Quantum dynamics of ultrafast energy transfer processes in light harvesting systems

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**QUANTUM DYNAMICS OF ULTRAFAST ENERGY
TRANSFER PROCESSES IN LIGHT HARVESTING SYSTEMS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

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A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Abstract

How to harvest sunlight efficiently for residential and industrial consumption is one of the most challenging problems faced by the modern energy-hungry world. However, underlying mechanisms of the nearly perfect energy transfer efficiency in light harvesting systems are not well understood despite many experimental and theoretical efforts devoted to unravelling these intricate processes. By formulating an accurate theoretical framework aided by the highly parallel Graphic Processing Unit (GPU) architecture, this thesis presents a comprehensive mechanistic study of the energy transfer processes in light harvesting systems.

We first develop two theoretical methods, i.e., a time-dependent variational approach utilizing a superposition of the Davydov D_1 and the Davydov D_2 ansätze, and an extended discretized Hierarchy Equation of Motion (HEOM) method that can accurately and efficiently characterize dynamics of the Holstein polaron in the presence of both diagonal and off-diagonal exciton-phonon coupling. Polaron dynamics of the Holstein model in various parameter regimes are systematically scrutinized by a combination of the two methods. Our formalism making use of the Davydov D_1 trial state is also applied to explore the coherent energy transport in engineered nano-arrays of pigments taken from natural photosynthetic systems.

Next, the HEOM method is applied to study dissipative dynamics at a conical intersection, which plays an important role in the ultrafast energy relaxation processes in polyatomic systems. We analyze the ultrafast nonadiabatic dynamics for a two-state two-mode conical

intersection in pyrazine which is bilinearly coupled to a bath of an infinite number of harmonic oscillators by calculating the diabatic and adiabatic populations of electronic states as well as wave packets of individual vibrational modes. While the population of the upper adiabatic electronic state is effectively quenched by the system-bath coupling, that of the diabatic electronic state exhibits long-lived quantum beating driven by the motion of the tuning mode. It is found that even weak coupling to the bath may effectively suppress the erratic oscillatory features of the nonadiabatic wave packet motion of an isolated two-mode conical intersection, and the main effect of the bath is to direct the wave packet to the lower adiabatic energy surface.

Furthermore, a first principles recipe has been developed for describing femtosecond double-pump single molecule signals of molecular aggregates by incorporating the vibrational modes with significant exciton-phonon coupling into a system Hamiltonian and treating the corresponding dynamics in terms of the Davydov D_1 ansatz, while the effect of remaining intra and inter-molecular modes treated as a bath are accounted for through the lineshape function formalism. We then apply our theory to calculate the single molecule signal of LHCII, and it is found that signal oscillations are of vibronic origin, and the oscillation periods are dependent on the exciton-phonon coupling strength.

Finally, a theoretical framework is developed to calculate 2D spectra of molecular aggregates by integrating the Davydov trial states into the non-linear response theory. We first apply this theory to calculate a model J aggregate in the presence of exciton-phonon coupling and bath-induced relaxation and dephasing. It is found that the 2D spectra at weak diagonal (off-diagonal) exciton-phonon coupling exhibits similar patterns as those of a two-level system, while multi-peak structures accompanied with the population relaxation from high to low energy regions for large population time dominate for the large diagonal (off-diagonal) coupling. The application of our theory to the calculation of 2D spectra of LHCII reveals coherent energy transport between different excitonic states within Chlb and Chla bands.

To summarize, through this work we have developed theoretical frameworks to systematically study energy transfer processes starting from basic model systems to realistic light harvesting systems. Specifically, we have investigated nonadiabatic wave packet motion of a two-state two-mode conical intersection in pyrazine, oscillatory features of the single molecule signal of LHCII, and the coherent energy transport between different excitonic states within Chlb and Chla bands of LHCII. It is our hope that this work may help provide guiding principles for the relationship between the structure of the light harvesting systems and optimal energy transfer pathways.

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Abbreviations

RC	reaction center
ATP	adenosine triphosphate
NADPH	nicotinamide adenine dinucleotide phosphate
NPQ	non-photochemical quenching
FMO	Fenna-Matthews-Olson
LHCII	light harvesting complex II
OSCs	organic solar cells
HEOM	hierarchical equation of motion
CI	conical intersection
PE	potential energy
LH2	light-harvesting complex 2
2DES	2D electronic spectroscopy
EET	excitation energy transfer
CPU	central processing units
GPU	Graphic Processor Units
HPC	high-performance computation
ETE	energy transfer efficiency
ENAQT	environment-assisted quantum transport
GBR	generalized Bloch-Redfield
PC 645	phycocyanin 645
NIBA	noninteracting blip approximation
FRET	Föster resonant energy transfer

CT	charge transfer
KMC	kinetic Monte-Carlo
2D DAS	two dimensional decay-associated spectra
MSD	Matsubara spectrum decomposition
PSD	Pade spectrum decomposition
QUAPI	quasiadiabatic propagator path integral
QME	quantum master equations
MSD	mean square displacement
HO	harmonic oscillator
MCTDH	multiconfigurational time-depedent Hartree
BO	Bloch oscillations

Chapter 1

Introduction

In this chapter, we first give a brief introduction to the research topic of the energy transfer in light harvesting systems. We then discuss the significance and novelty of the research topic. Finally, we list several objectives achieved through this work.

Decoding the numerous enigmatic facets of one of the most crucial biochemical processes occurring on Earth—photosynthesis, has been an active area of research over many decades. This intricate process starts from the absorption of solar energy by specialized light harvesting complexes, and the triggered excitation energy is then transferred with nearly perfect efficiency to a special site called reaction center (RC), where a chain of complicated electron transfer processes take place resulting in the synthesis of adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH) [1, 2]. Through millennia of evolution, many light harvesting organisms from primitive bacteria to high-order green plants have developed elegant ways to capture and convert the solar energy to chemical energy with remarkable efficiency and adaptability. At low light intensities, nearly every absorbed photon is transmitted instantaneously into RC, where subsequent electron transfer reactions convert nearly all the solar energy into chemical energy. On the other hand, at high light intensities, the rate of energy conversion occurring in the reaction centers saturates but that of energy absorption, which occurs in light harvesting pigment-protein antennae continues. The excess excitation energy poses a severe threat to the photosynthetic machinery due to the increased probability of formation of harmful singlet oxygen species via generation of long-lived triplet states of chlorophylls [3, 4]. In order to prevent such damage of the photosynthetic machinery, green plants have developed an elegant photo-protective mechanism called non-photochemical quenching (NPQ), which dissipates the excess energy as heat in a harmless way. When the ambient light intensity returns to normal level, the functionalities of the photosynthetic organisms get restored quickly [4]. Experimental and theoretical studies have revealed many interesting aspects of photosynthesis, yet, a complete understanding of molecular level mechanism remains elusive.

The mechanisms that underlie the near-perfect efficiency of light harvesting organisms are not fully understood, however, the situation started to improve with the advent of ultrafast laser spectroscopy. With recent technological advances, the technique of two dimensional (2D) Fourier transform electronic spectroscopy has dramatically expanded our understanding of energy transfer processes in light harvesting complexes [5, 6, 7, 8]. The application of

this technique to the Fenna-Matthews-Olson (FMO) pigment-protein complex in *Chlorobium tepidum* suggests that dominant energy transfer pathways depend on the spatial distribution of the excited state wave function of the entire complex [6]. The observation of quantum beats due to light induced oscillations between donors and acceptors provides direct evidence of quantum coherence. The fact that quantum coherence lasts for at least 660 fs is quite astonishing since it is contrasted with the general notion that electronic decoherence time is on the timescales of 10-100 fs in such warm, wet and noisy biological systems [9, 10]. The authors then claimed that this wavelike characteristic of the energy transfer rather than incoherent hopping might dramatically increase the efficiency of electronic energy transfer [6]. It is noted that the initial experiments are conducted at a low temperature (77 K), recent studies show that the quantum coherence can last up to 300 fs even at room temperature [7, 8]. Moreover, the existence of quantum coherence in light harvesting complex II (LHCII), the main light harvesting complexes in green plants, points to the possible universality of quantum coherence as an integral part of photosynthetic organisms [11]. While various experimental and theoretical studies provide fruitful information about the potential role of quantum coherence, the underlying mechanism of the observed long-lived quantum coherence and its potential role in promoting the energy transfer efficiency in photosynthetic organisms are far from reached. Resolving and extracting the mechanisms that underpin the remarkable efficiency of energy transfer in natural light harvesting systems help the design of artificial photosynthetic devices with great efficiency and robustness.

1.1 Research Scope: Significance and Novelty

Energy derived from the sunlight may provide the most abundant source of energy available on Earth. Specialized light harvesting complexes, during perhaps the longest stint on the evolutionary ladder, have developed a sophisticated and intricate system to harvest light energy and convert it to chemical forms via photosynthesis. Understanding of such funda-

mental process is not only important for our knowledge of primary energy and charge transfer mechanisms in natural light harvesting systems, but also foundational for the development of renewable energy technologies with the possibility to devise general optimal design principles for human-engineered complex devices/nano-materials capable of solar energy harvesting. Organic photovoltaic devices, for example, are regarded as a promising low-cost technology. However, organic solar cells (OSCs) have yet to possess the photocurrent efficiencies of their inorganic counterparts, thereby limiting their large-scale applications in commercial markets. Fortunately, recent technological advances in solution-processed OSCs based on polymer/fullerence-blend film have opened up a new pathway to develop bulk heterojunction devices as the next generation of OSCs. It is thus imperative that uncovering the energy and charge transfer mechanisms will immensely facilitate the design of solar-to-electric energy conversion devices with high efficiency and robustness.

While significant efforts have been devoted to the understanding of the energy transfer in light harvesting systems, accurate theoretical treatments of energy transfer processes are still rare due to intricate interplay between interchromophoric electronic interactions and excitation-environment coupling. Energy transfer in light harvesting system is usually described by electronic dynamics coupled to the thermal environment. The fact that the electronic coupling between pigments and the excitation-environment coupling characterized by reorganization energy are comparable in many light harvesting systems excludes traditional second-order perturbation theories, such as Föster and Redfield theories based on the perturbative treatments with respect to the electronic coupling and excitation environment interactions, respectively. In addition, the strong non-Markovian effect in which the environmental reorganization and system dynamics are on the similar timescales in these systems indicates that theories based on the Markovian approximation also fail. As a result, accurate treatments of these non-perturbative, non-Markovian regimes are challenging from a theoretical point of view. In theory, the Holstein model, with a long and rich history dating back to as early as 1950s when Holstein pioneered the concept of the small polaron, is usually used to study energy and charge transport

in light harvesting systems. A variety of theoretical methods only consider original Holstein model with diagonal exciton-phonon coupling. However, simultaneous presence of diagonal and off-diagonal exciton-phonon couplings seems crucial to characterize the energy and charge transport in light harvesting systems. Due to inherent difficulties to obtain the reliable solution, theoretical methods that can accurately treat off-diagonal exciton-phonon coupling seldom appear in the polaron literature. We tackle aforementioned problems by developing numerically efficient and accurate Davydov trial states and the numerically exact hierarchical equation of motion (HEOM) methods, thus providing microscopic modeling of polaron dynamics of Holstein model in the presence of both diagonal and off-diagonal exciton-phonon coupling.

Conical intersections (CI) of potential energy (PE) surfaces, characterized by the features of strong vibrational mode coupling resulting from pronounced local anharmonicity of the adiabatic PE surfaces and the breakdown of the Born-Oppenheimer approximation in the vicinity of the CI, play a crucial role in the ultrafast energy relaxation processes in polyatomic systems. It is known that energy relaxation through CI involves several active vibrational modes, the so called coupling modes and tuning modes, and these active modes are in turn coupled to a large body of spectroscopically inactive modes which results in the cooling of the modes actively in the energy relaxation process typically on a timescale of picoseconds. Theoretical treatments of the effect of dissipative bath modes on the dynamics of a CI are computationally challenging due to a large number of vibrational degree of freedoms. It is thus imperative to develop numerically efficient and accurate methods that can investigate the electronic and vibrational dynamics in the vicinity of CIs for various system parameters and system-bath coupling strengths, thus uncovering their potential roles in ultrafast energy relaxation processes.

The advancement of femtosecond nonlinear optical spectroscopy has dramatically expanded our understanding of ultrafast energy transfer processes in light harvesting systems. However, due to the large energetic and structural disorder of photosynthetic antenna proteins, the responses measured in conventional femtosecond spectroscopy are subject to inhomogeneous

broadening and dephasing. To overcome this ensemble averaging, ultrafast single molecule technique has been developed to investigate the excitation energy transfer pathways and asymmetric fluctuating shapes of light harvesting complex II (LH2) on a single molecular level. The advent of fluorescence-detection single molecule spectroscopy with a temporal resolution of ~ 10 fs has enabled simultaneous detection of electronic populations and coherences in individual molecule. This technique has recently been applied to study coherent energy transfer in a single LH2 complex. Adequate theoretical simulations of single molecule spectra involve non-perturbative treatments of field-matter, exciton-exciton and exciton-phonon interactions. We thus propose a theoretical framework that can accurately describe the fluorescence single molecule spectra of light harvesting systems for wide range of parameter regimes.

Technological advances of 2D electronic spectroscopy (2DES) have enabled researchers to probe vibrational dynamics as well as excitation transfer and relaxation, thus set to unravel the ultrafast energy transfer processes of photosynthesis. The claimed direct observation of electronic quantum coherence in FMO complex by 2DES attracted huge interest in the past few years. It is conjectured that the subtle quantum mechanical interference between different excited states allows simultaneous sampling of all energy transfer pathways as well as identification of the most efficient one to funnel solar energy from pigments to RCs. However, the underlying mechanisms of the observed long-lived coherence and its potential roles in photosynthetic light harvesting are still not well understood. We propose that the long-lasting coherence may arise from intricate system-environment interactions. We will combine the experimental and theoretical analysis to elucidate the electronic and vibronic coherence, and understand the interplay between these two types of coherence in the excitation energy transfer (EET) processes in light harvesting systems.

