Excitation-energy transfer from weak to strong coupling: Role of initial system-bath correlations

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Excitation-energy transfer problems in molecular aggregates have attracted intensive research interests for their fundamental importance. It is usually supposed that the total density operator at time $t = 0$ is a factorized product of single-excitation system state and thermal equilibrium bath state. The Franck-Condon principle ensures that it is a good approximation for a rapid photoexcitation. For natural photosynthesis, however, the transfer process in light-harvesting complexes mostly is initialized from an excited molecule, not direct absorption of a photon. Such intermolecular excitations span the same time scale as the transfer dynamics, and longer than the characteristic time of bath relaxation. Therefore, the initial system-bath correlations should be reconsidered. This work extends the coherent resonant energy transfer theory by including initial system-bath correlations. Within the approach of a second-order time-convolutionless quantum master equation in the polaron frame, a general time evolution equation for the reduced system density operator is obtained, including detailed expressions for both homogeneous and inhomogeneous terms. Two essentially distinct kinds of nonequilibrium are identified: one stems from subsistent initial system-bath correlations, while the other is from the theory of polaron transformation itself. The two kinds of nonequilibrium can accelerate or slow down the dynamical evolution for different energetic situations. Rate equations based on Förster-Dexter theory with and without initial correlations are also derived for comparison. Besides, our conclusions provide a positive perspective accounting for the quantum coherence induced by initial system-bath correlations, which may help to clarify the long-lasting issue of whether quantum phenomenons might be observed under natural conditions of excitation by incoherent solar light, and deepen understandings of the physical mechanisms underlying the natural photosynthesis process.

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I. INTRODUCTION

Excitation-energy transfer (EET) is a ubiquitous process with significant importance in fundamental scientific phenomena and technical implications, such as photosynthesis, photocatalytic chemistry, and operation of optoelectronic devices [1]. For instance, in natural photosynthesis, the sophisticated antenna molecule harvests a photon and creates an excitation in one location (the donor) and passes the excitation to another location (the acceptor), under the influence of the protein scaffold and surrounding solvent environment [2–5]. Quantitative elucidations of excitation dynamics in such systems become an increasingly attractive research area. For this purpose, identification of an appropriate and reliable theory that correctly accounts for the influence of environment is necessary.

In this work, we employ the polaron quantum master equation to study excitation transfer process. This theory combines a second-order time local quantum master equation with small polaron transformation [6–22]. Compared with the well-known Förster-Dexter theory [23,24] and Redfield (or Lindblad) [25,26] type master equation theory, it can interpolate between weak- and strong-coupling regimes and gives a reliable result to describe the transfer dynamics for intermediate system-bath coupling strength, allowing for a consistent exploration from coherent to incoherent evolution with the theoretical solutions according well with the experimental results [27–29], though it is based on a perturbative approach. Meanwhile, it is also more computational acceptable than numerically exact nonperturbative approaches, such as the quasiadiabatic propagator path integral [30,31], the hierarchy equations of motion [32–34], and the multiconfiguration time-dependent Hartree approach [35–37].

The polaron master equation, to our best knowledge, generally assumes a separable initial state with an excitation on the donor while the environment is in a thermal equilibrium state. Physically, this corresponds to preparation of an excited state in the system, which is originally in the ground electronic state with the bath in thermal equilibrium, by an impulsive excitation at time $t = 0$. Thus the system with single excitation has no correlation with surrounding environment or bath. This is a good approximation for photoexcitations, the time duration of which is much shorter than that of excitation transfer dynamics and bath relaxation [27–29], and it is in accordance with the Franck-Condon principle. In general, nevertheless, this initial condition might not be appropriate since it does not account for the subsistent initial correlation between the single excitation system and the bath. For natural photosynthesis, the excitation transfer in light-harvesting complexes mostly is initialized from an excited molecule, not direct absorption of

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a photon [2,3]. Since the duration of intermolecular excitation is the same with that of transfer dynamics, thus longer than the characteristic time of bath relaxation [27–29,38], initial correlations may play a nonignorable role [39–43]. Thus we should consider this initial correlation seriously to assess its influence on the transfer dynamics. Similar investigations of the effects of initial bath preparation focus on a "shifted" initial condition originating from a fluctuation in the bath coordinates of the system site [39–43]. In this work, we assume an initial nonequilibrium bath state which is prepared from a thermal equilibrium state of the total system, and contains initial system-bath correlations. The excitation transfer dynamics subjected to this initial condition is investigated within the polaron master equation formulism that is capable of interpolating between weak- and strong-coupling regimes.

In addition, from the point of view of quantum open system theory, we usually have to adopt various approximations or assumptions to get a master equation such that it can be solved analytically or numerically. One common assumption is that the initial system-bath state is a factorized state with the system and the thermal equilibrium bath being initially uncorrelated. This is justified for the weak system-bath coupling regime as well as a Markovian bath. For natural photosynthetic systems, however, these two conditions become untenable. The system-bath coupling is significant and ever present and, moreover, the surrounding solvent and protein scaffold act as a "memory" for the system [20,44–50]. These lead to the assumption of the initial factorized state to be invalid. Therefore, it is clearly worth investigating to what extent the transfer dynamics are modified by a initial correlated condition. In this respect, several proposals have been made. Many previous works focus on an exactly solvable model with a Hamiltonian of particular form [51–54]. Another one is the correlated projection superoperator technique which considers the relevant part of the dynamics as a correlated system-bath state [55–57]. A third approach is based on the reduced hierarchy equations of motion [58], which are suited for exponentially decaying bath correlation function. A joint transfer-tensor-hierarchy equation approach [59] is also developed to calculate emission spectra of multichromophoric systems. The next proposal considers a reduced propagator of the evolution operator in a Bargmann coherent-state basis on a weak system-bath coupling approximation [60]. In [61], a standard projection operator technique in combination with a weak-coupling expansion is adopted, assuming that the system is initially prepared from a correlated system-bath state such that the initial correlations are inherited due to the interaction terms in the total Hamiltonian. A master equation is constructed to explore the impact of initial system-bath correlations. Since the weak-coupling expansion is employed, it is also valid only in the weak system-bath coupling regime. In this work, we extend this method to go beyond this limit, through combining the weak-coupling expansion with the polaron master equation, and apply it to investigate the transfer process in a donor-acceptor system, the coupling of which to its surrounding bath varies in a wide range.

The remainder of the paper is organized as follows. In Sec. II, a donor-acceptor model is introduced to describe the transfer process. Then we show the formulism of the polaron master equation and explicit initial state preparation for our model. Under the assumption of super-Ohmic spectral densities, a general time evolution equation for the reduced system density operator is obtained, including detailed expressions for both homogeneous and inhomogeneous terms. Two essentially distinct kinds of nonequilibrium are identified in this method. In Sec. III, we focus on the time evolution of the population in the donor state to assess the influence of initial system-bath correlations as well as nonequilibrium preparation due to the polaron transformation under two different energetic situations. We compare the two kinds of nonequilibrium in variant system-bath coupling regimes. Rate equations based on Förster-Dexter theory with and without initial correlations are also derived for comparison. At last, Sec. IV is devoted to concluding remarks. Some details of derivations are left to the Appendix.

