

## Resonant energy transfer assisted by off-diagonal coupling

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Dynamics of resonant energy transfer of a single excitation in a molecular dimer system are studied in the simultaneous presence of diagonal and off-diagonal exciton-phonon coupling. It is found that, at given temperatures, the off-diagonal coupling can enhance both the coherence of the resonant energy transfer and the net quantity of energy transferred from an initially excited monomer to the other. Also studied is the dynamics of entanglement between the dimer system and the phonon bath as measured by the von Neumann entanglement entropy, and the inter-monomer entanglement dynamics for the excitonic system. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3697817>]

### INTRODUCTION

Resonant energy transfer (RET) is a ubiquitous phenomenon in diverse fields such as physics, chemistry, and biology. Recently, there emerged several remarkable reports on sustained quantum coherence at elevated or physiological temperatures in photosynthetic light-harvesting systems<sup>1-3</sup> and conjugated polymers.<sup>4</sup> While the coherence duration may be considered short by some measures, it is sufficient to allow energy transfer to take place in those systems at astonishingly high efficiencies. Much theoretical attention has since been devoted to this issue, and various mechanisms supporting quantum coherence at high temperatures have been proposed.<sup>5-16</sup>

In this work we propose a new mechanism that can be responsible to sustain quantum coherence at high temperatures, namely, the effect of off-diagonal exciton-phonon coupling on excitonic transport. Diagonal coupling is defined as a nontrivial dependence of the exciton site energies on the phonon coordinates, and off-diagonal coupling as a nontrivial dependence of the exciton transfer integral on the phonon coordinates. Off-diagonal coupling as appeared in the Su-Schrieffer-Heeger model<sup>17</sup> and the Peierls-type models modulates the transfer integral, and has a strong influence on transport properties of organic materials such as conducting polymers.<sup>18</sup> In natural photosynthetic systems, off-diagonal coupling may play a very important role in ultra-efficient energy transfer (see, e.g., Ref. 19 for a recent study addressing this issue). As pointed out by Mahan,<sup>20</sup> what excludes the seemingly natural introduction of electron-phonon interactions of types other than the diagonal one from most polaron discussions is often the sheer difficulty in obtaining reliable solutions in their presence.<sup>21-28</sup>

Using a generalized Holstein Hamiltonian of two monomers,<sup>23</sup> diagonal and off-diagonal couplings are treated on an equal footing. Our main goal is to investigate the impact of off-diagonal coupling on the RET process in the dimer system. It is found in this work that within some proper pa-

rameter range, a coherent component of the exciton energy transfer exists at arbitrary temperature for a non-vanishing off-diagonal coupling strength, and the oscillation frequency of site populations increases with the off-diagonal coupling strength. We calculated the evolution of the entanglement between the monomer system and the phonon bath and also the entanglement between the two monomers. The former shows oscillating behaviors in the off-diagonal coupling regime, in agreement with the coherent energy transfer. The latter revives in the same regime and reaches its maxima as the excitation is completely delocalized between the two monomers. Furthermore, due to the fact that the off-diagonal coupling is anti-symmetric, the total net population transferred from the initially excited monomer to the acceptor monomer at long times is an increasing function of the off-diagonal coupling strength at fixed temperatures.

The rest of the paper is organized as follows. The next section comprises of the methodology employed in this work. Details of analytical as well as numerical results are presented in the Results and Discussion section. Conclusions are drawn in the final section.

### METHODOLOGY

For simplicity, we consider a molecular dimer composed of a donor and an acceptor located at  $\mathbf{R}_{1,2} = \pm \mathbf{d}/2$  and coupled linearly to a common phonon bath via simultaneous diagonal and off-diagonal exciton-phonon coupling. These considerations lead to a two-site generalized Holstein Hamiltonian

$$H = \sum_{i=1,2} \epsilon_i a_i^\dagger a_i + J(a_1^\dagger a_2 + a_2^\dagger a_1) + \sum_q \omega_q b_q^\dagger b_q + \sum_q \left( \sum_{i=1,2} f_{ii}^q a_i^\dagger a_i + f_{12}^q a_1^\dagger a_2 - f_{21}^q a_2^\dagger a_1 \right) (b_q^\dagger + b_{-q}), \quad (1)$$

where the operator  $a_i^\dagger$  ( $a_i$ ) creates (destroys) an excitation of energy  $\epsilon$  at site  $i$ , and  $b_q^\dagger$  ( $b_q$ ) creates (destroys) a phonon of frequency  $\omega_q$  with wave vector  $q$ . Equation (1) is some-