The theoretical studies are generally accompanied by numerical simulations that employ the computational capabilities of the traditional central processing units (CPU)-based high-performance computational (HPC) clusters. However, despite the CPU-based HPC technol-

ogy, fully quantum mechanical calculations on systems sufficiently complex enough to mimic realistic conditions, remain computationally infeasible. The advent of the graphics processing unit (GPU) driven acceleration in very recent times has opened up the possibility of developing hybrid CPU-GPU architectures that yield very high computational speed-up and superior memory management as compared to the purely CPU-based architecture. Through the formulation of a unified framework of accurate theoretical models and state of the art computational techniques based on GPU acceleration that can capture the energy transfer processes in realistic systems, we can obtain energy transfer time scales, uncover coherent and incoherent energy transfer mechanisms, and facilitate understanding of spectra measurement.

1.2 Objectives

By formulating systematic quantum mechanical models for theoretical analysis and augmenting them with state-of-the-art GPU acceleration, this thesis aims at developing a unified framework to describe accurately the energy transfer processes in light harvesting systems. Insights obtained are expected to provide guiding principles for optimal design of molecular structures to best enhance the efficiency and robustness of light-harvesting. Specific objectives of the thesis are given as follows:

1. To develop theoretical frameworks that can provide efficient and accurate description of polaron dynamics of the Holstein model in the presence of both diagonal and off-diagonal exciton-phonon coupling in order to elucidate the complex interplay between the electron and its surrounding phonon environment. This study involves extending original single Davydov trial states to their multiple ansatz versions, i.e., a superposition of the D_1 or the D_2 ansätze, referred to the ‘multi- D_1 ’ or ‘multi- D_2 ’ ansätze, in order to accurately describe the Holstein model in various parameter regimes, as defined by transfer integral, phonon bandwidth, and diagonal and off-diagonal exciton-phonon coupling strengths. In addition, as a benchmark-

ing tool, an extended, numerically exact HEOM approach that is capable of treating electron-phonon coupling in a nonperturbative manner and applicable to any temperature, will also be derived. Finally, as an application of aforementioned methods, the Davydov D_1 trial state will be applied to explore the coherent energy transport in a one-dimensional chain as well as the engineered nano-arrays of pigments taken from LH2 complex.

2. To apply the HEOM approach aided with the GPU acceleration to study the ultrafast energy relaxation processes in the vicinity of CI. This study aims at uncovering the mechanisms responsible for vibrational energy redistribution and electronic relaxation processes. The potential role of intricate electronic and vibrational coherence will be scrutinized by analyzing the electronic population as well as vibrational probability densities.

3. Inspired by recent fluorescence single molecule spectra experiment, a theoretical description of femtosecond double-pump single molecule signals of molecular aggregates will be formulated. This new method includes the vibrational modes with significant exciton-phonon coupling into the system Hamiltonian, while the remaining intra- and inter-molecular vibrational modes are responsible for the excitation energy relaxation. This new theory, capable of dealing with broad parameter regimes from intermediate to strong electron-phonon and electron-electron coupling strengths, will be utilized to calculate the single molecule signal of LHCII. Specifically, the effect of exciton-phonon coupling strengths, system-bath coupling, the orientation of transition dipole moments as well as the distribution of site energies will be investigated in detail.

4. 2DES technique provides a nice tool to directly resolve the electron-electron interactions as well as dephasing and relaxation processes in polyatomic systems. This study aims at developing theoretical framework that incorporate the description of the system dynamics in terms of the Davydov ansätze into nonlinear response function theory, which will be utilized to simulate the 2DES of Holstein model in the presence of both diagonal and off-diagonal

exciton-phonon couplings. Furthermore, this theoretical framework will also be applied to analyze and understand the experimental 2DES of LHCII. Special attentions will be paid to the elucidation of the interplay between electronic and vibrational coherence in the EET process as well as to understand to what extent quantum coherence contributes to interband as compared to intraband EET processes in LHCII complexes.

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Chapter 2

Literature Review

In this chapter, we review recent experimental and theoretical progresses on the studies of energy transfer in light harvesting systems. In Section 2.1, we give a brief overview of various factors affecting the quantum efficiency. In Section 2.2, we comment experimental and theoretical demonstrations of the potential role of the quantum coherence in enhancing the energy transfer efficiency. Likely mechanisms of non-photochemical quenching in protecting the green plants under rapidly varying conditions of illumination are illustrated in Section 2.3. Spectroscopic measurements together with model simulations revealing charge transfer pathways in reaction center are presented in Section 2.4. Finally, we review recent theoretical treatments investigating the energy transfer processes in light harvesting systems in Section 2.5.

2.1 Quantum efficiency and average trapping time

Figure 2.1 Three energy flow pathways of an exciton system: dissipate energy to an environmental bath, subject to irreversible energy loss processes arising from trapping at the RC and decay to the ground state (adapted from Ref. [1]).

In an energy transfer process characterized by quantum coherence, trapping, and dissipation, how can different factors work harmoniously to yield maximum efficiency [1]? Fig. 2.1 depicts a simple model in which the excitonic dynamics in light harvesting systems is inevitably coupled to a dissipative environment and subjected to the non-radiative decay to ground state and trapping at the RC. The exciton dynamics in light harvesting systems can be described by the Liouville equation [1, 2, 3]

$$\dot{\rho}(t) = -\mathcal{L}\rho(t) = -[\mathcal{L}_{\text{sys}} + \mathcal{L}_{\text{dissp}} + \mathcal{L}_{\text{decay}} + \mathcal{L}_{\text{trap}}]\rho(t) \quad (2.1)$$

where ρ is the reduced density matrix of the excitonic system. In Eq. (2.1), $\mathcal{L}_{\text{sys}}$ is the evolution operator of the pure exciton system and can be defined as $\mathcal{L}_{\text{sys}}\rho = i[H, \rho]/\hbar$, where $[H]_{nm} = (1 - \delta_{nm})J_{nm} + \delta_{nm}\epsilon_n$ with $J_{nm} = J_{mn}^*$ being the nearest neighbouring coupling constant and ϵ being the site energy. $\mathcal{L}_{\text{decay}}$ and $\mathcal{L}_{\text{trap}}$ denote Liouville operators characterizing two irreversible energy loss processes arising from the decay of the exciton to the ground state and the trapping of the exciton at RC, respectively, which can be defined as $[\mathcal{L}_{\text{decay}}]_{mn} = (k_{d,m} +$

$k_{d,n})/2$, and $[\mathcal{L}_{\text{trap}}]_{mn} = (k_{t,m} + k_{t,n})/2$ with $k_{d,n}$ and $k_{t,n}$ being the decay and trapping rates. $\mathcal{L}_{\text{dissp}}$ represents environment-induced excited state relaxation and dephasing, which depends on the system-bath Hamiltonian [2, 3, 4]. In the white noise and infinite temperature limit, the coupling to the environment can be described by the Bloch-Redfield equation, $[\mathcal{L}_{\text{dissp}}]_{nm} = (1 - \delta_{nm})\Gamma_{nm}^*$, with Γ^* being the pure dephasing rate [5]. More complicated forms of quantum master equations can be incorporated in a systematic fashion when the detailed balance and the memory effect of the bath are taken into account [6].

According to Eq. (2.1), $\mathcal{L}_{\text{decay}}$ and $\mathcal{L}_{\text{trap}}$ represent two possible pathways for irreversible energy loss with the later being beneficial for the overall efficiency [7, 8]. The quantum efficiency of photosynthesis can be quantitatively measured by the quantum yield q , namely, the trapping probability [1, 9, 10]

$$q = \frac{\sum_n k_{t,n}\tau_n}{\sum_n k_{t,n}\tau_n + \sum_n k_{d,n}\tau_n} \quad (2.2)$$

Here, $\tau_n = \int_0^\infty \rho_n(t)dt$ is the mean residence time at site n with ρ_n denoting the exciton population. It is noted that the trapping rate in photosynthetic systems is typically much larger than the decay rate, thereby indicating the near-unity quantum yield. Thus, the quantum yield can be conveniently approximated as $q \approx \frac{1}{1+\langle k_d \rangle}$, where $\langle t \rangle = \sum_n \tau_n(k_d = 0)$ is the mean first passage time to the trap site in the absence of the constant decay, i.e., the average trapping time [1, 11]. Single molecule statistics have been widely used to study the quantum yield and the average trapping time [12, 13].

More and more evidences from recent experimental and theoretical investigations have shown that environmental noise plays an important role in quantum transport and the intricate interactions between system and environment can be optimized to enhance the energy transfer efficiency (ETE) [7, 10, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23]. By using the Haken-Strobl model, Rebentrost *et al.* have found that ETE in the FMO protein complex can be enhanced by environment-induced pure dephasing [7]. The left panel of Fig. 2.2 depicts the quantum transport network structure of the FMO protein, and the right panel of Fig. 2.2 displays the efficiency

and transfer time as a function of the pure-dephasing rate. It is argued that the static disorder in the system inhibits transport at low noise levels, while decoherence takes a dominant role thus also suppressing transport at a very high noise level. However, at intermediate noise levels, the dynamical interplay of dissipated environment and system collaborates to achieve the optimal quantum efficiency, the so called environment-assisted quantum transport (ENAQT) [7]. Although it is built under the assumption of Markovian bath fluctuations and in the high temperature limit, the Haken Strobl model, in general, captures the dephasing behavior of the environment in a phenomenological way. In order to circumvent aforementioned drawbacks in the Haken-Strobl model, Wu *et al.* have discussed how various physical parameters, such as reorganization energy, temperature and spatial-temporal correlation in noise, affect the quantum efficiency of FMO protein and phycocyanin 645 (PC 645) by utilizing the generalized Bloch-Redfield (GBR) equation [24]. It is found that the maximum ETE can be achieved at some intermediate value of various variables. Quite interestingly, only in certain parameter regimes can ETE change non-monotonically with the temperature or the spatial correlation, and thus

Figure 2.2 (Left panel) Pigments arrangement in FMO structure. Pigments 1 and 6 are initial excitation sites, while pigment 3 is the trapping site. (Right panel) Efficiency (blue) and transfer time (red) versus the pure-dephasing rate for the FMO complex. The vertical line is the room temperature pure-dephasing rate achieving the maximal efficiency at a trapping rate of 1 ps^{-1} (adapted from Ref. [7]).

can be optimized for these two variables. In addition, spatial and temporal correlations behave differently in the optimization of ETE, albeit both of them can enhance quantum coherence [24]. While aforementioned studies on the efficiency of EET adopt the seven-pigment model structure of the FMO complex, the most recent crystallographic analysis of FMO reveals the existence of an eighth chromophore, which is thought to serve as a linker between the chlorosome and other seven chromophores [25, 26]. Moix *et al.* then use the GBR equation and the noninteracting blip approximation (NIBA) to investigate the influence of incorporation of this additional chromophore on the dynamics and efficiency of FMO in detail [27]. It is found that, due to the initial preparation, the observed population oscillations between sites 1 and 2 in the seven-site model may be completely suppressed in the eight-site model. The presence of the eighth site does not significantly change the ETE, and the energy flow in the eight-site model can be described by an effective three-site system.

Despite considerable theoretical advances in the understanding of ETE, the question as to why maximum energy transfer efficiency can be achieved at intermediate noise levels remains unanswered. Huelga *et al.* propose a simple principle which states that two exciton states are tuned to harvest environmental fluctuations such that the energy difference of the exciton states matches the maximum of the environmental spectral density [28]. At a low environmental noise level, the system is highly coherent and delocalized in the space, thus resulting in a low ETE. On the other hand, the formation of the exciton states is largely suppressed at high noise level with little improvement for the ETE. As a result, the interplay of system and environment necessitates an intermediate regime in which the strength of electronic coupling between chromophores and system-bath coupling characterized by reorganization energy are comparable with each other for the optimal EET. In fact, the intermediate regime is typical for photosynthetic EET [29]. It seems that Mother Nature never ceases to astonish us with numerous elegant design principles that facilitate the EET in biological photosynthetic systems.

2.2 Quantum coherence and its interplay with protein environments

The first experimental observation of long lived quantum coherence in FMO complexes [14, 30] pioneered by Fleming and coworkers has laid the foundation to unravel the underlying mechanism of near-perfect ETE in natural light harvesting organisms. Although quantum beats arising from possible electronic coherence were predicted and observed indirectly in anisotropy measurements, the standard model based on step-wise Förster resonant energy transfer (FRET) along a discrete energy ladder excludes intricate coherent wave-packet dynamics. To clearly demonstrate quantum coherence as the key to the remarkable speed up of photosynthetic energy transfer, 2DES is developed to monitor the excitation energy flow through molecular complexes in the femtosecond timescale. The application of this technique to the FMO complex isolated from *Chlorobaculum tepidum* at 77 K has revealed the long-lived quantum coherence as evidenced by the observation of quantum beats of cross-peak in the 2D spectra [14]. It is argued that the subtle quantum mechanical interference allows simultaneous sampling of vast areas of phase space to find the most efficient to funnel solar energy from pigments to RCs, thus achieving the nearly perfect efficiency [14]. Later 2DES experiments on FMO complexes at physiological temperatures have shown that the electronic coherence could survive for at least 300 fs even at a physiological temperature of 277 K, and correlated motions within the protein environment play an important role for the observed long-lived quantum coherence [16]. These ground-breaking experiments stimulated a series of research thrusts on the fundamental understanding of mechanisms that underlie the long-lived quantum coherence and its potential role in enhancing the ETE in light harvesting complexes [1, 8, 20, 21, 31, 32, 33, 34, 35, 36].

