Artificial Light Harvesting by Dimerized Möbius Ring

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We theoretically study artificial light harvesting by a dimerized Möbius ring. When the donors in the ring are dimerized, the energies of the donor ring are split into two sub-bands. Because of the nontrivial Möbius boundary condition, both the photon and acceptor are coupled to all collective-excitation modes in the donor ring. Therefore, the quantum dynamics in the light harvesting are subtly influenced by the dimerization in the Möbius ring. It is discovered that energy transfer is more efficient in a dimerized ring than that in an equally-spaced ring. This discovery is also confirmed by the calculation with the perturbation theory, which is equivalent to the Wigner-Weisskopf approximation. Our findings may be beneficial to the optimal design of artificial light harvesting.

I. INTRODUCTION

Photosynthesis is the main resource of energy supply for living beings on earth. Therein, efficient light harvesting process, which delivers the captured photon energy to the reaction center, plays a crucial role in natural photosynthesis [1–4]. Because a series of experimental and theoretical explorations [5–9] have demonstrated that quantum coherent phenomena might exist and even optimize the natural photosynthesis, much effort has been made to reveal the effect of quantum coherence on efficient light harvesting [10–17].

The researches on optimal geometries for efficient energy transfer are rare [12, 18–21]. Wu et al. demonstrated the trapping-free mechanism for efficient light harvesting in a star-like artificial system [18]. Hoyer et al. showed ratchet effect for quantum coherent energy transfer in a one-dimensional system [19]. In 2013, one of the authors Q.A. and his collaborators elucidated that clustered geometries utilize exciton delocalization and energy matching condition to optimize energy transfer in a generic tetramer model [12] as well as in Fenna-Matthews-Olson complex [22, 23]. However, photosynthesis with ring-shape geometry is more frequently observed in natural photosynthetic complexes, e.g. LH1 and LH2 [10, 24]. This observation inspired Yang et al. to prove that symmetry breaking in B850 ring of LH2 complex boosts efficient inter-complex energy transfer [20]. Dong et al. further proposed that a perfect donor ring for artificial light harvesting makes full use of collective excitation and dark state to enhance the energy transfer efficiency [21].

Mathematically speaking, the rings as in LH1 and LH2 are topologically trivial, since both the photon and acceptor are only coupled to the zero-momentum collective-excitation mode regardless of the dimerization as shown in Appendix III. On the other hand, Möbius strips [25–28] manifest novel physical properties and can be used to fabricate novel devices and materials [29], e.g. topological insulators and negative-index metamaterials [30–32]. In these Möbius strips, the electrons in the ring experience different local effective fields at different positions due to the topologically non-trivial boundary condition. This observation enlightens us on the investigation of the Möbius strips in artificial light harvesting. When the donors in the ring are dimerized, there are two energy sub-bands for collective excitation modes. Due to the Möbius boundary condition, both the photon and acceptor interact with all collective excitations in the ring. This is in remarkable contrast to the case in Ref. [21], where they are only coupled to single collective excitation mode.

This paper is organized as follows: the donor ring with Möbius boundary condition in introduced for light harvesting in the next section. Then, in Sec. III the energy transfer efficiency is numerically simulated for various of parameter regimes. Finally, the main results are summarized in the Conclusion part. In Appendix I a brief description of diagonalizing a dimerized ring with Möbius boundary condition is given. In Appendix II we prove that both the photon and acceptor only interact with one of the collective excitation modes in the ring with periodic boundary condition, no matter whether the dimerization exists in the ring or not. In Appendix III we present a detailed perturbation theory for describing energy transfer in a ring with Möbius boundary condition.
II. DIMERIZED RING WITH MÖBIUS BOUNDARY CONDITION

In this paper, we consider the light harvesting in a Peierls distorted chain with Möbius boundary condition. The quantum dynamics of the whole system is governed by the Hamiltonian

$$H = \omega b^\dagger b + \varepsilon_A A^\dagger A + H_{PM} + \sum_{j=1}^{N} (\xi d_j^\dagger A + Jd_j^\dagger b) + \text{h.c.},$$

where $b^\dagger (b)$ is the creation (annihilation) operator of photon with frequency $\omega$. $A^\dagger (A)$ is the creation (annihilation) operator of excitation at the acceptor with site energy $\varepsilon_A$. $d_j^\dagger (d_j)$ is the creation (annihilation) operator of an excitation at $j$th donor, and the Peierls distorted ring with Möbius boundary condition is described by

$$H_{PM} = \sum_{j=1}^{N-1} g[1-(-1)^j\delta]d_{j+1}^\dagger d_j - g|1-(-1)^N\delta]d_N^\dagger d_N + \text{h.c.}$$

with $g$ being coupling constant between nearest neighbors and $\delta$ being dimerization constant. Notice that the minus sign before the second term on the r.h.s. indicates the Möbius boundary condition, and the site energies of donors are homogeneous and chosen as the zero point of energy. Here we assume that the photon and acceptor are coupled to all donors with equal coupling strength $J$ and $\kappa$, respectively.

By the diagonalization method of $H_{PM}$ in Appendix I, the total Hamiltonian is rewritten as

$$H = \omega b^\dagger b + \varepsilon_A A^\dagger A + \sum_k \varepsilon_k (A_k^\dagger A_k - B_k^\dagger B_k) + H_1.$$ (3)

There are two energy bands in the donor ring denoted by the annihilation (creation) operators

$$A_k = \sum_{j=1}^{N/2} \frac{e^{-ikj}}{\sqrt{N}} (e^{i(2j-1)\frac{\pi}{N}} d_{2j-1} + e^{i(\theta_k+2j)\frac{\pi}{N}} d_{2j}),$$

$$B_k = \sum_{j=1}^{N/2} \frac{e^{-ikj}}{\sqrt{N}} (e^{i(2j-1)\frac{\pi}{N}} d_{2j-1} - e^{i(\theta_k+2j)\frac{\pi}{N}} d_{2j}).$$

$(A_k^\dagger$ and $B_k^\dagger$) with the eigen energies being $\pm \varepsilon_k$, where

$$\varepsilon_k = 2g \sqrt{\cos^2(\frac{k}{2} - \frac{\pi}{N}) + \delta^2 \sin^2(\frac{k}{2} - \frac{\pi}{N})},$$

and the momentum

$$k = \frac{4\pi}{N} (0, 1, 2, \ldots, \frac{N}{2} - 1) - \pi + \frac{2\pi}{N}.$$ (7)

The interaction Hamiltonian among the photon and acceptor and donor ring is

$$H_1 = \sum_k (\xi A_k^\dagger A_k + \xi B_k B_k^\dagger A + (J_A A_k^\dagger B_k^\dagger + J_B B_k A_k^\dagger) b + \text{h.c.}$$

$$= \sum_k (h_A A_k^\dagger H_k + h_B B_k^\dagger (\xi A + Jb) + \text{h.c.}.$$ (8)
with the $k$-dependent factors
\begin{align}
\hspace{1cm} h_{Ak} &= \frac{1}{\sqrt{N}} \sum_{j=1}^{N/2} e^{-ikj} e^{-i(2j-1)\frac{\pi}{N}} (1 + e^{i\delta \kappa} e^{i\frac{\pi}{N}}), \\
\hspace{1cm} h_{Bk} &= \frac{1}{\sqrt{N}} \sum_{j=1}^{N/2} e^{-ikj} e^{-i(2j-1)\frac{\pi}{N}} (1 - e^{i\delta \kappa} e^{i\frac{\pi}{N}}),
\end{align}
\hspace{1cm}
\hspace{1cm}
e^{i\delta_k} = \frac{g}{\varepsilon_{k}} [(1 + \delta) e^{-i \frac{\pi}{N}} + (1 - \delta) e^{-i(k - \frac{\pi}{N})}].
\hspace{1cm}
\hspace{1cm}
Before investigating the quantum dynamics of light harvesting, we shall analyze the energy spectrum of Möbius ring for different dimerization $\delta$. As shown in Fig. 2, the characteristics of the energy spectrum vary remarkably in response to the change of $\delta$. When the donors in the ring are equally distributed, i.e. $\delta = 0$, the energy spectrum $\varepsilon_k = 2g \cos(k/2)$ changes over a range $2g$. For other parameters, i.e. $0 < |\delta| < 1$, the energy spectrum $\varepsilon_k$, which lies in the range $|2g| |\delta|, 2g$, shrinks as $|\delta|$ approaches unity. There is an energy gap between the two sub-bands $4g |\delta|$.

