Dimerization-assisted energy transport in light-harvesting complexes

S. Yang
Institute of Theoretical Physics, Chinese Academy of Sciences, Beijing 100190, China
D. Z. Xu
Institute of Theoretical Physics, Chinese Academy of Sciences, Beijing 100190, China
Z. Song
School of Physics, Nankai University, Tianjin 300071, China
C. P. Sun
Institute of Theoretical Physics, Chinese Academy of Sciences, Beijing 100190, China

We study the role of the dimer structure of light-harvesting complex II (LH2) in excitation transfer from the LH2 (without a reaction center (RC)) to the LH1 (surrounding the RC), or from the LH2 to another LH2. The excited and un-excited states of a bacteriochlorophyll (BChl) are modeled by a quasi-spin. In the framework of quantum open system theory, we represent the excitation transfer as the total leakage of the LH2 system and then calculate the transfer efficiency and average transfer time. For different initial states with various quantum superposition properties, we study how the dimerization of the B850 BChl ring can enhance the transfer efficiency and shorten the average transfer time.

I. INTRODUCTION

To face the present and forthcoming global energy crisis, human should search for clean and effective energy source. Recently the investigations on the basic energy science for this purpose has received great attention and experienced impressive progress based on the fundamental physics.1-6 In photosynthetic process, the structural elegance and chemical high efficiency of the natural system based on pigment molecules in transferring the energy of sunlight have stimulated a purpose driven investigation7,8 finding artificial analogs of porphyrin-based chromophores. These artificial systems replicate the natural process of photosynthesis so that the much higher efficiencies could be gained than that obtained in the conventional solid systems.9 It is because one of the most attractive features of photosynthesis is that the light energy can be captured and transported to the reaction center (RC) within about 100ps and with more than 95% efficiency.10-12

Actually, in most of the plants and bacterium, the primary processes of photosynthesis are almost in common:1-12,15: Light is harvested by antenna proteins containing many chromophores; then the electronic excitations are transferred to the RC sequentially, where photochemical reactions take place to convert the excitation energy into chemical energy. Most recent experiments have been able to exactly determine the time scales of various transfer processes by the ultra-fast laser technologies.16-18 These great progresses obviously offer us a chance to quantitatively make clear the underlying physical mechanism of the photosynthesis, so that people can construct the artificial photosynthesis devices in the future to reach the photon-energy and photon-electricity conversions with higher efficiency. For example, quantum interference effects in energy transfer dynamics has been studied for the Fenna-Matthews-Olson (FMO) protein complex, and it was found that, for such molecular arrays, the spatial correlations in the phonon bath and its induced decoherence could affect on the efficiency of the primary photosynthetic event. The present paper will similarly study the influences of spatial structure on the primary processes of photosynthesis for the light-harvesting complexes II (LH2).

In the past, by making use of the x-ray crystallographic techniques, the structure of light-harvesting system has been elucidated.15,19 In the purple photosynthetic bacteria, there exist roughly two types of light-harvesting complexes, referred to as light-harvesting complex I (LH1) and light-harvesting complex II (LH2). In LH1, the RC is surrounded by a B875 bacteriochlorophyll (BChl) ring with maximum absorption peak at 875 nm. The LH2 complex, however, does not contain the RC, but can transfer energy excitation to the RC indirectly through LH1. In the purple bacterium, LH2 is a ring-shaped aggregate built up by 8 (or 9) minimal units, where each unit consists of an αβ-heterodimer, three BChls, and one carotenoid. The αβ-heterodimers, i.e., α-apoproteins and β-apoproteins constitute the skeleton of LH2, while the BChls are embedded in the scaffold to form a double-layered ring structure. The top ring including 16 (or 18) BChl molecules is named as B850 since it has the lowest-energy absorption maximum at 850 nm. The bottom ring with 8 BChls is called B800 because it mainly absorbs light at 800 nm. In every minimal unit, the carotenoid connects B800 BChl with one of the two B850 BChls. Excitation is transferred from one pigment to the neighbor one through the Förster mechanism, while the electron is spatially transferred via the Marcus mechanism.20 Generally, it is independent of the global geometry configuration of the system.

In the present paper, we will study the energy transfer procedure in LH2 by considering the structure dimerization of the B850 ring. It has been conjectured that the dimerized inter-pigment couplings can cause the energy gap to protect the collective excitations.15 Indeed, like the the Su-Schrieffer-Heeger model for the flexible polyacetylene chain,21 the dimerization of the spatial configuration with the Peierls distorted ground state will minimize the total energy for the phonon plus electron. As it is well known, this model exhibits a rich variety of nonlinear phenomena and topological excitations including the topological protection of the quantum state transfer.22 Similarly, we will show that, when the B850 ring
in LH2 is dimerized the excitation transfer efficiency may be enhanced to some extent.

Based on the open quantum system theory, we simply model the excited and un-excited states of a BChl pigment as a quasispin. The excitation transfer is represented by the total leakage from a LH2. Using the master equation, we calculate the efficiency of excitation transfer and the average transfer time in low temperature for various initial states with different superposition properties. The results explicitly indicate that the dimerization of couplings indeed enhances the quantum transport efficiency and shortens the average transfer time.

This paper is organized as follows. In Sec. II, a double-ring XY model with \( N \) unit cells is presented to simulate the LH2 system. In Sec. III, the energy transfer process is described by the quantum master equation. The transfer efficiency \( \eta (t) \) and the average transfer time \( \tau \) are introduced to characterize the dynamics of the system. In Sec. IV, we represent the master equation in the momentum space and show that only the \((k,k)\)-blocks of the density matrix are relevant to energy transfer. In Sec. V, it is found that the transfer efficiency \( \eta (t) \) and the average transfer time \( \tau \) of an arbitrary initial state can be obtained through the channel decomposition. Some numerical analysis of \( \eta^{(k,k)}(t_0) \) and \( \tau^{(k,k)} \) for all the \( k \)-channels are presented in Sec. VI. They show that a suitable dimerization of the B850 BChl ring can enhance the transfer efficiency and shorten the average transfer time. Conclusions are summarized at the end of the paper. In Appendix A, we provide an alternative way to deal with the energy leakage problem. In Appendix B, detail derivations of transforming the master equation from the real space to the \( k \)-space are given. The approximate solution of \( \tau^{(k,k)} \) for \( k = 0 \) and \( k = \pm \pi \) channel is shown in Appendix C.

