

Theory of coherent resonance energy transfer

Seogjoo Jang,^{1,a)} Yuan-Chung Cheng,² David R. Reichman,³ and Joel D. Eaves³

¹Department of Chemistry and Biochemistry, Queens College of the City University of New York, 65-30 Kissena Boulevard, Flushing, New York 11367, USA

²Department of Chemistry, University of California, Berkeley, California 94720, USA

³Department of Chemistry, Columbia University, 3000 Broadway, New York, New York 10027, USA

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A theory of coherent resonance energy transfer is developed combining the polaron transformation and a time-local quantum master equation formulation, which is valid for arbitrary spectral densities including common modes. The theory contains inhomogeneous terms accounting for nonequilibrium initial preparation effects and elucidates how quantum coherence and nonequilibrium effects manifest themselves in the coherent energy transfer dynamics beyond the weak resonance coupling limit of the Förster and Dexter (FD) theory. Numerical tests show that quantum coherence can cause significant changes in steady state donor/acceptor populations from those predicted by the FD theory and illustrate delicate cooperation of nonequilibrium and quantum coherence effects on the transient population dynamics. © 2008 American Institute of Physics.

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The resonance energy transfer (RET) of electronic excitations¹ is an indispensable step in photosynthesis² and organic optoelectronic processes.³ It also has a powerful spectroscopic application called fluorescence RET (FRET), which can determine 2–10 nm distances in biological systems.⁴ How RET occurs is well understood at the level of the Förster and Dexter (FD) theory,^{5–7} where the transfer rate can be calculated assuming incoherent quantum mechanical transitions. What happens if the transition falls in the coherent regime has become a topic of prime interest in recent years.^{8–11} The utilization of coherence may lead to highly efficient solar energy conversion devices¹² and has significant implications in enhancing the sensitivity of FRET at short distances.¹³ However, the presence of coherence makes the definition of a transfer rate ambiguous, and assessing its effect on the overall RET dynamics has remained a difficult theoretical and experimental issue. The theory developed in this Communication elucidates some of these issues and provides a quantitative means to describe the RET dynamics in various limits.

Let us consider the simplest system consisting of single chromophoric energy donor (D) and acceptor (A). The state where both D and A are in the ground electronic state is denoted as $|g\rangle$. The state where only D (A) is excited while A (D) is in the ground electronic state is denoted as $|D\rangle$ ($|A\rangle$). Only single electronic excitations are considered, and the three states constitute a complete set of system states. Initially, the system is in $|g\rangle$, and the bath—all other degrees of freedom—is in equilibrium with $|g\rangle$, with a corresponding Hamiltonian H_b .

At time $t=0$, a laser pulse with duration τ_{pulse} selectively excites $|g\rangle$ to $|D\rangle$. It is assumed that $\tau_{\text{pulse}} \ll \tau_{\text{RET}}$, where the latter is the time scale of the RET dynamics. This in turn is

assumed to be much smaller than τ_{sd} , the spontaneous decay time to the ground state. Then, the RET dynamics for $t > 0$ (after the cessation of the pulse) can be described by a total Hamiltonian, $H = H_s^p + H_s^c + H_{sb} + H_b$, where H_s^p and H_s^c are system Hamiltonians (with superscripts p and c representing population and coherence), and H_{sb} is the system-bath interaction Hamiltonian. These have the following forms:

$$H_s^p = E_D |D\rangle\langle D| + E_A |A\rangle\langle A|, \quad (1)$$

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

$$H_{sb} = B_D |D\rangle\langle D| + B_A |A\rangle\langle A|, \quad (3)$$

where E_D (E_A) is the energy of state $|D\rangle$ ($|A\rangle$) relative to $|g\rangle$, J is the resonance coupling between $|D\rangle$ and $|A\rangle$, and B_D (B_A) represents the bath operator coupled to $|D\rangle$ ($|A\rangle$). The total density operator at time t is denoted as $\rho(t)$. The initial condition corresponding to the physical situation described above is $\rho(0) = \sigma(0)e^{-\beta H_b}/Z$, where $\beta = 1/k_B T$, $Z = \text{Tr}_b\{e^{-\beta H_b}\}$, and $\sigma(0) = |D\rangle\langle D|$.