Previously, Möbius strip [24, 27, 28] was proposed to fabricate novel devices and materials [29], e.g. topological insulators and negative-index metamaterials [30, 32]. Although it seems that the ring with Möbius boundary condition in this paper is somewhat different from Möbius strip in Refs. [28, 30, 32], we remark that the ring with Möbius boundary condition can be considered as Möbius strip in the Hilbert space. Further comparison shows that the ring with Möbius boundary condition is not even twisted as the previous Möbius strip. As a result of Möbius boundary condition, the photon and acceptor are coupled to all the collective modes in the ring, and thus leads to different quantum dynamics as compared to that for a ring with periodic boundary condition.

III. NUMERICAL RESULTS

In this section, we consider the quantum dynamics of light harvesting by a Peierls distorted chain with Möbius boundary condition. For an initial state $|\psi(0)\rangle = |1_b\rangle \equiv |1_b, 0_A, 0_{Ak}, 0_{Bk}\rangle$, the state of the total system at any time $t$
\begin{equation}
|\psi(t)\rangle = \alpha_b|1_b\rangle + \alpha_A|1_A\rangle + \sum_k \beta_{Ak}|1_{Ak}\rangle + \sum_k \beta_{Bk}|1_{Bk}\rangle,
\end{equation}
\hspace{1cm}

with $|1_A\rangle \equiv |0_b, 1_A, 0_{Ak}, 0_{Bk}\rangle$, $|1_{Ak}\rangle \equiv |0_b, 0_A, 1_{Ak}, 0_{Bk}\rangle$, $|1_{Bk}\rangle \equiv |0_b, 0_A, 0_{Ak}, 1_{Bk}\rangle$, is governed by the Schrödinger equation
\begin{equation}
i \partial_t |\psi(t)\rangle = H |\psi(t)\rangle,
\end{equation}
\hspace{1cm}

if the system does not interact with the environment. However, an open quantum system inevitably suffers from decoherence due to the couplings to the environment. Generally speaking, the quantum dynamics in the presence of decoherence is described by the master equation instead of Schrödinger equation. Despite this, it has been shown that the quantum dynamics for light harvesting can be well simulated by the quantum jump approach with a non-Hermitian Hamiltonian where the imaginary parts in the diagonal terms represent the decoherence processes [24, 35]. In this case, the Hamiltonian $H$ in Eq. 3 is obtained by replacing the energies of the acceptor and collective-excitation modes in the following way, i.e.
\begin{align}
A : \varepsilon_A &\rightarrow \varepsilon_A' = \varepsilon_A - i\Gamma, \\
A_k : \varepsilon_k &\rightarrow \varepsilon_k' = \varepsilon_k - i\kappa, \\
B_k : -\varepsilon_k &\rightarrow -\varepsilon_k' = -(\varepsilon_k + i\kappa),
\end{align}
\hspace{1cm}

where $\kappa$ and $\Gamma$ are respectively the fluorescence rate at the donors and the charge separation rate at the acceptor.

It was shown [21] that in a composite system including

FIG. 3: (color online) Population dynamics of acceptor $P_a(t) = |\alpha_A|^2$ with Möbius ring for red solid line $\delta = 0$, blue dash-dotted line $\delta = 0.3$, and black dashed line $\delta = 0.6$. Other parameters are $N = 8, \omega/\varepsilon_A/\xi = -6, J/\xi = 1, g/\xi = 1, \Gamma/\xi = 0.3$ and $\kappa/\Gamma = 1$ with $\xi = 10$ps$^{-1}$.

FIG. 4: (color online) Transfer efficiency $\eta$ vs detuning $\Delta = \omega - \varepsilon_A$ for (a) a large fluorescence rate $\kappa/\xi = 1$; (b) a small fluorescence rate $\kappa/\xi = 0.1$. In each subfigure, we plot the efficiency for a dimerized Möbius ring with $\delta = 0.6$ (red dashed line) and for an equally-spaced Möbius ring with $\delta = 0$ (blue solid line). Other parameters are $N = 8, \varepsilon_A/\xi = -6, J/\xi = 1, g/\xi = 1$, and $\Gamma/\xi = 0.3$ with $\xi = 10$ps$^{-1}$.
a photon, and an acceptor, and a perfect ring with periodic boundary condition, the quantum dynamics of the total system can be effectively modeled as the interaction of photon and acceptor with the donor’s single collective-excitation mode. Furthermore, as proven in Appendix III both the photon and acceptor are still coupled to the same collective mode of donor ring even when the ring is dimerized. However, the situation is different when we explore the coherent energy transfer in a dimerized Möbius ring. In Fig. 4, we plot population of acceptor $P_a(t) = |\alpha_A(t)|^2$ vs time for three cases with different $\delta$. Clearly, the quantum dynamics in Möbius ring is subtly influenced by the dimerization. In all cases, the populations quickly rise to a maximum and then it is followed by damped oscillations. After $t \approx 10$, all three curves converge to a similar same exponential decay as the charge separation rates are the same for all three cases.

To quantitatively characterize the energy transfer, there is the transfer efficiency $\eta$ defined as

$$\eta = 2\Gamma \int_0^\infty |\alpha_A(t)|^2 dt. \quad (15)$$

In Fig. 4(a), we investigate the dependence of transfer efficiency on the detuning $\Delta = \omega - \varepsilon_A$ for a fast fluorescence decay $\kappa/\xi = 1$. For an evenly-distributed donor ring, i.e. $\delta = 0$, the transfer efficiency reaches maximum near the resonance, i.e. $\Delta = 0$, which is slightly different from that discovered in Ref. 21. As the photon frequency deviates from the resonance, the transfer efficiency quickly drops. When we further investigate the case for a dimerized ring with $\delta = 0.6$, the transfer efficiency has been increased over the whole range of photon frequency, especially in the blue-detuned regime. The same characteristics has also been observed in the case with a slow fluorescence decay $\kappa/\xi = 0.1$ as shown in Fig. 4(b).

To validate the above numerical simulation, we also calculate the quantum dynamics and light-harvesting efficiency by the perturbation theory. The details are presented in Appendix III. In Ref. 39, it has been proven that the Wigner-Weisskopf approximation is equivalent to the perturbation theory in the study of an excited state coupled to a continuum. Here we generalize the perturbation theory to the investigation of coherent energy transfer between few bodies via a continuum. In Fig. 5, the energy transfer efficiency of a dimerized ring is generally larger than that of an equally-spaced ring. This result is qualitatively consistent with Fig. 4(a).