**II. MODEL SETUP**

The simplified model of LH2 is shown in Fig. 1. All the bacteriochlorophylls (big and small green squares) are modeled by the two-level systems with excited state \( |e_j^{[c]}\rangle \), ground state \( |g_j^{[c]}\rangle \), and energy level spacing \( \Omega \). The raising and lowering quasi-spin operators of the \( j \)th two-level system on the \([c]\) ring is expressed as

\[
\sigma_j^{+(c)} = |e_j^{[c]}\rangle\langle g_j^{[c]}|, \quad \sigma_j^{-(c)} = |g_j^{[c]}\rangle\langle e_j^{[c]}|,
\]

where \([c] = [a] ([b])\) denotes the B800 (B850) BChl ring. Approximately, all the couplings are supposed to be of XY type. This simplification enjoys the main feature of excitation transfer. The Hamiltonians

\[
H_a = \frac{\Omega}{2} \sum_{j=1}^N \sigma_j^{[a]} + J_1 \sum_{j=1}^N (\sigma_j^{+[a]}\sigma_{j+1}^{-[a]} + \text{H.c.})
\]

and

\[
H_b = \frac{\Omega}{2} \sum_{j=1}^{2N} \sigma_j^{[b]} + J_2 \sum_{j=1}^N [(1 + \delta) \sigma_{2j-1}^{+[b]}\sigma_{2j}^{-[b]} + (1 - \delta) \sigma_{2j}^{+[b]}\sigma_{2j+1}^{-[b]} + \text{H.c.}]
\]

with \( N = 8 \), describe the excitations of the B800 and B850 BChl rings, respectively. In the B850 BChl ring, the parameter \( \delta \neq 0 \) characterizes the dimerization due to the spatial deformation of the flexible B850 BChl ring in LH2. The coupling constants of \( H_b \) are dimerized as \( J_2 (1 + \delta) \) and \( J_2 (1 - \delta) \) since the intra-unit and inter-unit Mg-Mg distance between neighboring B850 BChls may be different. The non-local XY type interaction

\[
H_{ab} = g_1 \sum_{j=1}^N \left[ \sigma_j^{+[a]} \left( \sigma_{2j-1}^{-[b]} + \sigma_{2j}^{-[b]} \right) + \text{H.c.} \right] + g_2 \sum_{j=1}^N \left[ \sigma_j^{+[a]} \left( \sigma_{2j-3}^{-[b]} + \sigma_{2j-2}^{-[b]} + \sigma_{2j+1}^{-[b]} + \sigma_{2j+2}^{-[b]} \right) + \text{H.c.} \right]
\]

is used to describe the interaction between the B800 and B850 BChl rings.

In the single excitation case, the quasi-spin can be represented with a spinless fermion with the mapping

\[
\sigma_j^{+[a]} \leftrightarrow A_j^{+}, \sigma_j^{-[b]} \leftrightarrow B_j^{+}, C_j^{+} \leftrightarrow C_j
\]

from the spin space \( V_s = C_{2N}^{\otimes 3} \) to the subspace \( V_F \) of the Fermion Fock space spanned by

\[
\{ |O, j \rangle = O_j^+ |0\rangle | O = A, B, C; j = 1, 2, \ldots, N \}
\]

Hereafter, let us represent the site index as \( (O, j) \), where \( j \) refers to a unit cell shown in Fig. 1 and \( O = A, B, C \) to a position type inside the unit cell. In the subscripts, the site

![Figure 1](image_url)
index \((O, j)\) is written as \(Oj\) for simplicity. The vacuum state of the Fermion system \(|0\rangle\) corresponds to the state that all the quasi-spins are in their ground states,

\[
|0\rangle \leftrightarrow \prod_{j=1}^{N} \left|g_{j}^{(0)}\right\rangle \otimes \prod_{j=1}^{2N} \left|g_{j}^{(1)}\right\rangle.
\]

Then the total Hamiltonian \(H_S = H_a + H_b + H_{ab}\) of LH2 is mapped into

\[
H_S = \sum_{j=1}^{N} \left[ \Omega_a A_j^\dagger A_j + \Omega_b \left( B_j^\dagger B_j + C_j^\dagger C_j \right) \right] + \sum_{j=1}^{N} \left[ J_1 A_j^\dagger A_{j+1} + g_1 A_j^\dagger \left( B_j + C_j \right) \right] + J_2 \left[ (1 + \delta) B_j^\dagger C_j + (1 - \delta) C_j^\dagger B_{j+1} \right] + g_2 A_j^\dagger \left( B_{j+1} + B_{j-1} + C_{j+1} + C_{j-1} \right) + \text{H.c.}. \tag{8}
\]

In the present work, no multi-fermion interactions are considered for simplicity. On the other hand, we use the Holstein-Primakoff transformation\(^{23}\) to map the quasi-spin into bosons. The excitations of the BChls can be described by quasi-spins with the transformation

\[
\text{time spanned by}
\]

\[
|D\rangle = \prod_{j=1}^{n} \left( |0\rangle + A_j^\dagger |1\rangle + B_j^\dagger |2\rangle + C_j^\dagger |3\rangle \right). \tag{9}
\]

For \(S > 1/2\), one local bacteriochlorophyll has more than one excited states. In this case, higher order coherence could be included for further generalization.

In the following, we focus on the single excitation case. Then the temperature should be suitable to ensure there is no higher order excited state.

### III. TRANSFER EFFICIENCY AND AVERAGE TRANSFER TIME VIA THE MASTER EQUATION

Next we consider the energy transfer from an initial state

\[
\tilde{\rho}(0) = \sum_{\{A, j\}} \rho_{A_jA_{j+1}}(0) |A, j\rangle \langle A, j|,
\]

which is a coherent superposition or a mixture of those local states \(|A, j\rangle\) on the B800 ring. As time goes by, the initial state will evolve a state distributing around both the B800 and the B850 rings. Since there exists a difference of chemical potential, \(\Delta \Omega = \Omega_a - \Omega_b\), energy is transferred between the two rings during the time evolution. For an isolated LH2 system, such energy transfer is coherent, namely, the system oscillates between the B800 and the B850 rings. However, when a LH2 is coupled to a heat reservoir with infinite degrees of freedom, irreversible energy transfer occurs. As illustrated in Fig. 2 in the real photosynthetic system, energy is transferred from one LH2 to another LH2 or LH1 through the B850 ring.\(^{15}\) Therefore, we regard the first excited LH2 as an open system, and the sum of others as the a heat reservoir. The energy transfer now can be manipulated as the energy leakage from the B850 ring to the environment.

