{\rho}_3(0)$ and $\tilde{\rho}_{13}(0)$ contained in the total density operators for the polaron-transformed initial state $\tilde{\rho}(0)$ in Eq. (24) or (41), the expressions of which are, respectively,

$$\tilde{\rho}_3(0) = \frac{1}{Z'} |I_D|^2 I_D I_A^* |D\rangle\langle A| \times [\langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle \rho_b B - \alpha \rho_b \langle\langle D|E_0(\beta)|D\rangle B\rangle] \quad (45)$$

and

$$\tilde{\rho}_{13}(0) = \frac{1}{Z'} |I_D|^2 I_A I_D^* |A\rangle\langle D| \times [\langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle B^\dagger \rho_b - \alpha B^\dagger \rho_b \langle\langle D|E_0(\beta)|D\rangle]. \quad (46)$$

In view of the Hermiticity of $\rho_b \langle\langle D|E_0(\beta)|D\rangle$ that has been manifested in Ref. [68], it is easy to conclude that $\tilde{\rho}_3(0)$ and $\tilde{\rho}_{13}(0)$ are conjugate pairs. We choose such conjugate pairs as an example just for the convenience of written description. Then, subtracting $\mathcal{P}\tilde{\rho}_{3(13)}(0) = \rho_b \tilde{\sigma}_{3(13)}(0)$ from $\tilde{\rho}_{3(13)}(0)$ results in

$$\mathcal{Q}\tilde{\rho}_3(0) = (1 - \mathcal{P})\tilde{\rho}_3(0) = \frac{|I_D|^2 I_D I_A^*}{Z'} |D\rangle\langle A| \delta\rho_{b3} \quad (47)$$

and

$$\mathcal{Q}\tilde{\rho}_{13}(0) = (1 - \mathcal{P})\tilde{\rho}_{13}(0) = \frac{|I_D|^2 I_A I_D^*}{Z'} |A\rangle\langle D| \delta\rho_{b13}, \quad (48)$$

where

$$\delta\rho_{b3} = \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle \rho_b \tilde{B} - \alpha \rho_b (\langle\langle D|E_0(\beta)|D\rangle B - \langle\langle D|E_0(\beta)|D\rangle B\rangle) \quad (49)$$

and

$$\delta\rho_{b13} = \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle \tilde{B}^\dagger \rho_b - \alpha (B^\dagger \rho_b \langle\langle D|E_0(\beta)|D\rangle - \rho_b \langle\langle D|E_0(\beta)|D\rangle B^\dagger) \quad (50)$$

can be obtained straightforwardly. The first-order term of inhomogeneous contribution (15) with $\tilde{\rho}_3(0)$ and $\tilde{\rho}_{13}(0)$ can be written as

$$-i\alpha \text{Tr}_b\{\tilde{\mathcal{L}}_{1,t}(t)\mathcal{Q}\tilde{\rho}_3(0)\} - i\alpha \text{Tr}_b\{\tilde{\mathcal{L}}_{1,t}(t)\mathcal{Q}\tilde{\rho}_{13}(0)\} = -i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_3(0)]\} + \text{H.c.} \quad (51)$$

After substituting Eqs. (47) and (48), and employing the cyclic symmetry of trace operation, one can decouple the

bath correlation functions from the system operators. Then, Eq. (51) is shown to be

$$\begin{aligned}
 & -i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_3(0)]\} + \text{H.c.} \\
 & = -i\alpha |I_D|^2 I_D I_A^* \frac{J}{Z'} \text{Tr}_b\{\tilde{B}(t)\delta\rho_{b3}\}[\mathcal{T}(t), |D\rangle\langle A|] + i\alpha |I_D|^2 I_D I_A^* \frac{J}{Z'} \text{Tr}_b\{\tilde{B}^\dagger(t)\delta\rho_{b3}\}[|D\rangle\langle A|, \mathcal{T}^\dagger(t)] + \text{H.c.}
 \end{aligned} \tag{52}$$

Next, with the expressions of B , \tilde{B} , and $\langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle$ defined in Eqs. (A4), (A10), and (28), respectively, and inserting Eq. (25), the bath average quantities in Eq. (52) can be calculated as follows:

$$\begin{aligned}
 \text{Tr}_b\{\tilde{B}(t)\delta\rho_{b3}\} & = w^2 \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle (e^{S(0,t)} - 1) - \alpha w^3 J \int_0^\beta d\lambda (e^{S(\lambda,t)+S(\lambda,0)+S(0,t)} - e^{S(\lambda,0)} - e^{S(0,t)} + 1)(dazDD - dayDA) \\
 & + (e^{-S(\lambda,t)-S(\lambda,0)+S(0,t)} - e^{-S(\lambda,0)} - e^{S(0,t)} + 1)[adzDD + (adx - ady)DA]
 \end{aligned} \tag{53}$$

and

$$\begin{aligned}
 \text{Tr}_b\{\tilde{B}^\dagger(t)\delta\rho_{b3}\} & = w^2 \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle (e^{-S(0,t)} - 1) - \alpha w^3 J \int_0^\beta d\lambda (e^{-S(\lambda,t)+S(\lambda,0)-S(0,t)} - e^{S(\lambda,0)} - e^{-S(0,t)} + 1)(dazDD - dayDA) \\
 & + (e^{S(\lambda,t)-S(\lambda,0)-S(0,t)} - e^{-S(\lambda,0)} - e^{-S(0,t)} + 1)[adzDD + (adx - ady)DA].
 \end{aligned} \tag{54}$$

The Hermitian conjugate term in Eq. (51) or (52) can be calculated in a similar way. Now, the first-order term of the inhomogeneous contribution (15) with $\tilde{\rho}_3(0)$ and $\tilde{\rho}_{13}(0)$ is determined.

The second-order term of the inhomogeneous contribution (15) can be expressed as

$$\begin{aligned}
 & -\alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_3(0)\} - \alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_{13}(0)\} \\
 & = -\alpha^2 J^2 \int_0^t d\tau \{ \text{Tr}_b([\tilde{B}(t)\mathcal{T}(t), [\tilde{B}(\tau)\mathcal{T}(\tau), \mathcal{Q}\tilde{\rho}_3(0)]] + [\tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), [\tilde{B}(\tau)\mathcal{T}(\tau), \mathcal{Q}\tilde{\rho}_3(0)]] \\
 & + [\tilde{B}(t)\mathcal{T}(t), [\tilde{B}^\dagger(\tau)\mathcal{T}^\dagger(\tau), \mathcal{Q}\tilde{\rho}_3(0)]] + [\tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), [\tilde{B}^\dagger(\tau)\mathcal{T}^\dagger(\tau), \mathcal{Q}\tilde{\rho}_3(0)]] \} + \text{H.c.}
 \end{aligned} \tag{55}$$

Substituting Eqs. (47)–(50) into (55), one can obtain the explicit expression for the second-order term (55) of the inhomogeneous contribution denoted by Eq. (15) with $\tilde{\rho}_3(0)$ and $\tilde{\rho}_{13}(0)$ as follows:

$$\begin{aligned}
 & -\alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_3(0)\} - \alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_{13}(0)\} \\
 & = -\alpha^2 J^2 \int_0^t d\tau \left\{ \sum_{l=3,13} \mathcal{K}_{(1),l}(t, \tau)[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)] + \mathcal{K}_{(2),l}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)] \right. \\
 & \left. + \mathcal{K}_{(3),l}(t, \tau)[\mathcal{T}(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_l^{(0)}(0)] + \mathcal{K}_{(4),l}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_l^{(0)}(0)] \right\} + \text{H.c.},
 \end{aligned} \tag{56}$$

where $\tilde{\sigma}_{3(13)}^{(0)}(0)$ is the zeroth-order term of $\tilde{\sigma}_{3(13)}(0)$. It should be noted that Eq. (15) or (55) is of the second order in coupling strength designated by the dimensionless parameter α^2 . As a consequence, the zeroth-order term in coupling strength of Eq. (49) or (50) is preserved while the first-order term can be ignored when we derive Eq. (56). Under this circumstance, the partition function Z that guarantees the normalization condition $\text{Tr}_{s,b}[\rho(0)] = 1$ is rewritten as

$$Z = \text{Tr}_{s,b}[\tilde{\rho}(0)] = Z''Z_b, \tag{57}$$

where $Z_b = \text{Tr}_b\{e^{-\beta H_b}\}$, and

$$\begin{aligned}
 Z'' & = w[|I_D|^2 I_A I_D^* \langle D|e^{-\beta\tilde{H}_{0,s}}|A\rangle + |I_A|^2 I_D I_A^* \langle A|e^{-\beta\tilde{H}_{0,s}}|D\rangle \\
 & + |I_D|^2 I_D I_A^* \langle A|e^{-\beta\tilde{H}_{0,s}}|D\rangle + |I_A|^2 I_A I_D^* \langle D|e^{-\beta\tilde{H}_{0,s}}|A\rangle]
 \end{aligned}$$

$$\begin{aligned}
 & + |I_D|^2 |I_D|^2 \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle + |I_A|^2 |I_A|^2 \langle A|e^{-\beta\tilde{H}_{0,s}}|A\rangle \\
 & + |I_D|^2 |I_A|^2 \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle + |I_D|^2 |I_A|^2 \langle A|e^{-\beta\tilde{H}_{0,s}}|A\rangle.
 \end{aligned} \tag{58}$$

The zeroth-order term of $\tilde{\sigma}_3(0)$ and $\tilde{\sigma}_{13}(0)$ represented by $\tilde{\sigma}_3^{(0)}(0)$ and $\tilde{\sigma}_{13}^{(0)}(0)$, respectively, then can be shown to be

$$\tilde{\sigma}_3^{(0)}(0) = \frac{1}{Z''} |I_D|^2 I_D I_A^* |D\rangle \langle A| \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle w \tag{59}$$

and

$$\tilde{\sigma}_{13}^{(0)}(0) = \frac{1}{Z''} |I_D|^2 I_A I_D^* |A\rangle \langle D| \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle w. \tag{60}$$