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times referred<sup>29</sup> to as the Su-Schrieffer-Heeger Hamiltonian despite the classical treatment of configuration coordinates in the original model.<sup>17</sup> Note that we have chosen the off-diagonal coupling to be anti-symmetric so that the two molecules are indeed nonequivalent. This can be viewed as some kind of “parity violation” and will lead to interesting long-time behaviors of the dynamics as we will show later. We consider a form of diagonal electron-phonon coupling  $f_{11}^q = g_q e^{i\mathbf{q}\cdot\mathbf{R}_1}$ ,  $f_{22}^q = g_q e^{i\mathbf{q}\cdot\mathbf{R}_2}$ , and that of off-diagonal coupling  $f_{ij}^q = \lambda g_q (e^{i\mathbf{q}\cdot\mathbf{R}_i} - e^{i\mathbf{q}\cdot\mathbf{R}_j})/2$  ( $i, j = 1, 2$ ),<sup>23–25</sup> where  $\lambda/2$  is the relative strength of the off-diagonal coupling. Note that this particular choice enables both the diagonal and off-diagonal coupling share the same bath properties, which, in turn, makes the overall analysis easier. One of the well-known microscopic transport theories concerning the off-diagonal coupling is the Munn-Silbey approach,<sup>23–25</sup> which was based on a canonical transformation technique with an element of optimization. Our solution to Eq. (1) here follows a similar transformation of the Hamiltonian.

We confine ourselves in the one exciton subspace  $\sum_{i=1,2} a_i^\dagger a_i = 1$ . Within this one-exciton subspace, the two exciton operators can be viewed as two types of Schwinger bosons of the spin-one-half operators  $a_1^\dagger a_2 \rightarrow S_+$ ,  $a_2^\dagger a_1 \rightarrow S_-$ , and  $(a_1^\dagger a_1 - a_2^\dagger a_2)/2 \rightarrow S_z$ . To proceed, we introduce a canonical transformation<sup>23,25,30</sup>

$$U = \exp \left[ \frac{1}{2} (1 + \sigma_z + \lambda \sigma_x) \sum_q A_q (b_q^\dagger - b_{-q}) + \frac{1}{2} (1 - \sigma_z - \lambda \sigma_x) \sum_q B_q (b_q^\dagger - b_{-q}) \right], \quad (2)$$

where  $A_q = f_{11}^q/\omega_q$  and  $B_q = f_{22}^q/\omega_q$ . Up to a constant term, the transformed Hamiltonian reads

$$\begin{aligned} \tilde{H} = U H U^\dagger &= \sum_q \omega_q b_q^\dagger b_q + \frac{1}{1 + \lambda^2} \left( \frac{\epsilon}{2} + \lambda J \right) (\sigma_z + \lambda \sigma_x) \\ &+ \frac{1}{1 + \lambda^2} \left( \frac{\epsilon}{2} \lambda - J \right) (\lambda \sigma_z - \sigma_x) \cosh Z \\ &- \frac{i}{\sqrt{1 + \lambda^2}} \left( \frac{\epsilon}{2} \lambda - J \right) \sigma_y \sinh Z, \end{aligned} \quad (3)$$

where the energy detuning is labeled as  $\epsilon = \epsilon_1 - \epsilon_2$ , and  $Z = \sqrt{1 + \lambda^2} \sum_q (A_q - B_q) (b_q^\dagger - b_{-q})$ . As usual, the linear coupling terms disappear, with the pay that the on-site energy and transfer integral are both renormalized by the phonon degrees of freedom via operator  $Z$  in a very complicated way. Following Ref. 21, we invoke a thermal mean-field treatment to separate the transformed Hamiltonian into a free part and a perturbation part. This separation is believed to yield a weak residual exciton-phonon coupling even in the presence of strong exciton-phonon coupling.