In order to describe such a procedure that the excitations are finally transferred from the B850 ring to the heat reservoir, the Markovian master equation

\[
\frac{d\rho}{dt} = -i[H_S, \rho] + \mathcal{L}(\rho) \tag{11}
\]

in the Lindblad form is employed for determining the time-evolution of the density matrix. Here two kinds of loss processes, dissipation and dephasing, are considered as Lindblad terms

\[
\mathcal{L}(\rho) = \sum_{j=1}^{N} \left[ \mathcal{L}_{\text{diss},j}(\rho) + \mathcal{L}_{\text{deph},j}(\rho) \right]. \tag{12}
\]

We suppose that each quasi-spin on the B850 ring is coupled to an independent heat reservoir, which reflects the local modes of phonons and other local fluctuations. Then the dissipation from the \(j\)th unit cell is described as

\[
\mathcal{L}_{\text{diss},j}(\rho) = \Gamma_j \sum_{O=B,C} (O_j \rho O_j^\dagger - \frac{1}{2} [O_j^\dagger O_j, \rho]), \tag{13}
\]

where \([\cdot, \cdot]\) denotes the anti-commutator. Here, the sink rate \(\Gamma_j\) at the \(j\)th point may be site dependent. For the dynamics constrained on the subsystem described by \(O\) operators, the last term of \(\mathcal{L}_{\text{diss},j}(\rho)\) gives contribution \(-\Gamma \rho O_j O_j^\dagger\) to \(d\rho_{O_j O_j^\dagger}/dt\), thus dissipation results in the reduction of the total population. Therefore, the dissipation term Eq. (13) represents the incoherent transfer of energy into the environment.

On the other hand, the dephasing term reads

\[
\mathcal{L}_{\text{deph},j}(\rho) = \Gamma_j \sum_{O=B,C} (O_j^\dagger \rho O_j^\dagger O_j - \frac{1}{2} [O_j^\dagger O_j, \rho]). \tag{14}
\]
Compared with the dissipation term, the dephasing one \( L_{\text{deph}} \) does not contribute to any time local change of the probability distribution, i.e., the derivative of the diagonal elements of the density matrix is irrelevant to this term. Thus the total population \( \sum_{O=A,B,C} \sum_j \rho_{O,j,j}(t) \) would be conserved if only the dephasing term were present. However, the dephasing process is also incoherent since it makes the nondiagonal elements of the density matrix tend to zero.

The above two contributions force the LH2 system to ultimately reach a steady state \( \hat{\rho}_{\text{steady}} = |0\rangle \langle 0| = \hat{\rho}_{\text{v,v}} \), namely, in the long-time limit, all excitations are sinked away. The same steady state is obtained from Eq. (11) in the super-operator form

\[
\frac{d}{dt} [\rho] = M[\rho],
\]

where \([\rho]\) denotes the column vector defined by all matrix elements in some order, and the super-operator \(M\) is determined by

\[
M[\rho] = -i[H_S, \hat{\rho}] + L(\hat{\rho}).
\]

In this sense the steady state is just the non-trivial eigenstate of \(M\) with vanishing eigen-energy. Usually, from \(\det M = 0\), the steady state can be found.

However, we are interested in the system dynamics on a short timescale, i.e., how soon can the excitations be transferred from one LH2 to the other light-harvesting complexes? To this end, the transfer efficiency \(\eta(t)\) is defined as the population \(\rho_{\text{v,v}}(t)\) of the vacuum state \(|0\rangle\) at time \(t\),

\[
\eta(t) = \rho_{\text{v,v}}(t).
\]

The corresponding master equation (11)

\[
\frac{d\rho_{Oj}}{dt} = \sum_{j=1}^{N} \Gamma_{j} \langle 0| (B_{j} \hat{\rho} B_{j}^{\dagger} + C_{j} \hat{\rho} C_{j}^{\dagger}) |0\rangle = \sum_{j=1}^{N} \Gamma_{j} \sum_{\sigma=B,C} \rho_{O,j,j}(t') dt'.
\]

means that only the first term of \(L_{\text{diss}}(\hat{\rho})\) contributes to the time derivatives of \(\rho_{\text{v,v}}(t)\). The transfer efficiency is given by the integral of the above formula (15),

\[
\eta(t) = \int_{0}^{t} \sum_{j=1}^{N} \Gamma_{j} \sum_{\sigma=B,C} \rho_{O,j,j}(t') dt'.
\]

The average transfer time \(\tau\) is further defined as

\[
\tau = \lim_{t \to \infty} \frac{1}{\eta(t)} \int_{0}^{t} \sum_{j=1}^{N} \Gamma_{j} \sum_{\sigma=B,C} \rho_{O,j,j}(t') dt'.
\]

where usually

\[
\overline{\eta} = \lim_{t \to \infty} \eta(t) = 1.
\]
In the subspace of the single excitation plus the vacuum with the basis
\[ |O, k\rangle \equiv O_k^\dagger |0\rangle |k\rangle = \frac{2\pi l}{N}; l = 1, 2, \cdots N; O = A, B, C, \]
the general density matrix is decomposed into
\[ \hat{\rho} = \hat{\rho}_{v,v} + \sum_{k_1,k_2} \hat{\rho}_{k_1,k_2} + \sum_{k} \left( \hat{\rho}_{v,k} + \hat{\rho}_{k,v} \right). \]
(26)
where
\[ \hat{\rho}_{v,v} = \rho_{v,v} |0\rangle \langle 0| \]
(27)
is the vacuum block while
\[ \hat{\rho}_{k_1,k_2} = \sum_{O, O' = A, B, C} \rho_{O k_1, O' k_2} |O, k_1\rangle \langle O', k_2|, \]
(28)
is called the \((k_1, k_2)\)-block. For fixed \(k_1\) and \(k_2\), \(\rho_{O k_1, O' k_2}\) form a matrix
\[ \begin{pmatrix}
\rho_{A k_1, A k_2} & \rho_{A k_1, B k_2} & \rho_{A k_1, C k_2} \\
\rho_{B k_1, A k_2} & \rho_{B k_1, B k_2} & \rho_{B k_1, C k_2} \\
\rho_{C k_1, A k_2} & \rho_{C k_1, B k_2} & \rho_{C k_1, C k_2}
\end{pmatrix}. \]
(29)
The \(k\)-space representation of the density matrix is illustrated in Fig. 3 for the \(N = 8\) system.
In the \(k\)-space, the master equation \((11)\) is reduced to
\[ \frac{d\hat{\rho}_{k_1,k_2}}{dt} = -i \left( H_k \hat{\rho}_{k_1,k_2} - \hat{\rho}_{k_1,k_2} H_k \right) \\
+ \sum_{O, O' = A, B, C} \left\{ \left( \Gamma' \right) \rho_{O, k_1, O', k_2} \right\} \rho_{O', k_1, k_2} + \rho_{k_1,k_2} \rho_{O', k_1} \rho_{O, k_2} \\
- \frac{1}{2} \left( \Gamma + \Gamma' \right) \left( \rho_{O, k_1} \rho_{O', k_2} + \rho_{O', k_1} \rho_{O, k_2} \right) \}
\]
(30)
for all the \(k_1, k_2\),
\[ \frac{d\hat{\rho}_{v,v}}{dt} = -i \left( H_k \hat{\rho}_{v,v} - \frac{1}{2} \left( \Gamma + \Gamma' \right) \right) \sum_{O, O' = A, B, C} \rho_{O, k_1} \rho_{O', k_2} \]
\[ \frac{d\hat{\rho}_{v,k}}{dt} = -i \left( H_k \hat{\rho}_{v,k} - \frac{1}{2} \left( \Gamma + \Gamma' \right) \right) \sum_{O, O' = A, B, C} \rho_{O, k_1} \rho_{O', k_2} \]
(31)
for all the \(k\), and
\[ \frac{d\hat{\rho}_{k,v}}{dt} = \sum_{O, O' = A, B, C} \Gamma O_{O, k_1} O_{O', k_2} \]
(32)
The details of the calculation are shown in Appendix B.
We notice that the equations about \(\hat{\rho}_{v,k}\) and \(\hat{\rho}_{k,v}\) are completely decoupled from \(\hat{\rho}_{k_1,k_2}\) and \(\hat{\rho}_{v,v}\). It follows from Eq. (30) that when no dephasing exists, i.e., \(\Gamma' = 0\), the \((k_1, k_2)\)-block \(\hat{\rho}_{k_1,k_2}\) is decoupled with other \(\hat{\rho}_{k_1,k_2}\) for \(\left(k_1', k_2'\right) \neq (k_1, k_2)\). Thus \(\hat{\rho}_{k_1,k_2}\) only evolves in the \((k_1, k_2)\)-block. However, when the dephasing is present \((\Gamma' \neq 0)\), the term
\[ \sum_{O, O' = A, B, C} \Gamma O_{O, k_1} O_{O', k_2} \rho_{k_1,k_2} \rho_{O, k_1} \rho_{O', k_2} \]
(33)
actually induces the coupling between the \((k_1, k_2)\)-block and the \((k, k_2 + k - k_1)\)-block. The initial \(\hat{\rho}_{k_1,k_2}\) may evolves to \(\hat{\rho}_{k_2+k-k_1}\) as time goes by. A typical example of \((k, k_2 + k - k_1)\)-blocks are shown by the black hollow dot-dash squares in Fig. 3. The momentum difference \(k_1 - k_2\) is conserved during the evolution since
\[ k_2 - k_1 = (k_2 + k - k_1) - k. \]
(34)
In addition, Eq. (32) means that only the \((k, k)\)-blocks of the density matrix result in energy transfer, which are marked by the 8 green solid squares in Fig. 3. All the other \(k_1 \neq k_2\) blocks do not affect the transfer efficiency \(\eta(t)\) and average transfer time \(\bar{t}\) at all. Especially, the initial component \(\hat{\rho}_{k_1,k_2}\) with \(k_1 \neq k_2\) will not influence \(\eta(t)\) or \(\bar{t}\) at any time \(t\) afterwards since it cannot evolve to the blocks with \(k_1 = k_2\). Therefore, only considering the dynamics of the \((k, k)\)-blocks are enough for the present purpose.

