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A coherent modified Redfield theory for excitation energy transfer in molecular aggregates

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ABSTRACT

Excitation energy transfer (EET) is crucial in photosynthetic light harvesting, and quantum coherence has been recently proven to be a ubiquitous phenomenon in photosynthetic EET. In this work, we derive a coherent modified Redfield theory (CMRT) that generalizes the modified Redfield theory to treat coherence dynamics. We apply the CMRT method to simulate the EET in a dimer system and compare the results with those obtained from numerically exact path integral calculations. The comparison shows that CMRT provides excellent computational efficiency and accuracy within a large EET parameter space. Furthermore, we simulate the EET dynamics in the FMO complex at 77 K using CMRT. The results show pronounced non-Markovian effects and long-lasting coherences in the ultrafast EET, in excellent agreement with calculations using the hierarchy equation of motion approach. In summary, we have successfully developed a simple yet powerful framework for coherent EET dynamics in photosynthetic systems and organic materials.

1. Introduction

Excitation energy transfer (EET) is a crucial process in photosynthetic light harvesting. The near unity efficiency of photosynthetic EET from the antenna to the reaction center ensures the success of energy collections in light reactions, and thus enables the subsequent sugar-production reactions that support life forms on earth [1,2]. In addition to natural photosynthesis, EET also occurs in synthetic photosensitive molecules and conjugate polymers, which are potential materials for energy applications. Because of the importance and ubiquity of EET, its mechanism and accurate dynamical simulations have become an intriguing subject to scientists for decades [3,4]. Recent ultrafast time-resolved spectroscopic experiments revealing the existence of long-lived quantum coherence in photosynthetic complexes and conjugated polymer systems have been a major breakthrough in this field [5–8]. Although the significance of coherent EET in photosynthetic efficiency remains controversial, these experiments clearly demonstrate that conventional theories for EET can not adequately describe ultrafast (<picosecond time scale) transfer dynamics that are commonly observed in photosynthesis and bulk organic optoelectronic materials.

The major difficulty in describing coherent EET in molecular aggregate systems is how to appropriately treat the electronic coupling between the pigments and the exciton–phonon coupling between the excitations and their surrounding environments in a balanced way. A number of new frameworks employing various techniques, such as polaron transformation [9–12], quantum–classical hybrid methods [13–15], and non-perturbative approaches [16–25], have been suggested recently. In this study we turn to the modified Redfield theory [26,27], which has been applied to describe population dynamics and spectra of many photosynthetic systems. Unlike the conventional Redfield theory, the modified Redfield theory treats only the off-diagonal part of the exciton–phonon coupling matrix as the perturbation. As a result, it correctly and smoothly interpolates between the Förster and the Redfield theories at their respective limits [27,28]. Thus, the modified Redfield theory has been a popular tool in studies of light harvesting EET [29,28,3,30]. Recently, Novoderezhkin and van Grondelle have comprehensively evaluated the validity of the modified Redfield theory by benchmarking it against other theoretical methods [28,4] and by applying it to fit experimental data [31,29,32]. They conclude that a combination of modified Redfield approach and generalized Förster theory [33] yields excellent simulations of EET dynamics in photosynthetic systems [32]. Despite its popularity in photosynthetic EET, the modified Redfield theory cannot be applied to model coherent EET since coherence dynamics are neglected fully. Therefore, recently revealed coherent EET

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phenomena in natural photosynthetic systems can not be described by the conventional modified Redfield theory.

Previously, Golosov and Reichmen have proposed a pure dephasing reference system (PDRS) master equation that in essence is the full quantum master equation in the same basis of the modified Redfield theory [34,35]. The PDRS approach was shown to provide excellent results in a broad parameter space of the electron transfer problem, however, the complicated equation of motion made its application to large multichromophoric photosynthetic systems a formidable task.

In this work, we aim to derive a simple yet powerful quantum master equation based on the framework of the modified Redfield approach. This coherent modified Redfield theory (CMRT) allows the description of coherent EET dynamics as well as time-resolved spectroscopic signals that depend on the coherences. Additionally, to capture non-equilibrium bath relaxation effects, we do not apply the Markovian approximation, and thus the dissipation tensor is kept time-dependent. We also consider a generalized form of lineshape functions that enables the treatment of correlated-bath effects. Furthermore, we present the applications of this new framework, with comparisons to numerically exact methods. We explore the properties of CMRT in a simple two-site system and compare the results with those obtained from the quasi-adiabatic propagator path integral (QUAPI) approach. Finally, we compare our simulation of EET dynamics in the Fenna–Matthews–Olson complex with the exact results from the reduced hierarchy equation approach to show the effectiveness of the CMRT approach for coherent EET dynamics in photosynthetic systems.

2. Theoretical method

In order to develop a general theory for EET we adopted the modified Redfield theory [26] and extended it to treat coherent evolution of excitonic systems. In this section we describe the derivation of the CMRT equation of motion.