In Eq. (56), $\mathcal{K}_{(n),l}$ is the bath correlation function accounting for bath relaxation with the following expressions:

$$\mathcal{K}_{(1),3}(t, \tau) = \mathcal{K}_{(8),13}^*(t, \tau) = \text{Tr}_b[\tilde{B}(t)\tilde{B}(\tau)\rho_b\tilde{B}] = w^2[e^{S(0,\tau-t)}(e^{S(0,t)+S(0,\tau)} + 1) - e^{S(0,\tau)} - e^{S(0,t)} + 2], \quad (61)$$

$$\mathcal{K}_{(2),3}(t, \tau) = \mathcal{K}_{(7),13}^*(t, \tau) = \text{Tr}_b[\tilde{B}^\dagger(t)\tilde{B}(\tau)\rho_b\tilde{B}] = w^2[e^{-S(0,\tau-t)}(e^{-S(0,t)+S(0,\tau)} + 1) - e^{S(0,\tau)} - e^{-S(0,t)} + 2], \quad (62)$$

$$\mathcal{K}_{(3),3}(t, \tau) = \mathcal{K}_{(6),13}^*(t, \tau) = \text{Tr}_b[\tilde{B}(t)\tilde{B}^\dagger(\tau)\rho_b\tilde{B}] = w^2[e^{-S(0,\tau-t)}(e^{S(0,t)-S(0,\tau)} + 1) - e^{-S(0,\tau)} - e^{S(0,t)} + 2], \quad (63)$$

$$\mathcal{K}_{(4),3}(t, \tau) = \mathcal{K}_{(5),13}^*(t, \tau) = \text{Tr}_b[\tilde{B}^\dagger(t)\tilde{B}^\dagger(\tau)\rho_b\tilde{B}] = w^2[e^{S(0,\tau-t)}(e^{-S(0,t)-S(0,\tau)} + 1) - e^{-S(0,\tau)} - e^{-S(0,t)} + 2], \quad (64)$$

$$\mathcal{K}_{(5),3}(t, \tau) = \mathcal{K}_{(4),13}^*(t, \tau) = \text{Tr}_b[\rho_b\tilde{B}\tilde{B}(\tau)\tilde{B}(t)] = w^2[e^{S(0,t-\tau)}(e^{S(0,t)+S(0,\tau)} + 1) - e^{S(0,\tau)} - e^{S(0,t)} + 2], \quad (65)$$

$$\mathcal{K}_{(6),3}(t, \tau) = \mathcal{K}_{(3),13}^*(t, \tau) = \text{Tr}_b[\rho_b\tilde{B}\tilde{B}(\tau)\tilde{B}^\dagger(t)] = w^2[e^{-S(0,t-\tau)}(e^{-S(0,t)+S(0,\tau)} + 1) - e^{S(0,\tau)} - e^{-S(0,t)} + 2], \quad (66)$$

$$\mathcal{K}_{(7),3}(t, \tau) = \mathcal{K}_{(2),13}^*(t, \tau) = \text{Tr}_b[\rho_b\tilde{B}\tilde{B}^\dagger(\tau)\tilde{B}(t)] = w^2[e^{-S(0,t-\tau)}(e^{S(0,t)-S(0,\tau)} + 1) - e^{-S(0,\tau)} - e^{S(0,t)} + 2], \quad (67)$$

$$\mathcal{K}_{(8),3}(t, \tau) = \mathcal{K}_{(1),13}^*(t, \tau) = \text{Tr}_b[\rho_b\tilde{B}\tilde{B}^\dagger(\tau)\tilde{B}^\dagger(t)] = w^2[e^{S(0,t-\tau)}(e^{-S(0,t)-S(0,\tau)} + 1) - e^{-S(0,\tau)} - e^{-S(0,t)} + 2]. \quad (68)$$

Up to now, the derivations of the inhomogeneous term (15) with $\tilde{\rho}_3(0)$ and $\tilde{\rho}_{13}(0)$ have been expounded. Results for the other terms contained in the the polaron-transformed initial state $\tilde{\rho}(0)$ in Eq. (24) or (42) are presented in Appendix E.

E. Expressions of the system operators in the exciton basis

For numerical calculation, it is convenient to express the system operators by the eigenstates of the zeroth-order Hamiltonian $\tilde{H}_{s,0}$, i.e., the renormalized exciton basis, which is defined by

$$\tilde{H}_{s,0}|\pm\rangle = \varepsilon_\pm|\pm\rangle, \quad (69)$$

with the eigenvalues of $\tilde{H}_{s,0}$ being

$$\varepsilon_\pm = \frac{1}{2}[(\tilde{E}_D + \tilde{E}_A) \pm \sqrt{4J^2w^2 + (\tilde{E}_D - \tilde{E}_A)^2}]. \quad (70)$$

The corresponding eigenstates are related with local excitation states $|D\rangle$ and $|A\rangle$ through

$$|+\rangle = \cos\frac{\theta}{2}|D\rangle + \sin\frac{\theta}{2}|A\rangle, \quad (71)$$

$$|-\rangle = \sin\frac{\theta}{2}|D\rangle - \cos\frac{\theta}{2}|A\rangle, \quad (72)$$

where $\tan\theta = 2Jw/(\tilde{E}_D - \tilde{E}_A)$. Inserting Eqs. (71) and (72) into the homogeneous and inhomogeneous terms (11) and (15), respectively, the explicit form of these terms now can be obtained by expressing the commutators in the exciton basis. Then, we get the matrix elements of the QME (11).

F. Definition of spectral densities

We assume the following form for the spectral density to treat system-bath couplings:

$$\mathcal{J}_D(\omega) = \sum_k g_{kD}^2 \delta(\omega - \omega_k), \quad (73)$$

$$\mathcal{J}_A(\omega) = \sum_k g_{kA}^2 \delta(\omega - \omega_k), \quad (74)$$

$$\mathcal{J}_c(\omega) = -\sum_k g_{kD}g_{kA} \delta(\omega - \omega_k), \quad (75)$$

where \mathcal{J}_D and \mathcal{J}_A describe diagonal couplings of bath modes to the $|D\rangle$ and $|A\rangle$, respectively, while \mathcal{J}_c is for the common

modes shared between $|D\rangle$ and $|A\rangle$. Thus, cross correlations between energy fluctuations on different sites can be included in this formalism. All the bath correlation functions appearing in the master equation derived in Secs. II B, II C, and II D can be expressed with linear combinations of the spectral densities defined above. For example, Eq. (14) can be rewritten as

$$\mathcal{S}(\lambda, t) = -\frac{1}{2} \int_0^\infty \frac{\mathcal{J}_s(\omega)}{\omega^2} \left[\coth\left(\frac{\beta\omega}{2}\right) (e^{\lambda\omega - i\omega t} + e^{-\lambda\omega + i\omega t}) - (e^{\lambda\omega - i\omega t} - e^{-\lambda\omega + i\omega t}) \right], \quad (76)$$

where \mathcal{J}_s , according to Eq. (14), can be given by

$$\mathcal{J}_s(\omega) = \mathcal{J}_D(\omega) + \mathcal{J}_A(\omega) + 2\mathcal{J}_c(\omega). \quad (77)$$

III. RESULTS AND DISCUSSIONS

With the preliminary derivations, we proceed to investigate the dynamics of donor population $\sigma_{DD}(t)$ in our donor-acceptor system with the arbitrary coherent initial system condition (9). Two cases will be considered in this paper: the dynamics of $\sigma_{DD}(t)$ (i) with initial correlated state (10) or (24), i.e., with initial system-bath correlations, (ii) with initial uncorrelated state (8) or (16), i.e., without initial system-bath correlations but the inhomogeneous term (15) due to nonequilibrium preparation of initial bath state in the polaron frame exist. Since the population elements of the reduced system density operator are invariant under the polaron transformation, $\sigma_{DD}(t)$ can be obtained directly from the master equation for $\tilde{\sigma}_I(t)$ given by Eq. (11). Besides, the effects of common bath modes on the dynamics are also studied.

A. Model spectral density

We perform numerical calculations for the following three super-Ohmic spectral densities with the same exponential cutoff frequency:

$$\mathcal{J}_D(\omega) = \frac{\eta_A}{3!} \frac{\omega^3}{\omega_c^2} e^{-\omega/\omega_c}, \quad (78)$$

$$\mathcal{J}_A(\omega) = \frac{\eta_D}{3!} \frac{\omega^3}{\omega_c^2} e^{-\omega/\omega_c}, \quad (79)$$

$$\mathcal{J}_c(\omega) = \frac{\eta_c \omega^3}{3! \omega_c^2} e^{-\omega/\omega_c}, \quad (80)$$

$$\mathcal{J}_s(\omega) = \frac{\eta_s \omega^3}{3! \omega_c^2} e^{-\omega/\omega_c}, \quad (81)$$

where η_D, η_A are the dimensionless system-bath coupling strength. η_c is called cross coupling that is bounded by Schwarz inequality $\eta_c \leq \sqrt{|\eta_D \eta_A|}$. According to Eq. (75), positive η_c indicates the common bath modes couple to the exciton differently while negative η_c similarly. The effective system-bath coupling η_s is then given by

$$\eta_s = \eta_D + \eta_A + 2\eta_c. \quad (82)$$

The reciprocal of the cutoff frequency ω_c represents the relaxation time of the bath. This form of spectral density takes no account of subsistent localized vibration modes described by a delta function, which also contribute significantly to the exciton dynamics. Further work will be devoted to this issue. In addition, in realistic photosynthesis-related EET, the continuous part of spectral densities typically consists of more spectral weight at lower frequencies than a super-Ohmic density [69]. An Ohmic form thus seems more appropriate to account for the influence of these lower frequencies. However, a notable question of the Ohmic spectral density is that the renormalization factors exhibit a well-known infrared divergence [36] that may lead to electronic couplings being renormalized to zero for arbitrary values of system-bath coupling strength. By contrast, the super-Ohmic form gets rid of this problem and one can obtain analytical expressions for correlation functions within the polaron formalism [30–34,41–47] in terms of the spectral densities introduced in Eqs. (78)–(81), such that a simple picture for describing the system-bath coupling is available. For each of the two cases described above, two different energetic situations are under consideration in the following calculation: $\Delta E = \tilde{E}_D - \tilde{E}_A = \pm 1$. For numerical calculations throughout the paper, units are chosen such that $\hbar = \omega_c = 1$. This is equivalent to assuming that the unit of time is $1/(2\pi\omega_c)$ and the unit of energy is $\hbar\omega_c$. It is also assumed that $\beta = 1$ and $J = 1$. With these choices, if $\hbar\omega_c = 200 \text{ cm}^{-1}$, $J = 200 \text{ cm}^{-1}$, $T \approx 290 \text{ K}$, and the unit of time is about 1 ps [30–34,39–46]. With these parameters, in the entire regime of system-bath coupling strength, the measure of the electronic coupling fluctuations as introduced in Eq. (A12) remains smaller than the onsite energy gap $|\Delta E|$ and the cutoff frequency ω_c of spectral densities, which guarantees the validity of the present polaron treatment [32,34].

In this work, calculations of time-dependent evolution based on the theory of Förster-Dexter energy transfer (FDET) are also performed for comparison:

$$\frac{d}{dt} \sigma_{DD}(t) = -k_{DA}(t) \sigma_{DD}(t) + k_{AD}(t) [1 - \sigma_{DD}(t)], \quad (83)$$

where $k_{DA}(t)$ is the time-dependent Förster-Dexter rate [16–18] from D to A given by

$$k_{DA}(t) = \frac{2J^2}{\hbar^2} e^{S(0,0)} \text{Re} \int_0^t d\tau [e^{i(E_D - E_A)\tau/\hbar} f(t) \times f(\tau - t) (e^{-S(0,\tau)} - 1)], \quad (84)$$

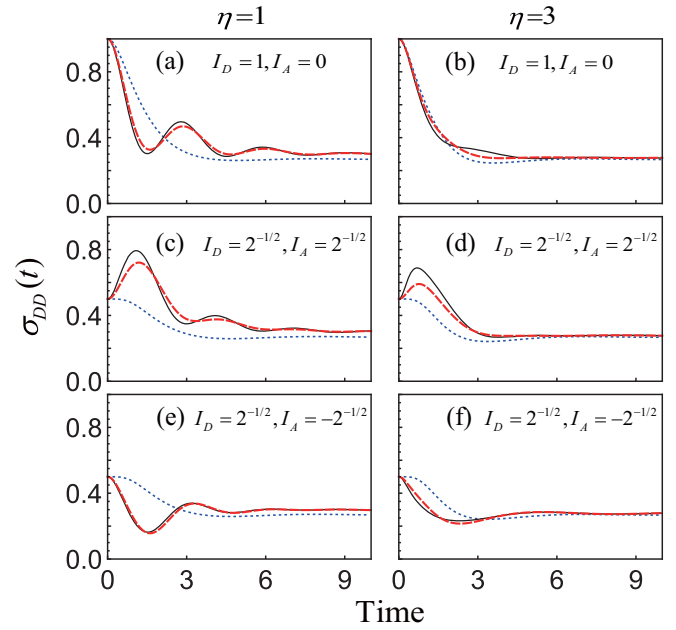


FIG. 1. Time evolution of donor population $\sigma_{DD}(t)$ in the units where $J = 1$, $\omega_c = 1$, $\beta = 1$ and $\Delta E = \tilde{E}_D - \tilde{E}_A = 1$ for different initial system conditions and system-bath coupling strength η (1 or 3). Black solid curves correspond to the results for initial correlated state (10) or (24), i.e., with initial system-bath correlations. Red dashed curves correspond to the results for initial uncorrelated state (8) or (16), i.e., without the initial correlations but the inhomogeneous term (15) exists. Blue dotted curves are based on the results from the theory of Förster-Dexter energy transfer (FDET).

while $k_{AD}(t)$ is the same as $k_{DA}(t)$ except for the replacement $E_D - E_A \rightarrow E_A - E_D$. The expression for $f(t)$ is presented in Appendix E. The validity of this theory relies on the smallness of the electronic coupling J . The resulting Förster-Dexter rate equations give account of purely incoherent hopping processes and are successfully applied in wide varieties of situations.