V. TRANSFER EFFICIENCY AND AVERAGE TRANSFER TIME WITH CHANNEL DECOMPOSITION

In this section we use the \(k\)-space representation of master equation to calculate the average transfer time and transfer efficiency by the standard open quantum system method. As a highly organized array of chlorophyll molecules, the LH2 acts cooperatively to shuttle the energy of photons to elsewhere when sunlight shines on it. In this sense, we use the density matrix
\[ \hat{\rho}(0) = \sum_{k_1,k_2} \rho_{O k_1, O' k_2} |O, k_1\rangle \langle O', k_2| \]
(35)
to describe the excitations in the initial state. From the discussions in the last section, only the \(k_1 = k_2 = k\) blocks relevant to energy transfer. Therefore, there exists an equivalence class of initial states
\[ \langle \hat{\rho}'(0) | = | \langle O, k| \hat{\rho} |O', k\rangle = \rho_{O k, O' k} \rangle \]
(36)
that results in the same transfer efficiency and average transfer time as that for \(\hat{\rho}(0)\). For further use, a special density matrix is chosen from the equivalence class \(\hat{\rho}'(0) \in [\hat{\rho}'(0)]\)
\[ \hat{\rho}(0) = \sum_{k} \rho_{O k, O' k} |O, k\rangle \langle O', k| \]
\[ = \sum_{k} \hat{\rho}^{[k]}(0), \]
(37)
which satisfies \(\langle O, k| \hat{\rho}(0)|O', k\rangle = \rho_{O k, O' k} \rangle\) for \(k_1 = k_2 = k\), and \(\langle O, k| \hat{\rho}(0)|O', k\rangle = 0\) for \(k_1 \neq k_2\). \(\hat{\rho}(0)\) plays an equivalent role for determining the transfer efficiency and average transfer time. Here,
\[ \hat{\rho}^{[k]}(0) = \sum_{O, O' = A, B, C} \rho_{O k, O' k} |O, k\rangle \langle O', k| \]
(38)
\( \tilde{\varrho}^{k_1} (0) \) as the initial state to obtain the final state \( \tilde{\varrho}^{k_1} (t) \), which gives the \( k \)-channel transfer efficiency at time \( t \),

\[
\eta^{k_1} (t) = \Gamma \int_0^t \sum_{k'} \sum_{0=B,C} \varrho^{k_1}_{0k',0k} (t') \, dt', \tag{39}
\]

and the \( k \)-channel average transfer time

\[
\tau^{k_1} = \frac{\Gamma}{\eta} \int_0^\infty t' \sum_{k'} \sum_{0=B,C} \varrho^{k_1}_{0k',0k} (t') \, dt'. \tag{40}
\]

Then we prove a general proposition:

*For an arbitrary initial state \( \tilde{\varrho} (0) \) (Eq. 55) of the LH2 complex, the transfer efficiency at time \( t \) and the average transfer time are the sum of \( \eta^{k_1} (t) \) and \( \tau^{k_1} \) over all \( k \)-channels, respectively.*

\[
\eta (t) = \sum_k \eta^{k_1} (t) \quad \tau = \sum_k \tau^{k_1}. \tag{41}
\]

In order to prove the above proposition we notice that the effective initial state \( \tilde{\varrho} (0) \) evolves to

\[
\tilde{\varrho} (t) = \sum_k \tilde{\varrho}^{k_1} (t) \tag{42}
\]

Since the corresponding transfer efficiency and average transfer time of \( \tilde{\varrho} (0) \) are

\[
\eta (t) = \Gamma \int_0^t \sum_{k'} \sum_{0=B,C} \varrho^{k_1}_{0k',0k} (t') \, dt' \quad \tau = \frac{\Gamma}{\eta} \int_0^\infty t' \sum_{k'} \sum_{0=B,C} \varrho^{k_1}_{0k',0k} (t') \, dt', \tag{43}
\]

Eq. (41) is obtained from Eqs. (39), (40), (42), and (43). Namely, \( \eta (t) \) and \( \tau \) are the sum of \( \eta^{k_1} (t) \) and \( \tau^{k_1} \) for different momentum \( k \) channels.