By assuming that the phonon bath is in thermal equilibrium at temperature  $T = (k_B \beta)^{-1}$  with Boltzmann constant  $k_B$ , it is easy to show that  $\langle \sinh Z \rangle_{\text{ph}} = 0$ , and

$$\langle \cosh Z \rangle_{\text{ph}} \equiv \Theta = e^{-\frac{1+\lambda^2}{2} \sum_q |A_q - B_q|^2 \coth(\beta \omega_q/2)},$$

where  $\langle \dots \rangle_{\text{ph}}$  denotes the thermal average. The mean-field like separation is accomplished by substituting the two nonlinear phonon operators above with their thermal averages. Then the transformed Hamiltonian is divided into the following three parts, i.e., the free phonon part  $\tilde{H}_b = \sum_q \omega_q b_q^\dagger b_q$ , the excitation part

$$\tilde{H}_e = \frac{\tilde{\epsilon}}{2} \sigma_z + \tilde{J} \sigma_x \quad (4)$$

with  $\tilde{\epsilon} = (1 + \lambda^2)^{-1} [\epsilon(1 + \lambda^2 \Theta) + 2\lambda J(1 - \Theta)]$  and  $\tilde{J} = (1 + \lambda^2)^{-1} [\epsilon \lambda(1 - \Theta)/2 + J(\lambda^2 + \Theta)]$ , and the residual interaction

$$\tilde{H}_r = \sum_{\alpha=1,2} A_\alpha \otimes B_\alpha, \quad (5)$$

which we believe to be small and will be treated as a perturbation.<sup>32–34</sup> Here  $A_1 = (1 + \lambda^2)^{-1} (\epsilon \lambda/2 - J)(\lambda \sigma_z - \sigma_x)$ ,  $B_1 = \cosh Z - \Theta$ ,  $A_2 = -(1 + \lambda^2)^{-1/2} (\epsilon \lambda/2 - J) \sigma_y$ , and  $B_2 = i \sinh Z$ . Clearly, in  $\tilde{H}_e$  the renormalized energy mismatch  $\tilde{\epsilon}$  and transfer integral  $\tilde{J}$  depend on the off-diagonal coupling strength  $\lambda$  nonlinearly, and this term describes a polaron indeed. In the following we will only consider the case of resonant energy transfer, i.e.,  $\epsilon = 0$ .

Treating the residual term perturbatively to the second order and using the Born-Markov approximation, the quantum master equation in the Schrodinger picture without the rotating-wave approximation (RWA) can be derived as<sup>31</sup>

$$\begin{aligned} \frac{d}{dt} \tilde{\rho}(t) &= -i[\tilde{H}_e, \tilde{\rho}(t)] \\ &- \sum_{\alpha=1,2} \sum_{\omega=0, \pm\tilde{\eta}} \{ \Gamma_{\alpha\alpha}(\omega) [A_\alpha, A_\alpha(\omega) \tilde{\rho}(t)] + h.c. \}. \end{aligned} \quad (6)$$

Here  $\tilde{\eta} = (\tilde{\epsilon}^2 + 4\tilde{J}^2)^{1/2}$  is the polaron bandwidth, and the two eigenstates of  $\tilde{H}_e$  in the one exciton subspace can be labeled as  $|\pm \frac{\tilde{\eta}}{2}\rangle$ . It follows that  $A_\alpha(\tilde{\eta}) = \langle -\frac{\tilde{\eta}}{2} | A_\alpha | \frac{\tilde{\eta}}{2} \rangle \cdot | -\frac{\tilde{\eta}}{2} \rangle \langle \frac{\tilde{\eta}}{2} | = A_\alpha^\dagger(-\tilde{\eta})$ ,  $A_\alpha(0) = \sum_{\epsilon=\pm\frac{\tilde{\eta}}{2}} \langle \epsilon | A_\alpha | \epsilon \rangle | \epsilon \rangle \langle \epsilon |$ . In addition,

$$\Gamma_{\alpha\alpha}(\omega) = \int_0^\infty ds e^{i\omega s} C_{\alpha\alpha}(s) = \frac{1}{2} \gamma_{\alpha\alpha}(\omega) + i S_{\alpha\alpha}(\omega), \quad (\alpha = 1, 2) \quad (7)$$

is the one-sided Fourier transforms of the bath correlation functions

$$\begin{aligned} C_{11}(s, \lambda) &= \frac{\Theta^2}{2} [e^{\phi(s, \lambda)} + e^{-\phi(s, \lambda)} - 2], \\ C_{22}(s, \lambda) &= \frac{\Theta^2}{2} [e^{\phi(s, \lambda)} - e^{-\phi(s, \lambda)}], \end{aligned}$$

where  $\phi(s, \lambda) = (1 + \lambda^2) \sum_q |A_q - B_q|^2 (\coth \frac{\beta \omega_q}{2} \cos \omega_q s - i \sin \omega_q s)$ . The residual interaction term is small in the sense that by construction its thermal average vanishes and it is weak in the polaron frame. Therefore, the quantum master equation, truncated in finite orders of the interaction, can be treated by the Born-Markov approximation. The role of the canonical transformation is not to impose actual formation of polaron, but to help identify a Hamiltonian

term that remains minute beyond the usual regime of weak system-bath coupling.