Now that most of recent experiments take FMO complex as a prototype system to study quantum coherence in light harvesting systems, it is a natural question as to whether such long-lived quantum coherence is a universal phenomenon. Two-color photon echo experiment studies on the RC of purple bacterium *Rhodobacter Sphaeroides* [17] have revealed dephasing

times of 440 and 310 fs at 77 and 180 K, respectively, substantially longer than another experimental estimation of about 250 fs [37]. It is argued that the strongly correlated protein-induced fluctuations in the transition energy of neighboring chromophores facilitate the coherent EET and trapping in photosynthesis [17]. Calhoun *et al.* performed 2DES experiment [38] to study energy transfer processes in LHCII, which has a trimeric structure with each monomer containing eight chlorophylls a (Chla) and six chlorophylls b (Chlb) [39]. The left panel of Fig. 2.3 presents the real part of the non-rephasing 2DES at a waiting time of 250 fs, and the corresponding amplitude of the diagonal cut as a function of waiting time are shown in the right panel of Fig. 2.3. As shown in the right panel of Fig. 2.3, quantum beatings are clearly observed in the high and low energy regimes corresponding to the Chlb and Chla bands, respectively. Then the coherence power spectrum with easily discernable individual exciton energy can be obtained through the Fourier transformation of the waiting time variable. Through the analysis of the power spectrum, it is revealed that the evenly spaced energetic surface in LHCII facilitates the ultrafast intracomplex energy transfer.

Figure 2.3 (Left panel) Contour plot of nonrephasing 2DES of LHCII for a waiting time of 250 fs. (Right panel) The amplitude of exciton energy as a function of waiting time (adapted from Ref. [38]).

While above experimental 2DES studies advance our understanding of the potential role of quantum coherence in EET in light harvesting complexes, the precise theoretical explanations of the observed long-lasting quantum coherence are still elusive. The electronic coupling

between chromophores and system-environment coupling characterized by the reorganization energy are two key parameters in the theoretical description of EET in light harvesting complexes [40, 41]. When the electronic coupling is weaker than the system-environment coupling, the electronic coupling can be treated perturbatively, leading to the Förster theory [42]. This theory describes the incoherent hopping of the excitation energy excluding intricate coherent wave-packet dynamics, resulting in coupled rate equations with the hopping rate related to the overlap of absorption and emission spectra of donor and acceptor pigments, respectively. On the other hand, the well-known Redfield theory [43], which treats system-environment coupling perturbatively, can describe the population relaxation as well as evolution of exciton coherence in the weak system-bath coupling regime. Although it is widely used to study energy relaxation processes in many biological systems, the Redfield theory is based on the Markovian approximation which neglects the memory effect induced by the slow bath relaxation and on the assumption of weak system-environment coupling. However, there exists a so-called intermediate regime commonly found in light harvesting complexes [29], where the electronic coupling and the reorganization energy are comparable, making perturbative theories invalid to treat EET dynamics [40, 41]. In addition, the fact that characteristic timescales of system dynamics and environmental reorganization have often the same magnitude implies the failure of Markovian approximation [40, 41]. It is thus highly challenging to describe EET dynamics in the intermediate regime, several theoretical methods have been devised to non-perturbative and non-Markovian dynamics [44, 45, 46, 47, 48, 49, 50, 51, 52, 53].

It is conjectured that quantum coherence may allow simultaneous sampling of all energy transfer pathways and funnel the excitation energy to the lowest energy state through optimal route [14]. By using the language of quantum information, the system is said to actually perform quantum computing, searching multiple states simultaneously and choosing the optimal pathways to transport solar energy from pigments to RCs. This process is similar to Grover's algorithm [54], which is designed to search an element in an array of disordered data with quadratical speedup as compared to that of the classical random walk algorithm [55]. It is later

argued that the purely unitary Grover algorithm can not explain the high EET efficiency in FMO complexes, and certain non-unitary generalization of quantum search algorithms should be constructed to adequately describe the interplay of quantum coherence and environment-induced dephasing [21]. Application of quantum random walk algorithm to the problem of quantum speedup in the FMO complex has shown that there exists only very short lived quantum speedup (70 fs), in contrast to the several hundred femtoseconds timescale of the observed quantum coherence [56]. This investigation revealed that quantum coherence may contribute to other aspects of EET, such as the overall efficiency and/or robustness instead of yielding dynamical speed up in natural light harvesting systems.

Figure 2.4 Two speculated primary energy transfer pathways with corresponding site energy profile in the FMO protein: baseplate $\rightarrow$ BChls 1 $\rightarrow$ 2 $\rightarrow$ 3 $\rightarrow$ 4 (A) and baseplate $\rightarrow$ Bchls 6 $\rightarrow$ 5,7,4 $\rightarrow$ 3 (B) (adapted from Ref. [57]).

By applying the HEOM method, Ishizaki and coworkers systematically investigated the spatial and temporal dynamics of EET within the FMO complex [57]. It is revealed that the FMO complex may function as a ‘rectifier’ for the unidirectional energy flow from the peripheral chlorosome to RC as the quantum coherence and the environmental noise may be well tuned to enter a fruitful interplay. It is further proposed that quantum coherence can avoid the traps of excitation energy at local energetic minima, thus facilitate the search of the optimal pathways to funnel the solar energy to the sink sites (which, in the isolated FMO complex, are linker pigments facing the RC). A schematic view of the energy landscapes along the two

primary transfer pathways in the FMO complex are shown in Fig. 2.4. On the one hand, the large energy gap between BChl 2 and BChl 3 greatly suppressed the backward transfer of excitation energy away from RC, and thus guaranteed that BChl 3 is well populated as depicted in Fig. 2.4A. On the other hand, the quantum superposition between BChls 1 and 2 inhibited the trapping of the excitation at BChl 1. Fig. 2.4B demonstrates that ultrafast delocalization of excitation in BChl 6 can aid the unidirectional and efficient energy transfer with the help of BChls 4, 5, 7. It should be noted that recent 2DES experiments have proposed an alternative EET pathway from the Chlorosome to RC, which includes all the states of baseplate and FMO complexes [58].

2.3 Non-photochemical Quenching

During the millennia of their evolution, green plants have developed a key regulatory mechanism called non-photochemical quenching (NPQ) [59], in response to the need to adapt to widely and rapidly varying conditions of illumination. Under high intensity light, the rate of energy conversion occurring in the reaction center saturates but that of energy absorption, which occurs in light harvesting pigment protein antennae continues to increase, as shown schematically in Fig. 2.5. The excess excitation energy poses a severe threat to the photosynthetic machinery due to the increased probability of formation of harmful singlet oxygen species via generation of long-lived triplet states of chlorophylls [60]. NPQ provides regulatory mechanisms to dissipate this energy as heat in a harmlessly and efficiently way while keep up an optimal photosynthetic yield. When the ambient light intensity returns to the normal level, the photosynthetic systems switch to the original mode of solar energy capture and conversion to chemical energy quickly. Understanding of this fundamental process is not only important for our knowledge of the primary photosynthetic dynamics in nature, but also foundational for development of multitude of renewable energy technologies including a possibility to turn biomimetic photo protective mechanisms into any human engineered complex devices/nano-

materials capable of solar energy harvesting.

Figure 2.5 Illustration of energy absorption and photochemical utilization as a function of incident light intensity in PSII of green plants.

Experimental and theoretical studies so far have unraveled many fascinating aspects of NPQ, the core molecular mechanisms governing the crucial processes of NPQ in green plants are however far from being achieved [61]. An increasing body of evidences suggest that the change in lumen pH under high light conditions may play a crucial role in the process of NPQ *in vivo*. The pH gradient activates a small protein PsbS and leads to the formation of zeaxanthin in a light-dependent and reversible conversion of violaxanthin to zeaxanthin process [62, 63]. It is proposed that the decrease in the thylakoid lumen pH causes an increase in aggregation of major LHCII trimer complexes in the PS-II supercomplexes [64, 65], which can be indicated from the much reduced excited state lifetime of the aggregated LHCII complex isolated from membranes as compared to that *in vivo* [66]. In addition, it is generally believed that special Chl pairs induced by the conformation changes may form the quenching sites for NPQ. By analyzing the ultrafast fluorescence of intact leaves, Holzwarth *et al.* demonstrate two independent NPQ quenching sites *in vivo* with the first site depending strictly on PsbS while the second site depending on the presence of zeaxanthin [67].

An important aspect of uncovering the mechanisms of NPQ inevitably involves identification of the sites at which it takes place and characterizing their special properties. However, whether there exists any particular site in the entire LHC-II trimer complex that acts as a radiationless drain or whether a number of components of PS-II play roles in parallel is a matter of debate. It is generally believed that the most likely site of quenching is composed of either closely spaced (excitonically coupled) chlorophyll molecules of the major trimeric LHCII or hetero-dimers/trimers of chlorophyll and carotenoid molecules [68]. Depending upon the orientation of Chls in different statistical pairs, i.e., two Chls that are spaced by less than a certain threshold distance, one may obtain H-type (shoulder-to-shoulder geometry) or J-type (head-to-tail geometry) dimers with respect to the directions of their transition dipole moments. While the latter possesses the lowest excited state that is optically bright; in the former, it is optically dark. Geometric considerations render the formation of the H-type pairs much more likely than those of the J-type. This view serves as the basis for the explanation of concentration fluorescence quenching [69, 70, 71, 72], a phenomenon analogously related to NPQ. Alternatively, recent experiments also suggest the possibility of an important role played by charge transfer (CT) states formed by chlorophyll dimers/trimers in quenching [73, 74, 75, 76]. With consideration of the structural complexity in LHCII, more than one mechanism for energy dissipation can be proposed as suggested by Krüger *et al.* [77]. High resolution NMR measurements on LHCII systems have revealed that the switch into a dissipative state involves the subtle conformational changes in some of the C-atoms of Chl macrocycles [78]. The results further suggest that the modulation of Chl-lutein and Chl-neoxanthin induce subtle changes in the Chla ground state electronic structures, pointing to its potential role in NPQ process. Detecting peculiar sites that exhibit high potential for NPQ to take place, thus will pave way for better understanding of the energy transfer/dissipation pathways in green plants.

Theoretical modeling of energy transfer and decay processes in green plants are generally based on the technique of kinetic Monte-Carlo (KMC), where a subset of Chls will be randomly selected to serve as the initially excited molecules and subsequent evolution of

excitation energy may take one of the possible routes including transfer to a neighbouring molecule/pigment-aggregate, fluorescence decay and non-radiative quenching, i.e., the NPQ. Based on the supramolecular structures of PSII and LHCII, van Amerongen and coworkers have developed a simple coarse-grained model to investigate the energy transfer and charge separation processes [79, 80]. Results showed that the overall efficiency of NPQ is hardly affected by the precise location of quenchers within the supercomplexes. Similar model for dimeric PSII with each of the major and minor PS-II complexes treated as same unit was subsequently studied in the group of Valkunas [81]. It was concluded that the requirement for the highest quenching efficiency is that the NPQ quenchers are localized in LHCII, achieving fast excitation relaxation in this state. In further studies where the random distribution of the NPQ traps within the LHCII aggregates was considered, they obtained an estimation of one NPQ-trap per 100 monomeric LHCII complexes [82]. Zaks *et al.* have developed a mathematical model which is applicable to describe the kinetics of NPQ at varying light intensities, and suggested that the trigger of NPQ, i.e., the lumen pH is not affected by NPQ [83]. This finding shows that NPQ functions as regulator for dissipating the excess energy, while sustaining the photochemical processes.

2.4 Charge separation in reaction center

The crucial step taking place in RC is charge separation, which drives water-splitting and generates trans-membrane electrochemical potential that is used in the synthesis of ATP and NADPH [84]. Since the first experimental determination of 3D structure of the bacterial RC from *Rhodospseudomonas viridis* by Deisenhofer and coworkers [85], RC structures for many photosynthetic organisms, such as Photosystem I (PSI) [86, 87, 88], Photosystem II (PSII) [89, 90, 91, 92, 93, 94] and purple bacteria [95, 96], at high resolutions have been obtained. As detailed structures differ for different photosynthetic organisms, we take the PSII RC complex as an example. In the PSII RC complex, four Chlorophylls (Chls, labeled as P_{D1} , P_{D2} ,

Chl_{D1} and Chl_{D2}), two pheophytins (Phe_s, labeled as Phe_{D1} and Phe_{D2}) and two quinone (Q) molecules in the center of the complex are arranged in two asymmetric branches (D₁ and D₂ branches). Two additional Chl molecules, Chl_{SZ}, are located on the opposite side of the RC with a distance larger than 20 Å apart from P_{D1} and P_{D2} central special pair. The central cofactors (P_{D1}, P_{D2}, Chl_{D1}, Chl_{D2}, Phe_{D1} and Phe_{D2}) give rise to different charge separation pathways that mainly occur along the D₁ branch [97, 98]. In contrast, pump-probe experiments have revealed multiple pathways of charge separation in the bacteria RC [99, 100]

Although the RC crystal structures of various photosynthetic organisms have been determined, molecular mechanisms regarding the charge separation process are still not well understood. Spectroscopic techniques have been utilized to study charge separation and electron transfer processes in PSII RC. It is proposed that upon excitation an electronically excited state, which is delocalized among the cofactors, is mixed with the CT state giving rise to ultrafast pathways for exciton relaxation and charge transfer. However, dynamical and static disorder arising from the fast nuclear motion (intra- and inter-molecular vibrations) and slow protein motion will modulate intra-molecular electronic transfer integral as well as electronic transitions, which may be detrimental to charge separation. Fortunately, PSII has developed an elegant design to initiate multiple charge separation pathways from various combinations of cofactors [99, 101, 102, 103, 104]. By applying an exciton model with the inclusion of coupling to a CT state for PSII RC, Novoderezhkin *et al.* modeled a whole set of experimental spectra including absorption, linear dichroism, circular dichroism, steady-state fluorescence, triplet-minus-singlet and Stark spectra [103]. Results revealed two possible disorder-controlled charge separation pathways with $P_{D1}^- P_{D2}^+$ and $Phe_{D1}^- Chl_{D1}^+$ as the primary charge-separated states. Further calculation of Stark spectra on a series of site-directed PSII RC mutants have demonstrated that three mixed exciton-CT states, $(P_{D2}^{\delta+} P_{D1}^{\delta-} Chl_{D1})_{673nm}^*$, $(Chl_{D1}^{\delta+} Phe_{D1}^{\delta-})_{681nm}^*$ and $(P_{D2}^+ P_{D1}^-)_{684nm}^{\delta*}$, contribute to the initial charge separation processes, and the corresponding charge separation pathways can be represented as [105]

and

respectively.