In order to explore the underlying physical mechanism, we turn to coupling constants $|h_{Ak}|$ and $|h_{Bk}|$ as shown in Fig. 4. Although the coupling constants $|h_{Ak}|$ for $\delta = 0$ almost coincide with the ones for $\delta = 0.6$, the coupling constants $|h_{Bk}|$ are significantly suppressed when the dimerization occurs. Furthermore, because $|h_{Ak}|$ are generally larger than $|h_{Bk}|$ by an order, the transfer efficiency is slightly tuned by the dimerization.

IV. CONCLUSION

In this paper, we investigate the quantum dynamics of light harvesting in a Peierls distorted ring with Möbius boundary condition. Due to the nontrivial Möbius topology, there are two energy bands for the excitation in the ring when the donors in the ring are dimerized. Because both the photon and acceptor interact with all collective-excitation modes in the Möbius ring, the quantum dynamics and thus the efficiency for light harvesting is effectively influenced by the presence of dimerization. By numerical simulations, we show that when the donors in the Möbius ring are dimerized, the energy transfer is generally optimal for a wide range of photon frequencies. Our discoveries together with previous findings 12, 18, 20, 21, 40 may be beneficial for the future design of optimal artificial light harvesting.

In addition, we also remark that in fact change of protein environment inevitably leads to static and dynamic disorders in the transition energies of chlorophylls in natural photosynthesis 22, 41, 42. In Ref. 21, assuming that all site energies of donors are homogeneous, the ab-
sorbed photon energy utilizes dark-state mechanism to effectively avoid fluorescence loss via the donors. However, this mechanism might not work well when the static and dynamic disorders take place.

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1. Diagonalization of Möbius Hamiltonian

The dimerized ring with Möbius boundary condition is described by

$$H_{PM} = \sum_{j=1}^{N-1} g[1 - (-1)^j \delta] d_{j+1}^\dagger d_j - g[1 - (-1)^N \delta] d_1^\dagger d_N + \text{h.c.},$$

where $|\delta| \leq 1$ is a dimensionless dimerization constant. By applying a unitary transformation

$$U = \sum_j e^{i j \pi} d_j^\dagger d_j,$$

the Hamiltonian reads

$$U H_{PM} U^\dagger = \sum_{j=1}^{N-1} g[1 - (-1)^j \delta] e^{i j \pi} d_{j+1}^\dagger d_j - g[1 - (-1)^N \delta] e^{-i (N-1) \pi} d_1^\dagger d_N + \text{h.c.},$$

$$= \sum_{j=1}^{N} g_0 [1 - (-1)^j \delta] d_{j+1}^\dagger d_j + \text{h.c.},$$

$$= \sum_{j=1}^{N/2} g_0 [1 - \delta] d_{2j+1}^\dagger d_{2j} + g_0 [1 + \delta] d_{2j+1} d_{2j+2} + \text{h.c.},$$

where

$$g_0 = g e^{i \pi}.$$

After the unitary transformation, the Möbius boundary condition has been canceled.

By defining fermion operators $\begin{pmatrix} 43 \end{pmatrix}$

$$\alpha_k = \frac{1}{\sqrt{N}} \sum_{j=1}^{N/2} e^{-ikj} (d_{2j-1} + e^{i\delta_k} d_{2j}),$$

$$\beta_k = \frac{1}{\sqrt{N}} \sum_{j=1}^{N/2} e^{-ikj} (d_{2j-1} - e^{i\delta_k} d_{2j}),$$

with inverse transformation

$$d_{2j-1} = \frac{1}{\sqrt{N}} \sum_{k=1}^{N/2} e^{ikj} (\alpha_k + \beta_k),$$

$$d_{2j} = \frac{1}{\sqrt{N}} \sum_{k=1}^{N/2} e^{ij(k-\delta_k)} (\alpha_k - \beta_k),$$

where the momentum is

$$k = \frac{4\pi}{N} (0, 1, 2, \cdots \frac{N}{2} - 1) - \pi + \frac{2\pi}{N},$$

$$e^{i\theta_k} = \frac{g}{\delta_k} [(1 + \delta) e^{-i \frac{\pi}{N}} + (1 - \delta) e^{-i(k-\frac{\pi}{N})}],$$

$$\varepsilon_k = 2g \sqrt{\cos^2 \left( \frac{k}{N} \right) - \delta^2 \sin^2 \left( \frac{k - \pi}{N} \right)}$$

is the eigen energy, $N$ is an even number,

$$U H_{PM} U^\dagger = \sum_k \varepsilon_k (\alpha_k^\dagger \alpha_k - \beta_k^\dagger \beta_k).$$

Here the momentum is chosen in such way that $\cos \left( \frac{k}{N} - \frac{\pi}{N} \right) \geq 0$ for $\delta = 0$ and thus the eigen energies $\varepsilon_k = 2g \cos \left( \frac{k}{N} - \frac{\pi}{N} \right)$. Therefore, the original Hamiltonian can be diagonalized as

$$H_{PM} = \sum_k \varepsilon_k (A_k^\dagger A_k - B_k^\dagger B_k),$$

where the annihilation operators of collective excitation modes of the two bands are

$$A_k = \alpha_k U = \sum_{j=1}^{N/2} \frac{e^{-ikj}}{\sqrt{N}} (e^{i(2j-1)\pi} d_{2j-1} + e^{i(\theta_k+2j)\pi} d_{2j}),$$

$$B_k = \beta_k U = \sum_{j=1}^{N/2} \frac{e^{-ikj}}{\sqrt{N}} (e^{i(2j-1)\pi} d_{2j-1} - e^{i(\theta_k+2j)\pi} d_{2j}).$$

According to Eq. (11), there are two sub-bands in the dimerized chain, i.e. $\varepsilon_k$ and $-\varepsilon_k$. For the upper band, there is a minimum $2|g\delta|$ at $k = \pi + \frac{2\pi}{N}$, while for the lower band, there is a maximum $-2|g\delta|$ also at $k = \pi + \frac{2\pi}{N}$. Therefore, there is an energy gap between the two sub-bands $4|g\delta|$ as long as the ring is dimerized.
II. LIGHT HARVESTING BY RING WITH PERIODICAL BOUNDARY CONDITION

The Hamiltonian for a dimerized ring with periodical boundary condition reads

\[ H = \omega b^\dagger b + \varepsilon_A A^\dagger A + \sum_j g(1 - (-1)^j)\delta d_j^\dagger d_{j+1} \]
\[ + \sum_j (Jd_j^\dagger b + \xi d_j^\dagger A) + \text{h.c.} \tag{1} \]

We define two sets of collective-excitation operators

\[ \alpha_k = \frac{1}{\sqrt{N}} \sum_{j=1}^{N/2} e^{-ikj}(d_{2j-1} - e^{i\theta_k}d_{2j}), \tag{2a} \]
\[ \beta_k = \frac{1}{\sqrt{N}} \sum_{j=1}^{N/2} e^{-ikj}(d_{2j-1} + e^{i\theta_k}d_{2j}), \tag{2b} \]

and the reverse transformation is

\[ d_{2j-1} = \frac{1}{\sqrt{N}} \sum_{j=1}^{N/2} e^{-ikj}(\alpha_k + \beta_k), \tag{3a} \]
\[ d_{2j} = \frac{1}{\sqrt{N}} \sum_{j=1}^{N/2} e^{-ikj-i\theta_k}(\beta_k - \alpha_k), \tag{3b} \]

where \( k = 4\pi(n-1)/N, n = 1, 2, ..., N/2, \) and

\[ e^{i\theta_k} = \left[(1 + \delta) + (1 - \delta)e^{-ik}\right]g/\varepsilon_k, \tag{4} \]
\[ \varepsilon_k = 2g\sqrt{\cos^2(k/2) + \delta^2\sin^2(k/2)}. \tag{5} \]