If  $\rho_T(t)$  and  $\tilde{\rho}_T(t) = \tilde{\rho}(t) \otimes \rho_B$  are the total density matrices in the original and the polaron basis, respectively, then the Bloch vector  $(\langle \sigma_x \rangle, \langle \sigma_y \rangle, \langle \sigma_z \rangle)$  has components  $\langle \sigma_i \rangle = \text{Tr}(\rho_T \sigma_i) = \text{Tr}(U^\dagger \tilde{\rho}_T U \sigma_i) = \text{Tr}(\tilde{\rho}_T U \sigma_i U^\dagger)$ , where the trace is taken over both the system and the bath degrees of freedom. By calculating the transformed Pauli matrices  $\tilde{\sigma}_i = U \sigma_i U^\dagger$  and combining them with Eq. (6), one arrives at a set of Bloch equations

$$\begin{pmatrix} \langle \dot{\sigma}_x \rangle \\ \langle \dot{\sigma}_y \rangle \\ \langle \dot{\sigma}_z \rangle \end{pmatrix} = M(\lambda) \begin{pmatrix} \langle \sigma_x \rangle \\ \langle \sigma_y \rangle \\ \langle \sigma_z \rangle \end{pmatrix} + \begin{pmatrix} -(\lambda\kappa_1 + \Theta\kappa_2) \\ \Theta S_3 \\ \Theta\lambda\kappa_2 - \kappa_1 \end{pmatrix} \quad (8)$$

with the Bloch matrix

$$M(\lambda) = \begin{pmatrix} \lambda^2 \Lambda_1 - \Gamma_3 & 0 & -\lambda \Lambda_2 \\ S_1 - \lambda \Omega & \lambda^2 \Lambda_1 - \Lambda_2 & -(\lambda S_1 + \Omega) \\ \lambda \Lambda_1 & T_2 & -(\Lambda_2 + \Gamma_3) \end{pmatrix}, \quad (9)$$

where detailed expressions for the auxiliary functions  $\Omega$ ,  $\Lambda_1$ ,  $\Lambda_2$ ,  $S_1$ ,  $T_2$ ,  $\Gamma_3$ ,  $\kappa_1$ ,  $\kappa_2$ , and  $S_3$  are given in the Appendix. The first six auxiliary functions appear in the Bloch matrix  $M$  governing the reduced dynamics, while the last three are responsible for the determination of the steady state.

The case of  $\lambda = 0$  has been studied in Ref. 34. Let us first look at the qualitative impact of a weak off-diagonal coupling on the dynamics. If we define  $\Delta M = M(\lambda) - M(0)$ , then in the limit of weak off-diagonal exciton-phonon coupling ( $\lambda \ll 1$ ), we have the small- $\lambda$  correction to  $\Delta M$  as follows:  $\Delta M_{11} = O(\lambda^2)$ ,  $\Delta M_{12} = 0$ ,  $\Delta M_{12} = -2J^2\gamma_{11}^{(0)}(0)\lambda + O(\lambda^3)$ ,  $\Delta M_{21} = 2J\lambda[1 + \frac{J}{\Theta_0}(S_{11}^{(0)}(\eta) - S_{11}^{(0)}(-\eta)) - \Theta_0^2] + O(\lambda^3)$ ,  $\Delta M_{22} = O(\lambda^2)$ ,  $\Delta M_{23} = O(\lambda^2)$ ,  $M_{31} = \lambda \frac{J^2}{\Theta_0^2}[2(1 - \Theta_0^2)\gamma_{11}^{(0)}(0) - (\gamma_{11}^{(0)}(\eta) + \gamma_{11}^{(0)}(-\eta))] + O(\lambda^3)$ ,  $\Delta M_{32} = O(\lambda^2)$ ,  $\Delta M_{33} = O(\lambda^2)$ , here  $\Theta_0$  and  $\gamma_{ii}^{(0)}$  are the corresponding quantities for  $\lambda = 0$ . We observe that the weak coupling mainly affects the matrix elements  $M_{13}$ ,  $M_{21}$ , and  $M_{31}$  in the sense that they are of first order in  $\lambda$ .