B. Effects of initial system condition and system-bath coupling strength

Figure 1 depicts the time-dependent donor population $\sigma_{DD}(t)$ for specific classes of parameters: $\eta_D + \eta_c = \eta_A + \eta_c = \eta$ where $\eta = 1$ or 3. These settings represent both the case of no common mode $\eta_c = 0$ and the case with finite η_c given that $\eta_D = \eta_A = \eta - \eta_c$. Three initial system states including that localized on the donor site are compared to examine the effects of initial system-bath correlations as well as system-bath coupling strength on the dynamics. It can be observed that the nonequilibrium, contained in the inhomogeneous terms (15) as a result of the initial system-bath correlations, have an obvious effect on enlarging the amplitude of population oscillation, especially for favorable initial condition like $|I\rangle = \frac{1}{\sqrt{2}}(|D\rangle + |A\rangle)$. When the excitation is localized on the donor site or in an unfavorable initial condition like $|I\rangle = \frac{1}{\sqrt{2}}(|D\rangle - |A\rangle)$, however, this effect is not obvious for the parameters adopted here. Thus, we see that the effects of quantum coherence involved in the initial system

state $|I\rangle$ and nonequilibrium due to the initial system-bath correlations, depend on the relative phase of $|D\rangle$ and $|A\rangle$. It can be expected that the relative magnitudes of $|D\rangle$ and $|A\rangle$ also have an important influence on the role of initial system-bath correlation, as we will see in a later section. This nonequilibrium-induced oscillation provides a positive theoretical instance accounting for the origin of quantum coherence that might be observed under the influence of ambient protein scaffold and solvent environment that are often defined as hot and wet [2–5]. Whereas for the dynamics based on FDET theory, all of these effects disappear, and in a weak system-bath coupling regime ($\eta = 1$) the stationary limit is distinct from the results obtained by the polaron master equation. This is because the electronic coupling J is not small enough (for the parameter $J = 1$ we choose here) to guarantee the validity of FDET theory, which breaks the detailed balance based on the Golden rule type transfer rate equation (83). When $\eta = 3$, the system-bath coupling becomes strong enough to damp the oscillation amplitude. Distinctions between the dynamics with and without initial correlation seem more pronounced than those of the cases when $\eta_D + \eta_c = \eta_A + \eta_c = 1$ as shown in Figs. 1(a), 1(c), and 1(e). Therefore, it can be pointed out that the initial system-bath correlations play an increasingly significant role in the strong coupling regime. From the point of view of quantum open system theory, the systematically increasing error due to the neglect of initial system-bath correlations as in Eq. (8) is introduced when increasing the system-bath coupling strength. Physically, this is for the reason that strong system-bath couplings greatly modify the bath and meanwhile make the modified bath have more access to take effect on the system evolution. In addition, the time-dependent donor population predicted by the two theories gradually approaches in the primary stage as well as stationary regime owing to the successful application of FDET theory in describing energy transfer when the system-bath coupling strength is strong enough compared to the electronic resonance interactions J .

From Fig. 1, the difference between the dynamics with and without initial correlations can only be observed in primary evolution stages. As time goes on, the two curves of polaron dynamics gradually overlap, indicating that the system will gradually “forget” the influence of nonequilibrium caused by initial system-bath correlations in the long-time limit. Mathematically, the transfer dynamics with both the uncorrelated initial condition (8) and correlated initial condition (10) goes to the Markovian limit. To be specific, it can be proved numerically that in the QME (11), the inhomogeneous term (15) arising from Eq. (8) or (10) decays to zero in the long-time limit as the upper integration limit becomes ∞ instead of t and, as a consequence, has a negligible contribution to system evolution. Therefore, it can be inferred that the effects of initial system-bath correlations become irrelevant in Markovian bath.

Figure 2 displays the case for the energetic situation $\Delta E = -1$. Similarly, behavior of dynamical evolution but with opposite trends can be observed. For certain initial system condition $|I\rangle = \frac{1}{\sqrt{2}}(|D\rangle + |A\rangle)$, the initial system-bath correlations induced nonequilibrium lead to larger amplitude of population oscillation, and more obvious distinctions can

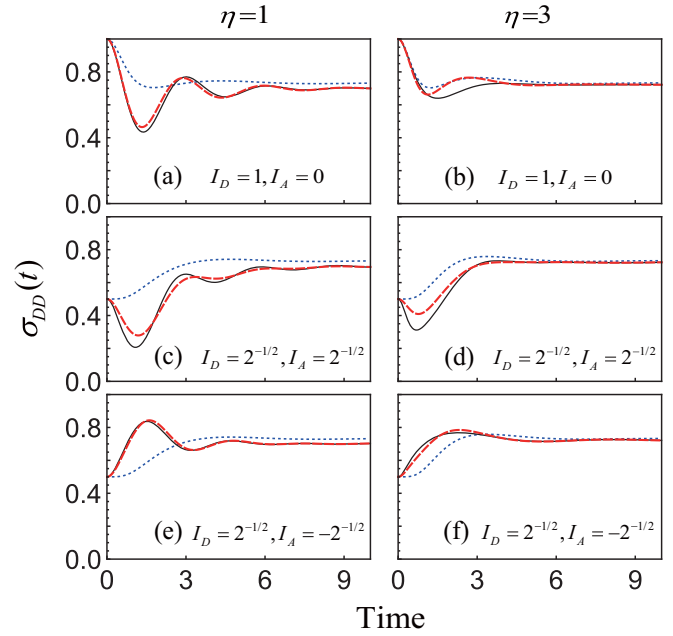


FIG. 2. Time evolution of donor population $\rho_{DD}(t)$ in the units where $J = 1$, $\omega_c = 1$, $\beta = 1$, and $\Delta E = \bar{E}_D - \bar{E}_A = -1$ for different initial system states and system-bath coupling strength η (1 or 3). Other conventions are the same as in Fig. 1.

be seen for larger system-bath coupling strength η . Likewise, the difference is obvious only in primary stages. At longer times, the nonequilibrium due to the initial system-bath correlations becomes much less important. So, the two curves of polaron dynamics overlap as well in the long-time limit. Besides, stronger system-bath coupling damps the oscillative population and makes the time-dependent evolution overlap with those obtained by the rate equation (83), for the same reason as the case of $\Delta E = 1$.

C. Effects of common bath modes

The effects of common bath modes are illustrated in Fig. 3 with fixed values of $\eta_D = \eta_A = 1$, and three different values of η_c (± 0.5 or 0) are examined. From Fig. 3, the duration of population oscillation gets shorter, i.e., the quantum coherence is gradually damped with increasing cross-coupling strength η_c for both the initial system conditions tested: $|I\rangle = \frac{1}{\sqrt{2}}(|D\rangle \pm |A\rangle)$. This can be understood easily since larger η_c gives rise to increased effective system-bath coupling η_s that is directly relevant to the evolution dynamics. Thus, we see that even when the donor and acceptor couple to the bath modes with the same strength $\eta_D = \eta_A = 1$, how the common bath modes respond to the excitations, differently (positive η_c) or similarly (negative η_c), plays an important role in influencing the duration of population oscillation. That is to say, the nature of common bath modes determines whether the quantum coherence is protected or destroyed during the evolution process. Besides, the nonequilibrium induced by the initial system-bath correlations makes more contribution to change the population evolution especially for the initial condition $|I\rangle = \frac{1}{\sqrt{2}}(|D\rangle + |A\rangle)$, which implies that the relative

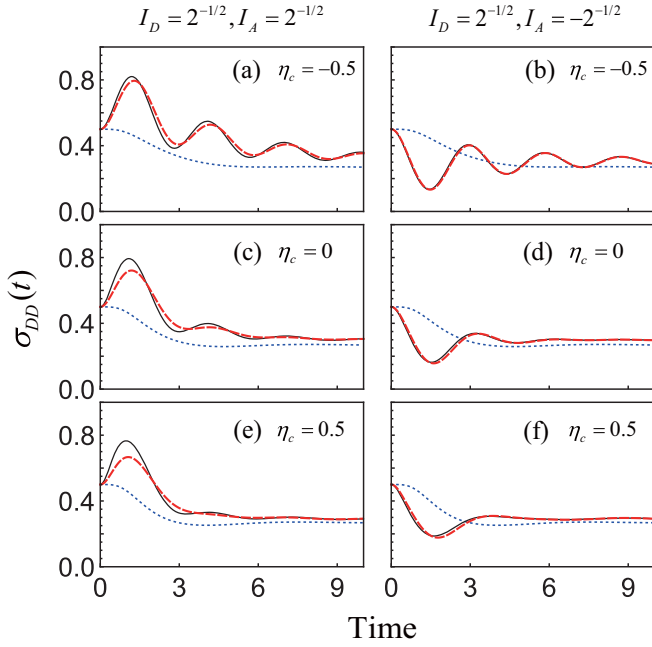


FIG. 3. Time evolution of donor population $\sigma_{DD}(t)$ in the units where $J = 1$, $\omega_c = 1$, $\beta = 1$, and $\Delta E = \tilde{E}_D - \tilde{E}_A = 1$ for different initial system states and cross-coupling strength η_c (± 0.5 or 0). Other conventions are the same as in Fig. 1.

phase of $|D\rangle$ and $|A\rangle$ also determines whether the initial system-bath correlations have more access to influence the dynamics for certain bath modes. For $|I\rangle = \frac{1}{\sqrt{2}}(|D\rangle - |A\rangle)$, the difference between the two curves of polaron dynamics is insignificant in both the primary stages and stationary limits. Thus, $|I\rangle = \frac{1}{\sqrt{2}}(|D\rangle - |A\rangle)$ is unfavorable for the initial system-bath correlations to take effect.

D. Effects of the relative phase and magnitude of $|D\rangle$ and $|A\rangle$

Based on the preceding discussions, the role of initial correlations on the dynamics is quite sensitive to the initial system condition, i.e., the values of I_D and I_A . In this section, we shed light on this issue by examining a sample of initial system conditions with equal interval of $|I_D|^2$. The difference between the dynamics with and without initial correlations, i.e., the effects of initial correlations for different initial system conditions, is measured by the cumulative trace distance [63] which is defined as $D_S(\tilde{\sigma}^c(t), \tilde{\sigma}^{\text{unc}}(t)) = \int_0^\infty D[\tilde{\sigma}^c(t), \tilde{\sigma}^{\text{unc}}(t)]dt$ where $D[A, B] = \frac{1}{2}\text{Tr}\sqrt{(A - B)^\dagger(A - B)}$ represents the usual trace distance [70]. $\tilde{\sigma}^c(t)$ and $\tilde{\sigma}^{\text{unc}}(t)$ correspond to the time evolution of the reduced system state in the polaron frame with initial uncorrelated state (8) or (16) and correlated state (10) or (24), respectively. Figure 4 illustrates the result for the energetic situation $\Delta E = 1$ with the parameter $\eta_D + \eta_c = \eta_A + \eta_c = \eta$ where $\eta = 1.5$.