The present experimental observations have provided some potential pathways for light-harvesting. One of them originates from the excitations on the B800 BCHl ring. It shows that the excitations are transferred to the RC through B800 (LH2) \( \rightarrow \) B850 (LH2) \( \rightarrow \) B850 (another LH2) \( \rightarrow \) B875 (LH1) \( \rightarrow \) RC. As to our model, the initial state is specialized as

\[
\tilde{\varrho} (0) = \sum_{k_1,k_2} \rho_{A_k,A_k} (0) \langle A, k_1 | A, k_2 \rangle. \tag{44}
\]

Accordingly, the \( k \)-channel component of the effective initial state \( \tilde{\varrho} (0) \) becomes

\[
\tilde{\varrho}^{k_1} (0) = \rho_{A_k,A_k} (0) \langle A, k | A, k \rangle = \rho_{A_k,A_k} (0) \tilde{\varrho}^{A,A} (0). \tag{45}
\]

Taking

\[
\tilde{\varrho}^{A,A} (0) = | A, k \rangle \langle A, k | \tag{46}
\]

as the initial state, we obtain the transfer efficiency and the average transfer time

\[
\eta^{A,A} (t) = \Gamma \int_0^t \sum_{k'} \sum_{0=B,C} \varrho^{A,A}_{0k',0k} (t') \, dt' \quad \tau^{A,A} = \frac{\Gamma}{\eta} \int_0^\infty t' \sum_{k'} \sum_{0=B,C} \varrho^{A,A}_{0k',0k} (t') \, dt'. \tag{47}
\]

Hereafter, the superscript \( [A, k] \) denotes that the initial state is Eq. (46). Similar to the above analysis about the proposition, we present a corollary:

*The transfer efficiency \( \eta (t) \) and average transfer time \( \tau \) of the initial state in Eq. (A44) are the weighted average of \( \eta^{[A,k]} (t) \) and \( \tau^{[A,k]} \), respectively.*

\[
\eta (t) = \sum_k \rho_{A_k,A_k} (0) \eta^{[A,k]} (t) \quad \tau = \sum_k \rho_{A_k,A_k} (0) \tau^{[A,k]}. \tag{48}
\]

In the following, we will show the analytical and numerical results of \( \eta^{[A,k]} (t) \) and \( \tau^{[A,k]} \).

First we consider the case without dephasing, i.e., \( \Gamma' = 0 \). The time evolution from initial state \( \tilde{\varrho}^{A,A} (0) \) only takes place in the \( (k, k) \)-block. According to Eq. (40), the master equation of \( \rho_{kk} \)

\[
\frac{d \rho_{kk}}{dt} = -i (H_{kk} \rho_{kk} - \rho_{kk} H_{kk}) \tag{49}
\]

gives the average transfer time

\[
\tau^{[A,k]} = \frac{\Gamma}{\eta} \int_0^\infty t' \sum_{0=B,C} \varrho^{[A,k]}_{0k',0k} (t') \, dt'. \tag{50}
\]

When \( k = 0 \), Eq. (49) is rearranged as a system of differential equations about \( v_j (t) \) (\( j = 1, \cdots, 4 \)) and \( v_5 (t) = |v_4 (t)|^2 \):

\[
v_1 = \rho_{BB,Bk}, \quad v_2 = \rho_{CB,CK} + \rho_{CB,Bk}, \quad v_3 = \rho_{BB,CK}, \quad v_4 = \rho_{BB,Bk} + \rho_{BB,CK} + \rho_{BB,Bk}. \tag{51}
\]

It is

\[
\frac{dv_1}{dt} = i g_+ [v_4 (t) - v_5 (t)], \quad \frac{dv_2}{dt} = -i g_+ [v_4 (t) - v_5 (t)] - \Gamma v_2 (t), \quad \frac{dv_3}{dt} = -i g_+ [v_4 (t) - v_5 (t)] - \Gamma v_3 (t), \quad \frac{dv_4}{dt} = 2 i g_+ v_1 (t) - i g_+ [v_2 (t) + v_3 (t)] - [2 i (J_1 - J_2) + i \Delta \Omega + \frac{\Gamma}{2}] v_4 (t). \tag{52}
\]
with initial conditions

\[ v_1 (0) = 1, v_2 (0) = v_3 (0) = v_4 (0) = v_5 (0) = 0. \] (53)

Here \( g_+ = (g_1 + 2g_2) \). Solving the above differential equations, we obtain

\[
\tau^{[A,k=0]} = \frac{\Gamma}{\eta} \int_0^\infty v_2 (t') dt'
\]

\[
= \frac{g_s^2 + (J_1 - J_2 + \Delta \Omega/2)^2 + \Gamma_0^2/4}{g_s^2 \Gamma_0},
\] (54)

with \( \Gamma_0 = \Gamma/2 \), which is independent of the dimerization parameter \( \delta \). Similarly, when \( k = \pm \pi \), the average transfer time of \( g_+^{[A,k]} (t_0) \) is

\[
\tau^{[A,k=\pm \pi]} = \frac{g_s^2 + (J_1 + J_2 \delta - \Delta \Omega/2)^2 + \Gamma_0^2/4}{g_s^2 \Gamma_0},
\] (55)

where \( g_- = (g_1 - 2g_2) \). It is a quadratic function with respect to \( \delta \). The optimal parameter \( \delta \) with the shortest transfer time satisfies

\[
\frac{\delta^{[A,k=\pm \pi]}}{\delta_{\text{opt}}} = \frac{\Delta \Omega/2 - J_1}{J_2}.
\]

When \( g_1 = 2g_2 \), Eq. (55) shows that \( \tau^{[A,k=\pm \pi]} = \infty \), corresponds to \( \overline{\eta} = 0 \), the energy transfer is prevented at this time.

If the dephasing is present, i.e., \( \Gamma' \neq 0 \), we can provide approximate solutions for \( \tau^{[A,k=0]} \) and \( \tau^{[A,k=\pm \pi]} \),

\[
\tau^{[A,k=0]} = \frac{g_s^2 (4\Gamma_0 - \Gamma')/\Gamma + (2J_1 - 2J_2 + \Delta \Omega)^2 + \Gamma_0^2/4}{2g_s^2 \Gamma_0},
\]

\[
\tau^{[A,k=\pm \pi]} = \frac{g_s^2 (4\Gamma_0 - \Gamma')/\Gamma + (2J_1 + 2J_2 \delta - \Delta \Omega)^2 + \Gamma_0^2/4}{2g_s^2 \Gamma_0},
\] (56)

where \( \Gamma_0 = \Gamma + \Gamma' \). They almost exactly agree with the numerical calculation below, and can also be confirmed by Eq. (54) and (55) when \( \Gamma' = 0 \). The details are shown in Appendix C.