For the Hamiltonians defined above, the corresponding quantum Liouville operators¹⁴ are denoted as \mathcal{L} , \mathcal{L}_s^p , \mathcal{L}_s^c , \mathcal{L}_{sb} , and \mathcal{L}_b . Then, $\rho(t)$ is governed by

$$\frac{d\rho(t)}{dt} = -i\mathcal{L}\rho(t) = -i(\mathcal{L}_s^p + \mathcal{L}_s^c + \mathcal{L}_{sb} + \mathcal{L}_b)\rho(t). \quad (4)$$

The major issue in coherent RET is that \mathcal{L}_s^p , \mathcal{L}_s^c , and \mathcal{L}_{sb} are all comparable, which makes perturbation expansion in any of these unreliable. When the coupling to the bath is weak, the second order quantum master equation (QME) approach^{15,16} may be employed, while for strong coupling to the bath, the FD theory^{5,6} is applicable. Our approach developed below interpolates between these limits by combining the polaron transformation^{17–19} and a QME formulation²⁰ up to the second order. In order to make clear exposition of the theory, we here assume a spin-boson-type model.^{18,21} Thus,

^{a)}Author to whom correspondence should be addressed. Electronic mail: seogjoo.jang@qc.cuny.edu.

$H_b = \sum_n \hbar \omega_n (b_n^\dagger b_n + \frac{1}{2})$, where b_n^\dagger (b_n) is the creation (annihilation) operator of the n th mode with frequency ω_n , and $B_D = \sum_n \hbar \omega_n g_{nD} (b_n + b_n^\dagger)$ and $B_A = \sum_n \hbar \omega_n g_{nA} (b_n + b_n^\dagger)$. It is assumed that J in Eq. (2) is a time independent parameter. Numerous theoretical studies have been made for this model, but its dynamics in the ranges of parameters corresponding to coherent RET remains relatively unknown.¹¹

Applying the polaron transformation¹⁷⁻¹⁹ generated by $G = \sum_n (b_n^\dagger - b_n)(g_{nD}|D\rangle\langle D| + g_{nA}|A\rangle\langle A|)$ to Eq. (4), we obtain the following time evolution equation for $\tilde{\rho}(t) = e^G \rho(t) e^{-G}$:

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

where $\tilde{\mathcal{L}}_s^p$ and $\tilde{\mathcal{L}}_s^c$ are quantum Liouville operators for

$$\tilde{H}_s^p = \tilde{E}_D |D\rangle\langle D| + \tilde{E}_A |A\rangle\langle A|, \quad (6)$$

$$\tilde{H}_s^c = J(\theta_D^\dagger \theta_A |D\rangle\langle A| + \theta_A^\dagger \theta_D |A\rangle\langle D|). \quad (7)$$

In Eq. (6), $\tilde{E}_D = E_D - \sum_n g_{nD}^2 \hbar \omega_n$ and $\tilde{E}_A = E_A - \sum_n g_{nA}^2 \hbar \omega_n$. In Eq. (7), $\theta_D = e^{-\sum_n g_{nD} (b_n^\dagger - b_n)}$ and $\theta_A = e^{-\sum_n g_{nA} (b_n^\dagger - b_n)}$, and θ_D^\dagger and θ_A^\dagger are their Hermitian conjugates. Accordingly, the initial condition transforms to $\tilde{\rho}(0) = \sigma(0) \theta_D^\dagger e^{-\beta H_b} \theta_D / Z$, which is nonequilibrium with respect to the bath.²²

For the purpose of deriving the QME, we divide the total transformed Hamiltonian as $\tilde{H} = \tilde{H}_0 + \tilde{H}_1$. The zeroth order term \tilde{H}_0 is defined as

$$\tilde{H}_0 = \tilde{H}_s^p + \langle \tilde{H}_s^c \rangle + H_b = \tilde{H}_{0,s} + H_b, \quad (8)$$

where $\langle \cdots \rangle$ denotes average over $e^{-\beta H_b} / Z_b$, and

$$\tilde{H}_{0,s} = \tilde{E}_D |D\rangle\langle D| + \tilde{E}_A |A\rangle\langle A| + Jw(|D\rangle\langle A| + |A\rangle\langle D|). \quad (9)$$