II. THEORY

A. Model system

First, we introduce the model to be studied in this paper. We focus on a simple donor-acceptor pair. Each site can be regarded as a two-level system with the energy split ε_i ($i = D$ for donor and $i = A$ for acceptor). $|g\rangle$ stands for the state where both sites are in the ground electronic state at the beginning. $|D\rangle$ ($|A\rangle$) is designated as the case where only D (A) is excited while A (D) remains in the ground electronic state. Here, we are interested in the case of single excitation. The bath is treated as harmonic oscillators with different frequencies. The system, initially in $|g\rangle$, is in equilibrium with the bath. Then, an excitation is transferred from an antenna molecule to the donor-acceptor system, the duration of which is τ_{exc} (above a few hundred femtoseconds). It is generally believed that $\tau_{\text{exc}} \simeq \tau_{\text{EET}}$, where the latter is the time scale of excitation transfer process in the donor-acceptor system, and both in turn are longer than the characteristic time of bath relaxation [27–29,38]. Meanwhile, τ_{exc} and τ_{EET} are assumed to be much smaller than the duration of spontaneous decay to the ground state $|g\rangle$. Then the transfer between $|D\rangle$ and $|A\rangle$ is governed by a Frenkel exciton model Hamiltonian in the single exciton manifold, $H = H_s^p + H_s^c + H_b + H_{sb}$. H_s^p represents population while H_s^c coherence of the system Hamiltonian. H_b is the Hamiltonian of the surrounding bath with $b_k^\dagger$ (b_k) the creation or annihilation operator and ω_k the frequency of the kth phonon mode of bath. H_{sb} is the interaction Hamiltonian describing the coupling of our system to the bath, dominated by site energy fluctuations. g_{ki} is the coupling strength of site i to the kth mode of the bath. These terms are as follows:

$$H_s^p = \sum_{i=D,A} E_i |i\rangle\langle i|, \tag{1}$$

$$H_s^c = J(|D\rangle\langle A| + |A\rangle\langle D|), \tag{2}$$

$$H_b = \sum_k \omega_k b_k^\dagger b_k, \tag{3}$$

$$H_{sb} = \sum_{i=D,A} \sum_k g_{ki}(b_k^\dagger + b_k)|i\rangle\langle i|. \tag{4}$$

The corresponding quantum Liouville equation can then be written as

$$\frac{d\rho(t)}{dt} = -i\mathcal{L}\rho(t) = -i\big(\mathcal{L}_s^p + \mathcal{L}_s^c + \mathcal{L}_b + \mathcal{L}_{sb}\big)\rho(t), \tag{5}$$

where $\mathcal{L}_s^p$, $\mathcal{L}_s^c$, $\mathcal{L}_b$, and $\mathcal{L}_{sb}$ correspond to the Hamiltonians defined above respectively and $\mathcal{L}$ is the total Liouville operator.

With the application of 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. (5), we obtain the following quantum Liouville equation for $\tilde{\rho}(t) = e^G\rho(t)e^{-G}$:

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

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

$$\tilde{H}_s^p = \sum_{i=D,A} \tilde{E}_i|i\rangle\langle i|, \tag{7}$$

$$\tilde{H}_s^c = J(B|D\rangle\langle A| + B^\dagger|A\rangle\langle D|), \tag{8}$$

while H_b remains unchanged. Here, $\tilde{E}_i$ $(i = D, A)$ is shifted by its corresponding site-dependent reorganization energy $\lambda_i = \sum_k \frac{g_{ki}^2}{\omega_k}$, such that $\tilde{E}_i = E_i - \lambda_i$ for the donor $(i = D)$ and acceptor $(i = A)$ site, respectively. In Eq. (8), $B = \theta_D^\dagger\theta_A$, where θ_i is a displacement operator 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 $\theta_D^\dagger$ and $\theta_A^\dagger$ being their Hermitian conjugates.

The transformed Hamiltonian $\tilde{H}$ can be divided into the zeroth- and first-order Hamiltonian as $\tilde{H} = \tilde{H}_0 + \tilde{H}_1$ such that

$$\tilde{H}_0 = \tilde{H}_s^p + \big\langle\tilde{H}_s^c\big\rangle + H_b = \tilde{H}_{0,s} + H_b, \tag{9}$$

where the zeroth-order system Hamiltonian $\tilde{H}_{0,s} = \tilde{H}_s^p + \langle\tilde{H}_s^c\rangle$ can be expressed explicitly as

$$\tilde{H}_{0,s} = \sum_{i=D,A} \tilde{E}_i|i\rangle\langle i| + Jw(|D\rangle\langle A| + |A\rangle\langle D|). \tag{10}$$

In Eq. (10), the so-called Franck-Condon factor is expressed as $w = \langle\theta_D^\dagger\theta_A\rangle = \langle\theta_A^\dagger\theta_D\rangle = e^{-\frac{1}{2}\sum_k \frac{\delta g_k^2}{\omega_k^2}\coth(\frac{\beta\omega_k}{2})}$ where $\delta g_k = g_{kD} - g_{kA}$ is the bath-induced renormalization factor. Here, $\langle\cdots\rangle$ denotes average over $e^{-\beta H_b}/Z_B$. The remaining first-order term of $\tilde{H}$ is given by

$$\tilde{H}_1 = \tilde{H}_s^c - \big\langle\tilde{H}_s^c\big\rangle = J(\tilde{B}|D\rangle\langle A| + \tilde{B}^\dagger|A\rangle\langle D|), \tag{11}$$

where $\tilde{B} = \theta_D^\dagger\theta_A - w$. By construction, $\langle\tilde{H}_1\rangle = 0$ since $\langle\tilde{B}\rangle = \langle\tilde{B}^\dagger\rangle = 0$. It is designed to guarantee the validity of the second-order master equation in both weak and strong system-bath coupling limits. In the formulism of polaron theory, the energy scale related to the fluctuations of the electronic coupling assigned in Eq. (11) should be the smallest in the system. As a measure of the magnitude of such fluctuations, the following parameter can be introduced [12,15]:

$$\gamma = J\langle|\tilde{B}|^2\rangle^{1/2} = J(1 - w^2)^{1/2}. \tag{12}$$

Therefore, the renormalized system-bath coupling Hamiltonian $\tilde{H}_1$ remains bounded by J in the limit of strong system-bath coupling, and vanishes in the weak-coupling limit. Small γ guarantees the smallness of $\tilde{H}_1$, and if γ is sufficiently small, $\tilde{H}_1$ can serve as a proper perturbative term in theoretical treatment and the resulting second-order quantum master equation is an improvement over that with respect to the bare system-bath coupling.

Based on the expressions of $\tilde{H}_0$ and $\tilde{H}_1$, the first-order Hamiltonian in the interaction picture with respect to $\tilde{H}_0$ becomes

$$\tilde{H}_{1,I}(t) = J(\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t)), \tag{13}$$

where $\tilde{B}(t) = e^{iH_bt}\tilde{B}\,e^{-iH_bt}$ and $\mathcal{T}(t) = e^{i\tilde{H}_{0,s}t}|D\rangle\langle A|e^{-i\tilde{H}_{0,s}t}$. Accordingly, the polaron transformed total density operator $\tilde{\rho}_I(t) = e^{i\tilde{\mathcal{L}}_0t}\rho(t)$ in the interaction picture is governed by

$$\frac{d\tilde{\rho}_I(t)}{dt} = -i\tilde{\mathcal{L}}_{1,I}\tilde{\rho}_I(t). \tag{14}$$

To obtain the quantum master equation governing the time evolution of the reduced system density operator $\tilde{\sigma}_I(t) = \mathrm{Tr}_b[\tilde{\rho}_I(t)]$, we apply the standard projection operator technique [62] with the usual definition of the projection operator $\mathcal{P}(\cdot) = \rho_b\mathrm{Tr}_b\{\cdot\}$ and its complement $\mathcal{Q} = 1 - \mathcal{P}$ to Eq. (14). A formally exact time-convolutionless quantum master equation for $\mathcal{P}\tilde{\rho}_I(t)$ can then be derived as follows:

$$\frac{d}{dt}\mathcal{P}\tilde{\rho}_I(t) = \mathcal{K}(t)\tilde{\rho}_I(t) + \mathcal{I}(t)\tilde{\rho}_I(0), \tag{15}$$

with the time-convolutionless generator given by

$$\mathcal{K}(t) = \alpha\mathcal{P}\tilde{\mathcal{L}}_{1,I}(t)[1 - \Sigma(t)]^{-1}\mathcal{P} \tag{16}$$

and

$$\mathcal{I}(t) = \alpha\mathcal{P}\tilde{\mathcal{L}}_{1,I}(t)[1 - \Sigma(t)]^{-1}\mathcal{G}(t)\mathcal{Q}, \tag{17}$$

where α serves as a parameter that keeps track of the order of the system-bath coupling strength. For practical calculations, a commonly used approximation needs to be made, that is the second-order approximation with respect to $\tilde{H}_{1,I}(t)$. Since $[1 - \Sigma(t)]^{-1}$ and $\mathcal{G}(t)$ can be expanded in powers of α, we can truncate the exact expression to second order in $\tilde{H}_{1,I}(t)$. It's notable that the inhomogeneous terms should be included since they are nonvanishing in this lowest-order approximation. Taking the trace over the bath degrees of freedom, the resulting quantum master equation for $\tilde{\sigma}_I(t) = \mathrm{Tr}_b[\tilde{\rho}_I(t)]$ reads

$$\frac{d}{dt}\tilde{\sigma}_I(t) = \mathrm{Tr}_b\big[\mathcal{K}(t)\tilde{\rho}_I(t)\big] + \mathrm{Tr}_b\big[\mathcal{I}(t)\tilde{\rho}_I(0)\big]. \tag{18}$$