VI. ENERGY TRANSFER EFFICIENCY AND AVERAGE TRANSFER TIME IN NUMERICAL CALCULATION

For a general \( k \), the analytical solution of \( \eta^{[A,k]} (t) \) and \( \tau^{[A,k]} \) is not easy to get. Nevertheless, the numerical results of \( \tau^{[A,k]} \) as a function of \( \delta \) are plotted as blue scatter lines in Fig. 4.

Here we have chosen

\[ N = 8, \frac{J_1}{\Gamma} = 0.3, \frac{J_2}{\Gamma} = 1, \]

\[ \frac{g_1}{\Gamma} = 0.5, \frac{\Delta \Omega}{\Gamma} = 0.1, \frac{\Gamma'}{\Gamma} = 1, \] (57)

\( g_2/\Gamma = 0 \) for the upper panel, \( g_2/\Gamma = 0.125 \) for the lower panel, and \( \delta \) is in the unit of \( 1/\Gamma \) and is long enough to ensure \( \overline{\eta} = 1 \). It shows that when \( k \neq 0 \) and \( \delta \) varies from \(-1 \) to \( 1 \), there always exist optimum cases \( \delta_{\text{opt}}^{[A,k]} \neq 0 \) with and shorter average transfer time. This fact reflects the enhanced effect of dimerization.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4}
\caption{(color online) The average transfer time \( \tau^{[A,k]} \) of \( \widehat{\rho}^{[A,k]} (0) \) (blue scatter lines) and \( \tau_{\text{mix}} \) of the initial mixed state \( \widehat{\rho}_{\text{mix}} (0) \) (red solid lines) with respect to the dimerization degree \( \delta \) of the B850 BChl ring. Here \( N = 8, J_1/\Gamma = 0.3, J_2/\Gamma = 1, g_1/\Gamma = 0.5, \Delta \Omega/\Gamma = 0.1, \Gamma'/\Gamma = 1, g_2/\Gamma = 0 \) (upper panel) and \( g_2/\Gamma = 0.125 \) (lower panel). \( \tau \) is in the unit of \( 1/\Gamma \) and \( \overline{\eta} = 1 \). It shows that each \( \tau^{[A,k]} (k \neq 0) \) curve has a minimum at \( \delta_{\text{opt}}^{[A,k]} \neq 0 \). \( \tau_{\text{mix}} \) is the equal-weighted average of a complete set of \( \{\tau^{[A,k]}\} \).}
\end{figure}

We then take the mixed initial density matrix \( \widehat{\rho} (0) = \widehat{\rho}_{\text{mix}} (0) \) as an example,

\[
\widehat{\rho}_{\text{mix}} (0) = \sum_{j} N \rho_{A_j A_j} (0) |A, j\rangle \langle A, j|
\]

\[ = \sum_{k_1, k_2} \rho_{A_{k_1} A_{k_2}} (0) |A, k_1\rangle \langle A, k_2|. \] (58)

The weight \( \rho_{A_{k_1} A_{k_2}} \) always satisfies

\[
\rho_{A_{k_1} A_{k_2}} (0) = \frac{1}{N} \sum_{j=1}^N \rho_{A_j A_j} (0) = \frac{1}{N}. \] (59)

From Eq. (48), the transfer efficiency and the average transfer time of \( \widehat{\rho}_{\text{mix}} \) is

\[
\eta_{\text{mix}} (t) = \frac{1}{N} \sum_{k} \eta^{[A,k]} (t) \] (60)

\[
\tau_{\text{mix}} = \frac{1}{N} \sum_{k} \tau^{[A,k]}. \] (61)

\( \tau_{\text{mix}} \) is also verified numerically and shown in Fig. 4 as the red solid lines.

In order to see the dynamics of the transfer process clearly, we plot \( \eta_{\text{mix}} \) with respect to the dimerization degree \( \delta \) and time.
FIG. 5. (color online) (a) The contour map of the transfer efficiency of the initial mixed state $\eta_{mix}(\delta, t)$ as a function of dimerization degree $\delta$ and time $t$ for the same setup as that in the lower panel of Fig. 4(b). The profile of $\eta_{mix}$ along $t_0 = 12$ (black dashed line in (a)). (c) The profile of $\eta_{mix}$ along $\delta_0 = -0.5$ (red dot line in (a)). It shows that $\eta_{mix}(\delta, t)$ increases over time, and an optimum $\delta$ can enhance the transfer efficiency.

In Fig. 5(a), i.e., $\eta_{mix} = \eta_{mix}(\delta, t)$. At a certain initial time $t_0 = 12$, $\eta_{mix}(\delta, t_0)$ as a function of $\delta$ is plotted in Fig. 5(b), while for a certain dimerization degree $\delta_0 = -0.5$, $\eta_{mix}(\delta_0, t)$ as a function of $t$ is plotted in Fig. 5(c). Here the parameters are chosen as same as the ones in Fig. 4 except that $g_2/\Gamma = 0.125$. The contour map Fig. 5(a) and the profiles of $\eta_{mix}(\delta, t)$ in Fig. 5(b) and (c) show that (1) $\eta_{mix}(\delta, t)$ increases monotonously as time goes by. In the large $t$ limit, $\eta_{mix}(\delta, t)$ equals to 1. (2) At any certain short instant, an optimum $\delta$ can enhance the transfer efficiency.

Similar to $\eta_{mix}$ and $\tau_{mix}$, in general, there exists an optimal $\delta_{opt} \neq 0$ for an arbitrary initial $\rho(0)$, which means that a suitable distortion of the B850 ring is helpful for the excitation transfer. This result agrees with the x-ray observation that the Mg-Mg distance between neighboring B850 BCHls is 9.2 Å within the $\alpha\beta$-heterodimer and 8.9 Å between the heterodimers reported in Ref. 10. The B850 ring is indeed dimerized in nature.

As shown in Fig. 4, $\tau^{[A;k=\pm \pi]}$ and $\tau^{[A;k=\pi]}$ are particular since nearly all the other $\tau^{[A;k]}$ are within the range of $[\tau^{[A;k=0]}, \tau^{[A;k=\pm \pi]}]$, so is the average transfer time $\tau$ of an arbitrary $\rho(0)$. Besides, the absolute value of $|\delta_{opt}^{[A;k=\pm \pi]}|$ for the $k = \pm \pi$ case is larger than the one of other $\rho(0)$, i.e., $|\delta_{opt}^{[A;k=\pm \pi]}| \leq |\delta_{opt}^{[A;k=0]}|$. Hence, once we have known the properties of $\tau^{[A;k=0]}$ and $\tau^{[A;k=\pm \pi]}$, the behavior of a general $\tau$ can be conjectured to some extent. Compared the lower panel of Fig. 4 with the upper panel, a larger $g_2/\Gamma$ can increase $\tau^{[A;k=\pi]}$ but decrease $\tau^{[A;k=0]}$. In the $g_2/\Gamma = 0.125$ case, the homogeneous pure state $\rho^{[A;k=0]}(0)$ is better than the mixed state $\rho_{mix}^{[A;k=0]}(0)$ for energy transport. However, the upper panel with $g_2/\Gamma = 0$ gives the contrary result.