Here, $w = \langle \theta_D^\dagger \theta_A \rangle = \langle \theta_A^\dagger \theta_D \rangle = e^{-\sum_n \coth(\beta \hbar \omega_n / 2) \delta g_n^2 / 2}$ with $\delta g_n = g_{nD} - g_{nA}$. The remaining first order term \tilde{H}_1 is defined as

$$\tilde{H}_1 = \tilde{H}_s^c - \langle \tilde{H}_s^c \rangle = J(\tilde{B} |D\rangle\langle A| + \tilde{B}^\dagger |A\rangle\langle D|), \quad (10)$$

where $\tilde{B} = \theta_D^\dagger \theta_A - w$. By definition, $\langle \tilde{B} \rangle = \langle \tilde{B}^\dagger \rangle = 0$. A crucial point to note is that, unlike the usual assumption of the FD theory,^{5,6} we follow the approach of Abram and Silbey²³ and take $J\tilde{B}$ and $J\tilde{B}^\dagger$ as perturbations which remain small in both limits of weak and strong system-bath couplings. This allows for the second order QME with respect to \tilde{H}_1 to be valid in both limits.

In the interaction picture of \tilde{H}_0 , $\tilde{\rho}_I(t) = e^{i\tilde{\mathcal{L}}_0 t} \tilde{\rho}(t)$ is governed by the following time evolution equation:

$$\frac{d}{dt} \tilde{\rho}_I(t) = -i\tilde{\mathcal{L}}_{1,I}(t) \tilde{\rho}_I(t), \quad (11)$$

where $\tilde{\mathcal{L}}_{1,I}(t)$ is the quantum Liouville operator for

$$\tilde{H}_{1,I}(t) = J(\tilde{B}(t)\mathcal{T}(t) + \tilde{B}^\dagger(t)\mathcal{T}^\dagger(t)), \quad (12)$$

with $\tilde{B}(t) = e^{iH_b t/\hbar} \tilde{B} e^{-iH_b t/\hbar}$ and $\mathcal{T}(t) = e^{i\tilde{H}_{0,s} t/\hbar} |D\rangle\langle A| e^{-i\tilde{H}_{0,s} t/\hbar}$.

Applying the standard projection operator technique²⁰ with $\mathcal{P}(\cdot) \equiv \rho_b \text{Tr}_b\{\cdot\}$ and $\mathcal{Q} = 1 - \mathcal{P}$ to Eq. (11) and making second order approximations [with respect to $\tilde{\mathcal{L}}_{1,I}(t)$] for

both the homogeneous and inhomogeneous terms consistently, we obtain

$$\begin{aligned} \frac{d}{dt} \mathcal{P}\tilde{\rho}_I(t) &= -i\mathcal{P}\tilde{\mathcal{L}}_{1,I}(t)\mathcal{Q}\tilde{\rho}(0) - \int_0^t d\tau \mathcal{P}\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau) \\ &\quad \times (\mathcal{Q}\tilde{\rho}(0) + \mathcal{P}\tilde{\rho}_I(\tau)), \end{aligned} \quad (13)$$

where $\mathcal{P}\tilde{\mathcal{L}}_{1,I}(t)\mathcal{P} = 0$ has been used and $\mathcal{Q}\tilde{\rho}(0) = \sigma(0) \times (\theta_D^\dagger e^{-\beta H_b} \theta_D - e^{-\beta H_b}) / Z$. In Eq. (13), $\mathcal{P}\tilde{\rho}_I(\tau)$ can be replaced with $\mathcal{P}\tilde{\rho}_I(t)$ without affecting the accuracy up to the second order.²⁰ Taking the trace of the resulting equation over the bath degrees of freedom, we obtain the following time-local QME for $\tilde{\sigma}_I(t) = \text{Tr}_b\{\tilde{\rho}_I(t)\}$:

$$\frac{d}{dt} \tilde{\sigma}_I(t) = -\mathcal{R}(t)\tilde{\sigma}_I(t) + \mathcal{I}(t), \quad (14)$$

where

$$\mathcal{R}(t) = \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\tilde{\mathcal{L}}_{1,I}(\tau)\rho_b\}, \quad (15)$$

$$\begin{aligned} \mathcal{I}(t) &= -i \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\mathcal{Q}\tilde{\rho}(0)\} \\ &\quad - \int_0^t d\tau \text{Tr}_b\{\tilde{\mathcal{L}}_{1,I}(t)\mathcal{Q}\tilde{\mathcal{L}}_{1,I}(\tau)\tilde{\rho}(0)\}. \end{aligned} \quad (16)$$