Recently, 2DES has been widely used to study the primary charge separation and energy-transfer events in PSII RC [106, 107, 108]. Two dimensional decay-associated spectra (2D DAS) have determined the time scales of energy equilibrium throughout the PSII RC and charge transfer to be of 50-150 fs and 1-3 ps, respectively [106]. By combining the 2DES and the Redfield theory, Romero *et al.* have elucidated the correlation between quantum coherence and highly efficient charge separation processes in PSII RC [108]. Their results revealed that the presence of vibration-assisted electronic coherence as indicated by the relative quantum beat amplitude may drive ultrafast and efficient charge separation. They argued that PSII RC has come up with an elegant design to achieve efficient solar-energy conversion [108].

2.5 State of the art theoretical treatment of energy transfer in light harvesting systems

The remarkable efficiency of energy transfer in light-harvesting systems has inspired many scientists to emulate its design to harness solar energy. In the past decades, numerous theoretical methods have been developed to resolve the intricate energy and charge transfer processes in light harvesting complexes. Theoretical modeling of EET usually takes the assumption of a one-exciton manifold, i.e., at each time there is only one exciton in the system, which is valid as the time scale of exciton lifetime is several ns in Bchl aggregates [109]. As a result, an aggregate of N chromophores can be modeled as N two-level systems, which is usually formulated with a Holstein Hamiltonian describing an exciton system coupled to a bath of harmonic

oscillators

$$\begin{aligned}
H &= H_{\text{ex}} + H_{\text{bath}} + H_{\text{ex-bath}} \\
&= \sum_n \epsilon_n a_n^\dagger a_n + \sum_{n \neq m} J_{nm} a_n^\dagger a_m + \sum_q \omega_q b_q^\dagger b_q + \sum_{nq} g_{nq} \hbar \omega_q (b_q + b_q^\dagger) a_n^\dagger a_n \quad (2.3)
\end{aligned}$$

Here, $a_n^\dagger(a_n)$ is the creation (annihilation) operator of an excitation with site energy ϵ_n , and $b_q^\dagger(b_q)$ is the creation (annihilation) operator of a phonon with frequency ω_q . J_{nm} is the inter-chromophoric coupling strength between chromophores m and n . System-bath interactions are assumed to be of a site-diagonal form with exciton-phonon coupling strength g_{nq} .

Highly accurate and fast numerical techniques have been formulated to study energy transfer processes and optical properties of light harvesting systems. The fact that many light harvesting systems are open quantum systems coupled non-perturbatively with non-Markovian baths makes the traditional Förster and Redfield theories inappropriate for treating EET dynamics. As a non-perturbative and non-Markovian algorithm, the HEOM method allows the reduced density operator of primary interest to couple hierarchically with a set of well-defined auxiliary density operators, and has been widely used to study energy transfer processes in photosynthetic systems. For example, the HEOM provides first theoretical investigation of long-lived electronic coherence in the FMO complex [57]. It is well known that the number of auxiliary density operators in HEOM method increases dramatically for strong system-bath coupling, low temperatures and large system sizes, which limits its numerical efficiency. By taking advantage of parallel computers, Strümpfer *et al.* have improved the computational efficiency of the HEOM algorithm and applied it to the investigations of the EET processes in various light harvesting complexes, such as single LH2, LH2-LH2, LH1-LH2 and LH1-RC systems [110, 111, 112, 113]. With technological advances of Graphic Processor Units (GPU), the GPU accelerated HEOM algorithms (GPU-HEOM) have been implemented and applied to study EET in the FMO and the LHCII complexes [114, 115, 116]. Shi *et al.* proposed a filtering algorithm that automatically truncates the hierarchy with a preselected tolerance value, thus dramatically reducing the number of auxiliary density operators used in the HEOM method

[117]. The optimized algorithm is then applied to study energy transfer in LH2 [118, 119] and 2DES of the FMO complexes [120].

It should be noted that the Matsubara spectrum decomposition (MSD) used in the standard HEOM method is notorious for its slow convergence, which can be significantly improved by certain sum-over-pole schemes, such as the Pade spectrum decomposition (PSD) techniques [121, 122, 123]. Moreover, an optimized HEOM algorithm is achieved for quantum dissipative systems coupled to multiple Brownian oscillators by a universal pre-screening search [124]. In addition, a hybrid stochastic HEOM approach that alleviates the bottleneck of low-temperature bath correlation in the ordinary HEOM method was proposed [125]. However, the application of HEOM is still restricted to certain form of phonon spectral densities. The iterative real-time quasiadiabatic propagator path integral (QUAPI) provides another numerically exact method for studying EET for any form of spectral densities [126, 127]. Yet, it is computationally expensive in strong electron-phonon coupling regime, the quantum master equations (QME), on the other hand, can be an alternative in the interest of computational efficiency. The original QME method based on a polaron transformation is formulated for the strong electron-phonon coupling regime, but it suffers from the well-known infra-red divergence problem for Ohmic and sub-Ohmic phonon spectral densities. As a result, only incoherent dynamics can be captured for these spectral densities. Recently, McCutcheon *et al.* proposed a variational master equation with optimization on the Bogoliubov inequality, which can accurately describe the energy transfer when the electron-electron and electron-phonon couplings are comparable in strength [128, 129].

In order to circumvent aforementioned difficulties in various methods, a hierarchy of time dependent variational wave functions of varying sophistication, which includes the Davydov D_2 , D -tilde, and D_1 trial states have been proposed [52, 53]. Time-dependent variational parameters are optimized by employing the Dirac-Frenkel variational principle. The performance of the trial states can be judged by the estimation of the deviation vector, which quantifies how

faithfully a given trial state obeys the Schrödinger equation. Path-dependent EET dynamics in double-ring LH2 systems are investigated by the Davydov D_1 ansatz [11, 130], it is found that symmetry breaking induced by non-nearest neighboring interactions may increase energy transfer efficiency by introducing multiple energy transfer pathways. By exploiting the parallel architecture of GPU, accurate simulation of EET dynamics in chlorosome antenna complex consisting of thousands of interacting chromophores have been performed by explicitly integrate both electronic and vibrational degrees of freedom [131]. A new theoretical framework, which treats the interactions between the excitons and the primary intramolecular vibrations and remaining nuclear degrees of freedom of the environment responsible for population decays and dephasings through Davydov trial states and line-shape functions, respectively, has been proposed to calculate 2DES of molecular aggregates [132, 133]. This theory covers a broad range of parameters, from intermediate to strong electron-phonon and electron-electron coupling strengths. In addition, the proposed theory is also applied to simulate single molecule signals of the LHCII, which exhibits pronounced oscillations of a mixed electron-vibronic origin [134].

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Chapter 3

Overviews of theoretical tools

In this chapter, we present various theoretical methodologies to be employed to study energy transfer in light harvesting systems in the coming chapters. In Section 3.1, we give a brief overview of the Holstein molecular crystal model with simultaneous diagonal and off-diagonal exciton-phonon coupling together with the theoretical methods including the Davydov ansätze and the discretized HEOM algorithms used in the studies of Holstein polaron dynamics. In Section 3.2, we first introduce the conical intersection problem which plays an very important role in non-adiabatic relaxation processes between different potential energy surfaces, and then describe the theoretical treatment of this problem. Femtosecond double-pump single molecule signals of molecular aggregates and their theoretical treatment are discussed in Section 3.3. Finally, we present the procedure of calculating 2DES of molecular aggregates in Section 3.4.

3.1 Polaron model

3.1.1 Hamiltonian

The theoretical treatment of polaron dynamics of the 1D Holstein model can be traced back to the pioneering work of Holstein in the late 1950s [1, 2]. The Holstein model describes a lattice of two level molecules coupled linearly to a bath described by a set of harmonic oscillators, which can be written as [1, 2, 3, 4]

$$\hat{H} = \sum_n \Omega_n(\mathbf{Q}) \hat{a}_n^\dagger \hat{a}_n + \sum_{m \neq n} J_{m,n}(\mathbf{Q}) \hat{a}_m^\dagger \hat{a}_n + \hat{H}_{\text{ph}} \quad (3.1)$$

where $\hat{a}_n^\dagger (\hat{a}_n)$ are the exciton creation (annihilation) operators on the n th site, $\mathbf{Q}$ denotes the collective coordinate of vibrational modes, and $\hat{H}_{\text{ph}}$ is the bath Hamiltonian.

By making the Taylor series expansion of $\Omega_n(\mathbf{Q})$ and $J_{m,n}(\mathbf{Q})$ to the first order in terms of collective coordinates $\mathbf{Q}$ and considering only coupling between nearest neighboring molecules, one can obtain [5, 6, 7]

$$\hat{H} = \Omega \sum_n \hat{a}_n^\dagger \hat{a}_n - J \sum_n \hat{a}_n^\dagger (\hat{a}_{n+1} + \hat{a}_{n-1}) + \hat{H}_{\text{ph}} + \hat{H}_{\text{ex-ph}}^{\text{diag}} + \hat{H}_{\text{ex-ph}}^{\text{o.d.}} \quad (3.2)$$

Here, $\Omega = \Omega_n(\mathbf{Q} = \mathbf{0})$ denotes excitation energy for all sites in a rigid lattice, J is the inter-molecular coupling between nearest neighboring molecules $J_{m,n}(\mathbf{Q} = \mathbf{0}) = -J\delta_{m,n\pm 1}$. $\hat{H}_{\text{ex-ph}}^{\text{diag}} (\hat{H}_{\text{ex-ph}}^{\text{o.d.}})$ is the diagonal (off-diagonal) exciton-phonon coupling Hamiltonian which characterizes the effect of molecular distortion on the excitation energy (inter-molecular electronic coupling). By taking phonon dispersion relations into account and working in the one exciton subspace, the exciton, phonon, diagonal and off-diagonal exciton-phonon coupling

Hamiltonians read in the momentum space as [8]

$$\begin{aligned}
\hat{H}_{\text{ex}} &= -J \sum_n \hat{a}_n^\dagger (\hat{a}_{n+1}^\dagger + \hat{a}_{n-1}) \\
\hat{H}_{\text{ph}} &= \sum_q \omega_q \hat{b}_q^\dagger \hat{b}_q \\
\hat{H}_{\text{ex-ph}}^{\text{diag}} &= -g \sum_{nq} \omega_q \hat{a}_n^\dagger \hat{a}_n (e^{iqn} \hat{b}_q + e^{-iqn} \hat{b}_q^\dagger) \\
\hat{H}_{\text{ex-ph}}^{\text{o.d.}} &= \frac{1}{2} \phi \sum_{nq} \omega_q \left\{ \hat{a}_n^\dagger \hat{a}_{n+1} [e^{iqn} (e^{iq} - 1) \hat{b}_q + \text{H.c.}] + \hat{a}_n^\dagger \hat{a}_{n-1} [e^{iqn} (1 - e^{-iq}) \hat{b}_q + \text{H.c.}] \right\}
\end{aligned} \tag{3.3}$$

Here H.c. stands for Hermitian conjugate, $\hat{b}_q^\dagger (\hat{b}_q)$ is the creation (annihilation) operator of a phonon with momentum q , and $g(\phi)$ is the dimensionless diagonal (off-diagonal) exciton-phonon coupling constant. Typically, a linear dispersion phonon band $\omega_q = \omega_0 [1 + W(2|q|/\pi - 1)]$ is assumed with W and ω_0 denoting the phonon bandwidth and central phonon frequency, respectively.