In the presence of finite off-diagonal coupling, all the three components of dynamics are coupled rendering elusive an analytic solution of these coupled Bloch equations. To proceed with numerical analysis, we should make some basic assumptions about the bath properties. Assuming a linear phonon dispersion  $\omega_q = v|\mathbf{q}|$  ( $v$  is the sound speed), one has in the three-dimensional space

$$\sum_q f(\omega_q) |A_q - B_q|^2 = 2 \int_0^\infty d\omega f(\omega) \frac{J(\omega)}{\omega^2} \left(1 - \frac{\sin \omega t_d}{\omega t_d}\right),$$

where  $J(\omega)$  is the usual spectral density function of the phonon bath, and  $t_d = |d|/v$  is the time for the sound speed to traverse the inter-monomer distance. In order to keep vacuum contributions finite, a cutoff frequency  $\Omega_c$  is usually introduced for the bath spectrum, and with it, the shortest wavelength of the modes is  $\Lambda_c = 2\pi v/\Omega_c$ . When  $\Lambda_c \gg |d|$  (or  $\Omega_c t_d \ll 1$ ), the two molecules will see almost the same field so that the fluctuations are in the fully correlated regime<sup>10,34</sup> in which the coherence dynamics is well protected. The spectral density function<sup>37,39</sup> is usually given by  $J(\omega) = \kappa\omega_{\text{ph}}^{-2}\omega^s e^{-\omega/\Omega_c}$ .

A super-Ohmic (Ohmic) form is corresponding to the power  $s = 3$  ( $s = 1$ ).<sup>40</sup> Here  $\kappa$  is a dimensionless constant representing the exciton-phonon coupling strength, and  $\omega_{\text{ph}}$  is a typical bath-phonon frequency which is set to unity and used as the energy scale. Two forms of the spectral density function with  $s = 3$  and  $s = 1$  are employed in this work. Note that the analytic results for the super-Ohmic case can be obtained by using the property of the digamma function  $\psi(z)$ <sup>41</sup>

$$\begin{aligned} & \int_0^\infty dx e^{-bx} \frac{\sin ax}{\sinh \gamma x} \\ &= \frac{1}{2i\gamma} \left[ \psi\left(\frac{b + \gamma + ia}{2\gamma}\right) - \psi\left(\frac{b + \gamma - ia}{2\gamma}\right) \right], \end{aligned}$$

we have

$$\begin{aligned} \ln \Theta &= -\kappa(1 + \lambda^2) \left[ \frac{\Omega_c^4 t_d^2}{1 + \Omega_c^2 t_d^2} + 2k_B^2 T^2 \psi^{(1)}(1 + k_B T/\Omega_c) \right] \\ &+ i\kappa(1 + \lambda^2) t_d^{-1} k_B T [H_{k_B T(\Omega_c^{-1} - it_d)} - H_{k_B T(\Omega_c^{-1} + it_d)}], \end{aligned}$$

where  $\psi^{(1)}(z)$  is the trigamma function and  $H_z$  is the harmonic number.

## RESULTS AND DISCUSSION

We are now in a position to explore dynamical properties of the molecular dimer in the entire parameter regime. For both the super-Ohmic and Ohmic cases, the population difference between the monomers,  $P(t) = \langle a_1^\dagger a_1 - a_2^\dagger a_2 \rangle = \langle \sigma_z \rangle$ , is plotted in Figs. 1(a) and 1(b) as a function of time  $t$  and off-diagonal exciton-phonon coupling strength  $\lambda$  for a given parameter set of  $\Omega_c = 5$ ,  $J = 2.5$ ,  $T = 5$ ,  $\kappa = 0.1$ , and  $t_d = 4$ . The parameters chosen here are according to realistic situations. For instance, the typical distance between a pair of BChl *a* molecules in FMO is  $\sim 10$  Å.<sup>38</sup> Assum-