It should be noted that the cumulative trace distance D_S in Fig. 4 is plotted in the polaron frame. One may also attempt to inquire into D_S in the laboratory frame. Then, the off-diagonal elements $\sigma_{AD}(t)$ or $\sigma_{DA}(t)$ of system density operator $\sigma(t)$ in the laboratory frame have to be calculated. Because they

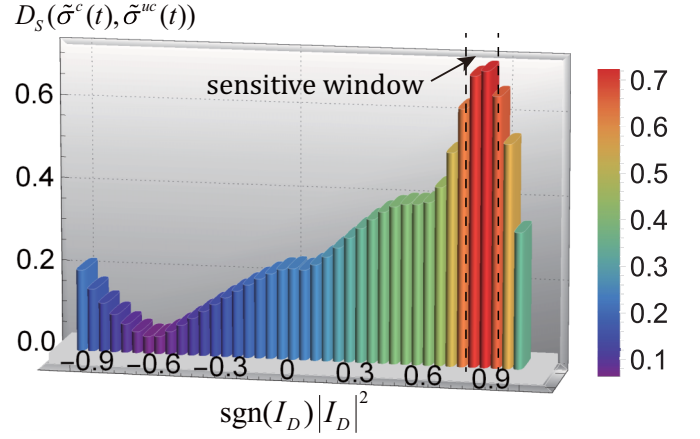


FIG. 4. Cumulative trace distance D_S with respect to different initial system states characterized by $|I_D|^2$ in the units where $J = 1$, $\omega_c = 1$, $\beta = 1$, $\eta = 1.5$, and $\Delta E = \tilde{E}_D - \tilde{E}_A = 1$. The “sensitive window” is centered around $|I_D|^2 \sim 0.85$ with I_D and I_A being the same sign.

do not commute with the polaron-transformation operator G , calculating $\sigma_{AD}(t)$ or $\sigma_{DA}(t)$ in the laboratory frame is much more involved. In addition, it would not offer a new result of the trend of cumulative trace distance D_S over $|I_D|^2$, compared with $D_S(\tilde{\sigma}^c(t), \tilde{\sigma}^{\text{unc}}(t))$ in the polaron frame. $D_S(\tilde{\sigma}^c(t), \tilde{\sigma}^{\text{unc}}(t))$ serves as a good measure to examine the role of initial system-bath correlations, and therefore we directly adopt $D_S(\tilde{\sigma}^c(t), \tilde{\sigma}^{\text{unc}}(t))$ without transforming back to the laboratory frame for simplicity.

As one can see from Fig. 4, the change of cumulative trace distance D_S over $|I_D|^2$ is not symmetry about the axis of $|I_D|^2 = 0$. Basically, the nonequilibrium caused by the initial correlations plays an apparent role when I_D and I_A are of the same sign. When I_D and I_A are of the opposite sign, however, D_S is much depressed, which can also be confirmed from Fig. 1 since the difference is of little consequence for $|I\rangle = \frac{1}{\sqrt{2}}(|D\rangle - |A\rangle)$. Thus, the effect of initial correlations is not manifested in the dynamical evolution under this circumstance. So, we confirm the crucial importance of the sign of the coefficients I_D and I_A , or the relative phase of $|D\rangle$ and $|A\rangle$ in determining whether the initial system-bath correlations would take effect.

The cumulative trace distance D_S also depends to a great degree on the magnitude of I_D and I_A as depicted in Fig. 4. Specifically, Fig. 4 clearly identifies a parameter range (between the two vertical black-dashed lines) in which D_S exhibits a dramatic increase. This means there exists a highly significant difference between the dynamics with and without initial correlations. The parameter range is centered around $|I_D|^2 \sim 0.85$ with I_D and I_A being the same sign. We plot the time evolution of donor population $\sigma_{DD}(t)$ under this corresponding condition within the specific parameter range $|I\rangle = \sqrt{0.85}|D\rangle + \sqrt{0.15}|A\rangle$, and the results are shown in Fig. 5. The population dynamics with and without initial correlations does show great difference for this initial system condition. The initial correlations cause large population oscillation, while for the case of initial uncorrelated state, oscillatory population is scarcely observed even in weak coupling regime

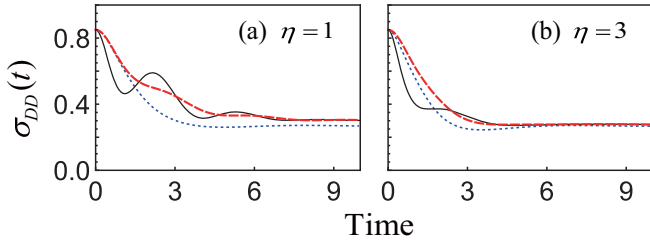


FIG. 5. Time evolution of donor population $\sigma_{DD}(t)$ in the units where $J = 1$, $\omega_c = 1$, $\beta = 1$, and $\Delta E = \tilde{E}_D - \tilde{E}_A = 1$ for different cross-coupling strength η (1 or 3) with initial system state $|I\rangle = \sqrt{0.85}|D\rangle + \sqrt{0.15}|A\rangle$. Other conventions are the same as in Fig. 1.

($\eta = 1$). This may be comprehended as follows: when the values of I_D and I_A lie within this range as specified in Fig. 4, excitation energy transfer in the donor-acceptor system is quite sensitive to the nature of the bath. Without initial correlations, population oscillation or quantum coherence is easily destroyed by the interaction with the bath compared to the results for other initial system conditions as shown in Fig. 1, even though the system-bath coupling strength remains small. By contrast, the initial correlations contained in the bath state give rise to long-lasting and greatly enhanced amplitude of population oscillation. So, this parameter range may be called as the “sensitive window” of the system. According to Fig. 4, one can say that when I_D and I_A are of the same sign, transfer dynamics in the donor-acceptor system is more sensitive to the bath compared to that of the case when I_D and I_A are of the opposite sign. Consequently, D_S is larger for the initial condition of the same sign of I_D and I_A . So, as previously mentioned, the relative sign of I_D and I_A is quite relevant.

In order to reveal the mechanisms underlying this phenomenon, one may observe the TCL master equation (11). The inhomogeneous term $\text{Tr}_b[\mathcal{I}(t)\tilde{\rho}_I(0)]$ is nonzero only when the initial bath state within the polaron frame differs from thermal equilibrium bath state. It represents the contribution due to the nonequilibrium preparation of initial bath state in the polaron frame, involving the influence of the initial system-bath correlations. Look at the explicit expressions for the homogeneous term, like for example Eq. (56), one can see that each term in Eq. (56) is the multiplication of system operator (e.g., $[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)]$) and bath correlation function [e.g., $\mathcal{K}_{(1),l}(t, \tau)$]. As is known, the bath correlation functions always decay to zero in the long-time limit, which leads the inhomogeneous terms also to decay to zero in the long-time limit. Then, the initial values of system operators are crucial to determine to what extent the inhomogeneous terms can modify the dynamics. For instance, if the initial preparation of $\tilde{\sigma}_3^{(0)}(0)$ denoted by I_A and I_D satisfies $[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)]|_{t=0} = 0$, the effect of this term is zero at time $t = 0$. By the time the system evolves to a state $\tilde{\sigma}(t)$ such that $[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)]$ is appreciably different from zero, $\mathcal{K}_{(1),l}(t, \tau)$ has decayed to almost zero. Therefore, in this case, this term $\mathcal{K}_{(1),l}(t, \tau)[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)]$ plays a negligible role. For general initial system state that does not satisfy $[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)]|_{t=0} = 0$, how the

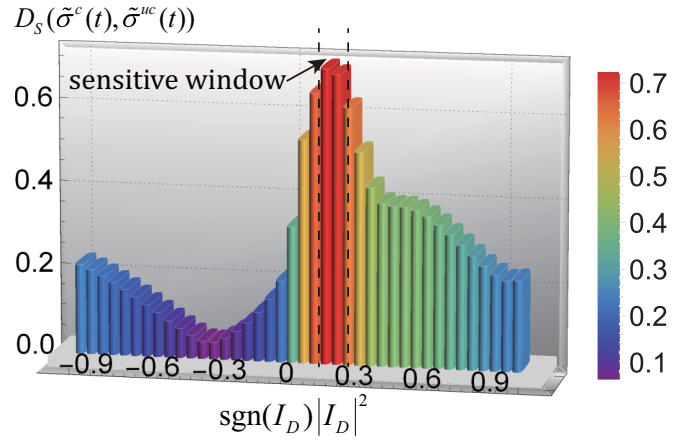


FIG. 6. Cumulative trace distance D_S with respect to different initial system states characterized by $|I_D|^2$ in the units where $J = 1$, $\omega_c = 1$, $\beta = 1$, $\eta = 1.5$, and $\Delta E = \tilde{E}_D - \tilde{E}_A = -1$. The “sensitive window” is centered around $|I_D|^2 \sim 0.15$ with I_D and I_A being the same sign.

initial system state is prepared determines the values of $[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)]$ at time $t = 0$, which in turn influences the effects of $\mathcal{K}_{(1),l}(t, \tau)[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)]$. Consequently, the initial state preparation denoted by I_D and I_A determines the initial values of various inhomogeneous terms shown in Eqs. (20), (52), (56), and the equations as listed in Appendix E, and obviously also determines the values of total inhomogeneous term $\text{Tr}_b[\mathcal{I}(t)\tilde{\rho}_I(0)]$ at time $t = 0$, which in turn influences the effects of total inhomogeneous term on the dynamics. Then, the difference between the total inhomogeneous term with and without initial system-bath correlations is decided by I_D and I_A . In this sense, one can say that the effects of initial system-bath correlations depend sensitively on the initial system state.

Figure 6 is plotted for the cumulative trace distance D_S in the polaron frame with respect to $|I_D|^2$ for the other energetic situation $\Delta E = -1$. It is notable that similarly behavior of the change of cumulative trace distance D_S over $|I_D|^2$ but with opposite trends can be observed. Likewise, the effect of the initial correlations is largely eliminated when I_D and I_A are of the opposite sign, which is also manifested as shown in Fig. 2. The sensitive window of the system appears within the parameter range centered around $|I_D|^2 \sim 0.15$ with I_D and I_A being the same sign. Time evolution of donor population for the initial system condition located in the sensitive window, $|I\rangle = \sqrt{0.15}|D\rangle + \sqrt{0.85}|A\rangle$, is plotted in Fig. 7, from which the same conclusion as that from Fig. 5 can be obtained. Thus, one can infer that the location of the sensitive window, i.e., the initial condition corresponding to the sensitive window appears to be closely related to the donor-acceptor energy difference, that is the intrinsic character of the system. For the parameter settings adopted in this work, when I_D and I_A share the same sign and the squared modulus of the higher-energy site is about 0.85, the transfer dynamics is especially vulnerable to the bath, and therefore the effects of the initial correlations become much more obvious.

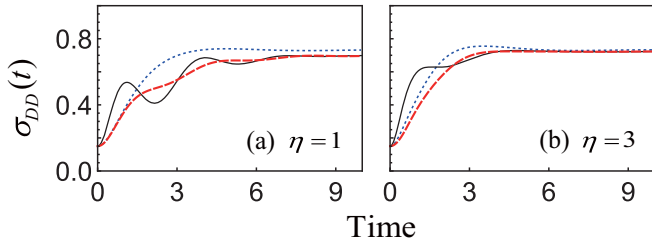


FIG. 7. Time evolution of donor population $\sigma_{DD}(t)$ in the units where $J = 1$, $\omega_c = 1$, $\beta = 1$, and $\Delta E = \tilde{E}_D - \tilde{E}_A = -1$ for different cross-coupling strength η (1 or 3) with initial system state $|I\rangle = \sqrt{0.15}|D\rangle + \sqrt{0.85}|A\rangle$. Other conventions are the same as in Fig. 1.

