Four-electron model for singlet and triplet excitation energy transfers with inclusion of coherence memory, inelastic tunneling and nuclear quantum effects

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ABSTRACT

A computational scheme to describe the coherent dynamics of excitation energy transfer (EET) in molecular systems is proposed on the basis of generalized master equations with memory kernels. This formalism takes into account those physical effects in electron-bath coupling system such as the spin symmetry of excitons, the inelastic electron tunneling and the quantum features of nuclear motions, thus providing a theoretical framework to perform an *ab initio* description of EET through molecular simulations for evaluating the spectral density and the temporal correlation function of electronic coupling. Some test calculations have then been carried out to investigate the dependence of exciton population dynamics on coherence memory, inelastic tunneling correlation time, magnitude of electronic coupling, quantum correction to temporal correlation function, reorganization energy and energy gap.

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1. Introduction

The excitation energy transfer (EET) phenomena in molecular systems often play key roles in the photophysical processes for a wide variety of problems in biophysics, chemical physics and materials science [1–3]. In biological context, the EET in photosynthetic systems has recently attracted much attention, in particular in association with the quantum coherence of exciton transfer [4,5]. As for the optoelectronic device applications employing organic semiconductors such as crystalline tetracene, the combined dynamics of singlet and triplet EETs are of great interest [6,7]. Fluorescence resonance energy transfer (FRET) provides another important research field for the application to bioimaging [8]. In order to understand the underlying mechanisms for these EET phenomena, one needs a comprehensive description concerning the dependence of exciton dynamics on relevent physical parameters in exciton-bath system such as the electronic coupling, the energy gap and the reorganization energy [1–3]. Although the model calculations in realistic situations are often very complicated, we would like to find a general formalism to allow for first-principles calculations to appropriately reproduce or predict the experimental observations. In addition to the theoretical eluci-

dation based on the conventional modeling employing the physical parameters above, we are also interested in the effects associated with the non-Condon, inelastic electron tunneling [9,10] and the quantum–mechanical features of nuclear motions [10–13], which have not been investigated well in previous studies.

The present study is thus focused not on the rate constant but on the time-dependent population dynamics of EET in order to describe the quantum coherence [14–27] as observed in photosynthetic systems such as the Fenna–Matthews–Olson (FMO) protein [28–31]. We start with the Liouville–von Neumann equation for the density operator and derive the generalized master equation for the exciton population [1], in which the memory kernel [32–34] plays a pivotal role. For the calculations of the memory kernel, we pay attention to the following issues: First, it has been recognized [12,13,35] that the electronic coupling, which causes the state transition and can be evaluated quantum–mechanically, dynamically fluctuates in its magnitude significantly due to structural fluctuations in biomolecular systems, as observed both in the cases of electron transfer and excitation energy transfer. This fact, in turn, would not allow the use of a constant value of the electronic coupling between donor and acceptor (Condon approximation) [36–38], and consequently would lead to the description of the inelastic effect of tunneling electrons [9,10] in which the temporal correlation function of the electronic coupling plays an essential role. The second issue, the nuclear effect described in terms of the Franck–Condon factor, is then taken into account in the theory [10–12] so that the nuclear

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degrees of freedom are dynamically coupled with the electronic ones. If we could quantitatively evaluate the spectral density [1–3] representing the electron–phonon or system-reservoir interactions through realistic molecular dynamics simulations, we could also account for the nuclear quantum effect [10–12] on the EET. Third, by considering the spin degrees of freedom of excitonic wave functions in terms of the four-electron model in the present study, we could describe the singlet–singlet and triplet–triplet excitation energy transfers [39–41] in a comprehensive manner. Thus, through a full account of known physical effects as much as possible, we could perform a very quantitative description for the coherent/incoherent dynamics of EET in molecular systems in such a way that is compatible with *ab initio* simulations.

In the following Section 2, the details of the present theory are illustrated so that the basic equations for describing the EET dynamics are derived in terms of the temporal correlation function of electronic coupling and the spectral density of the reservoir. Numerical calculations for some simplified models are then performed in Section 3 to see the dependence of EET dynamics on relevant physical parameters. Conclusions are given in Section 4.

2. Theory

2.1. Generalized master equation and second-order memory kernel

Let us consider a system-reservoir Hamiltonian [1],

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{1}$$

with the diagonal part,

$$\hat{H}_0 = \sum_a H_a |a\rangle\langle a| = \sum_a [E_a + H_R + V_{aa}(Z)]|a\rangle\langle a|. \tag{2}$$

Here, H_a is the vibronic Hamiltonian and $H_S = \sum_a E_a |a\rangle\langle a|$ is the electronic system Hamiltonian with system energy E_a for eigenstate $|a\rangle$; H_R is the reservoir (phonon) Hamiltonian and H_{S-R} represents the system-reservoir interaction, which yields

$$V_{ab}(Z) = \langle a|H_{S-R}|b\rangle, \tag{3}$$

where Z refers to the reservoir coordinates.

$$\hat{V} = \sum_{a,b}(1 - \delta_{ab})V_{ab}(Z)|a\rangle\langle b| \tag{4}$$

represents the off-diagonal part of the system-reservoir Hamiltonian, which is assumed to be small compared to the diagonal part.