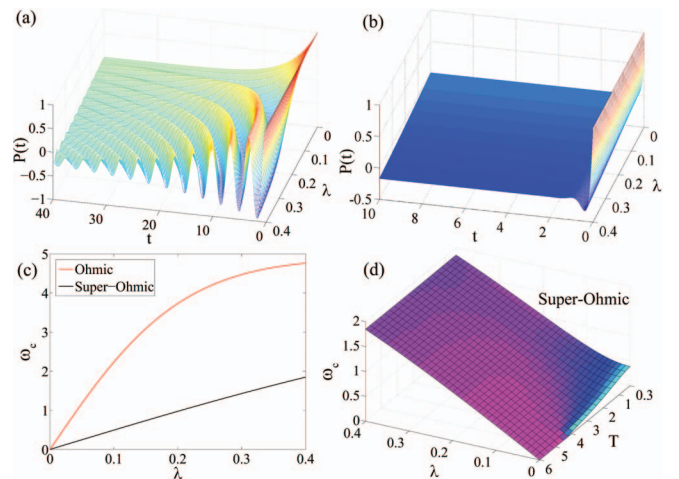


FIG. 1. (a) Population difference between the two monomers for super-Ohmic spectral density function,  $P(t) = \langle a_1^\dagger a_1 - a_2^\dagger a_2 \rangle = \langle \sigma_z \rangle$ , as a function of time and off-diagonal exciton-phonon coupling strength for the case of  $\Omega_c = 5$ ,  $J = 2.5$ ,  $T = 5$ ,  $\kappa = 0.1$ , and  $t_d = 4$ . (b) Population difference for Ohmic spectral density function, the same parameters are taken as (a). (c) Characteristic oscillating frequency of (a) and (b),  $\omega_c(\lambda)$ , is plotted as a function of the off-diagonal exciton-phonon coupling  $\lambda$ . (d) Characteristic oscillating frequency for the super-Ohmic case is shown as a function of temperature and off-diagonal exciton-phonon coupling strength.

ing  $\omega_{ph} = 41.67 \text{ cm}^{-1}$ , then  $T = 300 \text{ K}$ ,  $\Omega_c = 208.3 \text{ cm}^{-1}$ ,  $J = 104.17 \text{ cm}^{-1}$ . Initially, only the first monomer is excited electronically, and the excitation population is found to oscillate between the two due to the combined effect of  $J$  and  $\lambda$ . In the absence of off-diagonal coupling, it was found previously that there exists a crossover from coherent to incoherent transfer between the monomers as the temperature is increased, and the phonon cloud thickens.<sup>34</sup> Our choice of parameters guarantees that the  $\lambda = 0$  line in Figs. 1(a) and 1(b) falls in the regime of incoherent transfer as shown by the exponential decay of  $P(t)$  with time. However, coherence-induced oscillations of  $P(t)$  emerge with the introduction of a finite value off-diagonal coupling  $\lambda$ . It is found that the oscillations can last for a longer time in the super-Ohmic case, i.e., the super-Ohmic spectral density is conducive to the coherence transfer. Figure 1(b) seems to show an approximate off-resonance feature in the weak off-diagonal coupling ( $\lambda < 0.1$ ) because of the larger decay rate (that is, the dissipation of the system). More detailed results can be obtained by the solution to the Bloch equations which is a combination of an exponentially decaying component and an oscillating component with a characteristic frequency  $\omega_c(\lambda)$ . Unless  $\lambda$  vanishes, there always exists the oscillatory component of  $P(t)$ . As shown in Fig. 1(c), the characteristic frequency  $\omega_c(\lambda)$  is a monotonic function of  $\lambda$  for the two forms of the spectral density function. The Ohmic one reveals a saturation frequency as  $\lambda$  approaches 0.4, while the super-Ohmic case shows a linear relation in Fig. 1(c). It should be mentioned that in Ref. 35 there is a similar effect induced by a finite donor-acceptor energy mismatch in the high temperature limit, but the induced oscillations have an almost negligible amplitude, while our numerical analysis shows that the amplitude is very sensitive to the off-diagonal coupling strength. In addition, we investigate the characteristic frequency  $\omega_c(\lambda)$  for the super-Ohmic case as a function of the bath temperature  $T$ . As demonstrated in Fig. 1(d), the  $\lambda = 0$  transition temperature from coherent to incoherent transfer is found at  $T_c \simeq 4.2$ .<sup>34,35</sup> For  $T > T_c$ ,  $\omega_c$  is insensitive to the bath temperature  $T$ .