2.1. Model Hamiltonian

In this study, we employ the Frenkel exciton Hamiltonian to describe photoexcitations of a molecular aggregate with N sites. Written in the electronic eigenbasis (the so called exciton basis), the Hamiltonian reads ($\hbar = 1$):

$$H = H_e + H_{ph} + H_{e-ph},$$

$$H_e = \sum_{\alpha=1}^{N} \varepsilon_\alpha |\alpha\rangle\langle\alpha|, \tag{1}$$

$$H_{ph} = \sum_i \omega_i b_i^\dagger b_i, \tag{2}$$

$$\begin{aligned} H_{e-ph} &= \sum_{\alpha,\beta}^{N} |\alpha\rangle\langle\beta| \cdot \sum_{n=1}^{N}\sum_i c_n^\alpha c_n^{\beta*} g_{ni}\omega_i \left(b_i + b_i^\dagger\right) \\ &\equiv \sum_{\alpha,\beta}^{N} |\alpha\rangle\langle\beta| \cdot (H_{e-ph})_{\alpha\beta}, \end{aligned} \tag{3}$$

where $|\alpha\rangle$ denotes the αth exciton state, which is a delocalized linear combination of site excitations, $|\alpha\rangle = \sum_n^N c_n^\alpha |n\rangle$. In addition, ε_α denotes the excitation energy of $|\alpha\rangle$, $b_i^\dagger$ (b_i) is the creation (annihilation) operator of the ith phonon mode, ω_i is the frequency of the phonon mode, and g_{ni} is the exciton–phonon coupling constant between the localized electronic excitation on site n and the ith phonon mode. Note that we do not limit ourself to localized phonon modes, so general correlated baths are described in this model. The exciton–phonon coupling constant is related to the displacement of the phonon coordinate in the excited state, which also defines the site reorganization energy $\lambda_n = \sum_i \sum_n g_{ni}^2 \omega_i$. Finally, basis transformation from the site basis to the exciton basis yields the $\sum_n^N c_n^\alpha c_n^\beta$ factor, which can be considered as the overlap between exciton wavefunctions $|\alpha\rangle$ and $|\beta\rangle$.

The main idea behind the modified Redfield theory [26] is to partition the Hamiltonian into a zeroth-order Hamiltonian including the diagonal fluctuations in the exciton basis:

$$H_0 = H_e + H_{ph} + \sum_{\alpha=1}^{N} |\alpha\rangle\langle\alpha| \cdot (H_{e-ph})_{\alpha\alpha}$$

and a perturbation part:

$$V = \sum_{\alpha\neq\beta}^{N} |\alpha\rangle\langle\beta| \cdot (H_{e-ph})_{\alpha\beta}.$$

Specifically, the diagonal part of H_{e-ph} (Eq. (3)) is included in the zeroth-order Hamiltonian while the perturbation part includes only the off-diagonal part of H_{e-ph}. By treating the diagonal part of H_{e-ph} nonperturbatively, bath reorganizations and pure dephasing are treated exactly in this formalism. Moreover, multi-phonon effects are included [27,28]. Base on the same partitioning of the zeroth-order Hamiltonian, we derive a coherent modified Redfield theory for coherent EET dynamics.

2.2. Quantum master equation

The modified Redfield theory was derived with a diagonal projection operator, which omits the coherence part of the density matrix and only considers the population transfer between exciton states [26,27]. Given that recent experimental and theoretical studies have shown coherent EET dynamics in natural photosynthetic complexes and organic conjugated polymers, it is highly desirable to extend the modified Redfield theory to treat coherent dynamics. To this end, we start from a general time-local quantum master equation that is derived using a second-order cumulant expansion technique with respect to a perturbation V [36,37]. The quantum master equation written in the interaction picture of H_0 is

$$\dot{\sigma}_I(t) = -\int_0^t d\tau \mathrm{Tr}_B\left\{\left[V_I(t), \left[V_I(\tau), \sigma_I(t) \otimes \rho_b^{eq}\right]\right]\right\}, \tag{4}$$

where $V_I(t)$ is defined in the interaction picture of H_0, i.e. $V_I(t) = e^{iH_0 t} V(t) e^{-iH_0 t}$. Note that to derive Eq. (4), we have assumed a product-state initial condition, $\rho(0) = \sigma(0)\rho_b^{eq}$, where $\rho_b^{eq} = e^{-\beta H_{ph}}/Z$ is the equilibrium density matrix of the bath. This assumption is justified with photoinduced EET processes. Additionally, we also neglect the first-order average of the perturbation, i.e. $\langle V\rangle$ in the perturbation. This greatly simplifies the equation of motion, however, it can not be easily justified. In this work we perform numerical simulations to demonstrate that neglecting the first-order term does not contribute to significant error in a broad parameter regime.

In the Schrödinger picture, the reduced density matrix is calculated by

$$\sigma(t) = \mathrm{Tr}_B\left\{U_0(t)\sigma_I(t)\rho_b^{eq} U_0^\dagger(t)\right\}.$$

Note that $U_0(t)$ can not be simply separated into a system part and a bath part. Because the diagonal exciton–phonon coupling term contains both system and bath operators, the partial trace has to be taken *after* solving $U_0(t)\sigma_I(t)U_0^\dagger(t)$. Formally, the equation of motion for the reduced density matrix is

$$\begin{aligned} \dot{\sigma}(t) &= -i\mathrm{Tr}_B\left\{\left[H_0, \sigma(t) \otimes \rho_b^{eq}\right]\right\} \\ &\quad - \int_0^t \mathrm{Tr}_B\{[V, [V(-\tau), \sigma(t) \otimes \rho^{eq}]]\} d\tau \\ &= \dot{\sigma}^{(coh)}(t) + \dot{\sigma}^{(diss)}(t). \end{aligned} \tag{5}$$