IV. CONCLUSION

In this work, we extend the resonance energy transfer theory developed in Paper I for an initial coherent system state to account for the influence of the nonequilibrium bath containing the initial system-bath correlations. To this end, a quantum master equation with an initially direct product of the coherent system state and thermal equilibrium bath state is also derived. The inhomogeneous terms are much more complicated than those in Paper I because of the initial coherent system state. The explicit expressions for all of these terms are given in details within the model of super-Ohmic spectral densities. In addition, rate equations based on Förster-Dexter energy transfer theory are derived for comparison.

For a favorable initial system condition, the nonequilibrium which stems from the initial system-bath correlations is capable of giving rise to a larger amplitude of population oscillation. This may be a positive theoretical instance accounting for the long-lived quantum coherence that may be observed under the influence of “hot and wet” surrounding environment of the protein scaffold and solvent. The initial system condition, characterized by the relative phase and magnitude of the coefficients of $|D\rangle$ and $|A\rangle$, is shown to be of crucial importance in determining whether the effects of the initial system-bath correlations would be relevant in the transfer dynamics. We identify a parameter range in which the cumulative trace distance exhibits a dramatic increase. This implies the dynamics is especially vulnerable to the bath such that there exists a greatly obvious difference between the dynamics with initial correlated state and uncorrelated state. So, this parameter range is called the “sensitive window” of the system in which the role of initial correlations on the transfer dynamics is of critical significance.

Besides, the initial system-bath correlations play an increasingly significant role in the strong coupling regime since the modified bath has more access to take effect on the system evolution. Stronger coupling makes the time-dependent evolution overlap with those obtained by the rate equation based on FDET theory. At longer times, the influence of nonequilibrium as a result of initial system-bath correlations will gradually become of no consequence. Assuming super-Ohmic spectral densities, the effects of common bath modes are examined. The results show that smaller values of cross coupling η_c lead to long-lasting quantum coherence. It is because small η_c gives rise to reduced effective system-bath coupling η_s that is directly relevant to the evolution dynamics. Whether the

common bath modes respond differently or similarly to the excitations can influence the duration of population oscillation.

This work is an extension of the theory in Paper I, yet some important issues are not taken into account. In fact, we may expect a more significant effect of the initial system-bath correlations for the case of slow bath ($J < \omega_c$). However, if the bath is slow, there exists the problem of not being precise enough when utilizing the polaron master equation. We hope to make further improvement by employing more precise approaches, like a variational polaron master equation [71,72] and numerical methods such as the quadiabatic propagator path integral [21,22], the hierarchy equations of motion [23–25], and the multiconfiguration time-dependent Hartree approach [26–28]. In addition, a straightforward extension of this work is multistate generalization. A minimal model for the multistate system, for example, consists of donor-bridge-acceptor (D - B - A) states coupled to a phonon bath, which may help to understand the mechanism underlying the remarkably efficient EET across a 100-nm length scale. Then, the off-diagonal elements of reduced system density matrix, which are relevant to the calculation of the two-dimensional electronic spectroscopy in room temperature, are not included in this work. Since they do not commute with the polaron-transformation operator defined above, calculation of these elements in the laboratory frame is therefore more involved. For calculating the two-dimensional spectroscopy, coherent mixture of electronic ground state should also be included. The next one is the spectral density assumed. Here, as mentioned in the main text, with the use of super-Ohmic form spectral density, we ignore subsistent localized vibration modes which also contribute significantly to the exciton dynamics, and overestimate the contribution of the spectral weight at high frequencies of surrounding bath, though analytical expressions for correlation functions can be obtained in terms of this form. Accurately identifying the influence of quantized vibrations in energy transfer within in a variety of actual photosynthetic organisms is of critical importance. We hope to gain a thorough comprehension of the microscopic mechanism of excitation energy transfer in natural light-harvesting complexes by further exploration of these important issues.

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATIONS OF TIME-CONVOLUTIONLESS QUANTUM MASTER EQUATION IN THE POLARON FRAME

The application of the polaron transformation generated by $G = \sum_{i=D,A} \sum_k \frac{g_{ki}}{\omega_k} (b_k^\dagger - b_k) |i\rangle \langle i|$ to Eq. (6) results in the following quantum Liouville equation for the total density

operator in the polaron frame $\tilde{\rho}(t) = e^G \rho(t) e^{-G}$:

$$\frac{d\tilde{\rho}(t)}{dt} = -i\tilde{\mathcal{L}}\tilde{\rho}(t) = -i(\tilde{\mathcal{L}}_s^p + \tilde{\mathcal{L}}_s^c + \mathcal{L}_b)\tilde{\rho}(t), \quad (\text{A1})$$

where $\tilde{\mathcal{L}}$ is the quantum Liouville operator for the polaron-transformed system Hamiltonian $\tilde{H} = e^G H e^{-G} = \tilde{H}_s^p + \tilde{H}_s^c + H_b$ with $\tilde{\mathcal{L}}_s^p$ and $\tilde{\mathcal{L}}_s^c$ corresponding, respectively, to

$$\tilde{H}_s^p = \sum_{i=D,A} \tilde{E}_i |i\rangle \langle i| \quad (\text{A2})$$

and

$$\tilde{H}_s^c = J(B|D\rangle \langle A| + B^\dagger |A\rangle \langle D|), \quad (\text{A3})$$

while H_b remains unchanged. In Eq. (A2), $\tilde{E}_D = E_D - \sum_k \frac{g_{kD}}{\omega_k}$ and $\tilde{E}_A = E_A - \sum_k \frac{g_{kA}}{\omega_k}$. $\lambda_i = \sum_k \frac{g_{ki}}{\omega_k}$ is the site-dependent reorganization energy. In Eq. (A3), the bath operators B and B^\dagger are, respectively,

$$B = \theta_D^\dagger \theta_A = e^{\sum_k \frac{\delta g_k}{\omega_k} (b_k^\dagger - b_k)} \quad (\text{A4})$$

and

$$B^\dagger = \theta_A^\dagger \theta_D = e^{-\sum_k \frac{\delta g_k}{\omega_k} (b_k^\dagger - b_k)}, \quad (\text{A5})$$

where $\delta g_k = g_{kD} - g_{kA}$, and the displacement operators are defined by $\theta_D = e^{-\sum_k \frac{g_{kD}}{\omega_k} (b_k^\dagger - b_k)}$ and $\theta_A = e^{-\sum_k \frac{g_{kA}}{\omega_k} (b_k^\dagger - b_k)}$ with θ_D^\dagger and θ_A^\dagger being their Hermitian conjugates.

The transformed Hamiltonian \tilde{H} can then be divided into two parts in order to identify a small term:

$$\tilde{H} = \tilde{H}_0 + \tilde{H}_1. \quad (\text{A6})$$

In Eq. (A6), the zeroth-order Hamiltonian is defined as

$$\tilde{H}_0 = \tilde{H}_s^p + \langle \tilde{H}_s^c \rangle + H_b = \tilde{H}_{0,s} + H_b, \quad (\text{A7})$$

where the zeroth-order system Hamiltonian term $\tilde{H}_{0,s} = \tilde{H}_s^p + \langle \tilde{H}_s^c \rangle$ is given by

$$\tilde{H}_{0,s} = \sum_{i=D,A} \tilde{E}_i |i\rangle \langle i| + Jw(|D\rangle \langle A| + |A\rangle \langle D|). \quad (\text{A8})$$

$\langle B^\dagger \rangle$ ($\langle B^\dagger \rangle$) represents the average value taken over thermal equilibrium bath state $\rho_b = e^{-\beta H_b} / Z_b$. The bath-induced renormalization factor w is defined as $w = \langle \theta_D^\dagger \theta_A \rangle = \langle \theta_A^\dagger \theta_D \rangle = e^{-\frac{1}{2} \sum_k \frac{\delta g_k^2}{\omega_k} \coth(\frac{\beta \omega_k}{2})}$, which is also called the Franck-Condon factor. The explicit expression for w and λ_i in terms of spectral densities is presented in Appendix B.

The remaining first-order term of \tilde{H} in Eq. (A6) is the interaction Hamiltonian given by

$$\tilde{H}_1 = \tilde{H}_s^c - \langle \tilde{H}_s^c \rangle = J(\tilde{B}|D\rangle \langle A| + \tilde{B}^\dagger |A\rangle \langle D|). \quad (\text{A9})$$

Here,

$$\tilde{B} = \theta_D^\dagger \theta_A - w = e^{\sum_k \frac{\delta g_k}{\omega_k} (b_k^\dagger - b_k)} - w \quad (\text{A10})$$

and

$$\tilde{B}^\dagger = \theta_A^\dagger \theta_D - w = e^{-\sum_k \frac{\delta g_k}{\omega_k} (b_k^\dagger - b_k)} - w. \quad (\text{A11})$$

Therefore, \tilde{H}_1 denotes the fluctuations of the electronic coupling. It is easy to prove $\langle \tilde{B} \rangle = \langle \tilde{B}^\dagger \rangle = 0$, such that \tilde{H}_1 remains small for both weak and strong system-bath couplings In

fact, it is noteworthy that the energy scale related to these fluctuations of the electronic coupling should be the smallest in the system in order to guarantee the validity of second-order QME. As a measure of the magnitude of such fluctuations, one can consider the following parameter [32,34]:

$$\gamma = J \langle |\tilde{B}|^2 \rangle^{1/2} = J(1 - w^2)^{1/2}. \quad (\text{A12})$$

Therefore, in the weak system-bath coupling limit the renormalized system-bath interaction Hamiltonian \tilde{H}_1 vanishes, while it remains bounded by J in the strong coupling limit. Small γ guarantees the smallness of \tilde{H}_1 , and as long as γ is small in comparison to the onsite energy gap $|\Delta E|$ and the cutoff frequency ω_c of spectral densities, truncating the exact quantum master equation to the second order of \tilde{H}_1 is appropriate in theoretical treatment for the entire regime of system-bath couplings.