The first term on the right-hand side is the homogeneous term

$$\begin{aligned}\mathrm{Tr}_b[\mathcal{K}(t)\tilde{\rho}_I(t)]\\ &= -\alpha^2\int_0^t d\tau\,\mathrm{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\tilde{\sigma}_I(t)\otimes\rho_b\},\end{aligned} \tag{19}$$

which gives the standard second-order terms in the master equation. Inserting the interaction Hamiltonian (13) into (19) and using the cyclic invariance of the bath operators within $\mathrm{Tr}_b[\cdots]$, we obtain the resulting explicit expressions for the homogeneous term (19) (here we set $\alpha = 1$) as follows:

$$\begin{aligned}&\mathrm{Tr}_b[\mathcal{K}(t)\tilde{\rho}_I(t)]\\&\quad= -J^2 e^{\mathcal{S}(0,0)}\int_0^t d\tau\{(e^{\mathcal{S}(0,\tau-t)}-1)[\mathcal{T}(t),\mathcal{T}(\tau)\tilde{\sigma}_I(t)]\\&\qquad+(e^{-\mathcal{S}(0,\tau-t)}-1)[\mathcal{T}^\dagger(t),\mathcal{T}(\tau)\tilde{\sigma}_I(t)]\\&\qquad+(e^{-\mathcal{S}(0,\tau-t)}-1)[\mathcal{T}(t),\mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(t)]\\&\qquad+(e^{\mathcal{S}(0,\tau-t)}-1)[\mathcal{T}^\dagger(t),\mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(t)]\}+\mathrm{H.c.},\end{aligned}\tag{20}$$

in which

$$\begin{aligned}\mathcal{S}(\lambda,t) = &-\frac{1}{2}\sum_k\left(\frac{\delta g_k}{\omega_k}\right)^2\\&\times\left[\coth\left(\frac{\beta\omega_k}{2}\right)(e^{\lambda\omega_k-i\omega_k t}+e^{-\lambda\omega_k+i\omega_k t})\right.\\&\left.-(e^{\lambda\omega_k-i\omega_k t}-e^{-\lambda\omega_k+i\omega_k t})\right].\end{aligned}\tag{21}$$

The second term on the right-hand side of Eq. (18) is the inhomogeneous contribution

$$\begin{aligned}\mathrm{Tr}_b[\mathcal{I}(t)\tilde{\rho}_I(0)] = &-i\alpha\,\mathrm{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\mathcal{Q}\tilde{\rho}_I(0)\}-\alpha^2\int_0^t d\tau\,\mathrm{Tr}_b\\&\times\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\mathcal{Q}\tilde{\rho}_I(0)\},\end{aligned}\tag{22}$$

which is dependent on the initial state. Then all that's left is to substitute the initial condition $\tilde{\rho}_I(0)$ into Eq. (22). Usually, the initial uncorrelated state is employed:

$$\rho(0) = \sigma(0)\otimes\rho_b.\tag{23}$$

It is a direct product of system state $\sigma(0)$ and thermal equilibrium bath state $\rho_b = e^{-\beta H_b}/\mathrm{Tr}_b[e^{-\beta H_b}]$. This is equal to assuming that the system and the bath are interacting with vanishing interaction strength, so they are uncorrelated, and then one switches on the system-bath interaction H_{sb} at a particular instant t which we set to be zero. In most physical situations, however, the system and the bath have interacted for a long time beforehand; then it is practically impossible to avoid the interaction between the system and the bath before $t = 0$. The uncorrelated initial condition Eq. (23) is justified when the system-bath coupling is weak and the impact of the system on bath statistics can be ignored. Meanwhile, the bath is Markovian such that it "forgets" the initial correlations very quickly. For moderate- or strong-coupling strength and non-Markovian baths, which is the case in many realistic situations of experimental interest, like photosynthetic excitation transfer process discussed in this paper, the effect of initial system-bath correlations is non-negligible. The system-bath coupling is significant and ever present, which means it cannot be switched on or off at some particular instant. In most previous literatures, the initial condition (23) considered may be referred to as a "spectroscopic" preparation. This is a good approximation for a rapid photoexcitation from the ground state, which occurs in an antenna molecule that harvests a photon and creates an excitation. And it is in accordance with the Franck-Condon principle. In the experiments with light-harvesting complexes [27–29], a short laser pulse with duration τ_{pulse} (several tens of femtoseconds) much smaller than τ_{EET} (above a few hundred femtoseconds) and bath relaxation (a hundred femtoseconds) is employed to excite the pigment molecule. So this approximation is also tenable. In the biological functioning of systems such as the FMO complexes, however, the transfer process mostly is initialized from an excited molecule, not direct absorption of a photon. Recall that reaction centers or FMO complexes seldom absorb photons directly; instead they accept excitation energy from the antenna [2,3], the duration of which is τ_{exc}, since $\tau_{\mathrm{exc}} \simeq \tau_{\mathrm{EET}}$, which in turn is longer than the characteristic time of bath relaxation [27–29,38]. While the excitation is being transferred into the donor-accepter system, it begins to interact with the surrounding bath. It's been a while since the correlation between the single excitation system and the bath began to establish. Under these circumstances, if we set a particular instant at which the excitation is totally on the donor site as the initial moment for the transfer dynamics we are interested in, the bath state then cannot be a form of thermal equilibrium. Moreover, the surrounding solvent and protein scaffold acts as a "memory" for the system [20,44–50], and the system-bath coupling is significant; therefore, a nonequilibrium initial state of the bath, or that is to say, the initial system-bath correlated condition, is probably more appropriate. With these considerations in mind, it is clearly worthwhile to ask to what extent the transfer dynamics are modified by a initial correlated condition.

On the grounds of the above discussions, we consider the initial state to be of the form as follows, to account for initial correlations between the system and the bath:

$$\rho(0) = \sigma(0)\otimes\frac{\langle D|e^{-\beta H}|D\rangle}{Z},\tag{24}$$

though one may imagine a variety of different forms. The moment at which the excitation is totally on the donor site is set to be $t = 0$, i.e., the initial condition for the system is $\sigma(0) = |D\rangle\langle D|$. The solvent and protein scaffold bath is assumed to have been in equilibrium with the single-excitation system before $t = 0$ and now prepared in a nonequilibrium state $\rho_b(0) = \langle D|e^{-\beta H}|D\rangle/Z$, containing the system-bath correlations that have been established beforehand. Such an initial condition has been studied previously [54,61,63,64]. Without going into details of molecule structure, this assumed form of initial bath state might not be exactly the case for actual photosynthetic excitation transfer processes. One can even say it is some kind of artificial manipulation, rather than a natural process, yet it contains initial system-bath correlations which are usually neglected in previous works on photosynthesis. Physically, Eq. (24) means that the system and the bath, as a whole, are in equilibrium at a inverse temperature $1/\beta$ at time $t < 0$. Then one makes a measurement only on the system at time $t = 0$ to prepare the system in a pure state $\sigma(0) = |D\rangle\langle D|$. The combined system after the measurement can be described by Eq. (24) according to general principles of quantum measurement theory. For excitation transfer in light-harvesting complexes, the assumption of an excitation on the donor site at $t = 0$ may be comprehended as the measurement operation on the system. From Eq. (24), we see that the bath state has been modified due to the finite system-bath interaction, and correlations between the system and bath have been established before the measurement. Then any physical process of preparation of the initial state of the system would disturb the bath state. $\rho_b(0) = \langle D|e^{-\beta H}|D\rangle/Z$ is therefore not a canonical equilibrium state for the bath. It also depends on the system state $|D\rangle$ through the interaction term H_{sb} in total Hamiltonian H. It should be noted that this initial bath state differs from the thermal equilibrium state ρ_b. This is because ρ_b in Eq. (23) is a fixed bath state for all forms of initial system states $\sigma(0)$, which means the system and the bath are completely uncorrelated. Consequently, it is common to say that Eq. (24) contains initial system-bath correlations, though the density matrix in Eq. (23) and Eq. (24) are similar in form. What we should also note is that the initial bath state $\rho_b(0) = \langle D|e^{-\beta H}|D\rangle/Z$ is not equal to the reduced state of the total equilibrium state, i.e., $\mathrm{Tr}_S[e^{-\beta H}]/Z$, either. As a result, after the system preparation, the bath evolves under the action of the total Hamiltonian H and approaches this total system-bath equilibrium state. It is obvious from the initial condition (24) that the bath state depends on the system state $|D\rangle$ due to the interaction term H_{sb} in total Hamiltonian H, as described above, but the initial system state does not depend on the bath as a result of the projective measurement operation. During this evolution, however, the bath begins to have an important effect on the system dynamics, which will be shown below.

Accordingly, this initial condition should be transformed into the polaron frame, and its form can be written as

$$\tilde{\rho}(0) = \tilde{\sigma}(0) \otimes \frac{\langle D|e^{-\beta\tilde{H}}|D\rangle}{Z}, \tag{25}$$

with $\tilde{\sigma}(0) = \sigma(0) = |D\rangle\langle D|$. By expanding the bath state in powers of coupling strength, we can express the initial state (25) in the following form:

$$\tilde{\rho}(0) = \tilde{\sigma}(0) \otimes \left[\rho_b^{(0)} + \rho_b^{(1)} + \cdots\right], \tag{26}$$

with the superscript representing the order of coupling strength. From Eq. (18) we see that only $\rho_b^{(0)}$ and $\rho_b^{(1)}$ contribute to the master equation. Next, to get the explicit expression of $\rho_b^{(0)}$ and $\rho_b^{(1)}$ in Eq. (26), we should expand the initial state (24) in powers of α. For this purpose, the well-known Kubo identity can be employed,

$$e^{\beta(X+Y)} = e^{\beta X}\left(1 + \int_0^\beta d\lambda\, e^{-\lambda X} Y\, e^{\lambda(X+Y)}\right), \tag{27}$$

where X and Y are two arbitrary operators. For our model, these two operators are set to be $X = -(\tilde{H}_{0,s} + H_b)$ and $Y = -\tilde{H}_1$. It is easy to see that, to first order in system-bath coupling strength, $e^{-\beta\tilde{H}}$ can be expanded according to Kubo identity as follows:

$$e^{-\beta\tilde{H}} \approx e^{-\beta(\tilde{H}_{0,s}+H_b)}\left(1 - \int_0^\beta d\lambda\, e^{\lambda(\tilde{H}_{0,s}+H_b)}\alpha\tilde{H}_1 e^{-\lambda(\tilde{H}_{0,s}+H_b)}\right). \tag{28}$$

Then the initial condition (25) in the polaron frame can be expanded as

$$\tilde{\rho}(0) \approx \frac{\tilde{\sigma}(0)}{Z} \otimes \left(\langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle e^{-\beta H_b} - \alpha\, e^{-\beta H_b} E(\beta)\right), \tag{29}$$

where

$$\begin{aligned} E(\beta) = \int_0^\beta d\lambda \big(&e^{\lambda H_b} J\tilde{B}\, e^{-\lambda H_b}\langle D|e^{-\beta\tilde{H}_{0,s}} e^{\lambda\tilde{H}_{0,s}}|D\rangle\langle A|e^{-\lambda\tilde{H}_{0,s}}|D\rangle \\ &+ e^{\lambda H_b} J\tilde{B}^\dagger e^{-\lambda H_b}\langle D|e^{-\beta\tilde{H}_{0,s}} e^{\lambda\tilde{H}_{0,s}}|A\rangle\langle D|e^{-\lambda\tilde{H}_{0,s}}|D\rangle\big) \end{aligned} \tag{30}$$

is thus an operator acting in the Hilbert space of the bath only. It represents the first-order modification in the bath state due to the initial correlations. Z is the partition function such that $\mathrm{Tr}_{s,b}[\tilde{\rho}(0)] = 1$. To the first order in the coupling strength, it can be calculated that

$$Z = \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle - \alpha Z_b\langle E(\beta)\rangle_b = Z_b Z', \tag{31}$$

where $Z' = \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle - \alpha\langle E(\beta)\rangle_b$ and $\langle E(\beta)\rangle_b$ denotes the average value of $E(\beta)$ taken with respect to the equilibrium state $\rho_b = e^{-\beta H_b}/Z_b$. It can be shown from Eq. (30) that this term is generally zero. As a result, Z' is simply $\langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle$, the detailed expression of which is as follows:

$$\begin{aligned} Z' &= \langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle \\ &= \cosh\left(\frac{\beta\Delta\varepsilon}{2}\right) - \frac{\tilde{E}_D - \tilde{E}_A}{\Delta\varepsilon}\sinh\left(\frac{\beta\Delta\varepsilon}{2}\right), \end{aligned} \tag{32}$$

where

$$\Delta\varepsilon = \sqrt{\left(\frac{\tilde{E}_D - \tilde{E}_A}{2}\right)^2 + J^2 w^2}. \tag{33}$$

Now, the explicit expressions for the initial state (25) in powers of coupling strength are determined:

$$\rho_b^{(0)} = \rho_b \tag{34}$$

and

$$\rho_b^{(1)} = -\frac{1}{Z_b Z'}\alpha\, e^{-\beta H_b} E(\beta). \tag{35}$$

B. Master equation with correlated initial state

The next task is to go into the interaction picture, substitute this expanded initial state into Eq. (22), and take the average value of the bath operators with respect to the equilibrium state ρ_b. Then we give the explicit expressions for the inhomogeneous term (22)

$$\begin{aligned} \mathrm{Tr}_b[\mathcal{I}(t)\mathcal{Q}\tilde{\rho}_I(0)] = i\frac{J^2}{Z'}e^{\mathcal{S}(0,0)}\int_0^\beta d\lambda\big[&(e^{\mathcal{S}(\lambda,t)} - 1)\langle D|e^{(\lambda-\beta)\tilde{H}_{0,s}}|D\rangle\langle A|e^{-\lambda\tilde{H}_{0,s}}|D\rangle \\ &+ (e^{-\mathcal{S}(\lambda,t)} - 1)\langle D|e^{(\lambda-\beta)\tilde{H}_{0,s}}|A\rangle\langle D|e^{-\lambda\tilde{H}_{0,s}}|D\rangle\big][\mathcal{T}(t), \tilde{\sigma}_I(0)] + \mathrm{H.c.}, \end{aligned} \tag{36}$$

where $\mathcal{S}(\lambda, t)$ has been defined in Eq. (21). "H.c." denotes the Hermitian conjugates of all the previous terms. It should be noted that the projection operation $\mathcal{Q}\tilde{\rho}_I(0) = \alpha\tilde{\sigma}_I(0) \otimes \frac{1}{Z}[-e^{-\beta\tilde{H}_{0,s}}E(\beta)]$. Consequently, the second term in the inhomogeneous contribution (22) can be ignored, since only the terms up to the second order in coupling strength are taken into account. Thus we say that Eq. (36) represents the impact of initial system-bath correlations. The explicit expressions for Eq. (36) and Eq. (21) are provided in Appendix B.