While being time local, Eq. (14) can account for non-Markovian bath effects through the time dependence of $\mathcal{R}(t)$ and is expected to show good performance beyond the typical perturbative regime, as has been demonstrated for other cases.²⁴ As long as w defined below Eq. (9) is nonzero, it is simple to show that Eq. (14) captures the Redfield limit¹⁵ for long times and weak system-bath coupling limit. Two straightforward extensions of Eq. (14) are possible. The first is for more general initial condition with coherent mixture of $|D\rangle$ and $|A\rangle$, which is important for modeling pump-probe spectroscopy. The second is multistate generalization.

Inserting Eq. (12) into Eqs. (15) and (16) and using the cyclic invariance of the bath operators within $\text{Tr}_b\{\cdots\}$, we can explicitly decouple the bath correlation functions from the commutators of system operators. The resulting expression for Eq. (15), when applied to $\tilde{\sigma}_I(t)$, can be shown to be

$$\begin{aligned} \mathcal{R}(t)\tilde{\sigma}_I(t) &= \frac{J^2}{\hbar^2} e^{-\mathcal{K}(0)} \int_0^t d\tau \{ (e^{-\mathcal{K}(t-\tau)} - 1) [\mathcal{T}(t), \mathcal{T}(\tau)\tilde{\sigma}_I(\tau)] \\ &\quad + (e^{\mathcal{K}(t-\tau)} - 1) [\mathcal{T}^\dagger(t), \mathcal{T}(\tau)\tilde{\sigma}_I(\tau)] \\ &\quad + (e^{\mathcal{K}(t-\tau)} - 1) [\mathcal{T}(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(\tau)] \\ &\quad + (e^{-\mathcal{K}(t-\tau)} - 1) [\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau)\tilde{\sigma}_I(\tau)] \} + \text{H.c.}, \end{aligned} \quad (17)$$

where $\mathcal{K}(t) = \sum_n \delta g_n^2 \{ \coth(\beta \hbar \omega_n / 2) \cos(\omega_n t) - i \sin(\omega_n t) \}$ and ‘‘H.c.’’ represents the Hermitian conjugates of all the previous terms. The same convention will be used hereafter. The expression for Eq. (16) is more complicated because it involves nonequilibrium bath correlation functions. After careful examination, we find that it can be expressed compactly in terms of $\mathcal{K}(t)$, a new bath function $f(t) = e^{2i\sum_n g_{nD} \delta g_n \sin(\omega_n t)}$,

which represents the correlation of the initial donor bath, and $f_m(t, \tau) = f(t)f(\tau) - 1$ and $f_a(t, \tau) = f(t) + f(\tau) - 2$. Thus, Eq. (16) can be shown to be

$$\begin{aligned} \mathcal{I}(t) = & -\frac{iJ}{\hbar} e^{-\kappa(0)/2} (f(t) - 1) [\mathcal{T}(t), \sigma(0)] \\ & - \frac{J^2}{\hbar^2} e^{-\kappa(0)} \int_0^t d\tau \{F_{(1)}(t, \tau) [\mathcal{T}(t), \mathcal{T}(\tau) \sigma(0)] \\ & + F_{(2)}(t, \tau) [\mathcal{T}^\dagger(t), \mathcal{T}(\tau) \sigma(0)] \\ & + F_{(3)}(t, \tau) [\mathcal{T}(t), \mathcal{T}^\dagger(\tau) \sigma(0)] \\ & + F_{(4)}(t, \tau) [\mathcal{T}^\dagger(t), \mathcal{T}^\dagger(\tau) \sigma(0)]\} + \text{H. c.}, \end{aligned} \quad (18)$$

where $F_{(1)}(t, \tau) = f_m(t, \tau) e^{-\kappa(t-\tau)} - f_a(t, \tau)$, $F_{(2)}(t, \tau) = f_m(-t, \tau) e^{\kappa(t-\tau)} - f_a(-t, \tau)$, $F_{(3)}(t, \tau) = f_m(t, -\tau) e^{\kappa(t-\tau)} - f_a(t, -\tau)$, and $F_{(4)}(t, \tau) = f_m(-t, -\tau) e^{-\kappa(t-\tau)} - f_a(-t, -\tau)$. In the above expressions, the system-bath coupling is fully specified by two spectral densities, $\mathcal{J}_s(\omega) = \sum_n \delta(\omega - \omega_n) \omega_n^2 \delta g_n^2$ and $\mathcal{J}_i(\omega) = \sum_n \delta(\omega - \omega_n) \omega_n^2 g_{nD} \delta g_n$. These spectral densities can represent various situations including the cases where there are common bath modes²⁵ ($g_{nD} g_{nA} \neq 0$) between the donor and the acceptor.