Coherence properties are dictated by the interplay between the system coherence dynamics and the environment decoherence effects. Quantum properties such as entanglement rely critically on coherence and therefore it is essential to employ a model that accurately accounts for environmental effects on coherence to make predictions about entanglement in the system. If  $\rho$  is the reduced density matrix of the dimer system in the original basis, the von Neumann entropy of the system, which changes with time due to dephasing and relaxation processes induced by the bath, is given by

$$S(\rho) = -\text{Tr}(\rho \ln \rho), \quad (10)$$

quantifying the entanglement between the dimer system and the bath.<sup>36</sup> The von Neumann entropy is the quantum analog of the Shannon information entropy. Closely related to the so-called 2-Renyi entropy, the von Neumann entropy reflects inter-species entanglement in a reduced description, as compared to the intra-species entanglement to be introduced later.<sup>42-47</sup>

The von Neumann entanglement between the dimer system and the bath is plotted in Figs. 2(a) and 2(c) for the super-

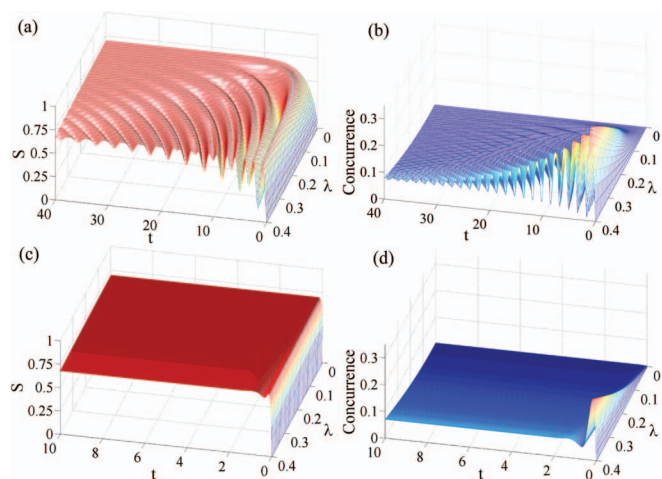


FIG. 2. The von Neumann entropy and the concurrence as a function of time and off-diagonal exciton-phonon coupling strength are plotted in (a) and (b) for the super-Ohmic case, and in (c) and (d) for the Ohmic case. The control parameters are  $\Omega_c = 5$ ,  $J = 2.5$ ,  $T = 5$ ,  $\kappa = 0.1$ , and  $t_d = 4$ .

Ohmic and Ohmic spectral density functions, respectively. Only the initial condition  $n_1(0) = a_1^\dagger(0)a_1(0) = 1$  is considered in our calculation. The entropy  $S(\rho)$  exhibits oscillatory behavior in the presence of off-diagonal coupling, signaling entanglement exchange between the dimer-bath type and the pure exciton type (to be quantified by the excitonic concurrence). It is also found that the oscillation frequency increases with the off-diagonal coupling strength. Comparing Fig. 2(a) with Fig. 2(c), it can be seen that the super-Ohmic spectral density function results in a much slower evolution of the coherent dynamics, as expected. In both cases, the final steady state of the entire system is reached in an entangled state.

Another interesting issue to look into is the time evolution of the entanglement between the two monomers as measured by the bipartite concurrence,  $C_{12} = 2|\rho_{12}|$ . This is the intra-species entanglement for the excitonic degrees of freedom. Given the two aforementioned forms of spectral density,  $C_{12}$  is displayed in Figs. 2(b) (super-Ohmic) and 2(d) (Ohmic) as a function of time and off-diagonal coupling strength. Initially, the concurrence is zero because only one of the monomers is excited. In the absence of off-diagonal exciton-phonon coupling (i.e.,  $\lambda = 0$ ), the concurrence cannot be revived in the Markovian approximation.<sup>48</sup> However, thanks to the inclusion of the off-diagonal coupling, concurrence oscillations soon emerge and their maxima coincide with where the excitation is completely delocalized, as demonstrated in Figs. 1(a), 1(b), 2(a), and 2(c). In the presence of the off-diagonal coupling, the entanglement between the two monomers is found to survive the long time limit.

It is also beneficial to examine the asymptotic dynamical behavior of the dimer system, and in particular, the steady-state population difference  $P(\infty)$  which is the Bloch-equation solution for  $\langle \sigma_z \rangle$  at long times. For example, it is revealing to study the total population transfer from the initially excited monomer to the other,  $n_2(\infty) = [1 - P(\infty)]/2$ . In the absence of off-diagonal exciton-phonon coupling,  $P(\infty)$  is always zero at any temperature, i.e., the electronic excitation initially localized at the donor molecule will be shared equally