C. Master equation with uncorrelated initial state

If we choose the initial uncorrelated state Eq. (23), it transforms into $\tilde{\rho}(0) = \tilde{\sigma}(0) \otimes \theta_D^\dagger e^{-\beta H_b}\theta_D/Z_b$, which is also nonequilibrium with respect to the bath due to the polaron transformation applied to the initial thermal equilibrium bath state ρ_b. After the same derivation procedure, we get the corresponding results for the inhomogeneous contribution (22) with the initial uncorrelated state (23), as shown to be

$$\begin{aligned}
&\mathrm{Tr}_b[\mathcal{I}(t)\mathcal{Q}\tilde{\rho}_I(0)]\\
&\quad = -iJ\, e^{\mathcal{S}(0,0)/2}[(f(t)-1)][\mathcal{T}(t), \tilde{\sigma}_I(0)]\\
&\qquad - J^2 e^{\mathcal{S}(0,0)}\int_0^t d\tau\{F_{(1)}(t,\tau)[\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_I(0)]\\
&\qquad + F_{(2)}(t,\tau)[\mathcal{T}^\dagger(t), \mathcal{T}(\tau)\tilde{\sigma}_I(0)]\\
&\qquad + F_{(3)}(t,\tau)[\mathcal{T}(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(0)]\\
&\qquad + F_{(4)}(t,\tau)[\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(0)]\} + \mathrm{H.c.}
\end{aligned} \tag{37}$$

Here, the bath function $f(t) = e^{2i\sum_k g_{nD}\delta g_k \sin(\omega_k t)}$ accounts for the cases where there are common bath modes shared between the donor and the acceptor. And $F_{(1)}(t,\tau) = f_m(t,\tau)\, e^{\mathcal{S}(0,\tau-t)} - f_a(t,\tau)$, $F_{(2)}(t,\tau) = f_m(-t,\tau)e^{-\mathcal{S}(0,\tau-t)} - f_a(-t,\tau)$, $F_{(3)}(t,\tau) = f_m(t,-\tau)e^{-\mathcal{S}(0,\tau-t)} - f_a(t,-\tau)$, and $F_{(4)}(t,\tau) = f_m(-t,-\tau)e^{\mathcal{S}(0,\tau-t)} - f_a(-t,-\tau)$, with $f_m(t,\tau) = f(t)f(\tau) - 1$ and $f_a(t,\tau) = f(t) + f(\tau) - 2$.

The nonzero inhomogeneous term (37) when we choose the initial uncorrelated state (23) corresponds to the contribution of nonequilibrium preparation of initial bath in the polaron frame. This nonequilibrium is different from that induced by initial system-bath correlations in the laboratory frame denoted by Eq. (36). Instead, it is a result of the polaron transformation applied to the initial thermal equilibrium bath state ρ_b, as well as the following projection operator formulism. To be specific, after the application of polaron transformation to the initial uncorrelated state (23), the initial thermal equilibrium state ρ_b therein or the zeroth-order term $\rho_b^{(0)}$ in Eq. (26) becomes $\theta_D^\dagger e^{-\beta H_b}\theta_D/Z_b$, from which we see that the initial bath state now is different from ρ_b (or $\rho_b^{(0)}$). That's to say, the bath is initially in nonequilibrium within the polaron frame. Consequently, applying the complementary super operator $\mathcal{Q}$, which is defined to project onto the irrelevant part of the density matrix, gives a nonzero inhomogeneous term in Eq. (37). From the above analysis, we identify two essentially distinct nonequilibrium: one stems from subsistent initial system-bath correlations as defined by Eq. (24), while the other from the theory of polaron transformation itself. Many previous literatures on the polaron theory [11–13,15] have focused on the role of this transformation-induced nonequilibrium preparation of initial bath state within the polaron frame. In Sec. III, we will compare the influence of these two kinds of nonequilibrium. For this purpose, we should also calculate $\tilde{\sigma}(t)$ without any inhomogeneous terms. Of the three cases, calculations with the initial uncorrelated state can be regarded as a benchmark.

Besides, we introduce two spectral densities to treat the system-bath couplings in the above expressions: $\mathcal{J}_s(\omega) = \sum_k \delta g_k^2 \delta(\omega - \omega_k)$ and $\mathcal{J}_i(\omega) = \sum_k g_{kD}\delta g_k \delta(\omega - \omega_k)$, both of which take into account various situations including the case of common bath modes.

III. RESULTS AND DISCUSSIONS

With the preliminary derivations, we proceed to investigate the transfer dynamics in our donor-acceptor system which can then be used to determine other physical observables of the system. For this purpose, we focus on the time evolution of the population in the donor state $|D\rangle$, $\sigma_{DD}(t) = \mathrm{Tr}_s[|D\rangle\langle D|\sigma(t)]$. In general, when calculating expectation values from a polaron master equation, one should be cautious about the transformation of physical observable between the polaron and the laboratory frame. Nevertheless, since $G = \sum_{i=D,A}\sum_k \frac{g_{ki}}{\omega_k}(b_k^\dagger - b_k)|i\rangle\langle i|$ commutates with $|D\rangle\langle D|$, $e^G|D\rangle\langle D|e^{-G} = |D\rangle\langle D|$, thus

$$\begin{aligned}
\sigma_{DD}(t) &= \mathrm{Tr}_s[|D\rangle\langle D|\sigma(t)]\\
&= \mathrm{Tr}_s[|D\rangle\langle D|e^{-G}\tilde{\sigma}(t)e^{G}]\\
&= \mathrm{Tr}_s[e^G|D\rangle\langle D|e^{-G}\tilde{\sigma}(t)]\\
&= \mathrm{Tr}_s[|D\rangle\langle D|\tilde{\sigma}(t)],
\end{aligned} \tag{38}$$

i.e., the population in state $|D\rangle$ remains unaffected by polaron transformation. We can obtain $\sigma_{DD}(t)$ directly from the master equation for $\tilde{\sigma}_I(t)$. Yet, the off-diagonal elements, which are relevant to the calculation of the linear spectra, do not commute with the polaron transformation operator G defined above; calculating $\sigma_{DA}(t)$ or $\sigma_{AD}(t)$ in the laboratory frame is therefore more involved. Further works will be committed to this aspect.

We perform numerical calculations for the following super-Ohmic spectral densities:

$$\mathcal{J}_s(\omega)/2 = \mathcal{J}_i(\omega) = \frac{\eta}{3!}\frac{\omega^3}{\omega_c^2}e^{-\omega/\omega_c}, \tag{39}$$

where η is the dimensionless system-bath coupling strength. ω_c is the cutoff frequency and its reciprocal represents the relaxation time of the bath. It should be noted that, in realistic situations, the localized vibration modes described by a delta function also contribute significantly to the spectral density [20,44–50]. This goes beyond the scope of this work and for simplicity only the continuous part is accounted for. Meanwhile, the continuous part of realistic spectral densities in photosynthesis-related EET typically have more weight at low frequencies than a super-Ohmic density [65]. It is thus more appropriate to adopt an Ohmic or sub-Ohmic form. Nevertheless, this spectral density of Eq. (39) provides a simple picture for describing the system-bath coupling and allows for analytical expressions for correlation functions as has been