The minimal $\tau^{[A;k=\pi]}$ is reachable at $\delta_{opt}^{[A;k=\pi]} = (\Delta \Omega/2 - J_1)/J_2$,

$$\tau_{\min}^{[A;k=\pi]} = \frac{(g_1 - 2g_2)^2(4\Gamma + 3\Gamma') + \Gamma'(\Gamma + \Gamma')^2}{2(g_1^2 - g_2^2)^2\Gamma(\Gamma + \Gamma')}.$$  

In the toy model illustrated in Fig. 4, $J_2 > J_1$ and $g_2 < g_1$. When $g_2/g_1 = \gamma_0 = 0.5$, we have $\tau_{\min}^{[A;k=\pi]} = \tau^{[A;k=0]}$, where

$$\xi = \frac{\Gamma + \Gamma'}{2(2J_2 - 2J_1 - \Delta \Omega)}.$$  

On the side of $0 < g_2/g_1 < \gamma_0$, $\tau_{\min}^{[A;k=\pi]} < \tau^{[A;k=0]}$, while on the other side $\gamma_0 < g_2/g_1 < 1$, $\tau_{\min}^{[A;k=\pi]} > \tau^{[A;k=0]}$.

In general, the shortest average transfer time of an arbitrary initial $\rho(0)$ is within the range of $[\tau_{\min}^{[A;k=\pi]}, \tau^{[A;k=0]}]$. The mean value of $\tau_{\min}^{[A;k=\pi]}$ and $\tau^{[A;k=0]}$ can roughly reflect the influence of parameters on the transfer process,

$$\overline{\tau} = \frac{1}{2}(\tau_{\min}^{[A;k=\pi]} + \tau^{[A;k=0]}).$$ 

In Fig. 6 we plot $\overline{\tau}$ with respect to $g_1/\Gamma$ for different $J_2/\Gamma = 0, 1, 2, 3$. Here, $J_1/\Gamma = 0.3$, $\delta = (\Delta \Omega/2 - J_1)/J_2$, $g_2/g_1 = 0.25$, $\Delta \Omega/\Gamma = 0.1$, $\Gamma'/\Gamma = 0.5$, and $\overline{\tau}$ is in the unit of (1/\Gamma). It shows that $\overline{\tau}$ decreases monotonously as $g_1/\Gamma$ increases. In the short $g_1/\Gamma$ limit, $\overline{\tau}$ tends to infinity, which is reasonable since the two BCHl rings are decoupled in this case. Moreover, $\overline{\tau}$ is larger when $J_2/\Gamma$ is larger.
VII. CONCLUSION

In summary, we have studied the craggy transfer in light-harvesting complex with dimerization. We employed the open quantum system approach to show that the dimerization of the B850 BChl ring can enhance the transfer efficiency and shorten the average transfer time for different initial states with various quantum superposition properties. Actually our present investigation only focuses on a crucial stage in photosynthesis – the energy transfer, which is carried by the coherent excitations in the typical light-harvesting complex II (LH2). Here the LH2 is modeled as two coupled bacteriochlorophyll (BChl) rings. With this modeling, the ordinary photosynthesis is roughly described as three basic steps: 1) stimulate an excitation in LH2; 2) transfer it to another LH2 or LH1; 3) the energy causes the chemical reaction that converts carbon dioxide into organic compounds.

Another important issues of the photosynthesis physics concerns about the quantum nature of light. Since the experiments have illustrated the role of the quantum coherence of collective excitations in LH complexes, it is quite natural to believe that the excitation coherence may be induced by the higher coherence of photon. Therefore, in a forthcoming paper we will report our systematical investigation on how the statistical properties of quantum light affects the photosynthesis.

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Appendix A: Equivalent non-Hermitian Hamiltonian

In the case without dephasing, i.e., $\Gamma' = 0$, an equivalent non-Hermitian Hamiltonian is introduced to study the dynamics of the open system,

$$H = H_S - i \sum_{j=1}^{N} \frac{\Gamma_j}{2} (B_j^\dagger B_j + C_j^\dagger C_j).$$

(A1)

The equivalence between Eq. (A1) and (11) is shown as follows. On the one hand, the Schrödinger equation

$$i \frac{d}{dt} |\psi\rangle = \left[ H_S + i \sum_{j=1}^{N} \frac{\Gamma_j}{2} (B_j^\dagger B_j + C_j^\dagger C_j) \right] |\psi\rangle.$$

(A2)

and its Hermitian conjugate

$$-i \frac{d}{dt} |\psi\rangle = |\psi\rangle \left[ H_S + i \sum_{j=1}^{N} \frac{\Gamma_j}{2} (B_j^\dagger B_j + C_j^\dagger C_j) \right].$$

(A3)

gives the evolution equation of the density matrix $\hat{\rho} = |\psi\rangle \langle \psi|$, and

$$\frac{d\hat{\rho}}{dt} = \left( \frac{d}{dt} |\psi\rangle \langle \psi| \right) \left( \frac{d}{dt} |\psi\rangle \langle \psi| \right).$$

(A4)

On the other hand, when the dephasing terms are absent, the master equation Eq. (11) becomes

$$\frac{d\hat{\rho}}{dt} = -i [H_S, \hat{\rho}] + \sum_{j=1}^{N} \sum_{O=B,C} \Gamma_j (O_j \hat{\rho} O_j^\dagger - \frac{1}{2} [O_j^\dagger O_j, \hat{\rho}]).$$

(A5)

The above equation is written on the expanded Hilbert space with an additive vacuum basis $|0\rangle$. Compared with Eq. (4), the additive term in Eq. (A5) $\sum_{j=1}^{N} \sum_{O=B,C} \Gamma_j (O_j \hat{\rho} O_j^\dagger - \frac{1}{2} [O_j^\dagger O_j, \hat{\rho}])$ has only contribution to $d\hat{\rho}_{\nu\gamma}/dt$, which does not change the dynamics of the system. The Eqs. (A4) and (A5) are equivalent for determining the time evolution of $\hat{\rho}_{Oj,Oj'}$.

For the non-Hermitian Hamiltonian, the corresponding transfer efficiency and the average transfer time are

$$\eta(t) = \int_0^\infty \sum_{j=1}^{N} \sum_{O=B,C} \frac{1}{\eta} \left| \langle O_j | \psi(t') \rangle \right|^2 dt'$$

$$\tau = \frac{1}{\eta} \int_0^\infty \sum_{j=1}^{N} \sum_{O=B,C} \left| \langle O_j | \psi(t') \rangle \right|^2 dt'.$$

(A6)

Due to the equivalence of the non-Hermitian Hamiltonian and the dissipative master equation, the results of Eq. (A6) are as same as the ones calculated by Eq. Eqs. (19) and (20). The non-Hermitian Hamiltonian method has an advantage over the master equation one for saving computer time. Instead of $N^2$ equations, only a system of $N$ equations are needed to be solved in the non-Hermitian Hamiltonian case.

