Research paper

Time-dependent renormalized Redfield theory II for off-diagonal transition in reduced density matrix

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ABSTRACT

In our previous letter (Kimura, 2016), we constructed time-dependent renormalized Redfield theory (TRRT) only for diagonal transition in a reduced density matrix. In this letter, we formulate the general expression for off-diagonal transition in the reduced density matrix. We discuss the applicability of TRRT by numerically comparing the dependencies on the energy gap of the exciton relaxation rate by using the TRRT and the modified Redfield theory (MRT). In particular, we roughly show that TRRT improves MRT for the detailed balance about the excitation energy transfer reaction.

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1. Introduction

Photosynthesis converts photo-energy into bio-energy in the form of carbohydrates. In the initial stages of photosynthesis, immediately following the absorption of photons, the electronically excited state of chlorophyll in the antenna protein is transferred to a reaction center with high quantum yield through strategies that remain unknown. The quantum effect of excitation energy transfer in the antenna system has recently been reported [1–3]. In particular, long-lasting quantum coherence via nuclear vibrations in photosynthetic antennas at room temperature has been the focus of research, and has been treated experimentally as well as theoretically [4].

When exciton coupling strength V^e is much smaller than the reorganization energy λ as $V^e \ll \lambda$, the localized excitation state as the donor molecule transfers to an energetically lower exciton state as the acceptor molecule. The excitation transfer rate has been expressed by Förster [5]. In the opposite limiting case ($V^e \gg \lambda$), the exciton state delocalizes in the system, and the relaxation process to the energetically lower delocalized exciton states occurs. The relaxation process can be expressed by Redfield theory [6].

While such a limiting case is easily treatable using a simple perturbation method, it is difficult to apply the perturbation method to it, especially in the case of intermediate coupling [4,7]. For such situations, Zhang et al. modified Redfield theory. The modified Redfield theory (MRT) treats electronic off-diagonal elements in

exciton-phonon interaction as a perturbation term [8,9]. In recent theoretical developments, a coherent modified Redfield theory (CMRT) was constructed by Hwang-Fu et al. [10,11] and was applied to the analysis of the energy transfer pathway in photosynthetic antenna systems [12].

We recently constructed a time-dependent renormalized Redfield theory (TRRT) and derived a formula to represent the exciton relaxation rate [13]. However, the rate formula could not analyze the physics of quantum coherence in such photosynthetic antenna systems due to the rate formula between the diagonal elements of the reduced density matrix element for delocalized exciton representation. Hence, in this letter, we extend the formalism of the previously expressed rate to analyze the transition rate between off-diagonal elements in the system.

The quantum master equation for the reduced density matrix element under second-order perturbative approximation by interaction representation is expressed by using the Nakajima-Zwanzig equation as [14,15]

$$i\hbar \frac{\partial \mathcal{P}\rho_I(t)}{\partial t} = \mathcal{P}[V_I(t), \mathcal{Q}\rho_I(0)] + \mathcal{P}[V_I(t), \mathcal{P}\rho_I(t)]$$
$$- \frac{i}{\hbar} \int_0^t dt' \mathcal{P}[V_I(t), \mathcal{Q}[V_I(t'), \mathcal{P}\rho_I(t')] \quad (1)$$

where $\mathcal{P}$ is the projection operator $\mathcal{P}A \equiv \rho_b \text{Tr}[A]$. ρ_b is expressed as $e^{-\beta H_B}/\text{Tr}[e^{-\beta H_B}]$. H_B is phonon-bath Hamiltonian. The operator $V_I(t)$ is perturbative Hamiltonian with interaction representation defined as $e^{iH_0t/\hbar}Ve^{-iH_0t/\hbar}$. The first term on the r.h.s. is an inhomogeneous term, which can be neglected due to proper initial conditions obtaining in the reduced density matrix. The third term of r.h.s.