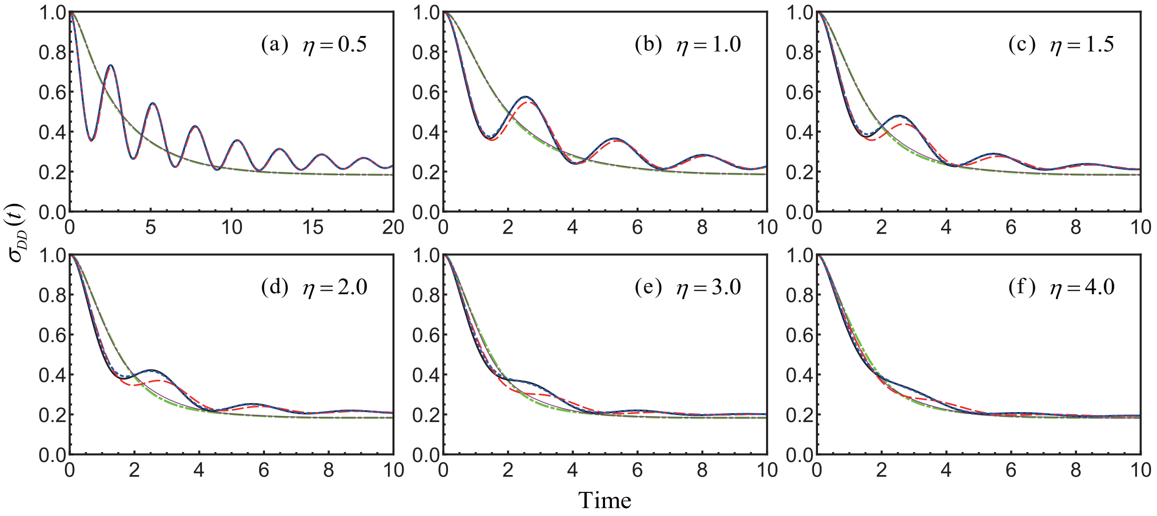

FIG. 1. Time evolution of donor population $\sigma_{DD}(t)$ in the units where $J = 1$, $\omega_c = 1.5$, $\beta = 1$, and $\Delta E = \tilde{E}_D - \tilde{E}_A = 1.5$ for different values of system-bath coupling strength η. Black solid curves correspond to the results with initial correlations represented by inhomogeneous term (36). Red dashed curves are for the case without the initial correlations but the inhomogeneous term (37) exists. Blue dotted curves are for the case without any inhomogeneous terms. Thin purple curves correspond to the results from the theory of Förster-Dexter energy transfer (FDET) with initial correlations (24), while green dot-dashed curves correspond to the results without initial correlations.

studied previously [11–22] in terms of polaron formulism. Especially, it avoids complications such as a well-known infrared divergence, which would be an issue for the case of Ohmic spectral density leading to electronic couplings being renormalized to zero in spite of the system-bath coupling strength. With these spectral densities, it is easy to write the detail expressions for the bath-induced Franck-Condon factor w, $\mathcal{S}(\lambda, t)$ and the bath function $f(t) = e^{2i\sum_k g_{nD}\delta g_k \sin(\omega_k t)}$, as well as the relevant coefficients involved in Eq. (37) (see Appendixes A and B). Time-dependent donor populations are calculated by solving Eq. (18).

For the system operators in Eqs. (20), (36), and (37), it is convenient to move into the exciton basis (see Appendix C). For each of the three cases described in Sec. II, calculations are performed with and without the inhomogeneous term (36) or (37) for comparison. For each case, two different energetic situations are taken into consideration: $\Delta E = \tilde{E}_D - \tilde{E}_A = \pm 1.5$. Throughout the paper, the parameters are $J = 1$, $\omega_c = 1.5$, and $\beta = 1$. In the entire regime of system-bath coupling strength, γ remains smaller than the onsite energy gap $|\Delta E|$, as well as the the characteristic frequency ω_c of spectral densities, which guarantees the accuracy of the present polaron master equation [12,15].

For comparison, calculations of time-dependent evolution based on the following rate equation for the case of initial correlated state (24) are also performed:

$$\frac{d}{dt}\sigma_{DD}(t) = -k_{DA}(t)\sigma_{DD}(t) + k_{AD}(t)[1 - \sigma_{DD}(t)] + I(t), \tag{40}$$

where $k_{DA}(t)$ is the time-dependent Förster-Dexter rate [23,24,66] from D to A, while $k_{AD}(t)$ from A to D. $I(t)$ represents the effects of initial system-bath correlations (24). The theory of Förster-Dexter energy transfer (FDET) gives an account of a Pauli-type population dynamics of individual chromophores being excited or deexcited, in terms of hopping processes. It is a successful application of Fermi's golden rule that relies on the smallness of the electronic resonance interactions. Expressions for $k_{DA(AD)}(t)$ and $I(t)$ are presented in Appendix D.

A. ΔE = 1.5

The time evolution of donor population σ_{DD} is plotted in Fig. 1 for $\Delta E = 1.5$. We observe that the initial correlations play an ignorable role in the weak-coupling regime according to the results of both polaron and Förster-Dexter theory. Physically, the system interacts weakly with the bath, so the bath is scarcely modified; the influence of initial correlations is insignificant. It is the same with the nonequilibrium induced by polaron transformation. Weak system-bath couplings make the modified bath have less access to affect the system evolution. Thus the three curves obtained by the polaron master equation nearly overlap for small η, and the same is true for the two curves obtained by the rate equation. Meanwhile, the polaron dynamics shows large oscillation that is not captured by Förster-Dexter theory, and the stationary limits calculated from the two theories also exhibit significant distinctions, since in the weak system-bath coupling regime Förster-Dexter theory becomes invalid, which can also be interpreted as the manifestation of quantum coherence that counteracts the results of the detailed balance based on the rate equation.

In moderate-coupling regimes, however, a visible difference between polaron dynamics with and without initial correlations emerges as illustrated in Fig. 1. The initial correlations seem to be capable of accelerating evolution, especially in primary stages. Nevertheless, the nonequilibrium due to the polaron transformation seems to slow down the dynamics if one compares the red-dashed curves and the blue dotted curves. As a result, the evolution rate of dynamics with initial system-bath correlations in the laboratory frame (black solid

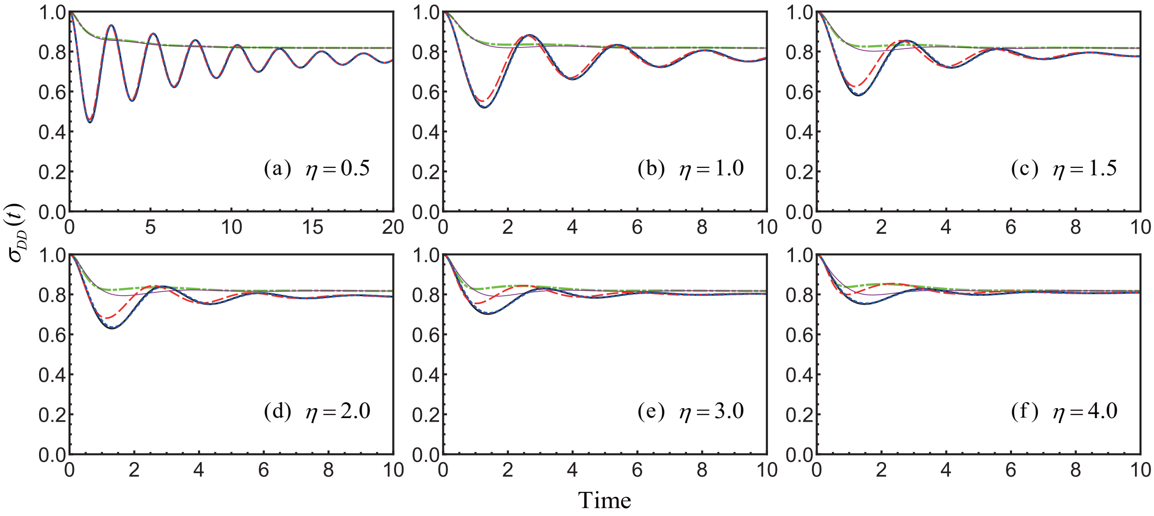

FIG. 2. Time evolution of donor population $\sigma_{DD}(t)$ for $\Delta E = \tilde{E}_D - \tilde{E}_A = -1.5$ and other conventions are the same as in Fig. 1.

curves) is almost the same as that without initial system-bath correlations either in the laboratory frame or in the polaron frame (blue dotted curves). The effects on the evolution rate of these two kinds of nonequilibrium neutralize each other. In addition, the initial system-bath correlations cause larger oscillation, especially for moderate-coupling strength ($1.5 < \eta < 3$). In this respect, the nonequilibrium due to the polaron transformation seems to damp the oscillation amplitude. As well, the effects on the oscillation amplitude of these two kinds of nonequilibrium neutralize each other. Consequently, the evolution curves of black solid and blue dotted have few differences. Besides, with further increasing η, the system-bath coupling becomes strong enough to damp the oscillation. The time-dependent donor population in the primary stage as well as stationary regime gradually overlap with those obtained by the rate equation. This is because of the successful application of Förster-Dexter theory in describing energy transfer when the electronic coupling strength between chromopheres is weak in comparison to their interaction with the bath degrees of freedom.