Thus, the Hamiltonian is transformed as

\[ H = \omega b^\dagger b + \varepsilon_A A^\dagger A + \sum_k \varepsilon_k(\beta_k^\dagger \beta_k - \alpha_k^\dagger \alpha_k) \]
\[ + \sqrt{N} \beta_0^\dagger (Jb + \xi A) + \text{h.c.} \tag{6} \]

Since only the zero-momentum mode

\[ \beta_0 = \frac{1}{\sqrt{N}} \sum_{j=1}^N d_j \tag{7} \]

with eigen energy \( \varepsilon_0 = 2g \) is coupled to the photon and acceptor, the effective Hamiltonian is further simplified as

\[ H_{\text{eff}} = \omega b^\dagger b + 2g\beta_0^\dagger \beta_0 + \varepsilon_A A^\dagger A \]
\[ + \sqrt{N} \beta_0^\dagger (Jb + \xi A) + \text{h.c.} \tag{8} \]

In conclusion, for a ring with periodical boundary condition, both the photon and acceptor are coupled to the same collective-excitation mode irrespective of the dimerization in the ring. In other words, we have proven that the quantum dynamics of light harvesting by a ring with periodical boundary condition is not affected by the dimerization.

III. EQUIVALENCE OF PRESENT THEORY AND WIGNER-WEISSKOPF APPROXIMATION

The quantum dynamics in light harvesting is governed by the Schrödinger equation, which is equivalent to a set of coupled differential equations. Formally, it can be solved by Laplace transformation. However, due to the presence of branch cut, the exact solution may not be easily obtained. Generally speaking, it can be solved by the Wigner-Weisskopf approximation \[44\text{-}46\]. In Ref. \[39\], it has been proven that the Wigner-Weisskopf approximation is equivalent to the perturbation theory in the study of excited state of a few-body system coupled to a continuum. Therefore, we make use of the perturbation theory to investigate the quantum dynamics of light-harvesting in a dimerized Möbius chain.

For an initial state \( |\psi(0)\rangle \equiv |1_b, 0_A, 0_A, 0_Bk\rangle \), the state of system at any time \( t \)

\[ |\psi(t)\rangle = \alpha_b(t)|1_b\rangle + \alpha_A(t)|1_A\rangle + \sum_k \beta_{Ak}(t)|1_{Ak}\rangle + \sum_k \beta_{Bk}(t)|1_{Bk}\rangle, \tag{1} \]

with \( |1_A\rangle \equiv |0_b, 1_A, 0_A, 0_Bk\rangle, |1_{Ak}\rangle \equiv |0_b, 0_A, 1_A, 0_Bk\rangle, |1_{Bk}\rangle \equiv |0_b, 0_A, 0_A, 1_Bk\rangle \), is governed by the Schrödinger equation

\[ i\partial_t|\psi(t)\rangle = H|\psi(t)\rangle. \tag{2} \]
We obtain a set of equations for the coefficients, i.e.

\[ i\dot{\alpha}_b = \omega \alpha_b + \epsilon \sum_k J_{Ak}^* \beta_{Ak} + \epsilon \sum_k J_{Bk}^* \beta_{Bk}, \]
\[ i\dot{\alpha}_A = \epsilon' \alpha_A + \epsilon \sum_k \xi_{Ak}^* \beta_{Ak} + \epsilon \sum_k \xi_{Bk}^* \beta_{Bk}, \]
\[ i\dot{\beta}_{Ak} = \epsilon_k \beta_{Ak} + \epsilon \xi_{Ak} \alpha_A + \epsilon J_{Ak} \alpha_b, \]
\[ i\dot{\beta}_{Bk} = -\epsilon_k^+ \beta_{Bk} + \epsilon \xi_{Bk} \alpha_A + \epsilon J_{Bk} \alpha_b, \]

(3a) (3b) (3c) (3d)

where the parameter \( \epsilon \) is introduced to keep track of the orders of perturbation.

By introducing renormalized frequencies, i.e.

\[ \Omega_b = \omega + \epsilon \Omega_b^{(1)} + \epsilon^2 \Omega_b^{(2)} + \epsilon^3 \Omega_b^{(3)} + \ldots, \]
\[ \Omega_A = \epsilon' \Omega_A + \epsilon^2 \Omega_A^{(2)} + \epsilon^3 \Omega_A^{(3)} + \ldots, \]
\[ \Omega_{Ak} = \epsilon_k^+ \Omega_{Ak} + \epsilon^2 \Omega_{Ak}^{(2)} + \epsilon^3 \Omega_{Ak}^{(3)} + \ldots, \]
\[ \Omega_{Bk} = -\epsilon_k^- \Omega_{Bk} + \epsilon^2 \Omega_{Bk}^{(2)} + \epsilon^3 \Omega_{Bk}^{(3)} + \ldots, \]

(4a) (4b) (4c) (4d)

we can define dimensionless times

\[ \tau_b = \Omega_b t, \tau_A = \Omega_A t, \tau_{Ak} = \Omega_{Ak} t, \tau_{Bk} = \Omega_{Bk} t, \]

(5)

and re-express the above differential equations as

\[ i\Omega_b \frac{\partial \alpha_b}{\partial \tau_b} = \omega \alpha_b + \epsilon \sum_k J_{Ak}^* \beta_{Ak} + \epsilon \sum_k J_{Bk}^* \beta_{Bk}, \]
\[ i\Omega_A \frac{\partial \alpha_A}{\partial \tau_A} = \epsilon' \alpha_A + \epsilon \sum_k \xi_{Ak}^* \beta_{Ak} + \epsilon \sum_k \xi_{Bk}^* \beta_{Bk}, \]
\[ i\Omega_{Ak} \frac{\partial \beta_{Ak}}{\partial \tau_{Ak}} = \epsilon_k \beta_{Ak} + \epsilon \xi_{Ak} \alpha_A + \epsilon J_{Ak} \alpha_b, \]
\[ i\Omega_{Bk} \frac{\partial \beta_{Bk}}{\partial \tau_{Bk}} = -\epsilon_k^+ \beta_{Bk} + \epsilon \xi_{Bk} \alpha_A + \epsilon J_{Bk} \alpha_b. \]

(6a) (6b) (6c) (6d)

By inserting Eq. (4) into Eq. (6), and expanding the coefficients as

\[ \alpha_b = \alpha_b^{(0)} + \epsilon \alpha_b^{(1)} + \epsilon^2 \alpha_b^{(2)} + \epsilon^3 \alpha_b^{(3)} + \ldots, \]
\[ \alpha_A = \alpha_A^{(0)} + \epsilon \alpha_A^{(1)} + \epsilon^2 \alpha_A^{(2)} + \epsilon^3 \alpha_A^{(3)} + \ldots, \]
\[ \beta_{Ak} = \beta_{Ak}^{(0)} + \epsilon \beta_{Ak}^{(1)} + \epsilon^2 \beta_{Ak}^{(2)} + \epsilon^3 \beta_{Ak}^{(3)} + \ldots, \]
\[ \beta_{Bk} = \beta_{Bk}^{(0)} + \epsilon \beta_{Bk}^{(1)} + \epsilon^2 \beta_{Bk}^{(2)} + \epsilon^3 \beta_{Bk}^{(3)} + \ldots, \]