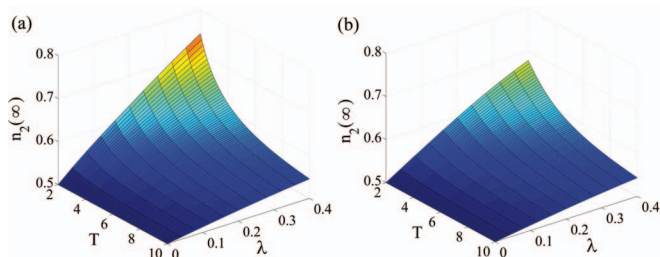


FIG. 3. Net population transfer  $n_2(\infty)$  from the excited monomer as a function of temperature and off-diagonal exciton-phonon coupling strength for the case of  $\Omega_c = 5$ ,  $J = 2.5$ ,  $\kappa = 0.1$ , and  $t_d = 4$ . (a) The super-Ohmic type. (b) The Ohmic type.

between the two monomers at long times. However, this is not the case for finite  $\lambda$ . Due to the anti-symmetric nature of the off-diagonal coupling, the site symmetry is violated. In Figs. 3(a) and 3(b), the steady-state population of the acceptor  $n_2(\infty)$  is plotted as a function of temperature and off-diagonal exciton-phonon coupling strength for the two spectral density functions. It is found that, at a given temperature, off-diagonal coupling increases the amount of energy transferred from the donor to the acceptor, although this increment decreases with the increasing temperature as expected.

## CONCLUSION

Motivated by recent experiments suggesting that coherent energy transfer may exist at physiological temperatures, we have studied the effect of off-diagonal exciton-phonon coupling on resonant energy transfer in a dimer system. We choose an anti-symmetric type of off-diagonal coupling, which leads to an inhomogeneous population distribution between the two monomers in the final steady state. By employing the polaron transformation and the second-order Born-Markov quantum master equation, a set of Bloch equations governing the dynamics of resonant energy transfer has been established, and numerical solutions to those equations are obtained for various parameter regimes. It is shown that the off-diagonal exciton-phonon coupling plays a crucial role in the energy transfer dynamics, and its presence adds a coherent contribution to the energy transfer dynamics. The characteristic frequency of such an induced coherence is an increasing function of the off-diagonal coupling strength. In addition, the final transferred population to the initially unexcited monomer is increased as a result of the anti-symmetric off-diagonal coupling. Our study suggests that in certain physical or chemical systems such as organic polymers and natural light-harvesting systems, the off-diagonal exciton-phonon coupling may play a possible role in their enhanced energy transfer dynamics at elevated temperatures.

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## APPENDIX: AUXILIARY FUNCTIONS FOR THE BLOCH EQUATIONS

This Appendix gives the detailed expressions for the inputs of the Bloch equation (Eq. (8)):

$$\begin{aligned}\Omega &= 2J\Theta^2(1 + \lambda^2)^{-1}, \\ \Lambda_1 &= J^2\xi^2(1 + \lambda^2)^{-1}\{2(1 - \Theta^2)\gamma_{11}(0) \\ &\quad - (1 + \lambda^2)[\gamma_{11}(\tilde{\eta}) + \gamma_{11}(-\tilde{\eta})]\}, \\ \Lambda_2 &= 2J^2(1 + \lambda^2)^{-2}\gamma_{11}(0), \\ S_1 &= 2J\lambda(1 + \lambda^2)^{-1}\{1 + J\xi[S_{11}(\tilde{\eta}) - S_{11}(-\tilde{\eta})]\}, \\ T_2 &= 2J + 2J^2\xi[S_{22}(\tilde{\eta}) - S_{22}(-\tilde{\eta})], \\ \Gamma_3 &= J^2(1 + \lambda^2)^{-1}[\gamma_{22}(\tilde{\eta}) + \gamma_{22}(-\tilde{\eta})], \\ \kappa_1 &= \lambda J^2\xi(1 + \lambda^2)^{-1}[\gamma_{11}(\tilde{\eta}) - \gamma_{11}(-\tilde{\eta}) + \gamma_{22}(\tilde{\eta}) \\ &\quad - \gamma_{22}(-\tilde{\eta})], \\ \kappa_2 &= J^2\xi\Theta(1 + \lambda^2)^{-1}[\gamma_{22}(\tilde{\eta}) - \gamma_{22}(-\tilde{\eta})], \\ S_3 &= -2J^2\xi^2\Theta\lambda[2S_{11}(0) - S_{11}(\tilde{\eta}) - S_{11}(-\tilde{\eta})],\end{aligned}$$

where  $\xi = (1 + \lambda^2)^{-1/2}(\lambda^2 + \Theta^2)^{-1/2}$ .

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