With the explicit expressions of \tilde{H}_0 and \tilde{H}_1 , we move into the interaction picture with respect to \tilde{H}_0 . The first-order Hamiltonian in the interaction picture is easily obtained as follows:

$$\tilde{H}_{1,I}(t) = J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t)], \quad (\text{A13})$$

where $\tilde{B}(t) = e^{iH_0 t} \tilde{B} e^{-iH_0 t}$ and $\mathcal{T}(t) = e^{i\tilde{H}_0 t} |D\rangle \langle A| e^{-i\tilde{H}_0 t}$. Accordingly, the time evolution of polaron-transformed total density operator $\tilde{\rho}_I(t) = e^{i\tilde{\mathcal{L}}_0 t} \tilde{\rho}(t)$ in the interaction picture is governed by

$$\frac{d\tilde{\rho}_I(t)}{dt} = -i\tilde{\mathcal{L}}_{1,I}\tilde{\rho}_I(t). \quad (\text{A14})$$

The next step is to obtain the QME for the reduced system density operator $\tilde{\sigma}_I(t) = \text{Tr}_b[\tilde{\rho}_I(t)]$. For this purpose, we apply the standard projection operator technique [50] to Eq. (A14). The projection operator \mathcal{P} and its complement \mathcal{Q} are defined as usual: $\mathcal{P}(\cdot) = \rho_b \text{Tr}_b\{\cdot\}$ and $\mathcal{Q} = 1 - \mathcal{P}$. With these definitions in mind, we write a formally exact time-convolutionless (TCL) quantum master equation for $\mathcal{P}\tilde{\rho}_I(t)$ as follows:

$$\frac{d}{dt} \mathcal{P}\tilde{\rho}_I(t) = \mathcal{K}(t)\tilde{\rho}_I(t) + \mathcal{I}(t)\tilde{\rho}_I(0), \quad (\text{A15})$$

with the TCL generator given by

$$\mathcal{K}(t) = \alpha \mathcal{P} \tilde{\mathcal{L}}_{1,I}(t) [1 - \Sigma(t)]^{-1} \mathcal{P} \quad (\text{A16})$$

and

$$\mathcal{I}(t) = \alpha \mathcal{P} \tilde{\mathcal{L}}_{1,I}(t) [1 - \Sigma(t)]^{-1} \mathcal{G}(t) \mathcal{Q}. \quad (\text{A17})$$

In Eqs. (A16) and (A17), α is a dimensionless parameter that keeps track of the order of system-bath coupling strength. Then, a second-order approximation with respect to $\tilde{H}_{1,I}(t)$ is made. Note that $[1 - \Sigma(t)]^{-1}$ and $\mathcal{G}(t)$ in the TCL generators can be expanded in powers of α , therefore, we can truncate the exact expression to second order in $\tilde{H}_{1,I}(t)$. In addition, the inhomogeneous terms in this lowest-order approximation are nonvanishing, so they should be included in deriving the master equation. After taking trace over the bath degrees of freedom, we obtain the TCL quantum master equation for $\tilde{\sigma}_I(t) = \text{Tr}_b[\tilde{\rho}_I(t)]$ in the following form:

$$\frac{d}{dt} \tilde{\sigma}_I(t) = \text{Tr}_b[\mathcal{K}(t)\tilde{\rho}_I(t)] + \text{Tr}_b[\mathcal{I}(t)\tilde{\rho}_I(0)]. \quad (\text{A18})$$

This is Eq. (11) of the main text.

APPENDIX B: REORGANIZATION ENERGY AND THE FRANCK-CONDON FACTOR

The bath-induced reorganization energy $\lambda_i = \sum_k \frac{g_{ki}^2}{\omega_k}$ can be evaluated in terms of the spectral densities defined by Eqs. (73)–(75) and (78)–(81). Then, it reads as

$$\lambda_i = \sum_k \frac{g_{ki}^2}{\omega_k} = \int_0^\infty \frac{J_i(\omega)}{2\omega} d\omega. \quad (\text{B1})$$

In the same way, the Franck-Condon factor that renormalizes the electronic couplings in the polaron frame are shown to be

$$w = \langle \theta_D^\dagger \theta_A \rangle = \langle \theta_A^\dagger \theta_D \rangle = e^{-\frac{1}{2} \sum_k \frac{g_{ik}^2}{\omega_k} \coth\left(\frac{\beta\omega_k}{2}\right)} = \exp\left\{-\frac{1}{2} \int_0^\infty \frac{J_s(\omega)}{\omega^2} \coth\left(\frac{\beta\omega}{2}\right) d\omega\right\}. \quad (\text{B2})$$

This factor captures the influence of the bath modes via incorporating temperature dependence into $\tilde{H}_{0,s}$.

APPENDIX C: BATH CORRELATION FUNCTIONS OF INHOMOGENEOUS TERMS WITH INITIAL UNCORRELATED STATE

For initial uncorrelated state (8) or (16), the bath correlation functions $C_l(t)$ and $\mathcal{F}_{(n),l}(t, \tau)$ due to the nonequilibrium preparation of the initial bath state in the polaron frame are listed below:

$$C_1(t) = w\{f_D(t) - 1\}, \quad (\text{C1})$$

$$C_2(t) = w\{e^{S(0,-t)} f_A(t) - 1\}, \quad (\text{C2})$$

$$C_3(t) = w\{e^{-S(0,-t)} f_D(t) - 1\}, \quad (\text{C3})$$

$$C_4(t) = w\{f_A(t) - 1\}, \quad (\text{C4})$$

$$\mathcal{F}_{(1),1}(t, \tau) = w^2\{[f_D(t)f_D(\tau) - 1]e^{S(0,\tau-t)} - f_D(t) - f_D(\tau) + 2\}, \quad (\text{C5})$$

$$\mathcal{F}_{(2),1}(t, \tau) = w^2\{[f_D(-t)f_D(\tau) - 1]e^{-S(0,\tau-t)} - f_D(-t) - f_D(\tau) + 2\}, \quad (\text{C6})$$

$$\mathcal{F}_{(3),1}(t, \tau) = w^2\{[f_D(t)f_D(-\tau) - 1]e^{-S(0,\tau-t)} - f_D(t) - f_D(-\tau) + 2\}, \quad (\text{C7})$$

$$\mathcal{F}_{(4),1}(t, \tau) = w^2\{[f_D(-t)f_D(-\tau) - 1]e^{S(0,\tau-t)} - f_D(-t) - f_D(-\tau) + 2\}, \quad (\text{C8})$$

$$\mathcal{F}_{(1),2}(t, \tau) = w^2\{e^{S(0,\tau-t)}[e^{S(0,-t)+S(0,-\tau)} f_A(t)f_A(\tau) - 1] - f_A(t)e^{S(0,-t)} - f_A(\tau)e^{S(0,-\tau)} + 2\}, \quad (\text{C9})$$

$$\mathcal{F}_{(2),2}(t, \tau) = w^2\{e^{-S(0,\tau-t)}[e^{-S(0,-t)+S(0,-\tau)} f_A(-t)f_A(\tau) - 1] - f_A(-t)e^{-S(0,-t)} - f_A(\tau)e^{S(0,-\tau)} + 2\}, \quad (\text{C10})$$

$$\mathcal{F}_{(3),2}(t, \tau) = w^2\{e^{-S(0,\tau-t)}[e^{S(0,-t)-S(0,-\tau)} f_A(t)f_A(-\tau) - 1] - f_A(t)e^{S(0,-t)} - f_A(-\tau)e^{-S(0,-\tau)} + 2\}, \quad (\text{C11})$$

$$\mathcal{F}_{(4),2}(t, \tau) = w^2\{e^{S(0,\tau-t)}[e^{-S(0,-t)-S(0,-\tau)} f_A(-t)f_A(-\tau) - 1] - f_A(-t)e^{-S(0,-t)} - f_A(-\tau)e^{-S(0,-\tau)} + 2\}, \quad (\text{C12})$$

$$\mathcal{F}_{(1),3}(t, \tau) = w^2\{e^{S(0,\tau-t)}[e^{-S(0,-t)-S(0,-\tau)} f_D(t)f_D(\tau) - 1] - f_D(t)e^{-S(0,-t)} - f_D(\tau)e^{-S(0,-\tau)} + 2\}, \quad (\text{C13})$$

$$\mathcal{F}_{(2),3}(t, \tau) = w^2\{e^{-S(0,\tau-t)}[e^{S(0,-t)-S(0,-\tau)} f_D(-t)f_D(\tau) - 1] - f_D(-t)e^{S(0,-t)} - f_D(\tau)e^{-S(0,-\tau)} + 2\}, \quad (\text{C14})$$

$$\mathcal{F}_{(3),3}(t, \tau) = w^2\{e^{-S(0,\tau-t)}[e^{-S(0,-t)+S(0,-\tau)} f_D(t)f_D(-\tau) - 1] - f_D(t)e^{-S(0,-t)} - f_D(-\tau)e^{S(0,-\tau)} + 2\}, \quad (\text{C15})$$

$$\mathcal{F}_{(4),3}(t, \tau) = w^2\{e^{S(0,\tau-t)}[e^{S(0,-t)+S(0,-\tau)} f_D(-t)f_D(-\tau) - 1] - f_D(-t)e^{S(0,-t)} - f_D(-\tau)e^{S(0,-\tau)} + 2\}, \quad (\text{C16})$$

$$\mathcal{F}_{(1),4}(t, \tau) = w^2\{[f_A(t)f_A(\tau) - 1]e^{S(0,\tau-t)} - f_A(t) - f_A(\tau) + 2\}, \quad (\text{C17})$$

$$\mathcal{F}_{(2),4}(t, \tau) = w^2\{[f_A(-t)f_A(\tau) - 1]e^{-S(0,\tau-t)} - f_A(-t) - f_A(\tau) + 2\}, \quad (\text{C18})$$

$$\mathcal{F}_{(3),4}(t, \tau) = w^2\{[f_A(t)f_A(-\tau) - 1]e^{-S(0,\tau-t)} - f_A(t) - f_A(-\tau) + 2\}, \quad (\text{C19})$$

$$\mathcal{F}_{(4),4}(t, \tau) = w^2\{[f_A(-t)f_A(-\tau) - 1]e^{S(0,\tau-t)} - f_A(-t) - f_A(-\tau) + 2\}, \quad (\text{C20})$$

where $f_D(t)$ and $f_A(t)$ are introduced:

$$f_D(t) = e^{2i \sum_k g_{kD} \delta g_k \sin(\omega_k t) / \omega_k^2}, \quad (\text{C21})$$

$$f_A(t) = e^{2i \sum_k g_{kA} \delta g_k \sin(\omega_k t) / \omega_k^2}. \quad (\text{C22})$$

Combining the definition of spectral densities (73)–(75), $f_D(t)$ and $f_A(t)$ can be expressed as

$$f_D(t) = e^{2i \int_0^\infty d\omega (\mathcal{J}_{iD}(\omega) / \omega^2) \sin(\omega t)}, \quad (\text{C23})$$

$$f_A(t) = e^{-2i \int_0^\infty d\omega (\mathcal{J}_{iA}(\omega) / \omega^2) \sin(\omega t)}, \quad (\text{C24})$$

with

$$\mathcal{J}_{iD}(\omega) = \mathcal{J}_D(\omega) + \mathcal{J}_c(\omega), \quad (\text{C25})$$

$$\mathcal{J}_{iA}(\omega) = \mathcal{J}_A(\omega) + \mathcal{J}_c(\omega). \quad (\text{C26})$$

It is easy to prove that $f_D(-t) = f_A(t)$ for the case of $\eta_D = \eta_A$ that is chosen for numerical calculations in the main text.