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represent dissipation, which is expressed by the time correlation of the perturbative Hamiltonian with interaction representation $V_I(t)$. The second term of the r.h.s. has been neglected by comparing the result according to the quantum master equation with that obtained by using numerically exact calculation. This elimination simplifies the equation of motion. However, it cannot be easily justified [16]. By using the renormalization approach, the time correlation function in the dissipation term of the quantum master equation becomes the formalism of the variance-covariance matrix. However, in case of interaction representation for the quantum master equation, it is difficult to analyze the temporal propagation of the reduced matrix element by Schrödinger representation. The CMRT overcomes this problem by dividing the quantum master equation into a coherent term and a dissipation term. The time-dependent renormalization approach in this letter improves the dissipation term in the CMRT.

In the remainder of this letter, the model Hamiltonian and analytical strategies are stated in Section 2. The requisite numerical analysis is conducted in Section 3. In Section 4, we discuss some findings and the conclusions that can be drawn from them. The details of the analytical expression are presented in Appendices.

2. Theory

2.1. Hamiltonian

Let us define the total Hamiltonian of the system. We express the ket vector $|n\rangle$ as the electronic excited state at the nth site, where the electronic site energy is E_n. The exciton coupling strength between the nth and mth molecules is expressed by V_{nm}^e. We introduce the pure exciton Hamiltonian as $\left[\sum_n E_n|n\rangle\langle n| + \sum_{n\neq m} V_{nm}^e[|n\rangle\langle m| + |m\rangle\langle n|]\right]|\mu\rangle = E_\mu|\mu\rangle$ where $|\mu\rangle$ is the ket vector in the pure exciton representation expressed by the site representation as

$$|\mu\rangle = \sum_n C_n^\mu|n\rangle. \tag{2}$$

For nuclear motion, we only consider the phonon bath, where the creation (annihilation) operator for the kth phonon mode is expressed as $b_k^\dagger$ (b_k), the frequency of which is ω_k. Finally, g_{nk} is introduced as the exciton-phonon coupling strength at the nth excited state: We introduce exciton-phonon coupling using pure exciton representation as

$$G_k^{\mu\nu} = \sum_n C_n^\mu C_n^\nu g_{nk}. \tag{3}$$

Hence, the total Hamiltonian based on pure exciton representation can be expressed as $H = H_0 + V$

$$H = H_0 + V, \tag{4}$$

$$H_0 = \sum_\mu [E_\mu + H_B + B_{\mu\mu}]|\mu\rangle\langle\mu|, \tag{5}$$

$$V = \sum_{\mu\neq\nu} B_{\mu\nu}|\mu\rangle\langle\nu|, \tag{6}$$

where $H_B = \sum_k \hbar\omega_k b_k^\dagger b_k$ is the phonon-bath Hamiltonian. Here, $B_{\mu\nu}$ is defined as

$$B_{\mu\nu} = \sum_k G_k^{\mu\nu}\left(b_k^\dagger + b_k\right). \tag{7}$$

We now introduce the shift operator $\theta \equiv e^S$, where S is defined as

$$S = \sum_\mu S_{\mu\mu} = \sum_{\mu k} \frac{G_k^{\mu\mu}}{\hbar\omega_k}\left(b_k^\dagger - b_k\right)|\mu\rangle\langle\mu|. \tag{8}$$

Using the shift operator, we apply a unitary transformation from Eq. (4) to the total Hamiltonian as $\theta H \theta^\dagger = H_0^R(t) + V^R(t)$ as in Section 2.3.

2.2. Renormalization strategy

We divide the total Hamiltonian H into two parts, renormalized non-perturbative Hamiltonian and its perturbative Hamiltonian as $H_0^R(t) + V^R(t)$, in advance. Based on the zeroth-order propagator $U(t_o)$ as $\exp_+\left[-\frac{i}{\hbar}\int_0^t dt_1 H_0^R(t_1)\right]$, by re-introducing the shift operator, we obtain a first-order expansion of the unitary-transformed propagator $e^{-iHt/\hbar}$ as

$$\langle f|\theta^\dagger e^{-iHt/\hbar}\theta|i\rangle = \langle f|\theta^\dagger U(t)\theta|i\rangle - \frac{i}{\hbar}\int_0^t dt_1 \langle f|\theta^\dagger U(t)V_I^R(t_1)\theta|i\rangle, \tag{9}$$

where we take the element in the electronic state, and $V_I^R(t)$ is the interaction representation of $V^R(t)$, defined as $U^\dagger(t)V^R(t)U(t)$.