3.1.2 The Davydov ansätze

In order to accurately characterize the polaron dynamics of the Holstein model, various efficient numerical methods have been formulated, including a time dependent density matrix renormalization group (t-DMRG) [9, 10, 11, 12], the Merrifield ansatz [13, 14], and variational exact diagonalization (VED) [15]. It should be noted that most of theoretical studies consider Holstein Hamiltonian with diagonal exciton-phonon coupling only. Theoretical methods that can accurately treat off-diagonal exciton-phonon coupling seldom appear in the polaron literature. A hierarchy of time-dependent variational wave functions of varying sophistication, which includes the Davydov D_2 , D -tilde, and D_1 trial states, have been proposed to study the dynamics of the Holstein polaron [16, 17]. Time-dependent variational parameters are optimized by employing the Dirac-Frenkel variational principle. Through the estimation of the

‘deviation vector’, it is easy to judge how faithfully a given trial state obeys the Schrödinger equation. Originally formulated for the purpose of explaining storage and transport of energy in protein molecules, two Davydov trial states with localized nature are written as

$$|D_1(t)\rangle = \sum_n \psi_n(t) \hat{a}_n^\dagger |0\rangle_{ex} \otimes \exp \left\{ \sum_n [\lambda_{nq} \hat{b}_q^\dagger - \text{H.c.}] \right\} |0\rangle_{ph} \quad (3.4)$$

and

$$|D_2(t)\rangle = \sum_n \psi_n(t) \hat{a}_n^\dagger |0\rangle_{ex} \otimes \exp \left\{ \sum_n [\lambda_q \hat{b}_q^\dagger - \text{H.c.}] \right\} |0\rangle_{ph} \quad (3.5)$$

Here, $\psi_n(t)$ and $\lambda_{nq}(\lambda_q)$ are variational parameters denoting the exciton amplitudes and phonon displacements, respectively. The only difference between the D_1 and D_2 ansatz is that the phonon amplitudes are exciton site independent for the latter. It is found that the D_1 ansatz works well for the dynamics study of Holstein model with diagonal coupling only. In comparison, the D_2 ansatz, a simplified version of D_1 ansatz, performs better in the case of off-diagonal coupling despite the relative large error to the exact Schrödinger equation dynamics. In order to improve the accuracy of the Davydov ansätze for describing the polaron dynamics of the Holstein model for a wide range of model parameters (including J , g , ϕ), a so-called multiple Davydov ansatz, which is a linear combination of single Davydov ansatz, has been proposed. The multiple Davydov trial state with the multiplicity M can be straightforwardly formulated as follows

$$|D_1^M(t)\rangle = \sum_i^M \sum_n^N \psi_{i,n} \hat{a}_n^\dagger |0\rangle_{ex} \exp \left\{ \sum_q [\lambda_{inq} \hat{b}_q^\dagger - \text{H.c.}] \right\} |0\rangle_{ph} \quad (3.6)$$

and

$$|D_2^M(t)\rangle = \sum_i^M \sum_n^N \psi_{i,n} \hat{a}_n^\dagger |0\rangle_{ex} \exp \left\{ \sum_q [\lambda_{iq} \hat{b}_q^\dagger - \text{H.c.}] \right\} |0\rangle_{ph} \quad (3.7)$$

where $\psi_{i,n}$ and $\lambda_{inq}(\lambda_{iq})$ represent exciton amplitudes and phonon displacements, respectively. Here index i and n denote i th coherent state and n th site, respectively. The case of $M = 1$ corresponds to the single Davydov ansatz.

There are several methods to solve the Schrödinger equation. In the language of Lagrangian dynamics, we first parameterize the time-dependent wave function $|\Phi(t)\rangle$ for Hamiltonian $\hat{H}$

by a set of time dependent parameters $\alpha_m(t)$ ($m = 1, \dots, M$), i.e., $|\Phi(t)\rangle = |\alpha_m(t)\rangle$, and then construct the Lagrangian L as follows

$$L = \langle \Phi(t) | i\hbar \frac{\overrightarrow{\partial}}{\partial t} - i\hbar \frac{\overleftarrow{\partial}}{\partial t} - \hat{H} | \Phi(t) \rangle \quad (3.8)$$

The equations of motion for the time dependent parameters $\alpha_m(t)$ and their time derivatives $\dot{\alpha}_m(t)$ ($m = 1, \dots, M$) can be obtained by following the Dirac-Frenkel time-dependent variational method [18]

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\alpha}_m^*} \right) - \frac{\partial L}{\partial \alpha_m^*} = 0 \quad (3.9)$$

From solving sets of equations of motion, one can obtain full information regarding the polaron dynamics. The equations of motion for the variational parameters are presented in Appendices A and B.

3.1.3 The discretized HEOM method

For the one-dimensional Holstein model (3.3), let us denote $|n\rangle = \hat{a}^\dagger |0\rangle_{\text{ex}}$ with $|0\rangle_{\text{ex}}$ representing the vacuum state of the exciton. Then we can easily write down the expression of the reduced density matrix for the exciton system under the factorized initial condition by applying the path integral theory [19]

$$\rho(n, n'; t) = \int \mathcal{D}n \int \mathcal{D}n' \rho(n_0, n'_0; t_0) \times e^{iS[n;t]} F(n, n'; t) e^{-iS[n';t]} \quad (3.10)$$

Here $S[n]$ denotes the action of the exciton system, and Feynman-Vernon influence functional $F[n, n']$ is defined as

$$F[n, n'] = \exp \left(- \sum_q \omega_q^2 \int_{t_0}^t ds \int_{t_0}^s ds' V_q^{*\times}(s) \times \left[V_q^\times(s') \coth(\beta\omega_q/2) \cos(\omega_q(s - s')) - iV_q^\circ(s') \sin(\omega_q(s - s')) \right] \right). \quad (3.11)$$

where $\beta = 1/k_B T$ is the inverse temperature, and we introduce abbreviations

$$V_q^\times = V_q(n) - V_q(n') \quad V_q^\circ = V_q(n) + V_q(n'), \quad (3.12)$$

with $\hat{V}_q^\dagger = -g \sum_n \hat{a}_n^\dagger \hat{a}_n e^{iqn} + \frac{1}{2} \phi \sum_n \left(\hat{a}_n^\dagger \hat{a}_{n+1} e^{iqn} (e^{iq} - 1) + \hat{a}_n^\dagger \hat{a}_{n-1} e^{iqn} (1 - e^{-iq}) \right)$. The influence functional (3.11) can be rewritten as

$$F[n, n'] = \exp \left(- \sum_q \omega_q^2 \int_{t_0}^t ds \int_{t_0}^s ds' V_q^{*\times}(s) \right. \\ \left. \times \left[\frac{e^{i\omega_q(s-s')}}{2} (V_q^\times(s') \coth(\beta\omega_q/2) - V_q^\circ(s')) + \frac{e^{-i\omega_q(s-s')}}{2} (V_q^\times(s') \coth(\beta\omega_q/2) + V_q^\circ(s')) \right] \right), \quad (3.13)$$

Taking derivative of Eq. (3.10) leads to

$$\frac{\partial}{\partial t} \rho(n, n'; t) = -i\mathcal{L} \rho(n, n'; t) - \sum_q \omega_q^2 V_q^{*\times}(t) \int \mathcal{D}n \int \mathcal{D}n' \rho(n_0, n'_0; t_0) \\ \int_0^t ds' \left[\frac{e^{i\omega_q(t-s')}}{2} (V_q^\times(s') \coth(\beta\omega_q/2) - V_q^\circ(s')) + \frac{e^{-i\omega_q(t-s')}}{2} (V_q^\times(s') \coth(\beta\omega_q/2) + V_q^\circ(s')) \right] \\ \times e^{iS[n, t]} F(n, n'; t) e^{-iS[n', t]} \quad (3.14)$$

We can further simplify Eqs. (3.13) and (3.14) as

$$F[n, n'] = \exp \left(- \sum_q \int_{t_0}^t ds \int_{t_0}^s ds' \Phi_q(s) \times [e^{i\omega_q(s-s')} \Theta_{q+}(s') + e^{-i\omega_q(s-s')} \Theta_{q-}(s')] \right) \quad (3.15)$$

$$\frac{\partial}{\partial t} \rho(n, n'; t) = -i\mathcal{L} \rho(n, n'; t) - \sum_q \Phi_q(t) \int \mathcal{D}n \int \mathcal{D}n' \rho(n_0, n'_0; t_0) \\ \int_0^t ds' [e^{i\omega_q(t-s')} \Theta_{q+}(s') + e^{-i\omega_q(t-s')} \Theta_{q-}(s')] \times e^{iS[n, t]} F(n, n'; t) e^{-iS[n', t]}, \quad (3.16)$$

by introducing super-operators

$$\hat{\Phi}_q(t) = \omega_q^2 \hat{V}_q^{\dagger\times}(t)/2, \quad (3.17)$$

$$\hat{\Theta}_{q\pm}(t) = \hat{V}_q^\times(t) \coth(\beta\omega_q/2) \mp \hat{V}_q^\circ(t). \quad (3.18)$$

The next crucial step is to construct auxiliary operator $\rho_{m_{1\pm}, m_{2\pm}, \dots, m_{N\pm}}(n, n'; t)$ with matrix elements

$$\rho_{m_{1\pm}, m_{2\pm}, \dots, m_{N\pm}}(n, n'; t) = \int \mathcal{D}n \int \mathcal{D}n' \rho(n_0, n'_0; t_0) \prod_{q=1}^N \\ \left(\int_{t_0}^t ds e^{i\omega_q(t-s)} \Theta_{q+}(s) \right)^{m_{q+}} \left(\int_{t_0}^t ds e^{-i\omega_q(t-s)} \Theta_{q-}(s) \right)^{m_{q-}} \times e^{iS[n, t]} F(n, n') e^{-iS[n', t]} \quad (3.19)$$

where $m_{1\pm}, m_{2\pm}, \dots, m_{N\pm}$ are non-negative integers. It should be noted that $\hat{\rho}_{0,\dots,0}(t) = \hat{\rho}(t)$ is the real reduced density matrix, and other auxiliary density matrices are introduced to describe non-Markovian effects and multiple-phonon excitation processes. By taking the derivative of $\rho_{m_{1\pm}, m_{2\pm}, \dots, m_{N\pm}}(n, n'; t)$ with respect to t , finally we obtain the hierarchy equation of motions in the operator form

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}_{m_{1\pm}, \dots, m_{N\pm}}(t) = & -i\mathcal{L} \hat{\rho}_{m_{1\pm}, \dots, m_{N\pm}}(t) - i \sum_q \omega_q (m_{q-} - m_{q+}) \hat{\rho}_{m_{1\pm}, \dots, m_{N\pm}}(t) \\ & - \sum_q \hat{\Phi}_q (\hat{\rho}_{m_{1\pm}, \dots, m_{q+}+1, m_{q-}, \dots, m_{N\pm}}(t) + \hat{\rho}_{m_{1\pm}, \dots, m_{q+}, m_{q-}+1, \dots, m_{N\pm}}(t)) \\ & + \sum_q (m_{q+} \hat{\Theta}_{q+} \hat{\rho}_{m_{1\pm}, \dots, m_{q+}-1, m_{q-}, \dots, m_{N\pm}}(t) + m_{q-} \hat{\Theta}_{q-} \hat{\rho}_{m_{1\pm}, \dots, m_{q+}, m_{q-}-1, \dots, m_{N\pm}}(t)) \end{aligned} \quad (3.20)$$

The fact that HEOM consists of an infinite number of equations necessitates the truncation of auxiliary density matrices at a certain hierarchy level. There are many truncation schemes, among which the simplest one is defining the following terminator

$$\frac{\partial}{\partial t} \hat{\rho}_{m_{1\pm}, \dots, m_{N\pm}}(t) = -(i\mathcal{L} + i \sum_q \omega_q (m_{q-} - m_{q+})) \times \hat{\rho}_{m_{1\pm}, \dots, m_{N\pm}}(t) \quad (3.21)$$

It should be noted that the error introduced by the truncation can be kept negligibly small by choosing a sufficiently large number of hierarchy levels. The total number of hierarchy elements can be easily calculated as $L_{\text{tot}} = (N_{\text{trun}} + 2N)! / N_{\text{trun}}! (2N)!$ with total number of termination elements $L_{\text{term}} = (N_{\text{trun}} + 2N - 1)! / (2N - 1)! N_{\text{trun}}!$, where N_{trun} is the truncation level for $m_{q\pm} (q = 1, \dots, N)$.

3.2 Conical intersection

3.2.1 Hamiltonian

Conical intersections of potential energy (PE) surfaces, also referred to as photochemical funnels, play a crucial role in ultrafast internal conversion processes. The Hamiltonian including the system part $H^{(S)}$, the bath part $H^{(B)}$ and the system-bath coupling $H^{(SB)}$ can be written as [20, 21, 22]

$$H = H^{(S)} + H^{(B)} + H^{(SB)}. \quad (3.22)$$

The system we consider is the minimal model of a conical intersection, which comprises two electronic states $|\varphi_1\rangle$ and $|\varphi_2\rangle$, and two vibrational modes, a coupling mode and tuning mode. The system Hamiltonian with only linear electronic-vibrational coupling can be written as

$$\begin{aligned} H^{(S)} &= \sum_{k=1,2} |\varphi_k\rangle h_k \langle \varphi_k| + (|\varphi_1\rangle \langle \varphi_2| + |\varphi_2\rangle \langle \varphi_1|) \lambda Q_c \\ h_k &= h_0 + E_k + \kappa_k Q_t, h_0 = h_c + h_t = \frac{1}{2} \sum_{j=c,t} \Omega_j \{P_j^2 + Q_j^2\} \end{aligned} \quad (3.23)$$

where Q_j , P_j and Ω_j denote the dimensionless coordinate, momentum and frequency of the coupling ($j = c$) and tuning ($j = t$) mode, respectively. We assume that excited state is shifted relative to the ground state with E_k and κ_k ($k=1,2$) representing vertical excitation energies and intra-state electron-vibrational coupling constants, respectively, and λ is the inter-state coupling constant.

After including the primary modes into the system Hamiltonian, we can simply treat the

remaining modes by a bath represented as a set of harmonic oscillators

$$H^{(B)} = \{|\varphi_1\rangle\langle\varphi_1| + |\varphi_2\rangle\langle\varphi_2|\} \sum_{\alpha} \sum_{j=\{c,t\}} \frac{1}{2} \omega_{\alpha,j} \{p_{\alpha,j}^2 + q_{\alpha,j}^2\}, \quad (3.24)$$

where $p_{\alpha,j}$, $q_{\alpha,j}$ and $\omega_{\alpha,j}$ are the dimensionless momentum, coordinate, and frequency of α th secondary bath mode attached to primary coupling ($j = c$) and tuning ($j = t$) modes, respectively.

The coupling and tuning vibrational modes are assumed to be bilinearly coupled to the respective heat bath with a system-bath coupling Hamiltonian

$$H^{(SB)} = \{|\varphi_1\rangle\langle\varphi_1| + |\varphi_2\rangle\langle\varphi_2|\} \sum_{\alpha} \sum_{j=\{c,t\}} \{c_{\alpha,j} q_{\alpha,j} Q_j\} \quad (3.25)$$

where $c_{\alpha,j}$ denotes the system-bath coupling constant between the α th bath mode with coupling mode ($j = c$) and tuning mode ($j = t$). The system-bath coupling strength is completely specified by spectral density.

$$J_j(\omega) = \sum_{\alpha} c_{\alpha,j}^2 \delta(\omega - \omega_{\alpha,j}) \quad j = c, t \quad (3.26)$$

for each system mode.