We also note that, as time goes on, the difference between the dynamics with and without initial correlations diminishes, which is true for both polaron and Förster-Dexter theory. After a period of evolution, the transfer dynamics goes to the Markovian limit as the upper integration limit becomes ∞ instead of t, and the inhomogeneous terms (37) decay to zero and therefore have an negligible contribution to system evolution. We can also prove numerically that Eq. (36) decays to zero in the long-time limit. Physically, at longer times, the system will gradually "forget" the influence of nonequilibrium, both from initial system-bath correlations in laboratory frame and from polaron transformation. Therefore, in the long-time limit, the three curves of polaron dynamics overlap as well. By the way, when $\Delta E = 1.5$, the slight difference between the Förster-Dexter dynamics with and without initial system-bath correlations can be observed only for moderate- and strong-coupling strength in a nonstationary regime, and to less extents than those between polaron dynamics.

B. $\Delta E = -1.5$

Figure 2 displays the case of the other energetic situation $\Delta E = -1.5$. One can observe that, for both polaron and Förster-Dexter theory, the dynamics exhibit no difference for small η, and a visible difference between the dynamics with and without initial correlations emerges in moderate- and strong-coupling regimes. Conversely, however, the initial system-bath correlations slow down the evolution with increasing η when $\Delta E = -1.5$, which is also the case of the results based on the Förster-Dexter rate equation, while the nonequilibrium preparation within the polaron frame accelerates the dynamics. Consequently, the evolution rates in these two cases are almost the same as shown by the red-dashed curves and the blue dotted curves in Fig. 2. What's more, we find that, analogous to the results for the case of $\Delta E = 1.5$, the initial system-bath correlation is capable of enlarging the oscillation amplitude for moderate-coupling strength ($1.5 < \eta < 3$), while the nonequilibrium due to the polaron transformation damp the oscillation. This is a positive instance accounting for the quantum coherence induced by initial system-bath correlations, and also provides the possibilities to interpret the origin of quantum coherence that might be observed under natural conditions of excitation by incoherent solar light, in view of the fact that a series of photosynthesis experiments have been performed utilizing coherent laser radiation as a resource. In fact, we may expect a more significant effect for the case of slow bath ($J > \omega_c$). Note that, however, the polaron master equation is not precise enough when the bath is slow [21]. This difficulty can be overcome by employing a variational polaron master equation, or numerical methods, such as the quasiadiabatic propagator path integral [30,31], the hierarchy equations of motion [32–34], and the multiconfiguration time-dependent Hartree approach [35–37]. Again, the effects on both the dynamical evolution rate and the oscillation amplitude of these two kinds of nonequilibrium neutralize each other. Therefore, the black solid and blue dotted evolution curves also nearly overlap, which is basically the same with the results from Fig. 1. In addition, with increasing η, the dynamical evolution predicted by the two theories gradually approaches in both early stage and stationary regime, for the same reason as the case of $\Delta E = 1.5$.

It can also be observed from Fig. 2 that the difference between these three curves is obvious only in primary stages. At longer times, the influence of nonequilibrium both from initial system-bath correlations in laboratory frame and from polaron transformation will gradually become much less significant or of no consequence. Again, the three curves of polaron dynamics overlap as well in the long-time limit. The same conclusion can be obtained for Förster-Dexter theory as well.

IV. CONCLUSION

In this work, we have investigated the excitation-energy transfer dynamics of the donor-acceptor model subjected to the conditions of initial system-bath correlations. We assume a product form of initial state, in which the bath part contains correlations with the single-excitation system. The polaron quantum master equation is employed such that we can investigate the dynamics from the weak to strong system-bath coupling regime. We apply the weak-coupling expansion to the initial bath state within the polaron formulism. Dynamical master equations with an initially direct product of the system and thermal equilibrium bath state are also derived. For comparison, calculations of time-dependent evolution based on the Förster-Dexter rate equation are also performed.

Two kinds of nonequilibrium are identified: one stems from subsistent initial system-bath correlations, while the other from the theory of polaron transformation itself. Under the assumption of super-Ohmic spectral densities, we obtain detailed expressions for both the homogeneous and inhomogeneous terms, the latter of which accounts for the contributions of the two kinds of nonequilibrium. The effects of two kinds of nonequilibrium for different system-bath coupling strength η and the evolution time t are discussed in detail under two different energetic situations $\Delta E = \pm 1.5$. We find that, when $\Delta E = 1.5$, the initial correlations can accelerate dynamical evolution, especially for moderate system-bath coupling, while the nonequilibrium due to the polaron transformation seems to slow down the dynamics. When $\Delta E = -1.5$, it is just the reverse: the nonequilibrium as a result of the polaron transformation speeds up the dynamics in moderate and strong system-bath coupling regimes, while the initial system-bath correlations slow down the evolution rates. These phenomena can also be observed for Förster-Dexter dynamics, but to less extent than those between polaron dynamics especially when $\Delta E = 1.5$. More importantly, the initial system-bath correlations cause larger oscillation, while the nonequilibrium due to the polaron transformation damp the amplitude of oscillation. This provides a positive perspective in that it suggests initial system-bath correlations induced quantum coherence, and also helps to clarify the long-lasting issue of whether the quantum phenomena might be observed under natural conditions of excitation by incoherent solar light rather than utilizing coherent laser radiation as a resource. Besides, further increasing system-bath coupling strength damps the oscillative evolution and makes the time-dependent population overlap with those obtained by the rate equation, which is a manifestation of the validity of Förster-Dexter theory in the strong system-bath coupling regime.

At longer times, the influence of nonequilibrium, both from initial system-bath correlations in laboratory frame and from polaron transformation, gradually vanishes since both kinds of inhomogeneous contributions decay to zero in the long-time limit. Their influence gradually becomes much less significant or of no consequence such that the system will forget the nonequilibrium effects from both initial system-bath correlations in the laboratory frame and polaron transformation. For the dynamical evolution calculated from Förster-Dexter theory, the same conclusion can be obtained as well.

We hope these may help to deepen the understanding of the excitation transfer process in the natural photosynthesis process.

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APPENDIX A: REORGANIZATION ENERGY AND THE FRANCK-CONDON FACTOR

The bath induced reorganization energy and the Franck-Condon factor can be evaluated in terms of spectral densities that describe the system-bath couplings. With the definitions given by Eq. (39), the reorganization energy can be expressed as

$$\lambda_i = \sum_k \frac{g_{ki}^2}{\omega_k} = \int_0^\infty \frac{J_i(\omega)}{2\omega} d\omega \tag{A1}$$

and the Franck-Condon factor

$$\begin{aligned} w &= \langle \theta_D^\dagger \theta_A \rangle = \langle \theta_A^\dagger \theta_D \rangle = e^{-\frac{1}{2}\sum_k \frac{\delta g_k^2}{\omega_k^2} \coth\left(\frac{\beta\omega_k}{2}\right)} \\ &= \exp\left\{-\frac{1}{2}\int_0^\infty \frac{J_s(\omega)}{\omega^2} \coth\left(\frac{\beta\omega}{2}\right) d\omega\right\}. \end{aligned} \tag{A2}$$

The electronic couplings in the polaron frame are renormalized by the Franck-Condon factor w, incorporating temperature dependence into $\tilde{H}_{0,s}$ to capture the influence of the bath on system evolution.

Besides, the bath function $f(t)$ can also be expressed as

$$f(t) = e^{2i\int_0^\infty d\omega \frac{J_i(\omega)}{\omega^2} \sin(\omega t)}. \tag{A3}$$

Then we can easily write the detailed expressions for the relevant coefficients involved in Eq. (37).