(7a) (7b) (7c) (7d)
we could obtain a set of equations for different orders of coefficients,

\[
\begin{align*}
i \left( \omega + \epsilon \Omega_b^{(1)} + \epsilon^2 \Omega_b^{(2)} + \epsilon^3 \Omega_b^{(3)} \ldots \right) & = \omega \left( \alpha_b^{(0)} + \epsilon \alpha_b^{(1)} + \epsilon^2 \alpha_b^{(2)} + \epsilon^3 \alpha_b^{(3)} \ldots \right) + \epsilon \sum_k J_k^* \beta_{Ak} + \epsilon \sum_k J_k^* \beta_{Bk}, \\
i \left( \varepsilon_A' + \epsilon \Omega_A^{(1)} + \epsilon^2 \Omega_A^{(2)} + \epsilon^3 \Omega_A^{(3)} \ldots \right) & = \varepsilon_A' \left( \alpha_A^{(0)} + \epsilon \alpha_A^{(1)} + \epsilon^2 \alpha_A^{(2)} + \epsilon^3 \alpha_A^{(3)} \ldots \right) + \epsilon \sum_k \xi_{Ak} \beta_{Ak} + \epsilon \sum_k \xi_{Bk} \beta_{Bk}, \\
i \left( \varepsilon_k' - \epsilon \Omega_{Ak}^{(1)} + \epsilon^2 \Omega_{Ak}^{(2)} + \epsilon^3 \Omega_{Ak}^{(3)} \ldots \right) & = \varepsilon_k' \left( \beta_{Ak}^{(0)} + \epsilon \beta_{Ak}^{(1)} + \epsilon^2 \beta_{Ak}^{(2)} + \epsilon^3 \beta_{Ak}^{(3)} \ldots \right) + \epsilon \sum_k \xi_{Ak} \alpha_A + \epsilon \sum_k \xi_{Ak} \alpha_A, \\
i \left( -\varepsilon_k^+ + \epsilon \Omega_{Bk}^{(1)} + \epsilon^2 \Omega_{Bk}^{(2)} + \epsilon^3 \Omega_{Bk}^{(3)} \ldots \right) & = -\varepsilon_k^+ \left( \beta_{Bk}^{(0)} + \epsilon \beta_{Bk}^{(1)} + \epsilon^2 \beta_{Bk}^{(2)} + \epsilon^3 \beta_{Bk}^{(3)} \ldots \right) + \epsilon \sum_k \xi_{Bk} \alpha_A + \epsilon \sum_k \xi_{Bk} \alpha_A.
\end{align*}
\]

For the zeroth-order coefficients, we have

\[
\begin{align*}
\omega (i \frac{\partial \alpha_b^{(0)}}{\partial \tau_b} - \alpha_b^{(0)}) & = 0, \\
\varepsilon_A' (i \frac{\partial \alpha_A^{(0)}}{\partial \tau_A} - \alpha_A^{(0)}) & = 0, \\
\varepsilon_k' (i \frac{\partial \beta_{Ak}^{(0)}}{\partial \tau_{Ak}} - \beta_{Ak}^{(0)}) & = 0, \\
\varepsilon_k^+ (i \frac{\partial \beta_{Bk}^{(0)}}{\partial \tau_{Bk}} - \beta_{Bk}^{(0)}) & = 0.
\end{align*}
\]

The solutions to the above equations are

\[
\begin{align*}
\alpha_b^{(0)} & = A_b e^{-i \tau_b}, \\
\alpha_A^{(0)} & = A_A e^{-i \tau_A}, \\
\beta_{Ak}^{(0)} & = B_{Ak} e^{-i \tau_{Ak}}, \\
\beta_{Bk}^{(0)} & = B_{Bk} e^{-i \tau_{Bk}}.
\end{align*}
\]

where the constants \(A_u (u = b,A)\) and \(B_{uv} (v = A,B)\) will be determined by the initial condition later.

For the first-order coefficients, we have

\[
\begin{align*}
\omega (i \frac{\partial \alpha_b^{(1)}}{\partial \tau_b} - \alpha_b^{(1)}) & = -i \Omega_b^{(1)} \frac{\partial \alpha_b^{(0)}}{\partial \tau_b} + \sum_k J^*_{Ak} \beta_{Ak}^{(0)} + \sum_k J^*_{Bk} \beta_{Bk}^{(0)}, \\
\varepsilon_A' (i \frac{\partial \alpha_A^{(1)}}{\partial \tau_A} - \alpha_A^{(1)}) & = -i \Omega_A^{(1)} \frac{\partial \alpha_A^{(0)}}{\partial \tau_A} + \sum_k \xi_{Ak} \beta_{Ak}^{(0)} + \sum_k \xi_{Bk} \beta_{Bk}^{(0)}, \\
\varepsilon_k' (i \frac{\partial \beta_{Ak}^{(1)}}{\partial \tau_{Ak}} - \beta_{Ak}^{(1)}) & = -i \Omega_{Ak}^{(1)} \frac{\partial \beta_{Ak}^{(0)}}{\partial \tau_{Ak}} + \xi_{Ak} \alpha_A^{(0)} + J_{Ak} \alpha_b^{(0)}, \\
\varepsilon_k^+ (i \frac{\partial \beta_{Bk}^{(1)}}{\partial \tau_{Bk}} - \beta_{Bk}^{(1)}) & = -i \Omega_{Bk}^{(1)} \frac{\partial \beta_{Bk}^{(0)}}{\partial \tau_{Bk}} + \xi_{Bk} \alpha_A^{(0)} + J_{Bk} \alpha_b^{(0)}.
\end{align*}
\]
The first terms on the r.h.s will lead to divergence in the long-time limit, because they are resonant driving. As a result, the first-order renormalizations to energies vanish, i.e.

$$\Omega_b(1) = \Omega_A(1) = \Omega_{Ak} = \Omega_{Bk} = 0.$$  \hfill (12)

By further inserting Eq. (11) into Eq. (11):

$$\omega(i \frac{\partial \alpha_{b}^{(1)}}{\partial \tau_b} - \alpha_{b}^{(1)}) = \sum_{k} J_{Ak}^{*} B_{Ak} e^{-i \tau_{Ak}} + \sum_{k} J_{Bk}^{*} B_{Bk} e^{-i \tau_{Bk}},$$  \hfill (13a)

$$\epsilon_{A}^{'}(i \frac{\partial \alpha_{A}^{(1)}}{\partial \tau_A} - \alpha_{A}^{(1)}) = \sum_{k} \xi_{Ak}^{*} B_{Ak} e^{-i \tau_{Ak}} + \sum_{k} \xi_{Bk}^{*} B_{Bk} e^{-i \tau_{Bk}},$$  \hfill (13b)

$$\epsilon_{k}^{'}(i \frac{\partial \beta_{Ak}^{(1)}}{\partial \tau_{Ak}} - \beta_{Ak}^{(1)}) = \xi_{Ak} A_{A} e^{-i \tau_{A}} + J_{Ak} A_{b} e^{-i \tau_{b}},$$  \hfill (13c)

$$- \epsilon_{k}^{'}(i \frac{\partial \beta_{Bk}^{(1)}}{\partial \tau_{Bk}} - \beta_{Bk}^{(1)}) = \xi_{Bk} A_{A} e^{-i \tau_{A}} + J_{Bk} A_{b} e^{-i \tau_{b}},$$  \hfill (13d)