Let us introduce a basis set, $\{n_c\}$, $\{n_t\}$ for the coupling and tuning mode, respectively, the total Hamiltonian can be rewritten in a matrix representation

$$H = \sum_{k,k'=1,2} \sum_{n_c n_t, n'_c n'_t} |\varphi_k\rangle |n_c\rangle |n_t\rangle H_{kn_c n_t, k' n'_c n'_t} \langle\varphi_{k'}| \langle n'_c| \langle n'_t| \quad (3.27)$$

where

$$\begin{aligned} H_{kn_c n_t, k' n'_c n'_t}^{(S)} &= \delta_{kk'} \delta_{n_c n'_c} \delta_{n_t n'_t} [\hbar \Omega_c (n_c + 1/2) + \hbar \Omega_t (n_t + 1/2) + E_k] \\ &\quad + \delta_{kk'} \delta_{n_c n'_c} \kappa_k A_{n_t n'_t} + (\delta_{k,k'-1} + \delta_{k,k'+1}) \delta_{n_t n'_t} \lambda A_{n_c n'_c} \end{aligned} \quad (3.28)$$

$$H_{kn_c n_t, k' n'_c n'_t}^{(SB)} = \delta_{kk'} \sum_{\alpha} \left\{ \delta_{n_t n'_t} A_{n_c n'_c} c_{\alpha,c} q_{\alpha,c} + \delta_{n_c n'_c} A_{n_t n'_t} c_{\alpha,t} q_{\alpha,t} \right\} \quad (3.29)$$

$$H_{kn_c n_t, k' n'_c n'_t}^{(B)} = \delta_{kk'} \delta_{n_c n'_c} \delta_{n_t n'_t} \sum_{\alpha} \sum_{j=\{c,t\}} \frac{1}{2} \hbar \omega_{\alpha,j} \{p_{\alpha,j}^2 + q_{\alpha,j}^2\}$$

with

$$A_{nn'} = \langle n|Q|n'\rangle = \delta_{n,n'+1}\sqrt{\frac{n'+1}{2}} + \delta_{n,n'-1}\sqrt{\frac{n'}{2}} \quad (3.30)$$

The bath Hamiltonian is, of course, a diagonal matrix. Finally, we obtain the total Hamiltonian in a matrix form

$$H = \mathbf{H}^{(S)} + \sum_{\alpha} \{c_{\alpha,c}q_{\alpha,c}\mathbf{V}^c + c_{\alpha,t}q_{\alpha,t}\mathbf{V}^t\} + H^{(B)} \quad (3.31)$$

where

$$\begin{aligned} V_{kn_cn_t,k'n'_cn'_t}^c &= \delta_{kk'}\delta_{n_t n'_t} A_{n_c n'_c} \\ V_{kn_cn_t,k'n'_cn'_t}^t &= \delta_{kk'}\delta_{n_c n'_c} A_{n_t n'_t} \end{aligned}$$

The dynamics of combined system and bath follow Liouville-von Neumann equation [23]

$$\frac{\partial}{\partial t}\rho_{\text{tot}}(t) = -\frac{i}{\hbar}[H, \rho_{\text{tot}}] \quad (3.32)$$

We can then obtain the dynamics of relevant system (denoted by ρ) by tracing out the bath degrees of freedom of the full density matrix ρ_{tot}

$$\rho(t) = \text{Tr}_B\{\rho_{\text{tot}}(t)\} \quad (3.33)$$

3.2.2 The HEOM approach

The bath is modeled by Drude spectral density, which can be described as in the overdamped Brownian oscillator model

$$J_j(\omega) = 2\lambda_j\gamma_j\omega/(\omega^2 + \gamma_j^2) \quad j = c, t \quad (3.34)$$

where λ_j and γ_j denote the system-bath coupling strength and Drude decay constant for each mode, respectively. For such a spectral density, the correlation function can be expressed as exponential functions, which facilitates the construction of HEOM method, a numerically exact

method that can treat open quantum system in a nonperturbative and non-Markovian manner [24, 25, 26, 27].

The hierarchy of coupled equations of motion for the reduced density matrix in the high temperature approximation ($\beta\hbar\gamma_j < 1$) can be derived as [24, 25, 26, 27, 28]

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{l_c l_t}(t) &= -(i\mathcal{L}^{(s)} + l_c \gamma_c + l_t \gamma_t) \rho_{l_c l_t}(t) + \Phi_c \rho_{l_c+1 l_t}(t) + \Phi_t \rho_{l_c l_t+1}(t) \\ &\quad + l_c \gamma_c \Theta_c \rho_{l_c-1 l_t}(t) + l_t \gamma_t \Theta_t \rho_{l_c l_t-1}(t) \end{aligned} \quad (3.35)$$

for sets of nonnegative integers, (l_c, l_t) . It should be noted that $\rho(t) = \rho_{00}(t)$ is the real reduced density matrix, while all other auxiliary density matrices are introduced to account for the non-Markovian and non-perturbative nature of the system-bath interactions. In Eq. (3.35), $\mathcal{L}^{(s)}$ is the Liouvillian super operator corresponding to the system Hamiltonian $H^{(s)}$, and the relaxation operators Φ and Θ are defined as

$$\Phi_j = iV_j^\times, \Theta_j = i\left(\frac{2\lambda_j}{\beta\hbar^2} V_j^\times - i\frac{\lambda_j}{\hbar} \gamma_j V_j^\circ\right) \quad (3.36)$$

with abbreviations $A^\circ \rho = A\rho + \rho A$ and $A^\times \rho = A\rho - \rho A$ for any operator A . The hierarchy of HEOM must be truncated at a certain level for the purpose of numerical calculations. It is shown that the condition $N = l_c + l_t \gg \frac{\omega^{(s)}}{\min(\gamma_1, \gamma_2)}$, where $\omega^{(s)}$ is the characteristic frequency for $\mathcal{L}^{(s)}$, is sufficient for this purpose. As a result, the terminator for the hierarchy can be chosen as

$$\frac{\partial}{\partial t} \rho_{l_c l_t}(t) = -i\mathcal{L}^{(s)} \rho_{l_c l_t}(t) \quad (3.37)$$

In the low temperature regime where the condition $\beta\hbar\gamma_j < 1$ is not satisfied, low temperature corrections should be included in Eq. (3.35) by [28]

$$\mathcal{L}^{(s)} \rightarrow \mathcal{L}^{(s)} - \sum_{j=c,t} \frac{2\lambda_j}{\beta\hbar^2} \frac{2\gamma_j}{\nu_1^2 - \gamma_j^2} V_j^\times V_j^\times, \Theta_j \rightarrow \Theta_j - \frac{2\lambda_j}{\beta\hbar^2} \frac{2\gamma_j^2}{\nu_1^2 - \gamma_j^2} V_j^\times \quad (3.38)$$

where $\nu_1 = 2\pi/\beta\hbar$ is the first bosonic Matsubara frequency. Including higher order Matsubara terms will further improve the performance of HEOM in the low temperature regime.

3.2.3 Observables of interest and computational details

The physical observables of interest can be easily calculated based on the reduced density matrix $\rho(t)$. With regard to the initial condition of $\rho(t)$, we assume instantaneous transition from ground state to higher excited state by a short laser pulse with an initial density matrix

$$\rho(0) = |\varphi_2\rangle|0\rangle\langle 0|\langle\varphi_2| \quad (3.39)$$

where $|0\rangle$ denotes the vacuum state of both the coupling and the tuning mode according to the Frank Condon principle.

The time-dependent population of diabatic electronic states characterizing the radiationless decay dynamics are defined as [20]

$$P_n^{\text{di}}(t) = \text{tr}_S\{|\varphi_n\rangle\langle\varphi_n|\rho(t)\} \quad (3.40)$$

Within the two-state model, it is easy to transform from the diabatic basis to the adiabatic basis through the transformation

$$|\tilde{\varphi}_n\rangle = \sum_{m=1,2} \mathbf{S}(Q_c, Q_t)_{nm} |\varphi_m\rangle, \quad n = 1, 2 \quad (3.41)$$

with [20, 29, 30, 31]

$$\mathbf{S}(Q_c, Q_t) = \begin{pmatrix} \cos \alpha(Q_c, Q_t) & -\sin \alpha(Q_c, Q_t) \\ \sin \alpha(Q_c, Q_t) & \cos \alpha(Q_c, Q_t) \end{pmatrix}$$

where $\alpha(Q_c, Q_t)$ is the diabatic-adiabatic mixing angle. Then, the population of adiabatic electronic states can be calculated as

$$P_n^{\text{ad}}(t) = \text{tr}_S\{|\tilde{\varphi}_n\rangle\langle\tilde{\varphi}_n|\rho(t)\} \quad (3.42)$$

The adiabatic population P_n^{ad} depicts electronic relaxation dynamics from the upper to lower adiabatic energy surface, while diabatic population P_n^{di} is more closely related to the time-resolved pump-probe spectra [29]

The expectation values of the position and the momentum operators of vibrational modes which are used to quantify the vibrational coherence are defined as [29]

$$\langle Q_j \rangle_t = \text{tr}_S \{ Q_j \rho(t) \}, \langle P_j \rangle_t = \text{tr}_S \{ P_j \rho(t) \} \quad (3.43)$$

In order to further decipher the complex interplay of electronic and nuclear motions in ultrafast internal-conversion processes, we represent the reduced density matrix in terms of vibrational coordinates in either diabatic or adiabatic basis.

$$\begin{aligned} \rho_{nn'}^{\text{di}}(Q_c, Q_t; Q'_c, Q'_t; t) &= \langle Q_c | \langle Q_t | \langle \varphi_n | \rho(t) | \varphi_{n'} \rangle | Q'_t \rangle | Q'_c \rangle \\ \rho_{nn'}^{\text{ad}}(Q_c, Q_t; Q'_c, Q'_t; t) &= \langle Q_c | \langle Q_t | \langle \tilde{\varphi}_n | \rho(t) | \tilde{\varphi}_{n'} \rangle | Q'_t \rangle | Q'_c \rangle \end{aligned} \quad (3.44)$$

We can then have a better view on the contribution of each single vibrational mode on the reduced density matrix by averaging over the remaining vibrational mode, thus defining the reduced probability for each vibrational mode as (in the adiabatic representation)

$$\begin{aligned} P_n^{\text{ad}}(Q_c, t) &= \int dQ_t \rho_{nn}^{\text{ad}}(Q_c, Q_t; Q_c, Q_t; t) \\ P_n^{\text{ad}}(Q_t, t) &= \int dQ_c \rho_{nn}^{\text{ad}}(Q_c, Q_t; Q_c, Q_t; t) \end{aligned} \quad (3.45)$$

3.3 Single molecule spectra of molecular aggregates

3.3.1 The model system

We consider a molecular aggregate embedded in a protein environment. The total Hamiltonian is composed of the system Hamiltonian, the bath Hamiltonian, and the system-bath interaction Hamiltonian

$$H = H_S + H_B + H_{SB} \quad (3.46)$$

The system Hamiltonian involves all electronic states (modeled by two-level systems) and strongly coupled high frequency vibrational modes, which can be written as [32, 33]

$$H_S = H_{\text{ex}} + H_{\text{ph}} + H_{\text{ex-ph}} \quad (3.47)$$

Here H_{ex} is the Frenkel-exciton Hamiltonian

$$H_{\text{ex}} = \epsilon_g |g\rangle\langle g| + \sum_{m=1}^N \epsilon_m |m\rangle\langle m| + \sum_{m=1}^N \sum_{n \neq m}^N J_{nm} |n\rangle\langle m|, \quad (3.48)$$

where $|g\rangle$ and $|m\rangle$ are the ground state and the m th singly-excited excitonic states with energy ϵ_m , respectively, and the J_{nm} are the inter-molecular electronic coupling between site n and m . H_{ph} describes a set of high frequency phonon modes modeled by harmonic oscillators

$$H_{\text{ph}} = \sum_q \hbar \omega_q b_q^\dagger b_q \quad (3.49)$$

The exciton-phonon coupling Hamiltonian $H_{\text{ex-ph}}$, which characterizes the shift of the equilibrium position of the singly excited state potential energy surface of each site as compared to that of the ground state potential energy surface, can be written as

$$H_{\text{ex-ph}} = \sum_q \sum_{m=1}^N \chi_{qm} \hbar \omega_q (b_q^\dagger + b_q) |m\rangle\langle m|. \quad (3.50)$$

where b_q ($b_q^\dagger$) is the annihilation (creation) operator of the phonon mode with frequency ω_q , and χ_{qm} denotes the exciton-phonon coupling strength, which is related to the Huang-Rhys factor $S_{qm} = \chi_{qm}^2$

The second and the third terms in Eq. (3.46) describe the interaction of H_S with the low-frequency intramolecular vibrations of the chromophore as well as intermolecular vibration modes of the environment. These vibrational modes account for the bath-induced relaxation and dephasing phenomenon. The corresponding Hamiltonian with the assumption of site-independent and site-diagonal system-bath coupling can be formulated as [34, 35, 36]

$$H_B = \sum_j \hbar \Omega_j a_j^\dagger a_j, \quad (3.51)$$

$$H_{SB} = \sum_j \sum_{m=1}^N \kappa_j \hbar \Omega_j (a_j^\dagger + a_j) |m\rangle \langle m|. \quad (3.52)$$

Here a_j ($a_j^\dagger$) is the annihilation (creation) operator of the j th bath mode with frequency Ω_j and corresponding system-bath coupling strength κ_j . The spectral density specifying the distribution of the system-bath coupling strength is defined as

$$D(\omega) = \sum_j \kappa_j^2 \Omega_j^2 \delta(\omega - \Omega_j) \quad (3.53)$$

It should be noted that single molecule spectra correspond to a specific realization of the local protein environment as well as the configuration of the chromophores. As a result, the parameters defining the Hamiltonian (i.e., the site energies ϵ_m , the exciton-phonon couplings χ_{qm} , and the system-bath couplings κ_j) in principle should be extracted from a certain distribution.