It is noteworthy to mention important qualitative features related to the characteristics of the spectral density. Let us assume that $\mathcal{J}_s(\omega) \propto \omega^p$ in the limit of $\omega \rightarrow 0$. If $p \leq 1$, $e^{-\kappa(0)} = 0$ and $\langle \tilde{H}_s^1 \rangle = 0$ at all temperatures. Then, the only surviving terms are those with $e^{-\kappa(0) + \kappa(t-\tau)}$ in Eq. (17) and those with $F_{(2)}(t, \tau)$ or $F_{(3)}(t, \tau)$ in Eq. (18). The resulting dynamics involves only population terms ($|D\rangle\langle D|$ and $|A\rangle\langle A|$) in a way similar to the noninteracting blip approximation,²¹ but our equations are time local and include inhomogeneous terms. On the other hand, for $p > 2$, $\langle \tilde{H}_s^1 \rangle$ and $e^{-\kappa(0)}$ are nonzero at all temperatures, and the dynamics always involves coherence terms, $|D\rangle\langle A|$ and $|A\rangle\langle D|$. However, caution is required, and it is important to identify the physical origin of the low frequency modes especially for the Ohmic density. If the low frequency modes have an anharmonic origin, they may not make full multiphonon contributions or remain virtually static during the lifetime of the electronic excitation. This situation can be accounted for by introducing a lower bound of order $1/\tau_{sd}$ in the frequency-domain integration of the spectral density. With this modification, our theory reduces to the Redfield approach for weak coupling limit even for Ohmic spectral densities.

For numerical calculations, it is convenient to express Eq. (14) in the eigenbasis of $\tilde{H}_{0,s}$. Detailed expressions are provided in the supporting document. Numerical tests have been made for the following super-Ohmic spectral densities: $\mathcal{J}_s(\omega)/2 = \mathcal{J}_i(\omega) = (\eta/3!) (\omega^3/\omega_c^2) e^{-\omega/\omega_c}$. In the units where $\omega_c = \hbar = 1$ and $k_B T = 1$, two different cases of $\eta = 1$ and 3 were considered for $\Delta E = \tilde{E}_D - \tilde{E}_A = \pm 1$. Calculations of $\tilde{\sigma}_I(t)$ have been made both with and without $\mathcal{I}(t)$ in Eq. (14), which can then be used to determine any physical observable of the system. Here, we focus only on the population of the excited donor, $P_D(t) = \langle D | e^{-i\tilde{H}_{0,s}t/\hbar} \tilde{\sigma}_I(t) e^{i\tilde{H}_{0,s}t/\hbar} | D \rangle$. In order to assess the role of quantum coherence, the population $P_D^r(t)$ based on the following rate equation was also calculated:

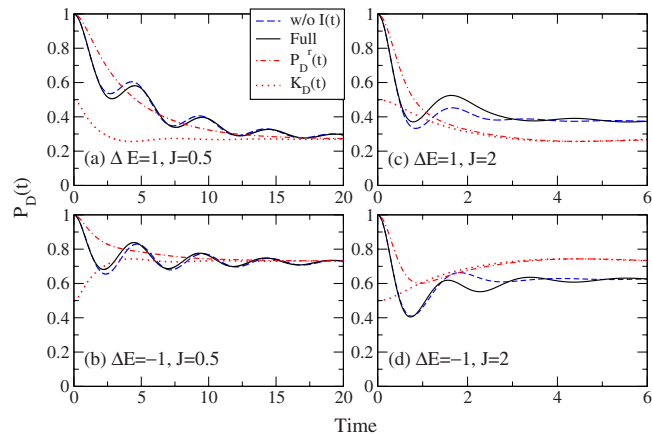


FIG. 1. (Color online) Time-dependent donor populations for $\eta=1$. Units are such that $\hbar = \omega_c = 1$ and $k_B T = 1$. Blue dashed lines [without $I(t)$] result from Eq. (14) with the inhomogeneous term $\mathcal{I}(t) = 0$, and black solid lines (full) correspond to the results of Eq. (14) employing the full expressions. Red dot-dashed lines represent results based on Eq. (19). Red dotted lines correspond to the time-dependent equilibrium donor population $K_D(t)$ as defined below Eq. (19). Different panels show results for different values of $\Delta E = E_D - E_A$ and J as indicated.