we obtain the first-order terms as

$$\alpha_{b}^{(1)} = \sum_{k} B_{Ak}^{*} \frac{\Omega_{b}^{*} J_{Ak}}{\omega(\Omega_{Ak} - \Omega_{b})} e^{-i \tau_{Ak}} + \sum_{k} B_{Bk}^{*} \frac{\Omega_{b}^{*} J_{Bk}}{\omega(\Omega_{Bk} - \Omega_{b})} e^{-i \tau_{Bk}},$$  \hfill (14a)

$$\alpha_{A}^{(1)} = \sum_{k} B_{Ak}^{*} \frac{\Omega_{A}^{*} \xi_{Ak}}{\epsilon_{A}^{*}(\Omega_{Ak} - \Omega_{A})} e^{-i \tau_{Ak}} + \sum_{k} B_{Bk}^{*} \frac{\Omega_{A}^{*} \xi_{Bk}}{\epsilon_{A}^{*}(\Omega_{Bk} - \Omega_{A})} e^{-i \tau_{Bk}},$$  \hfill (14b)

$$\beta_{Ak}^{(1)} = A_{A} \frac{\Omega_{Ak} \xi_{Ak}}{\epsilon_{Ak}^{*}(\Omega_{Ak} - \Omega_{A})} e^{-i \tau_{A}} + A_{b} \frac{\Omega_{Ak} J_{Ak}}{\epsilon_{Ak}^{*}(\Omega_{b} - \Omega_{Ak})} e^{-i \tau_{b}},$$  \hfill (14c)

$$\beta_{Bk}^{(1)} = A_{A} \frac{\Omega_{Ak} \xi_{Ak}}{\epsilon_{Ak}^{*}(\Omega_{Ak} - \Omega_{A})} e^{-i \tau_{A}} + A_{b} \frac{\Omega_{Bk} J_{Ak}}{\epsilon_{Ak}^{*}(\Omega_{b} - \Omega_{Bk})} e^{-i \tau_{b}}.$$  \hfill (14d)

In the same way, we can obtain the equations for the second-order coefficients as

$$\omega(i \frac{\partial \alpha_{b}^{(2)}}{\partial \tau_b} - \alpha_{b}^{(2)}) = -i\Omega_{b}(2) \frac{\partial \alpha_{b}^{(0)}}{\partial \tau_b} + \sum_{k} J_{Ak}^{*} B_{Ak} \frac{\Omega_{Ak} \xi_{Ak}}{\epsilon_{Ak}^{*}(\Omega_{Ak} - \Omega_{A})} e^{-i \tau_{Ak}} + A_{b} \frac{\Omega_{Ak} J_{Ak}}{\epsilon_{Ak}^{*}(\Omega_{b} - \Omega_{A})} e^{-i \tau_{b}}$$
$$+ \sum_{k} J_{Bk}^{*} B_{Bk} \frac{\Omega_{Bk} \xi_{Bk}}{\epsilon_{Bk}^{*}(\Omega_{Bk} - \Omega_{B})} e^{-i \tau_{Bk}} + A_{b} \frac{\Omega_{Bk} J_{Bk}}{\epsilon_{Bk}^{*}(\Omega_{b} - \Omega_{B})} e^{-i \tau_{b}},$$  \hfill (15a)

$$\epsilon_{A}^{'}(i \frac{\partial \alpha_{A}^{(2)}}{\partial \tau_{A}} - \alpha_{A}^{(2)}) = -i\Omega_{A}(2) \frac{\partial \alpha_{A}^{(0)}}{\partial \tau_{A}} + \sum_{k} \xi_{Ak}^{*} B_{Ak} \frac{\Omega_{Ak} \xi_{Ak}}{\epsilon_{Ak}^{*}(\Omega_{Ak} - \Omega_{A})} e^{-i \tau_{Ak}} + A_{b} \frac{\Omega_{Ak} J_{Ak}}{\epsilon_{Ak}^{*}(\Omega_{b} - \Omega_{A})} e^{-i \tau_{b}}$$
$$+ \sum_{k} \xi_{Bk}^{*} B_{Bk} \frac{\Omega_{Bk} \xi_{Bk}}{\epsilon_{Bk}^{*}(\Omega_{Bk} - \Omega_{B})} e^{-i \tau_{Bk}} + A_{b} \frac{\Omega_{Bk} J_{Bk}}{\epsilon_{Bk}^{*}(\Omega_{b} - \Omega_{B})} e^{-i \tau_{b}},$$  \hfill (15b)

$$\epsilon_{k}^{'}(i \frac{\partial \beta_{Ak}^{(2)}}{\partial \tau_{Ak}} - \beta_{Ak}^{(2)}) = -i\Omega_{Ak}(2) \frac{\partial \beta_{Ak}^{(0)}}{\partial \tau_{Ak}} + \xi_{Ak} \sum_{k'} B_{Ak'} \frac{\Omega_{Ak'} \xi_{Ak'}}{\epsilon_{Ak'}^{*}(\Omega_{Ak'} - \Omega_{A})} e^{-i \tau_{Ak'}} + \sum_{k'} B_{Bk'} \frac{\Omega_{Ak'} \xi_{Ak'}}{\epsilon_{Ak'}^{*}(\Omega_{Bk'} - \Omega_{A})} e^{-i \tau_{Bk'}}$$
$$+ J_{Ak} \sum_{k'} B_{Ak'} \frac{\Omega_{Ak'} J_{Ak'}}{\epsilon_{Ak'}^{*}(\Omega_{Ak'} - \Omega_{b})} e^{-i \tau_{Ak'}} + \sum_{k'} B_{Bk'} \frac{\Omega_{Ak'} J_{Ak'}}{\epsilon_{Ak'}^{*}(\Omega_{Bk'} - \Omega_{b})} e^{-i \tau_{Bk'}},$$  \hfill (15c)

$$- \epsilon_{k}^{'}(i \frac{\partial \beta_{Bk}^{(2)}}{\partial \tau_{Bk}} - \beta_{Bk}^{(2)}) = -i\Omega_{Bk}(2) \frac{\partial \beta_{Bk}^{(0)}}{\partial \tau_{Bk}} + \xi_{Bk} \sum_{k'} B_{Ak'} \frac{\Omega_{Bk'} \xi_{Bk'}}{\epsilon_{Ak'}^{*}(\Omega_{Ak'} - \Omega_{A})} e^{-i \tau_{Ak'}} + \sum_{k'} B_{Bk'} \frac{\Omega_{Bk'} \xi_{Bk'}}{\epsilon_{Ak'}^{*}(\Omega_{Bk'} - \Omega_{b})} e^{-i \tau_{Bk'}}$$
$$+ J_{Ak} \sum_{k'} B_{Ak'} \frac{\Omega_{Ak'} J_{Ak'}}{\epsilon_{Ak'}^{*}(\Omega_{Ak'} - \Omega_{b})} e^{-i \tau_{Ak'}} + \sum_{k'} B_{Bk'} \frac{\Omega_{Ak'} J_{Ak'}}{\epsilon_{Ak'}^{*}(\Omega_{Bk'} - \Omega_{b})} e^{-i \tau_{Bk'}}.$$  \hfill (15d)
Because the resonant-driving terms will result in divergence, the second-order energies are thus

\[ \Omega^{(2)}_b = \sum_k \left( \frac{\Omega_{Ak} J_{Ak}}{\varepsilon_k (\Omega_b - \Omega_{Ak})} + \frac{\Omega_{Bk} |J_{Bk}|^2}{-\varepsilon_k^*(\Omega_b - \Omega_{Bk})} \right), \]  
(16a)

\[ \Omega^{(2)}_A = \sum_k \left( \frac{\Omega_{Ak} \xi_{Ak}}{\varepsilon_k (\Omega_A - \Omega_{Ak})} + \frac{\Omega_{Bk} \xi_{Bk}}{-\varepsilon_k^*(\Omega_A - \Omega_{Bk})} \right), \]  
(16b)

\[ \Omega^{(2)}_{Ak} = \frac{\Omega_{Ak} \xi_{Ak}^2}{\varepsilon_A^*(\Omega_{Ak} - \Omega_A) + \omega(\Omega_{Ak} - \Omega_b)}, \]  
(16c)

\[ \Omega^{(2)}_{Bk} = \frac{\Omega_{Ak} \xi_{Bk}^2}{\varepsilon_A^*(\Omega_{Bk} - \Omega_A) + \omega(\Omega_{Bk} - \Omega_b)}, \]  
(16d)