APPENDIX B: DERIVATIONS OF THE EXPRESSION FOR EQ. (36) AND EQ. (21)

To determine the explicit expressions for Eq. (36) and Eq. (21), we invoke the identities

$$\begin{aligned} e^{\lambda\tilde{H}_{0,s}} |D\rangle\langle A| e^{-\lambda\tilde{H}_{0,s}} &= dax|D\rangle\langle A| + day(|D\rangle\langle A| - |A\rangle\langle D|) \\ &\quad + daz(|D\rangle\langle D| - |A\rangle\langle A|) \end{aligned} \tag{B1}$$

and

$$e^{\lambda\tilde{H}_{0,s}}|A\rangle\langle D|e^{-\lambda\tilde{H}_{0,s}} = adx|A\rangle\langle D| + ady(|D\rangle\langle A| - |A\rangle\langle D|) + adz(|D\rangle\langle D| - |A\rangle\langle A|), \tag{B2}$$

where

$$\begin{aligned} dax &= \frac{(\tilde{E}_D - \tilde{E}_A)^2}{\Delta\varepsilon^2}\cosh(\lambda\Delta\varepsilon) + \frac{4J^2w^2}{\Delta\varepsilon^2} + \frac{\tilde{E}_D - \tilde{E}_A}{\Delta\varepsilon}\sinh(\lambda\Delta\varepsilon), \\ day &= \frac{2J^2w^2}{\Delta\varepsilon^2}[\cosh(\lambda\Delta\varepsilon) - 1], \\ daz &= \frac{Jw(\tilde{E}_D - \tilde{E}_A)}{\Delta\varepsilon^2}[1 - \cosh(\lambda\Delta\varepsilon)] - \frac{Jw}{\Delta\varepsilon}\sinh(\lambda\Delta\varepsilon), \end{aligned} \tag{B3}$$

and

$$\begin{aligned} adx &= \frac{(\tilde{E}_D - \tilde{E}_A)^2}{\Delta\varepsilon^2}\cosh(\lambda\Delta\varepsilon) + \frac{4J^2w^2}{\Delta\varepsilon^2} - \frac{\tilde{E}_D - \tilde{E}_A}{\Delta\varepsilon}\sinh(\lambda\Delta\varepsilon), \\ ady &= \frac{2J^2w^2}{\Delta\varepsilon^2}[1 - \cosh(\lambda\Delta\varepsilon)], \\ adz &= \frac{Jw(\tilde{E}_D - \tilde{E}_A)}{\Delta\varepsilon^2}[1 - \cosh(\lambda\Delta\varepsilon)] + \frac{Jw}{\Delta\varepsilon}\sinh(\lambda\Delta\varepsilon). \end{aligned} \tag{B4}$$

The expression of $\langle D|e^{-\beta\tilde{H}_{0,s}}|D\rangle$ has been shown in Eq. (32). With this in mind, we obtain the final expressions for Eqs. (36) and (21), respectively:

$$\begin{aligned} &\mathrm{Tr}_b[\mathcal{I}(t)\mathcal{Q}\tilde{\rho}_I(0)] \\ &= i\frac{J^2}{Z'}e^{S(0,0)}\int_0^\beta d\lambda[(e^{S(\lambda,t)} - 1)(dazDD - dayDA) \\ &+ (e^{-S(\lambda,t)} - 1)[(adx - ady)DA + adzDD]] \\ &\times [\mathcal{T}(t), \tilde{\sigma}_I(0)] + \mathrm{H.c.}, \end{aligned} \tag{B5}$$

in which

$$\begin{aligned} S(\lambda, t) = -\frac{1}{2}\int_0^\infty d\omega \frac{J_s(\omega)}{\omega^2} &\times \left[\coth\left(\frac{\beta\omega}{2}\right)(e^{\lambda\omega - i\omega t} + e^{-\lambda\omega + i\omega t}) \right. \\ &\left. - (e^{\lambda\omega - i\omega t} - e^{-\lambda\omega + i\omega t})\right]. \end{aligned} \tag{B6}$$

APPENDIX C: EXPRESSIONS OF THE SYSTEM OPERATORS IN THE EXCITON BASIS

For numerical calculations, it is convenient to express the system operators in the renormalized exciton basis in which $\tilde{H}_{s,0}|\pm\rangle = \varepsilon_\pm|\pm\rangle$. The eigenvalues of the zeroth-order term $\tilde{H}_{s,0}$ are

$$\varepsilon_\pm = \tfrac{1}{2}[(\tilde{E}_D + \tilde{E}_A) \pm \sqrt{4J^2w^2 + (\tilde{E}_D - \tilde{E}_A)^2}], \tag{C1}$$

where $\tilde{E}_i = E_i - \lambda_i$, $(i = D, A)$ is the shifted energy for the donor and acceptor site, respectively, with the corresponding site-dependent reorganization energy λ_i defined in Eq. (A1). w is the Franck-Condon factor defined in Eq. (A2). The corresponding eigenstates are related with local excitation states $|D\rangle$ and $|A\rangle$ through

$$|+\rangle = \cos\frac{\theta}{2}|D\rangle + \sin\frac{\theta}{2}|A\rangle, \tag{C2}$$

$$|-\rangle = \sin\frac{\theta}{2}|D\rangle - \cos\frac{\theta}{2}|A\rangle, \tag{C3}$$

where $\tan\theta = 2Jw/(\tilde{E}_D - \tilde{E}_A)$. Inserting Eqs. (C2) and (C3) into Eqs. (20), (B5), and (37), 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 quantum master equation (18).

APPENDIX D: DERIVATION OF FORSTER-DEXTER RATE EQUATION

The theory of Förster-Dexter energy transfer that describes hopping dynamics treats the bare electronic coupling as a perturbation. The total Hamiltonian of the Frenkel exciton model studied in this paper now can be divided into the zeroth- and first-order part as follows:

$$H_0 = H_s^p + H_b + H_{sb}, \tag{D1}$$

$$H_1 = H_s^c, \tag{D2}$$

where H_s^p, H_b, H_{sb}, and H_s^c have been defined in Eqs. (1)–(4). In the interaction picture of H_0, $\rho_I(t) = e^{\frac{i}{\hbar}\mathcal{L}_0 t}\rho(t)$ is governed by the following time evolution equation:

$$\frac{d}{dt}\rho_I(t) = -\frac{i}{\hbar}\mathcal{L}_I(t)\rho_I(t), \tag{D3}$$

where $\mathcal{L}_0$ is the Liouville operator for H_0, and $\mathcal{L}_I(t)$ is for

$$H_1(t) = e^{iH_0t/\hbar}H_1e^{-iH_0t/\hbar}. \tag{D4}$$

Applying the standard projection operator technique [62] and following the same procedures of deriving the polaron master equation shown in the main text, one can obtain the rate equation (40) for the case of initial correlated state Eq. (24). The time-dependent Förster-Dexter rate from D to A is given by [23,24,66]

$$\begin{aligned} k_{DA}(t) = \frac{2J^2}{\hbar^2}e^{S(0,0)}\mathrm{Re}\int_0^t d\tau & \\ \times [e^{i(E_D - E_A)\tau/\hbar}f(t)f(\tau - t)(e^{-S(0,-\tau)} - 1)], & \end{aligned} \tag{D5}$$

while $k_{AD}(t)$ is the same as $k_{DA}(t)$ except for the replacement $E_D - E_A \to E_A - E_D$. In (D5), note that a contribution of zero phonon line to the rate has been subtracted within the integrand, which removes the singularity that can exist for the super-Ohmic spectral density adopted here.

The effects of initial system-bath correlations are involved in $I(t)$ which has a similar expression to the Förster-Dexter rate:

$$\begin{aligned} I(t) = \frac{2J^2}{\hbar^2}e^{S(0,0)}\mathrm{Re}\int_0^t d\tau[e^{i(E_D - E_A)\tau/\hbar} & \\ \times [f(t)f(\tau - t) - 1](e^{-S(0,-\tau)} - 1)]. & \end{aligned} \tag{D6}$$

If the initial state is uncorrelated [Eq. (23)], the time-dependent Förster-Dexter rates $k_{DA(AD)}(t)$ in the rate equation remain exactly the same, and the only difference lies in that $I(t) = 0$.

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