APPENDIX D: EXPRESSIONS FOR THE POLARON-TRANSFORMED INITIAL STATE (24)

Substituting (21) into (24), the polaron-transformed initial state (24) can be decomposed into 16 terms as listed below:

$$\tilde{\rho}_1(0) = \frac{1}{Z'} |I_D|^2 |I_D|^2 |D\rangle \langle D| [\langle D| e^{-\beta \tilde{H}_{0,s}} |D\rangle \rho_b - \alpha \rho_b \langle D| E_0(\beta) |D\rangle], \quad (\text{D1})$$

$$\tilde{\rho}_2(0) = \frac{1}{Z'} |I_D|^2 |I_A|^2 |D\rangle \langle A| [\langle D| e^{-\beta \tilde{H}_{0,s}} |A\rangle \rho_b - \alpha \rho_b \langle D| E_0(\beta) |A\rangle], \quad (\text{D2})$$

$$\tilde{\rho}_3(0) = \frac{1}{Z'} |I_D|^2 I_D I_A^* |D\rangle \langle A| [\langle D| e^{-\beta \tilde{H}_{0,s}} |D\rangle \rho_b B - \alpha \rho_b \langle D| E_0(\beta) |D\rangle B], \quad (\text{D3})$$

$$\tilde{\rho}_4(0) = \frac{1}{Z'} |I_D|^2 I_A I_D^* |D\rangle \langle D| [\langle D| e^{-\beta \tilde{H}_{0,s}} |A\rangle \rho_b B^\dagger - \alpha \rho_b \langle D| E_0(\beta) |A\rangle B^\dagger], \quad (\text{D4})$$

$$\tilde{\rho}_5(0) = \frac{1}{Z'} |I_A|^2 |I_D|^2 |A\rangle \langle D| [\langle A| e^{-\beta \tilde{H}_{0,s}} |D\rangle \rho_b - \alpha \rho_b \langle A| E_0(\beta) |D\rangle], \quad (\text{D5})$$

$$\tilde{\rho}_6(0) = \frac{1}{Z'} |I_A|^2 |I_A|^2 |A\rangle \langle A| [\langle A| e^{-\beta \tilde{H}_{0,s}} |A\rangle \rho_b - \alpha \rho_b \langle A| E_0(\beta) |A\rangle], \quad (\text{D6})$$

$$\tilde{\rho}_7(0) = \frac{1}{Z'} |I_A|^2 I_D I_A^* |A\rangle \langle A| [\langle A| e^{-\beta \tilde{H}_{0,s}} |D\rangle \rho_b B - \alpha \rho_b \langle A| E_0(\beta) |D\rangle B], \quad (\text{D7})$$

$$\tilde{\rho}_8(0) = \frac{1}{Z'} |I_A|^2 I_A I_D^* |A\rangle \langle D| [\langle A| e^{-\beta \tilde{H}_{0,s}} |A\rangle \rho_b B^\dagger - \alpha \rho_b \langle A| E_0(\beta) |A\rangle B^\dagger], \quad (\text{D8})$$

$$\tilde{\rho}_9(0) = \frac{1}{Z'} I_D I_A^* |I_D|^2 |D\rangle \langle D| [\langle A| e^{-\beta \tilde{H}_{0,s}} |D\rangle B \rho_b - \alpha B \rho_b \langle A| E_0(\beta) |D\rangle], \quad (\text{D9})$$

$$\tilde{\rho}_{10}(0) = \frac{1}{Z'} I_D I_A^* |I_A|^2 |D\rangle \langle A| [\langle A| e^{-\beta \tilde{H}_{0,s}} |A\rangle B \rho_b - \alpha B \rho_b \langle A| E_0(\beta) |A\rangle], \quad (\text{D10})$$

$$\tilde{\rho}_{11}(0) = \frac{1}{Z'} I_D I_A^* I_D I_A^* |D\rangle \langle A| [\langle A| e^{-\beta \tilde{H}_{0,s}} |D\rangle B \rho_b B - \alpha B \rho_b \langle A| E_0(\beta) |D\rangle B], \quad (\text{D11})$$

$$\tilde{\rho}_{12}(0) = \frac{1}{Z'} I_D I_A^* I_A I_D^* |D\rangle \langle D| [\langle A| e^{-\beta \tilde{H}_{0,s}} |A\rangle B \rho_b B^\dagger - \alpha B \rho_b \langle A| E_0(\beta) |A\rangle B^\dagger], \quad (\text{D12})$$

$$\tilde{\rho}_{13}(0) = \frac{1}{Z'} I_A I_D^* |I_D|^2 |A\rangle \langle D| [\langle D| e^{-\beta \tilde{H}_{0,s}} |D\rangle B^\dagger \rho_b - \alpha B^\dagger \rho_b \langle D| E_0(\beta) |D\rangle], \quad (\text{D13})$$

$$\tilde{\rho}_{14}(0) = \frac{1}{Z'} I_A I_D^* |I_A|^2 |A\rangle \langle A| [\langle D| e^{-\beta \tilde{H}_{0,s}} |A\rangle B^\dagger \rho_b - \alpha B^\dagger \rho_b \langle D| E_0(\beta) |A\rangle], \quad (\text{D14})$$

$$\tilde{\rho}_{15}(0) = \frac{1}{Z'} I_A I_D^* I_D I_A^* |A\rangle \langle A| [\langle D| e^{-\beta \tilde{H}_{0,s}} |D\rangle B^\dagger \rho_b B - \alpha B^\dagger \rho_b \langle D| E_0(\beta) |D\rangle B], \quad (\text{D15})$$

and

$$\tilde{\rho}_{16}(0) = \frac{1}{Z'} I_A I_D^* I_A I_D^* |A\rangle \langle D| [\langle D| e^{-\beta \tilde{H}_{0,s}} |A\rangle B^\dagger \rho_b B^\dagger - \alpha B \rho_b \langle D| E_0(\beta) |A\rangle B^\dagger]. \quad (\text{D16})$$

Combining the Hermiticity of $\rho_b\langle D|E_0(\beta)|D\rangle$ that has been proved in Ref. [68], it is easy to pick out conjugate pairs: $\tilde{\rho}_2(0)$ and $\tilde{\rho}_5(0)$, $\tilde{\rho}_3(0)$ and $\tilde{\rho}_{13}(0)$, $\tilde{\rho}_4(0)$ and $\tilde{\rho}_9(0)$, $\tilde{\rho}_7(0)$ and $\tilde{\rho}_{14}(0)$, $\tilde{\rho}_8(0)$ and $\tilde{\rho}_{10}(0)$, $\tilde{\rho}_{11}(0)$ and $\tilde{\rho}_{16}(0)$. The remaining terms $\tilde{\rho}_1(0)$, $\tilde{\rho}_6(0)$, $\tilde{\rho}_{12}(0)$, and $\tilde{\rho}_{15}(0)$, are Hermitian operators themselves.

APPENDIX E: EXPRESSIONS FOR INHOMOGENEOUS TERMS WITH INITIAL CORRELATED STATE

Following the procedure as shown in the main text, one can obtain explicit expressions for the inhomogeneous contribution (15) with the remaining terms contained in the the polaron-transformed initial state $\tilde{\rho}(0)$ in Eq. (24) or (42). Results for the first-order term of Eq. (15) are shown in the following. Each conjugate pair of $\tilde{\rho}_i(0)$ are given together for the convenience of written description, except that $\tilde{\rho}_1(0)$, $\tilde{\rho}_6(0)$, $\tilde{\rho}_{12}(0)$, and $\tilde{\rho}_{15}(0)$ are calculated individually:

$$-i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_1(0)]\} = -i\alpha|I_D|^4 \frac{J^2 w^2}{Z'} \int_0^\beta d\lambda \{(1 - e^{S(\lambda,t)})(dazDD - dayDA) \\ + (1 - e^{-S(\lambda,t)})(adx - ady)DA + adzDD\}[\mathcal{T}(t), |D\rangle\langle D|] + \text{H.c.}, \quad (\text{E1})$$

$$-i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_2(0)]\} - i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_5(0)]\} \\ = -i\alpha|I_D|^2|I_A|^2 \frac{J^2 w^2}{Z'} \int_0^\beta d\lambda \{(1 - e^{S(\lambda,t)})(dax + day)DD - dazDA\} + (1 - e^{-S(\lambda,t)})(adyDD - adzDA)\}[\mathcal{T}(t), |D\rangle\langle A|] \\ + i\alpha|I_D|^2|I_A|^2 \frac{J^2 w^2}{Z'} \int_0^\beta d\lambda \{(1 - e^{-S(\lambda,t)})(dax + day)DD - dazDA\} + (1 - e^{S(\lambda,t)})(adyDD - adzDA)\} [|D\rangle\langle A|, \mathcal{T}^\dagger(t)] + \text{H.c.}, \quad (\text{E2})$$

$$-i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_4(0)]\} - i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_9(0)]\} \\ = i\alpha|I_D|^2 I_A I_D^* \frac{J w^2}{Z'} \left\{ \langle D|e^{-\beta\tilde{H}_{0,s}}|A\rangle(1 - e^{-S(0,t)}) + \alpha w J \int_0^\beta d\lambda (a_4(\lambda, t)[(dax + day)DD - dazDA] \right. \\ \left. + a_3(\lambda, t)(adyDD - adzDA) \right\} [\mathcal{T}(t), |D\rangle\langle D|] - i\alpha|I_D|^2 I_A I_D^* \frac{J w^2}{Z'} \left\{ \langle D|e^{-\beta\tilde{H}_{0,s}}|A\rangle(1 - e^{S(0,t)}) \right. \\ \left. + \alpha w J \int_0^\beta d\lambda (a_2(\lambda, t)[(dax + day)DD - dazDA] + a_1(\lambda, t)(adyDD - adzDA)) \right\} [|D\rangle\langle D|, \mathcal{T}^\dagger(t)] + \text{H.c.}, \quad (\text{E3})$$

$$-i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_6(0)]\} = -i\alpha|I_A|^4 \frac{J^2 w^2}{Z'} \int_0^\beta d\lambda \{(1 - e^{S(\lambda,t)})(dax + day)AD - dazAA\} \\ + (1 - e^{-S(\lambda,t)})(adyAD - adzAA)\}[\mathcal{T}(t), |A\rangle\langle A|] + \text{H.c.}, \quad (\text{E4})$$

$$-i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_7(0)]\} - i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_{14}(0)]\} \\ = i\alpha|I_A|^2 I_D I_A^* \frac{J w^2}{Z'} \left\{ \langle A|e^{-\beta\tilde{H}_{0,s}}|D\rangle(1 - e^{S(0,t)}) + \alpha w J \int_0^\beta d\lambda [a_1(\lambda, t)(dazAD - dayAA) + a_2(\lambda, t)(adzAD \right. \\ \left. + (adx - ady)AA)] \right\} [\mathcal{T}(t), |A\rangle\langle A|] - i\alpha|I_A|^2 I_D I_A^* \frac{J w^2}{Z'} \left\{ \langle A|e^{-\beta\tilde{H}_{0,s}}|D\rangle(1 - e^{-S(0,t)}) + \alpha w J \int_0^\beta d\lambda [a_3(\lambda, t)(dazAD \right. \\ \left. - dayAA) + a_4(\lambda, t)(adzAD + (adx - ady)AA)] \right\} [|A\rangle\langle A|, \mathcal{T}^\dagger(t)] + \text{H.c.}, \quad (\text{E5})$$

$$-i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_8(0)]\} - i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_{10}(0)]\} \\ = i\alpha|I_A|^2 I_A I_D^* \frac{J w^2}{Z'} \left\{ \langle A|e^{-\beta\tilde{H}_{0,s}}|A\rangle(1 - e^{-S(0,t)}) + \alpha w J \int_0^\beta d\lambda (a_4(\lambda, t)[(dax + day)AD - dazAA] \right. \\ \left. + a_3(\lambda, t)(adyAD - adzAA) \right\} [\mathcal{T}(t), |A\rangle\langle D|] - i\alpha|I_A|^2 I_A I_D^* \frac{J w^2}{Z'} \left\{ \langle A|e^{-\beta\tilde{H}_{0,s}}|A\rangle(1 - e^{S(0,t)}) \right. \\ \left. + \alpha w J \int_0^\beta d\lambda [a_2(\lambda, t)(dax + day)AD - dazAA] + a_1(\lambda, t)(adyAD - adzAA) \right\} [|A\rangle\langle D|, \mathcal{T}^\dagger(t)] + \text{H.c.}, \quad (\text{E6})$$

$$\begin{aligned}
 & -i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_{11}(0)]\} - i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_{16}(0)]\} \\
 = & i\alpha I_D I_A^* I_D I_A^* \frac{Jw^5}{Z'} \left\{ \langle A|e^{-\beta\tilde{H}_{0,s}}|D\rangle(1 - e^{2S(0,t)}f^2(t)) \right. \\
 & + \alpha wJ \int_0^\beta d\lambda [c_1(\lambda, t)(dazAD - dayAA) + c_2(\lambda, t)(adzAD + (adx - ady)AA)] \left. \right\} [\mathcal{T}(t), |D\rangle\langle A|] \\
 & - i\alpha I_D I_A^* I_D I_A^* \frac{Jw^5}{Z'} \left\{ \langle A|e^{-\beta\tilde{H}_{0,s}}|D\rangle(1 - e^{-2S(0,t)}f^2(-t)) + \alpha wJ \int_0^\beta d\lambda [c_3(\lambda, t)(dazAD - dayAA) \right. \\
 & \left. + c_4(\lambda, t)(adzAD + (adx - ady)AA)] \right\} [|D\rangle\langle A|, \mathcal{T}^\dagger(t)] + \text{H.c.}, \tag{E7}
 \end{aligned}$$