However, when the dephasing terms are present, there is no equivalent non-Hermitian Hamiltonian. In this case, compared with Eq. (4), the additional term $\sum_{O=B,C} \Gamma_j (O_j \hat{\rho} O_j^\dagger - \frac{1}{2} [O_j^\dagger O_j, \hat{\rho}])$ cannot be omitted any more. It can also affect the evolution of the density matrix of the LH2 system.

Appendix B: Transform the master equation to the $k$-space

In this section, we will transform the master equation from the real space (Eqs. (11)-(14)) to the $k$-space (Eqs. (30)-(32)).
Since $H_S = \sum_k H_k$, and $\hat{\rho}$ is expressed as Eq. (26), we have
\[-i[H_S, \hat{\rho}] = -i \left( \sum_k H_k, \sum_{k_1,k_2} \hat{\rho}_{k_1,k_2} + \sum_k (\hat{\rho}_{v,k} + \hat{\rho}_{k,v}) \right)\]
\[-i \sum_{k_1,k_2} (H_k \hat{\rho}_{k_1,k_2} - \hat{\rho}_{k_1,k_2} H_k)\]
\[-i \sum_k (H_k \hat{\rho}_{k,v} - \hat{\rho}_{v,k} H_k). \] (B1)

Here $[H_S, \hat{\rho}_{v,v}] = 0$ since they are in the different subspaces.

According to the Fourier transformation Eq. (22), the term $\sum_j O_j \hat{\rho} O_j^\dagger$ becomes
\[\sum_j O_j \hat{\rho} O_j^\dagger = \sum_{k_1,k_2,k_3,k_4} \frac{1}{N} \sum_j e^{i(k_1-k_3)j} O_{k_4} \hat{\rho}_{k_1,k_2} O_{k_3}^\dagger \]
\[= \sum_{k_1,k_2} \frac{1}{N} \sum_j e^{i(k_1-k_2)j} O_{k_1} \hat{\rho}_{k_1,k_2} O_{k_2}^\dagger \]
\[= \sum_{k_1,k_2} \hat{\delta}_{k_1,k_2} O_{k_4} \hat{\rho}_{k_1,k_2} O_{k_2}^\dagger = \sum_k O_k \hat{\rho}_k O_k^\dagger. \] (B2)

The term $\sum_j O_j^\dagger O_j \hat{\rho}$ is transformed as
\[\sum_j O_j^\dagger O_j \hat{\rho} \]
\[= \sum_{k_1,k_3} \frac{1}{N} \sum_j e^{-i(k_1-k_3)j} O_{k_3}^\dagger O_{k_1} \left( \sum_k \hat{\rho}_{k_1,k_2} + \hat{\rho}_{k_2,v} \right) \]
\[= \sum_{k_1,k_3} \frac{1}{N} \sum_j e^{-i(k_1-k_3)j} O_{k_3}^\dagger O_{k_1} \left( \sum_k \hat{\rho}_{k_1,k_2} + \hat{\rho}_{k_2,v} \right) \]
\[= \sum_{k_1,k_3} \hat{\delta}_{k_1,k_3} O_{k_4}^\dagger O_{k_4} + O \hat{\rho}_{k_1,k_2} + \sum_k O_k \hat{\rho}_k O_k^\dagger. \] (B3)

Similarly,
\[\sum_j O_j^\dagger O_j \hat{\rho} = \sum_{k_1,k_2} \hat{\rho}_{k_1,k_2} O_{k_2}^\dagger + \sum_k \hat{\rho}_v O_k^\dagger O_k. \] (B4)

Finally, the term $\sum_j O_j^\dagger O_j \hat{\rho} O_j^\dagger O_j$ is written as
\[\sum_j O_j^\dagger O_j \hat{\rho} O_j^\dagger O_j \]
\[= \sum_{k_1,k_2,k_3,k_4,k_5,k_6} \frac{1}{N^2} \sum_j e^{-i(k_1-k_3-k_4+k_5-k_6)j} O_{k_4} O_{k_3} \hat{\rho}_{k_1,k_2} O_{k_6}^\dagger \]
\[= \sum_{k_1,k_2,k_3,k_4} \frac{1}{N^2} \sum_j e^{-i(k_1-k_3+k_5-k_6)j} O_{k_4} O_{k_3} \hat{\rho}_{k_1,k_2} O_{k_6}^\dagger \]
\[= \frac{1}{N} \sum_{k_1,k_2,k_3} \delta_{k_1+k_2+k_3} O_{k_4} \hat{\rho}_{k_1,k_2} O_{k_6}^\dagger \]
\[= \frac{1}{N} \sum_{k_1,k_2,k_3} O_{k_4} \hat{\rho}_{k_1,k_2} O_{k_6}^\dagger O_{k_3} O_{k_4}^{k_3-k_6}. \] (B5)

Therefore, Eqs. (30)–(32) are obtained by summarizing Eqs. (B1)–(B5).

Appendix C: Approximative master equations for special cases

In the cases of $k = 0$ and $k = \pm \pi$, we have the approximate master equation,
\[
\frac{d\rho_{k,k}}{dt} = \frac{-1}{2} \left( \Gamma + \Gamma^\prime \right) \rho_{k,k} + \sum_{O \in B,C} \left\{ \Gamma_k^O \rho_{k,k} O_k^O \right\}.
\] (C1)

It is verified numerically that the term $\Gamma_k^O \rho_{k,k} O_k^O$ in Eq. (C1) plays the same role as $\Gamma / N \sum_k \rho_{k,k} O_k^O$ in Eq. (30) for $k = 0, \pm \pi$. For the $(k = 0, k = 0)$-block, Eq. (52) becomes
\[
\frac{d}{dt} v_1(t) = i g_+ [v_4(t) - v_5(t)],
\]
\[
\frac{d}{dt} v_2(t) = -i g_+ [v_4(t) - v_5(t)] - \Gamma v_2(t),
\]
\[
\frac{d}{dt} v_3(t) = -i g_+ [v_4(t) - v_5(t)] - (\Gamma + \Gamma^\prime) v_3(t),
\]
\[
\frac{d}{dt} v_4(t) = 2i g_+ [v_1(t) - i] \left[ v_2(t) + v_3(t) \right] - \left[ 2i (\Gamma_1 - \Gamma_2) + i \Delta \Omega + \frac{\Gamma + \Gamma^\prime}{2} \right] v_4(t).
\] (C2)

Solving the above differential equation we have $\tau^{[A,k=0]}$ shown in Eq. (50). The average transfer time $\tau^{[A,k=\pm \pi]}$ for the $k = \pm \pi$ channel is also obtained similarly.

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