To describe the dynamics of excitation energy transfer, we consider the statistical operator (or the density operator) $\hat{W}(t)$ for the system-reservoir Hamiltonian above. In thermal equilibrium at temperature T, it reduces to the canonical density operator,

$$\hat{W}_{eq} = \sum_a \hat{W}_a = \sum_a \hat{R}_a \hat{\Pi}_a \tag{5}$$

with

$$\hat{R}_a = \frac{\exp(-H_a/k_B T)}{\mathrm{tr}_R\{\exp(-H_a/k_B T)\}} \tag{6}$$

and

$$\hat{\Pi}_a = |a\rangle\langle a|, \tag{7}$$

where k_B is the Boltzmann constant and tr_R means the trace over the reservoir coordinates. The projection operator $\tilde{\mathcal{P}}$ onto the diagonal part is then defined as

$$\tilde{\mathcal{P}}\hat{O} = \sum_a \hat{R}_a \mathrm{tr}_R\{\langle a|\hat{O}|a\rangle\}\hat{\Pi}_a \tag{8}$$

for any operator $\hat{O}$, and we find

$$\tilde{\mathcal{P}}\hat{W}(t) = \sum_a P_a(t)\hat{W}_a, \tag{9}$$

where $P_a(t)$ represents the time-dependent population of system eigenstate $|a\rangle$.

We rely on the Liouville–von Neumann equation for the statistical operator,

$$\frac{\partial}{\partial t}\hat{W}(t) = \frac{1}{i\hbar}\left[\hat{H}, \hat{W}(t)\right], \tag{10}$$

with the initial condition at $t = 0$,

$$\tilde{\mathcal{Q}}\hat{W}(0) = (1 - \tilde{\mathcal{P}})\hat{W}(0) = 0. \tag{11}$$

The generalized master equation (GME) for $P_a(t)$ is then derived with the aid of the projection operator technique [1] as

$$\frac{\partial}{\partial t}P_a(t) = \sum_b \int_0^t d\tau K_{ab}(\tau)P_b(t - \tau). \tag{12}$$

The memory kernel $K_{ab}(\tau)$ and its Fourier transform,

$$K_{ab}(\omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau}K_{ab}(\tau), \tag{13}$$

thus govern the dynamics of the population $P_a(t)$.

We consider the case in which the electronic coupling between the exciton donor and acceptor is relatively weak, thus allowing for a use of perturbation theory. Up to the second order of $\hat{V}$, the memory kernel can be expressed in terms of the reservoir correlation function $C_{ab}(t)$ as [1]

$$K_{ab}^{(2)}(\omega) = \int_0^{\infty} dt e^{i\omega t}[C_{ab}(t) + C_{ab}(-t)], \tag{14}$$

$$C_{ba}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t}C_{ba}(t), \tag{15}$$

$$C_{ba}(t) = \frac{1}{\hbar^2}\sum_{\mu,\nu}f_{a\mu}|\langle\Phi_{a\mu}|V_{ab}(Z)|\Phi_{b\nu}\rangle|^2 e^{i(\omega_{a\mu}-\omega_{b\nu})t}, \tag{16}$$

$$C_{ba}(\omega) = \frac{2\pi}{\hbar^2}\sum_{\mu,\nu}f_{a\mu}|\langle\Phi_{a\mu}|V_{ab}(Z)|\Phi_{b\nu}\rangle|^2\delta(\omega + \omega_{a\mu} - \omega_{b\nu}), \tag{17}$$

where $\Phi_{a\mu}$ refers to the eigenfunction (eigenstate) of the Hamiltonian H_a with the vibrational state μ, and $\hbar\omega_{a\mu}$ is the eigenvalue (energy) of H_a;

$$f_{a\mu} = \frac{\exp(-\hbar\omega_{a\mu}/k_B T)}{Z_a} \tag{18}$$

represents the equilibrium distribution with the partition function Z_a. It is straightforward to derive the Förster [42] and Dexter [43] formulae for the EET rate constant from Eqs. (12)–(17), as seen in Appendix A.

2.2. Four-electron model for two-state transition

In the following, we consider a two-state transition from the initial state $i = a$ to the final state $f = b$. In the initial state, the pigment A is electronically excited (*e*) and the pigment B is in the ground (*g*) state. In the final state, the pigment A is in the ground state and the pigment B is in the excited state. The total vibronic wavefunctions for the initial and final states are then expressed in terms of the product of the electronic (Ψ) and vibrational (χ) parts as

$$\Phi_i = \Psi_{Ae}\chi_{Ae\nu}(\boldsymbol{R}_A)\Psi_{Bg}\chi_{Bgu}(\boldsymbol{R}_B), \tag{19}$$