3.3.2 Response functions and measured signals

The field-matter interaction Hamiltonian in the dipole approximation and in the rotating wave approximation can be written as

$$H_F(t) = -\lambda[\varepsilon(t)X^\dagger + \varepsilon^*(t)X], \quad (3.54)$$

where

$$\varepsilon(t) = \varepsilon_1(t) + \varepsilon_2(t), \varepsilon_1(t) = E(t)e^{-i\omega_1 t}, \varepsilon_2(t) = E(t - \tau)e^{i(\phi - \omega_2 t)}. \quad (3.55)$$

Here, $\varepsilon_1(t)$ and $\varepsilon_2(t)$ represent two femtosecond pump pulses with the pulse carrier frequencies ω_1 and ω_2 , respectively. λ , $E(t)$, τ and ϕ are the amplitude, dimensionless envelope, time delay and the relative phase of the pulses, respectively. The transition dipole moment operator is defined as follows

$$X = \sum_{m=1}^N \mathbf{e}\boldsymbol{\mu}_m |g\rangle \langle m|, X^\dagger = \sum_{m=1}^N \mathbf{e}\boldsymbol{\mu}_m |m\rangle \langle g|. \quad (3.56)$$

where e denotes the polarization of the pulses, and μ_m is the transition dipole moment between ground state and excited state of site m .

The time evolution of the total density matrix of molecular aggregates coupled to the bath as well as excited by the laser pulses follows the Liouville-von Neumann equation

$$\partial_t \rho(t) = -i[H + H_F(t), \rho(t)]. \quad (3.57)$$

The measured signal is the total fluorescence from the lowest singly-excited optically bright excitonic state as a function of inter-pulse delay time [37], which is proportional to the total population of the singly-excited electronic states

$$S(\tau) = \text{Tr}\{\mathcal{P}_1 \rho(t \rightarrow \infty)\} \quad (3.58)$$

where

$$\mathcal{P}_1 = \sum_{m=1}^N |m\rangle\langle m| \quad (3.59)$$

with trace done over all nuclear degrees of freedom. Indeed, if the lowest excited state of the system is optically bright, then all the single-excited excitonic states will nonradiatively relax down to this state. If the lowest state is optically dark, then population of the lowest bright state will be proportional to the total population of the singly-excited electronic state weighted by the appropriate Boltzmann factor.

It is natural to rewrite Eq. (3.58) in terms of the total complex nonlinear polarization

$$P(t) = \text{Tr}\{X\rho(t)\} \quad (3.60)$$

as follows [38]:

$$S(\tau) = -2\text{Im} \int_{-\infty}^{\infty} dt \varepsilon^*(t) P(t). \quad (3.61)$$

Eq. (3.61) reminds us the formula used to calculate the integral transient absorption pump-probe signal, however it should be noted that $P(t)$ is the nonlinear total polarization which contains the contributions from all orders of system-field interaction λ .

We can also express the signal in power series of λ

$$S(\tau) = \sum_{k=1}^{\infty} \lambda^{2k} S_k(\tau). \quad (3.62)$$

where each contribution $S_k(\tau)$ is calculated through the $(2k - 1)$ -order response function [39, 40]. The weak laser pulses used in the experiment [37] ensure that the experiment was performed in the linear regime, thus avoiding the excited state absorption and stimulated emission. As a result, it is sufficient to evaluate $S(\tau)$ in the leading order $S_1(\tau)$

$$S_1(\tau) = \sum_{a,b=1}^2 \sigma_{ab}(\tau) \quad (3.63)$$

with

$$\sigma_{ab}(\tau) = 2\text{Re} \int_{-\infty}^{\infty} dt \int_0^{\infty} dt_1 \varepsilon_a^* \varepsilon_b(t - t_1) R(t_1) \quad (3.64)$$

Here

$$R(t) = \text{Tr}\{X^\dagger e^{iHt} \rho_0 X e^{-iHt}\} \quad (3.65)$$

is the linear response function, and

$$\rho_0 = Z^{-1} \exp\left\{-\frac{H}{k_B T}\right\} \quad (3.66)$$

is the initial state of the system and bath phonons according to the Boltzmann distribution (Z is the partition function, k_B is the Boltzmann constant, and T is the bath temperature). If the characteristic energies of the primary phonon modes are much higher than $k_B T$, we can assume that the system resides in its lowest exciton-phonon state $|g\rangle|0_{\text{ph}}\rangle$

$$\rho_0 = |g\rangle|0_{\text{ph}}\rangle\langle 0_{\text{ph}}|\langle g| \quad (3.67)$$

By taking in account the fact that the system Hamiltonian (3.47) commutes with the bath Hamiltonian (3.51) and the system-bath coupling Hamiltonian (3.52), $[H_S, H_{SB} + H_B] = 0$, we can describe the bath-induced relaxation in the framework of the second-order cumulant expansion [23], yielding

$$R(t) = e^{-g(t)} \sum_{n,n'} C(n, n') \langle 0_{\text{ph}} | \langle n | e^{-iH_S t} | n' \rangle | 0_{\text{ph}} \rangle \quad (3.68)$$

Here $C_{n,n'} = (\mathbf{e}\boldsymbol{\mu}_n)(\mathbf{e}\boldsymbol{\mu}_{n'})$ is the geometrical factor which accounts for statistical orientations of the chromophores in the laboratory frame, and the lineshape function is defined as [23]

$$g(t) = \int_0^\infty d\omega \frac{D(\omega)}{\omega^2} \times \left[\coth \frac{\hbar\omega}{2k_B T} (1 - \cos \omega t) + i(\sin \omega t - \omega t) \right]. \quad (3.69)$$

If we consider an ensemble experiment, the orientational averaging of $C_{n,n'}$ yields $\bar{C}_{n,n'} = (\boldsymbol{\mu}_n \boldsymbol{\mu}_{n'})/3$.

3.3.3 The Davydov ansatz

The next crucial step is to evaluate the propagator in Eq. (3.68) in terms of the Davydov D_1 ansatz

$$e^{-iH_S t} |n\rangle |\mathbf{0}_S\rangle = |\Psi_{D_1}(t)\rangle, \quad (3.70)$$

$$|\Psi_{D_1}(t)\rangle = \sum_n \alpha_n(t) |n\rangle \exp \left\{ \sum_q [\lambda_{nq}(t) b_q^\dagger - H.c.] \right\} |\mathbf{0}_{ph}\rangle. \quad (3.71)$$

By applying the Lagrangian formulation of the Dirac-Frenkel variational principle, the equations of motion for the variational parameters $\alpha_n(t)$ and $\lambda_{nq}(t)$ can be obtained as follows [16, 17, 41]

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\alpha}_n^*} \right) - \frac{\partial L}{\partial \alpha_n^*} = 0. \quad (3.72)$$

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\lambda}_{nq}^*} \right) - \frac{\partial L}{\partial \lambda_{nq}^*} = 0, \quad (3.73)$$

with the Lagrangian

$$L = \langle \Psi_{D_1}(t) | \frac{i}{2} \left(\overrightarrow{\frac{\partial}{\partial t}} - \overleftarrow{\frac{\partial}{\partial t}} \right) - H_S | \Psi_{D_1}(t) \rangle \quad (3.74)$$

Explicitly,

$$\begin{aligned}
\dot{\alpha}_n(t) &= -\frac{1}{2}\alpha_n \sum_q (\dot{\lambda}_{nq}\lambda_{nq}^* - H.c.) - i \sum_m J_{nm}\alpha_m S_{nm} \\
&\quad - i\alpha_n \left[\sum_q \omega_q |\lambda_{nq}|^2 - \sum_q g_q \omega_q (\lambda_{nq} + \lambda_{nq}^*) \right], \\
\dot{\lambda}_{nq}(t) &= -i[\alpha_n^{-1} \sum_m J_{nm}\alpha_m S_{nm} (\lambda_{mq} - \lambda_{nq}) + \omega_q \lambda_{nq} - g_q \omega_q].
\end{aligned} \tag{3.75}$$

Here

$$S_{nm}(t) = \exp\left\{ \sum_q [\lambda_{nq}^*(t)\lambda_{mq}(t) - \frac{1}{2}|\lambda_{nq}(t)|^2 - \frac{1}{2}|\lambda_{mq}(t)|^2] \right\} \tag{3.76}$$

is the Debye-Waller factor. The quality of ansatz (see Eq. (3.71)) is estimated by the deviation vector which shows how faithfully a given trial state obeys the Schrödinger equation [16, 17].

3.4 2DES of molecular aggregates

With recent technological advances, the 2DES technique has attracted increasing attentions due to its wide applications in studying energy and charge transfer processes in light harvesting systems [42, 43, 44, 45, 46, 47, 48]. Theoretical description of 2D spectroscopic signals is encoded in the third-order polarization $P^{(3)}(t)$, which can be described in the nonlinear response function theory. In this section, we briefly discuss how to use the Davydov trial states to efficiently handle the 2D spectra calculation. The theory is formulated such that we incorporate the vibrational modes with significant exciton-phonon coupling into the system Hamiltonian, and treat them by the Davydov trial states. The other nuclear degrees of freedom of the environment, which are responsible for phenomenological relaxation rates, are simply described through the nonlinear response function formalism.

The model system we considered is already described in Section 3.3.1. In order to calculate

the 2D spectra, we include in Eq. (3.46) an additional field-matter interaction Hamiltonian

$$H_F(t) = - \sum_{a=1}^3 \sum_{m=1}^N E_a(t - \tau_a) e^{i\mathbf{k}_a \mathbf{r} - \omega_a(t - \tau_a)} \mathbf{e}_a \boldsymbol{\mu}_m |m\rangle g| + \text{H.c.} \quad (3.77)$$

Here $\mathbf{e}_a$, $\mathbf{k}_a$, ω_a , $E_a(t)$, and τ_a represent the polarization, the wave vector, the carrier frequency, the dimensionless envelope, and the central time of the pulses, respectively. $\boldsymbol{\mu}_m$ is the transition dipole moment between the ground state and the excited state of site m .

In accord with the language of 2D spectra, we define the arrival times for three pulses as follows

$$\tau_1 = -T - \tau, \tau_2 = -T, \tau_3 = 0 \quad (3.78)$$

where τ and T are the coherence and population times, respectively. In a 2DES experiment and apparatus, the signal is measured in a given phase-matched direction. The signal measured in the direction $-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ gives rise to the so-called rephasing (subscript R) contribution $P_R^{(3)}(t)$, while that in the direction $\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$ gives rise to so-called non-rephasing (subscript NR) contribution $P_{NR}^{(3)}(t)$. We can then write the third-order polarization in terms of nonlinear response function R_i , $i = 1 - 4$, in the impulsive limit as follows [23]

$$\begin{aligned} P_R^{(3)}(t, T, \tau) &\sim -i [R_2(t, T, \tau) + R_3(t, T, \tau)], \\ P_{NR}^{(3)}(t, T, \tau) &\sim -i [(R_1(t, T, \tau) + R_4(t, T, \tau))] \end{aligned} \quad (3.79)$$

By taking 2D Fourier transformation of Eq. (3.79), one obtains the rephasing and non-rephasing 2D spectra as follows

$$\begin{aligned} S_R(\omega_t, T, \omega_\tau) &= \text{Re} \int_0^\infty \int_0^\infty dt d\tau i P_R^{(3)}(t, T, \tau) e^{-i\omega_t \tau + i\omega_t t}, \\ S_{NR}(\omega_t, T, \omega_\tau) &= \text{Re} \int_0^\infty \int_0^\infty dt d\tau i P_{NR}^{(3)}(t, T, \tau) e^{i\omega_\tau \tau + i\omega_t t} \end{aligned} \quad (3.80)$$

The total 2D spectra is simply the sum of the non-rephasing and the rephasing part

$$S(\omega_t, T, \omega_\tau) = S_R(\omega_t, T, \omega_\tau) + S_{NR}(\omega_t, T, \omega_\tau) \quad (3.81)$$