$$\frac{d}{dt} P_D^r(t) = -k_{DA}^r(t) P_D^r(t) + k_{AD}^r(t) (1 - P_D^r(t)), \quad (19)$$

where $k_{DA}^r(t)$ is the time-dependent FD rate⁷ from D to A given by

$$k_{DA}^r(t) = \frac{2J^2}{\hbar^2} e^{-\kappa(0)} \text{Re} \left[\int_0^t d\tau e^{i(\tilde{E}_D - \tilde{E}_A)t/\hbar} (e^{\kappa(t)} - 1) \right]. \quad (20)$$

The expression for $k_{AD}^r(t)$ is the same except for the replacement $\tilde{E}_D - \tilde{E}_A \rightarrow \tilde{E}_A - \tilde{E}_D$. The time-dependent equilibrium constant of the donor, $K_D(t) = k_{AD}^r(t) / (k_{DA}^r(t) + k_{AD}^r(t))$, was also calculated as a reference.

Figure 1 shows results for $\eta=1$. When $J=0.5$, the quantum coherence causes oscillatory donor population, but its average over the period and the steady state limit remain very close to those based on the rate equation, Eq. (19). When $J=2$, the quantum coherence has significant effects on the steady state donor population. For $\Delta E=1$, there is more donor population (less efficient transfer) than the prediction of the rate equation, Eq. (19). For $\Delta E=-1$, the opposite is true. Thus, quantum coherence (or tunneling) is shown to counteract the prescription of the detailed balance based on the FD rate equation (in the site localized basis).

Figure 2 shows results for $\eta=3$. When $J=0.5$, the system-bath coupling is large enough to damp the oscillatory population and to make the time-dependent population nearly overlap with that based on the rate equation. When $J=2$, there are slight transient oscillations at early times, and the steady state donor populations differ from those of the rate equation but to less extents than those in Fig. 1. Also shown are significant contributions of the inhomogeneous term $\mathcal{I}(t)$ on the transient behavior of population dynamics. This suggests the importance of including nonequilibrium effects for quantitative description of the ultrafast RET dynamics. For the modeling of nonlinear spectroscopy experiments being used to probe such dynamics in real time, fur-

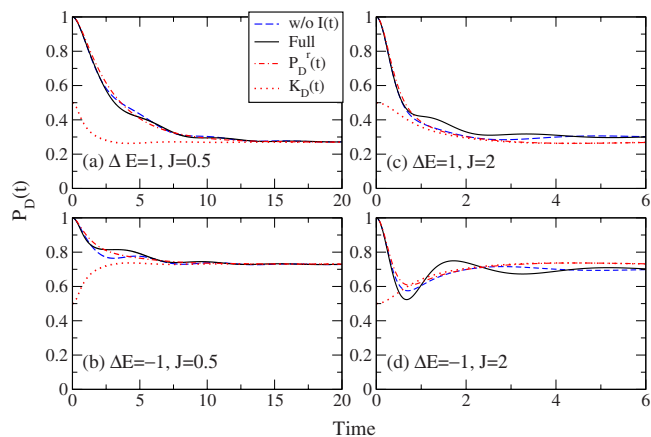


FIG. 2. (Color online) Time-dependent donor populations for $\eta=3$. All other details are the same as in Fig. 1.

ther extension of the theory for more general initial conditions as was done by Matro and Cina¹⁶ is needed, which is possible at the expense of more complicated $\mathcal{I}(t)$ in our formalism. Future theoretical efforts will be dedicated to this issue.

In summary, we have developed a theory of coherent RET including both nonequilibrium and quantum coherence effects. Numerical tests demonstrate the presence of oscillatory population dynamics even for moderately large system-bath coupling and interesting effects of quantum coherence on the steady state donor populations.

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