And the corresponding second-order coefficients are

\[ \alpha^{(2)}_b = \sum_k A_A \left( \frac{J_{Ak} \xi_{Ak} \Omega_{Ak}}{\varepsilon_k (\Omega_A - \Omega_{Ak})} + \frac{J_{Bk} \xi_{Bk} \Omega_{Bk}}{-\varepsilon_k^*(\Omega_A - \Omega_{Bk})} \right) \alpha_b e^{-i\tau_A}, \]  
(17a)

\[ \alpha^{(2)}_A = \sum_k A_b \left( \frac{J_{Ak} \xi_{Ak} \Omega_{Ak}}{\varepsilon_k (\Omega_A - \Omega_{Ak})} + \frac{J_{Bk} \xi_{Bk} \Omega_{Bk}}{-\varepsilon_k^*(\Omega_A - \Omega_{Bk})} \right) \Omega_A e^{-i\tau_A}, \]  
(17b)

\[ \beta^{(2)}_{Ak} = \sum_k B_A \left( \frac{\Omega_{Ak} \xi_{Ak} \xi_{Ak}^*}{\varepsilon_A^*(\Omega_{Ak} - \Omega_A)} + \frac{\Omega_{Ak} J_{Ak} J_{Ak}^*}{\omega(\Omega_{Ak} - \Omega_b)} \right) \xi_{Ak} e^{-i\tau_{Ak'}}, \]  
(17c)

\[ \beta^{(2)}_{Bk} = \sum_k B_A \left( \frac{\Omega_{Ak} \xi_{Bk} \xi_{Bk}^*}{\varepsilon_A^*(\Omega_{Bk} - \Omega_A)} + \frac{\Omega_{Ak} J_{Bk} J_{Bk}^*}{\omega(\Omega_{Bk} - \Omega_b)} \right) \xi_{Bk} e^{-i\tau_{Bk'}}, \]  
(17d)

where the prime over summation \( \sum' \) indicates that the term related to \( k' = k \) is removed from the summation.

For the third-order coefficients, we have

\[ i\omega \frac{\partial \alpha^{(3)}_b}{\partial \tau_b} - \omega \alpha^{(3)}_b = -i \Omega^{(2)}_b \frac{\partial \alpha^{(1)}_b}{\partial \tau_b} - i \Omega^{(3)}_b \frac{\partial \alpha^{(0)}_b}{\partial \tau_b} + \sum_k J_{Ak} \beta^{(2)}_{Ak} + \sum_k J_{Bk} \beta^{(2)}_{Bk}, \]  
(18a)

\[ i\varepsilon_A \frac{\partial \alpha^{(3)}_A}{\partial \tau_A} - \varepsilon_A \alpha^{(3)}_A = -i \Omega^{(2)}_A \frac{\partial \alpha^{(1)}_A}{\partial \tau_A} - i \Omega^{(3)}_A \frac{\partial \alpha^{(0)}_A}{\partial \tau_A} + \sum_k \xi_{Ak} \beta^{(2)}_{Ak} + \sum_k \xi_{Bk} \beta^{(2)}_{Bk}, \]  
(18b)

\[ -i \varepsilon_K \frac{\partial \beta^{(3)}_{Ak}}{\partial \tau_{Ak}} - \varepsilon_k \beta^{(3)}_{Ak} = -i \Omega^{(2)}_{Ak} \frac{\partial \beta^{(1)}_{Ak}}{\partial \tau_{Ak}} - i \Omega^{(3)}_{Ak} \frac{\partial \beta^{(0)}_{Ak}}{\partial \tau_{Ak}} + \xi_{Ak} \sum_k A_b \left( \frac{J_{Ak} \xi_{Ak} \Omega_{Ak}}{\varepsilon_k (\Omega_b - \Omega_{Ak})} + \frac{J_{Bk} \xi_{Bk} \Omega_{Bk}}{-\varepsilon_k^*(\Omega_b - \Omega_{Bk})} \right) \Omega_A e^{-i\tau_{b}}, \]  
(18c)

\[ -i \varepsilon_K \frac{\partial \beta^{(3)}_{Bk}}{\partial \tau_{Bk}} + \varepsilon_k \beta^{(3)}_{Bk} = -i \Omega^{(2)}_{Bk} \frac{\partial \beta^{(1)}_{Bk}}{\partial \tau_{Bk}} - i \Omega^{(3)}_{Bk} \frac{\partial \beta^{(0)}_{Bk}}{\partial \tau_{Bk}} + \xi_{Bk} \sum_k A_b \left( \frac{J_{Ak} \xi_{Ak} \Omega_{Ak}}{\varepsilon_k (\Omega_b - \Omega_{Ak})} + \frac{J_{Bk} \xi_{Bk} \Omega_{Bk}}{-\varepsilon_k^*(\Omega_b - \Omega_{Bk})} \right) \Omega_A e^{-i\tau_{b}}. \]  
(18d)

The coefficients of resonant terms are zero and thus lead to

\[ \Omega^{(3)}_b = \Omega^{(3)}_A = \Omega^{(3)}_{Ak} = \Omega^{(3)}_{Bk} = 0. \]  
(19)
In conclusion, to the order of $\epsilon^3$, the renormalized energies are

\[
\begin{align*}
\Omega_b &= \omega + \epsilon^2 \sum_k \left( \frac{|J_{Ak}|^2}{\omega - \epsilon_k} + \frac{|J_{Bk}|^2}{\omega + \epsilon_k} \right), \\
\Omega_A &= \epsilon_A' + \epsilon^2 \sum_k \left( \frac{|\xi_{Ak}|^2}{\epsilon_A' - \epsilon_k} + \frac{|\xi_{Bk}|^2}{\epsilon_A' + \epsilon_k} \right), \\
\Omega_{Ak} &= \epsilon_k' + \epsilon^2 \left( \frac{|\xi_{Ak}|^2}{\epsilon_k' - \epsilon_A'} + \frac{|J_{Ak}|^2}{\epsilon_k' - \omega} \right), \\
\Omega_{Bk} &= -\epsilon_k' + \epsilon^2 \left( \frac{|\xi_{Bk}|^2}{-\epsilon_k' - \epsilon_A'} + \frac{|J_{Bk}|^2}{-\epsilon_k' - \omega} \right).
\end{align*}
\]