The reduced density operator is expressed as

$$\rho(t) = \text{Tr}[\langle f|\theta^\dagger e^{-iHt/\hbar}\theta|i\rangle\rho_b\langle i'|\theta^\dagger e^{iHt/\hbar}\theta|f'\rangle], \tag{10}$$

where ρ_b is defined as $e^{-\beta H_B}/\text{Tr}[e^{-\beta H_B}]$. Inserting Eq. (9) into Eq. (10), we obtain

$$\rho(t) = \langle 1,1\rangle_t - \frac{i}{\hbar}\int_0^t dt_1\left[\langle 1, V_I^R(t_1)\rangle_t - \langle V_I^{R\dagger}(t_1), 1\rangle_t\right]$$
$$+ \frac{1}{\hbar^2}\int_0^t dt_1\int_0^t dt_1' \langle V_I^{R\dagger}(t_1'), V_I^R(t_1)\rangle_t, \tag{11}$$

where we introduce the new bracket as

$$\langle A, B\rangle_t \equiv \text{Tr}[\langle i'|\theta^\dagger A U^\dagger(t)\theta|f'\rangle\langle f|\theta^\dagger U(t)B\theta|i\rangle\rho_b]. \tag{12}$$

Apparently, in order to eliminate the first order term of the r.h.s. in Eq. (11), we need to introduce the average interaction Hamiltonian, which is independent of the phonon operator but depends on the electronic exciton states. In addition, the average interaction Hamiltonian needs to be a function of two type variables for time. One is the integral variable t_1; the other is the artificially observing time t. Hence, we redefine renormalized nonperturbative Hamiltonian $H_0^R(t_1) \equiv H_0(t_1) + v_c(t_1, t)$, and renormalized perturbative Hamiltonian as $V^R(t_1) \equiv V_0(t_1) - v_c(t_1, t)$. The average matrix element $v_c(t, t_1)$ is determined to satisfy the relation as $\langle 1, V_I^R(t_1)\rangle_t = \langle V_I^{R\dagger}(t_1), 1\rangle_t = 0$.

2.3. Renormalized Hamiltonian

Introducing the c-number as the strength of time-dependent interaction $v_{c\mu\nu}(t, t')$ and the renormalized exciton state $|\alpha(t)\rangle$ as below, we define the non-perturbative renormalized Hamiltonian H_0^R as

$$H_0^R(t) = \sum_\alpha [\epsilon_\alpha'(t) + H_B]|\alpha(t)\rangle\langle\alpha(t)|, \tag{13}$$

$$\left[\sum_\mu \epsilon_\mu|\mu\rangle\langle\mu| + \sum_{\mu\nu}^{\mu\neq\nu} v_{c\mu\nu}(t, t')|\mu\rangle\langle\nu|\right]|\alpha(t)\rangle = \epsilon_\alpha'(t)|\alpha(t)\rangle, \tag{14}$$

where the nuclear-relaxed exciton energy ϵ_μ is defined as

$$\epsilon_\mu = E_\mu - \sum_k G_k^{\mu\mu 2}/(\hbar\omega_k). \tag{15}$$

The renormalized perturbative Hamiltonian $V^R(t)$ is defined as

$$V^R(t) = \sum_{\mu\nu}^{\mu\neq\nu}[v_{q\mu\nu} - v_{c\mu\nu}(t, t')]|\mu\rangle\langle\nu|, \tag{16}$$

$$v_{q\mu\nu} \equiv \theta_\mu B_{\mu\nu}\theta_\nu^\dagger, \tag{17}$$