$$\begin{aligned}
 & -i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_{12}(0)]\} \\
 = & i\alpha I_D I_A^* I_D I_A^* \frac{Jw}{Z'} \left\{ \langle A|e^{-\beta\tilde{H}_{0,s}}|A\rangle(1 - f^2(t)) - \alpha wJf^2(t) \int_0^\beta d\lambda [(1 - e^{S(\lambda,t)})(dax + day)AD - dazAA] \right. \\
 & \left. + (1 - e^{-S(\lambda,t)})(adyAD - adzAA) \right\} [\mathcal{T}(t), |D\rangle\langle D|] + \text{H.c.}, \tag{E8}
 \end{aligned}$$

and

$$\begin{aligned}
 & -i\alpha \text{Tr}_b\{J[\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t), \mathcal{Q}\tilde{\rho}_{15}(0)]\} \\
 = & i\alpha I_A I_D^* I_D I_A^* \frac{Jw}{Z'} \left\{ \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle(1 - f^2(-t)) - \alpha wJf^2(-t) \int_0^\beta d\lambda [(1 - e^{S(\lambda,t)})(dazDD - dayDA) \right. \\
 & \left. + (1 - e^{-S(\lambda,t)})(adzDD + (adx - ady)DA)] \right\} [\mathcal{T}(t), |A\rangle\langle A|] + \text{H.c.}, \tag{E9}
 \end{aligned}$$

where

$$a_1(\lambda, t) = (e^{S(\lambda,t)+S(\lambda,0)+S(0,t)} - e^{S(\lambda,0)} - e^{S(0,t)} + 1), \tag{E10}$$

$$a_2(\lambda, t) = (e^{-S(\lambda,t)-S(\lambda,0)+S(0,t)} - e^{-S(\lambda,0)} - e^{S(0,t)} + 1), \tag{E11}$$

$$a_3(\lambda, t) = (e^{-S(\lambda,t)+S(\lambda,0)-S(0,t)} - e^{S(\lambda,0)} - e^{-S(0,t)} + 1), \tag{E12}$$

$$a_4(\lambda, t) = (e^{S(\lambda,t)-S(\lambda,0)-S(0,t)} - e^{-S(\lambda,0)} - e^{-S(0,t)} + 1), \tag{E13}$$

and

$$c_1(\lambda, t) = e^{S(\lambda,t)+2S(\lambda,0)+2S(0,t)}f^2(t) - e^{2S(\lambda,0)} - e^{2S(0,t)}f^2(t) + 1, \tag{E14}$$

$$c_2(\lambda, t) = e^{-S(\lambda,t)-2S(\lambda,0)+2S(0,t)}f^2(t) - e^{-2S(\lambda,0)} - e^{2S(0,t)}f^2(t) + 1, \tag{E15}$$

$$c_3(\lambda, t) = e^{-S(\lambda,t)+2S(\lambda,0)-2S(0,t)}f^2(-t) - e^{2S(\lambda,0)} - e^{-2S(0,t)}f^2(-t) + 1, \tag{E16}$$

$$c_4(\lambda, t) = e^{S(\lambda,t)-2S(\lambda,0)-2S(0,t)}f^2(-t) - e^{-2S(\lambda,0)} - e^{-2S(0,t)}f^2(-t) + 1. \tag{E17}$$

Then, the second-order terms of inhomogeneous contribution (15) are shown to be

$$\begin{aligned}
 & -\alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,l}(t)\tilde{\mathcal{L}}_{1,l}(\tau)\mathcal{Q}\tilde{\rho}_4(0)\} - \alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,l}(t)\tilde{\mathcal{L}}_{1,l}(\tau)\mathcal{Q}\tilde{\rho}_9(0)\} \\
 = & -\alpha^2 J^2 \int_0^t d\tau \left\{ \sum_{l=4,9} \mathcal{K}_{(4),l}(t, \tau)[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)] + \mathcal{K}_{(3),l}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)] \right. \\
 & \left. + \mathcal{K}_{(2),l}(t, \tau)[\mathcal{T}(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_l^{(0)}(0)] + \mathcal{K}_{(1),l}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_l^{(0)}(0)] \right\} + \text{H.c.}, \tag{E18}
 \end{aligned}$$

$$\begin{aligned}
 & -\alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,l}(t)\tilde{\mathcal{L}}_{1,l}(\tau)\mathcal{Q}\tilde{\rho}_7(0)\} - \alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,l}(t)\tilde{\mathcal{L}}_{1,l}(\tau)\mathcal{Q}\tilde{\rho}_{14}(0)\} \\
 = & -\alpha^2 J^2 \int_0^t d\tau \left\{ \sum_{l=7,14} \mathcal{K}_{(1),l}(t, \tau)[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)] + \mathcal{K}_{(2),l}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)] \right. \\
 & \left. + \mathcal{K}_{(3),l}(t, \tau)[\mathcal{T}(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_l^{(0)}(0)] + \mathcal{K}_{(4),l}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_l^{(0)}(0)] \right\} + \text{H.c.}, \tag{E19}
 \end{aligned}$$

$$\begin{aligned}
& -\alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_8(0)\} - \alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_{10}(0)\} \\
& = -\alpha^2 J^2 \int_0^t d\tau \left\{ \sum_{l=8,10} \mathcal{K}_{(4),I}(t, \tau)[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)] + \mathcal{K}_{(3),I}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)] \right. \\
& \quad \left. + \mathcal{K}_{(2),I}(t, \tau)[\mathcal{T}(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_l^{(0)}(0)] + \mathcal{K}_{(1),I}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_l^{(0)}(0)] \right\} + \text{H.c.}, \quad (\text{E20})
\end{aligned}$$

$$\begin{aligned}
& -\alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_{11}(0)\} - \alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_{16}(0)\} \\
& = -\alpha^2 J^2 \int_0^t d\tau \left\{ \sum_{l=11,16} \mathcal{M}_{(1),I}(t, \tau)[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)] + \mathcal{M}_{(2),I}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}(\tau)\tilde{\sigma}_l^{(0)}(0)] \right. \\
& \quad \left. + \mathcal{M}_{(3),I}(t, \tau)[\mathcal{T}(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_l^{(0)}(0)] + \mathcal{M}_{(4),I}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_l^{(0)}(0)] \right\} + \text{H.c.}, \quad (\text{E21})
\end{aligned}$$

$$\begin{aligned}
-\alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_{12}(0)\} & = -\alpha^2 J^2 \int_0^t d\tau \{ \mathcal{N}_{(1)}(t, \tau)[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_{12}^{(0)}(0)] + \mathcal{N}_{(2)}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}(\tau)\tilde{\sigma}_{12}^{(0)}(0)] \\
& \quad + \mathcal{N}_{(3)}(t, \tau)[\mathcal{T}(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_{12}^{(0)}(0)] + \mathcal{N}_{(4)}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_{12}^{(0)}(0)] \} + \text{H.c.}, \quad (\text{E22})
\end{aligned}$$

$$\begin{aligned}
-\alpha^2 \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_{15}(0)\} & = -\alpha^2 J^2 \int_0^t d\tau \{ \mathcal{N}_{(4)}(t, \tau)[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_{15}^{(0)}(0)] + \mathcal{N}_{(3)}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}(\tau)\tilde{\sigma}_{15}^{(0)}(0)] \\
& \quad + \mathcal{N}_{(2)}(t, \tau)[\mathcal{T}(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_{15}^{(0)}(0)] + \mathcal{N}_{(1)}(t, \tau)[\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_{15}^{(0)}(0)] \} + \text{H.c.}, \quad (\text{E23})
\end{aligned}$$

where $\tilde{\sigma}_i^{(0)}(0)$ represents the zeroth-order term of $\tilde{\sigma}_i(0)$ in which the first-order term in α is ignored. One can easily obtain the expressions for in the same way as shown in Eqs. (59) and (60). The bath correlation functions $\mathcal{K}_{(n),I}(t, \tau)$ have been calculated in Eqs. (61)–(68). $\mathcal{M}_{(n),I}(t, \tau)$ and $\mathcal{N}_{(n)}$ are determined as follows:

$$\mathcal{M}_{(1),11}(t, \tau) = \mathcal{M}_{(4),16}(t, \tau) = w^2 \{ e^{S(0, \tau-t)} [e^{2S(0,t)+2S(0,\tau)} f^2(t)f^2(\tau) - 1] - e^{2S(0,t)} f^2(t) - e^{2S(0,\tau)} f^2(\tau) + 2 \}, \quad (\text{E24})$$

$$\mathcal{M}_{(2),11}(t, \tau) = \mathcal{M}_{(3),16}(t, \tau) = w^2 \{ e^{-S(0, \tau-t)} [e^{-2S(0,t)+2S(0,\tau)} f^2(-t)f^2(\tau) - 1] - e^{-2S(0,t)} f^2(-t) - e^{2S(0,\tau)} f^2(\tau) + 2 \}, \quad (\text{E25})$$

$$\mathcal{M}_{(3),11}(t, \tau) = \mathcal{M}_{(2),16}(t, \tau) = w^2 \{ e^{-S(0, \tau-t)} [e^{2S(0,t)-2S(0,\tau)} f^2(t)f^2(-\tau) - 1] - e^{2S(0,t)} f^2(t) - e^{-2S(0,\tau)} f^2(-\tau) + 2 \}, \quad (\text{E26})$$

$$\mathcal{M}_{(4),11}(t, \tau) = \mathcal{M}_{(1),16}(t, \tau) = w^2 \{ e^{S(0, \tau-t)} [e^{-2S(0,t)-2S(0,\tau)} f^2(-t)f^2(-\tau) - 1] - e^{-2S(0,t)} f^2(-t) - e^{-2S(0,\tau)} f^2(-\tau) + 2 \}, \quad (\text{E27})$$

$$\mathcal{N}_{(1)}(t, \tau) = w^2 \{ e^{S(0, \tau-t)} (f^2(t)f^2(\tau) - 1) - f^2(t) - f^2(\tau) + 2 \}, \quad (\text{E28})$$

$$\mathcal{N}_{(2)}(t, \tau) = w^2 \{ e^{-S(0, \tau-t)} (f^2(-t)f^2(\tau) - 1) - f^2(-t) - f^2(\tau) + 2 \}, \quad (\text{E29})$$

$$\mathcal{N}_{(3)}(t, \tau) = w^2 \{ e^{-S(0, \tau-t)} (f^2(t)f^2(-\tau) - 1) - f^2(t) - f^2(-\tau) + 2 \}, \quad (\text{E30})$$

$$\mathcal{N}_{(4)}(t, \tau) = w^2 \{ e^{S(0, \tau-t)} (f^2(-t)f^2(-\tau) - 1) - f^2(-t) - f^2(-\tau) + 2 \}, \quad (\text{E31})$$

where $f(t)$ is defined as

$$f(t) = e^{i \sum_k (\delta g_k / \omega_k)^2 \sin(\omega_k t)}. \quad (\text{E32})$$

Combining the definitions of spectral densities [Eqs. (73)–(75) and (78)–(81)], $f(t)$ can be expressed as

$$f(t) = e^{i \int_0^\infty d\omega [\mathcal{J}_s(\omega) / \omega^2] \sin(\omega t)}. \quad (\text{E33})$$

Then, the relevant coefficients involved in the above expressions are finally determined.

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