To the order of $\epsilon^2$, the coefficients are

\[
\begin{align*}
\alpha_b(t) &= A_b e^{-i\tau_b} + \epsilon \sum_k [B_{Ak} \frac{\Omega_b J_{Ak}^*}{\omega(\Omega_{Ak} - \Omega_b)} e^{-i\tau_{Ak}} + B_{Bk} \frac{\Omega_b J_{Bk}^*}{\omega(\Omega_{Bk} - \Omega_b)} e^{-i\tau_{Bk}}] \\
&\quad + \epsilon^2 \sum_k A_b' \left[ J_{Ak}^* \xi_{Ak} \frac{\Omega_{Ak}}{\epsilon_k(\Omega_b - \Omega_{Ak})} + J_{Bk}^* \xi_{Bk} \frac{\Omega_{Bk}}{\epsilon_k(\Omega_b - \Omega_{Bk})} \right] \frac{\Omega_b e^{-i\tau_b}}{\omega(\Omega_{Ak} - \Omega_b)}, \\
\alpha_A(t) &= A_A e^{-i\tau_A} + \epsilon \sum_k [B_{Ak} \frac{\Omega_A \xi_{Ak}}{\epsilon_A'(\Omega_{Ak} - \Omega_A)} e^{-i\tau_{Ak}} + B_{Bk} \frac{\Omega_A \xi_{Bk}^*}{\epsilon_A'(\Omega_{Bk} - \Omega_A)} e^{-i\tau_{Bk}}] \\
&\quad + \epsilon^2 \sum_k A_b' \left[ J_{Ak}^* \xi_{Ak} \frac{\Omega_{Ak}}{\epsilon_k(\Omega_b - \Omega_{Ak})} + J_{Bk}^* \xi_{Bk} \frac{\Omega_{Bk}}{\epsilon_k(\Omega_b - \Omega_{Bk})} \right] \frac{\Omega_A e^{-i\tau_a}}{\omega(\Omega_{Ak} - \Omega_{Ak})}, \\
\beta_{Ak}(t) &= B_{Ak} e^{-i\tau_{Ak}} + \epsilon [A_A \left( \frac{\Omega_{Ak} \xi_{Ak}}{\epsilon_k(\Omega_b - \Omega_{Ak})} e^{-i\tau_A} + A_b \frac{\Omega_{Ak} J_{Ak}}{\epsilon_k(\Omega_b - \Omega_{Ak})} e^{-i\tau_b} \right)] \\
&\quad + \epsilon^2 \sum_{k'} B_{Ak'} \left[ J_{Ak}^* \xi_{Ak} \frac{\Omega_{Ak'}}{\epsilon_k'(\Omega_b - \Omega_{Ak})} + \Omega_{Ak} \frac{\Omega_{Ak}}{\epsilon_k'(\Omega_b - \Omega_{Ak})} \right] e^{-i\tau_{Ak'}}, \\
\beta_{Bk}(t) &= B_{Bk} e^{-i\tau_{Bk}} + \epsilon [A_A \left( \frac{\Omega_{Bk} \xi_{Bk}}{\epsilon_k(\Omega_b - \Omega_{Bk})} e^{-i\tau_A} + A_b \frac{\Omega_{Bk} J_{Bk}}{\epsilon_k(\Omega_b - \Omega_{Bk})} e^{-i\tau_b} \right)] \\
&\quad + \epsilon^2 \sum_{k'} B_{Bk'} \left[ J_{Bk}^* \xi_{Bk} \frac{\Omega_{Bk'}}{\epsilon_k'(\Omega_b - \Omega_{Bk})} + \Omega_{Bk} \frac{\Omega_{Bk}}{\epsilon_k'(\Omega_b - \Omega_{Bk})} \right] e^{-i\tau_{Bk'}}.
\end{align*}
\]

By using the initial condition

\[
\begin{align*}
\alpha_b(0) &= 1, \quad \alpha_A(0) = \beta_{Ak}(0) = \beta_{Bk}(0) = 0,
\end{align*}
\]

we can obtain the constants as
where we have taken $\epsilon$ to the order of $\epsilon^2$, the probability amplitudes are

$$A_b = 1 - \epsilon^2 \sum_k \left( \frac{|J_{Ak}|^2}{(\Omega_b - \Omega_{Ak})^2} + \frac{|J_{Bk}|^2}{(\Omega_b - \Omega_{Bk})^2} \right)$$

$$A_A = -\epsilon^2 \sum_k \frac{J_{Ak} \xi_{Ak} (\Omega_{Ak} - \Omega_A) + J_{Bk} \xi_{Bk} (\Omega_{Bk} - \Omega_B)}{(\Omega_b - \Omega_{Ak})(\Omega_{Ak} - \Omega_A)(\Omega_b - \Omega_{Bk})(\Omega_{Bk} - \Omega_B)}$$

$$B_k = -\epsilon \frac{J_{Ak}}{\Omega_b - \Omega_{Ak}} \sum_k \frac{B_{Ak} \xi_{Ak} (\Omega_{Ak} - \Omega_A) + B_{Bk} \xi_{Bk} (\Omega_{Bk} - \Omega_B)}{(\Omega_b - \Omega_{Ak})(\Omega_{Ak} - \Omega_A)(\Omega_b - \Omega_{Bk})(\Omega_{Bk} - \Omega_B)}$$

To the order of $\epsilon^2$, the probability amplitudes are

$$\alpha_b(t) = A_b e^{-i\tau b} + \sum_k \left[ \frac{B_{Ak}}{\omega(\Omega_{Ak} - \Omega_b)} e^{-i\omega t} + \frac{B_{Bk}}{\omega(\Omega_{Bk} - \Omega_b)} e^{-i\omega t} \right]$$

$$\alpha_A(t) = A_A e^{-i\tau_A} + \sum_k \left[ \frac{B_{Ak}}{\omega(\Omega_{Ak} - \Omega_A)} e^{-i\omega t} + \frac{B_{Bk}}{\omega(\Omega_{Bk} - \Omega_A)} e^{-i\omega t} \right]$$

$$\beta_A(t) = B_A e^{-i\tau_A} + \sum_k \left[ \frac{B_{Bk}}{\omega(\Omega_{Bk} - \Omega_A)} e^{-i\omega t} + \frac{B_{Bk}}{\omega(\Omega_{Bk} - \Omega_A)} e^{-i\omega t} \right]$$

$$\beta_B(t) = B_B e^{-i\tau_B} + \sum_k \left[ \frac{B_{Ak}}{\omega(\Omega_{Ak} - \Omega_B)} e^{-i\omega t} + \frac{B_{Ak}}{\omega(\Omega_{Ak} - \Omega_B)} e^{-i\omega t} \right]$$

where we have taken $\epsilon = 1$. Regardless of fluorescence in the donor ring, and assum-
ing there is a small imaginary part in $\omega$, we recover the result under Wigner-Weisskopf approximation, i.e.

$$\alpha_b(t) = A_b e^{-i\tau_b}$$

$$= \exp \left[ -i\omega t - it \sum_k \frac{|J_{Ak}|^2}{\omega - \varepsilon_k + i0^+} + \frac{|J_{Bk}|^2}{\omega + \varepsilon_k + i0^+} \right]$$

$$= \exp \left[ -i(\omega + \Delta') t - \gamma t \right], \quad (28)$$

where

$$\Delta' = \sum_k \psi \left( \frac{|J_{Ak}|^2}{\omega - \varepsilon_k} + \frac{|J_{Bk}|^2}{\omega + \varepsilon_k} \right), \quad (29a)$$

$$\gamma = \pi \sum_k \left( |J_{Ak}|^2 \delta(\omega - \varepsilon_k) + |J_{Bk}|^2 \delta(\omega + \varepsilon_k) \right). \quad (29b)$$

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