It is noted that the system Hamiltonian (3.47) commutes with the bath Hamiltonian (3.51) and the system-bath coupling Hamiltonian (3.52), $[H_S, H_{SB} + H_B] = 0$, we can thus separate the contributions to the nonlinear response function into system and bath parts. The former is treated by the Davydov trial states, while the latter can be taken into account through lineshape factors in the second-order cumulant expansion technique. Finally, we arrive at the expressions for the nonlinear response function [32]

$$\begin{aligned}
R_1(t, T, \tau) &= F_1(t, T, \tau) \sum_{n, n', n'', n'''} C_{n, n', n'', n'''} \langle 0 | \langle n | e^{iH_S T} | n' \rangle \langle n'' | e^{-H_S(t+T+\tau)} | n''' \rangle | 0 \rangle_{\text{ph}} \\
R_2(t, T, \tau) &= F_2(t, T, \tau) \sum_{n, n', n'', n'''} C_{n, n', n'', n'''} \langle 0 | \langle n | e^{iH_S(\tau+T)} | n' \rangle \langle n'' | e^{-H_S(t+T)} | n''' \rangle | 0 \rangle_{\text{ph}} \\
R_3(t, T, \tau) &= F_3(t, T, \tau) \sum_{n, n', n'', n'''} C_{n, n', n'', n'''} \langle 0 | \langle n | e^{iH_S \tau} | n' \rangle \langle n'' | e^{-H_S t} | n''' \rangle | 0 \rangle_{\text{ph}} \\
R_4(t, T, \tau) &= F_4(t, T, \tau) \sum_{n, n', n'', n'''} C_{n, n', n'', n'''} \langle 0 | \langle n | e^{-iH_S t} | n' \rangle \langle n'' | e^{-H_S \tau} | n''' \rangle | 0 \rangle_{\text{ph}} \quad (3.82)
\end{aligned}$$

with

$$C_{n, n', n'', n'''} = (\mathbf{e}_1 \boldsymbol{\mu}_n)(\mathbf{e}_2 \boldsymbol{\mu}_{n'})(\mathbf{e}_3 \boldsymbol{\mu}_{n''})(\mathbf{e}_4 \boldsymbol{\mu}_{n'''}) \quad (3.83)$$

denoting the geometrical factors. The reorientation of transition dipole moments $\boldsymbol{\mu}_n$, on the assumption of the same polarization for all laser fields, leads to the averaged geometrical factors

$$\tilde{C}_{n, n', n'', n'''} = \frac{1}{15} ((\boldsymbol{\mu}_n \boldsymbol{\mu}_{n'}) (\boldsymbol{\mu}_{n''} \boldsymbol{\mu}_{n'''}) + (\boldsymbol{\mu}_n \boldsymbol{\mu}_{n''}) (\boldsymbol{\mu}_{n'} \boldsymbol{\mu}_{n'''}) + (\boldsymbol{\mu}_n \boldsymbol{\mu}_{n'''}) (\boldsymbol{\mu}_{n'} \boldsymbol{\mu}_{n''})) \quad (3.84)$$

The lineshape factors F_i can be easily evaluated by cumulant expansion techniques [23]

$$\begin{aligned}
F_1(t, T, \tau) &= e^{-g^*(t)-g(\tau)-g^*(T)+g^*(T+t)+g(\tau+T)-g(\tau+T+t)} \\
F_2(t, T, \tau) &= e^{-g^*(t)-g^*(\tau)+g(T)-g(T+t)-g^*(\tau+T)+g^*(\tau+T+t)} \\
F_3(t, T, \tau) &= e^{-g(t)-g^*(\tau)+g^*(T)-g^*(T+t)-g^*(\tau+T)+g^*(\tau+T+t)} \\
F_4(t, T, \tau) &= e^{-g(t)-g(\tau)-g(T)+g(T+t)+g(\tau+T)-g(\tau+T+t)} \quad (3.85)
\end{aligned}$$

with the lineshape function $g(t)$ expressed as

$$g(t) = \int_0^\infty d\omega \frac{D(\omega)}{\omega^2} \times \left[\coth \frac{\hbar\omega\beta}{2} (1 - \cos \omega t) + i(\sin \omega t - \omega t) \right] \quad (3.86)$$

The final crucial step is to substitute the propagators by the corresponding Davydov ansätze

$$e^{-\frac{i}{\hbar}H_S t}|n\rangle|0\rangle_{\text{ph}} = |\Psi_\sigma(t)\rangle \quad (3.87)$$

with σ denoting the $D_1(D_2)$ (see Eqs. (3.4) and (3.5)) and the multiple $D_1(D_2)$ (see Eqs. (3.6) and (3.7))

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Chapter 4*

Dynamics of a one-dimensional Holstein polaron

In this chapter, we have systematically studied the polaron dynamics of one-dimensional Holstein molecular crystal model in the presence of both diagonal and off-diagonal exciton-phonon coupling by utilizing a multitude of the Davydov ansätze and the HEOM method. We first carefully examined the validity of Davydov trial states by using the relative deviation which quantifies how faithfully a given trial state obeys the Schrödinger equation. The small relative deviation for large multiplicity M demonstrates the superior accuracy of the multiple Davydov ansätze. Interestingly, it is found that the intricate interplay between transfer integral and off-diagonal coupling leads to the self-trapping of the exciton. We then devised a novel HEOM formalism that can treat the Holstein polaron in a nonperturbative way and at any temperatures. It is found that strong exciton-phonon coupling leads to exciton localization, while the transfer integral facilitates exciton transport. The scattering effect induced by the temperature can be also accounted for by this formalism. Finally, we applied Davydov D_1 ansatz to study exciton dynamics in a linear chain and LH2 rings in purple bacteria. The simulation results reveal that exciton transport exhibit superdiffusive characteristics.

* This section published substantially as references [5, 10, 15] shown in the List of Publications

4.1 Introduction

Theoretical studies of energy transfer processes in light harvesting systems are usually based on the Holstein molecular crystal model, which describes a lattice of molecular aggregates (each site modeled as a two-level system) coupled to a phonon environment. In the past decades, various numeric methods have been proposed to tackle the complicated dynamics of the Holstein polaron, such as t-DRMG [1, 2, 3, 4], the Merrifield ansatz [5, 6], and variational exact diagonalization (VED) [7]. However, most of these theoretical studies treat the conventional form of the Holstein Hamiltonian with the diagonal coupling only, and the case of off-diagonal is rarely considered in the literature due to inherent difficulties to obtain reliable results.

In this chapter, we utilize a superposition of the Davydov D_1 and D_2 ansatz (the multi- D_1 , and multi- D_2 ansatz) as well as a discretized HEOM method as discussed in Sections 3.1.2 and 3.1.3 to systematically study the polaron dynamics of Holstien model in the presence of both diagonal and off-diagonal exciton-phonon coupling. In Section 4.2, the multi- D_1 and multi- D_2 with enhanced efficiency and adequate accuracy are employed to investigate the dynamics properties of the Holstein polaron with both diagonal and off-diagonal exciton-phonon coupling. An extended, numerically exact HEOM approach is developed and applied to study the dynamics of a one-dimensional Holstein model under various physical parameters, such as exciton-phonon coupling, exciton transfer integral as well as temperature in Section 4.3. Finally, in Section 4.4, the exciton-phonon dynamics in a linear chain of pigments and in a multiple-ring LH2 are studied by using the Davydov D_1 ansatz.

4.2 Dynamics of a one-dimensional Holstein polaron with the multiple Davydov ansätze

4.2.1 Validity of variational dynamics

In this section, the validity of the Davydov ansätze are systematically scrutinized. For this purpose, we introduce a deviation vector $\vec{\delta}(t)$ to quantify how trial wave function follows the Schrödinger equation, which is defined as

$$\vec{\delta}(t) = \frac{1}{i\hbar} \hat{H} |D_{1,2}^M(t)\rangle - \frac{\partial}{\partial t} |D_{1,2}^M(t)\rangle. \quad (4.1)$$

As a result, the deviation of the ansätze from the exact Schrödinger equation solution can be quantified by the amplitude of the deviation vector $\Delta(t) = \|\vec{\delta}(t)\|$. We further define a dimensionless relative deviation σ as follows

$$\sigma = \frac{\max\{\Delta(t)\}}{\text{mean}\{N_{\text{err}}(t)\}}, \quad t \in [0, t_{\text{max}}]. \quad (4.2)$$

where $N_{\text{err}}(t)$ is simply calculated as

$$\begin{aligned} N_{\text{err}}(t) &= \sqrt{-\langle \frac{\partial}{\partial t} \Psi(t) | \frac{\partial}{\partial t} \Psi(t) \rangle} \\ &= \sqrt{\langle D_{1,2}^M(t) | \hat{H}^2 | D_{1,2}^M(t) \rangle} \\ &\approx \Delta E, \end{aligned} \quad (4.3)$$

We proceed to test the validity of multitude Davydov ansätze for various parameter sets (J, W, g, ϕ) in Figs. 4.1-4.3. As displayed in Fig. 4.1, the relative deviation σ is plotted as a function of $1/M$ for the diagonal coupling case of $J = 0.1, W = 0.5, g = 0.1$ and $\phi = 0$. It is found that the relative deviation σ monotonically decreases with the increase of M , and the results obtained by $D_1^{M=5}$ ansatz are already quite close to the exact Schrödinger equation dynamics ($\sigma = 0.067$), demonstrating the superiority of the multiple Davydov trial states.

Figure 4.1 M (multiplicity) dependent relative deviations σ of the multi- D_1 ansatz for a molecular ring with 16 sites. We set other parameters $J = 0.1$, $g = 0.1$, $W = 0.5$ and $\phi = 0$.

Fig. 4.2 displays the relative deviation σ of the multi- D_1 ansätze with $M = 1$ and 4 as a function of transfer integral J . Other parameters are $g = 0.1$, $W = 0.5$ and $\phi = 0$. For all values of J , the relative error σ dramatically decreases with the increase of multiplicity M . It is also shown that a large M is required to further decrease the relative error for a large transfer integral J due to the plane-wave nature of the phonon wave function.

Figure 4.2 J dependent relative deviations σ of the multi- D_1 ansätze with multiplicity $M = 1$ and 4, respectively. Other parameters $g = 0.1$, $W = 0.5$ and $\phi = 0$ are set.

Figure 4.3 g dependent relative deviations σ of the multi- D_1 ansätze with multiplicity $M = 1$ and $M = 4$, respectively. Other parameters $J = 0.1$, $W = 0.5$ and $\phi = 0$ are set.

The relative errors σ of the multi- D_1 ansätze with $M = 1$ and 4 as a function of diagonal coupling strength g are plotted in Fig. 4.3. Overall, the relative error for the case of $M = 4$

Figure 4.4 M dependent relative deviations σ of the multi- D_1 ansatz for the off-diagonal coupling strength $\phi = 0.4$. We set other parameters $J = W = g = 0$.

is rather small for all values of g . The results obtained by the $D_1^{M=4}$ ansatz exhibit significant improvement over that obtained by $D_1^{M=1}$ ansatz for very small g . It is also shown that the $D_1^{M=1}$ ansatz is sufficient to capture the correct dynamics for large diagonal coupling $g > 0.3$. Figs. 4.1-4.3 indicate that the multitude of the Davydov trial states provide accurate description of the delocalized state, while D_1 ansatz is sufficient to characterize the localized state.

Figure 4.5 M dependent relative deviations σ of the multi- D_2 ansatz for the off-diagonal coupling strength $\phi = 1$. We set other parameters $J = W = g = 0$. In the inset, the relationship $\sigma \sim M^{-\nu}$ is displayed on a log-log scale, and the dashed line represents a power-law fit.

Furthermore, the performance of multitude of the Davydov trial state in the off-diagonal coupling case of $J = W = g = 0, \phi = 0.4$ is also investigated, and results are shown in Fig. 4.4. The relative error σ decreases obviously as M increases, though the value of $\sigma(M = 6) = 0.544$ is still large. In order to achieve an accurate description of the off-diagonal coupling case, a large value of M should be used. This behavior is also reflected in Fig. 4.5, which plots the relative deviation σ calculated by multi- D_2 ansatz as a function of $1/M$ for the off-diagonal coupling case of $J = W = g = 0, \phi = 1$. As M increases, the relative deviation σ decreases and approaches zero as M goes to infinity. The power-law fitting $\sigma \sim M^{-\nu}$ with the exponent $\nu = 0.29$ further confirms the prediction of $\sigma = 0$ in the limit of $M \rightarrow \infty$. Due to

the localized nature of the coherent state, a large number of coherent states (a large M) should be used in the multi- D_1/D_2 ansatz to accurately characterize the complex dynamics for the off-diagonal coupling case. However, the computational burden of the multi- D_1 ansatz increases dramatically for large M , thus the computationally much cheaper multi- D_2 trial state is more suitable for the off-diagonal cases.

4.2.2 Exciton probabilities and phonon displacements

Figure 4.6 The propagation patterns of exciton probability $P_{\text{ex}}(t, n)$ calculated by the single D_1 ansatz (a), the $D_1^{M=8}$ (b) ansatz and the HEOM method (c), respectively. (d) displays the difference $\Delta P_{\text{ex}}(t, n)$ calculated by the $D_1^{M=8}$ and HEOM method. We set other parameters $J = 0.5, W = 0.5, g = 0.1, \phi = 0$ and $N = 10$.

We utilized the exciton probability $P_{\text{ex}}(t, n) = \langle D_{1,2}^M | \hat{a}_n^\dagger \hat{a}_n | D_{1,2}^M \rangle$ and the phonon displacements $X_{\text{ph}}(t, n) = \langle D_{1,2}^M | \hat{b}_n + \hat{b}_n^\dagger | D_{1,2}^M \rangle$ to characterize the dynamical properties of the Hol-

stein polaron. In Fig. 4.6, we compare the time evolution of the exciton probability $P_{\text{ex}}(t, n)$ calculated by the $D_1^{M=1}$ and $D_1^{M=8}$ ansätze as well as the numerically exact HEOM method. The parameters $J = 0.5, W = 0.5, g = 0.1, \phi = 0$ and $N = 10$ are set. As shown in Figs. 4.6a and 4.6b, the dynamics obtained by the $D_1^{M=8}$ ansatz exhibit distinguishable differences as compared to that obtained by $D_1^{M=1}$ ansatz, and is consistent with that obtained by the HEOM method (see Fig. 4.6c). In addition, the difference $\Delta P_{\text{ex}}(t, n)$ between the HEOM and the $D_1^{M=8}$ ansatz displayed in Fig. 4.6d is two orders of magnitude smaller than the value of $P_{\text{ex}}(t, n)$, further demonstrating the superiority of the multiple Davydov ansatz. We plot the exciton probabilities $P_{\text{ex}}(t, n)$ at sites $n = 5$ and 10 calculated by the single D_1 ansatz, the $D_1^{M=8}$ ansatz and the HEOM method in Fig. 4.7. The near overlap of curves obtained by the $D_1^{M=8}$ ansatz and the HEOM method reconfirms our contention.

Figure 4.7 The exciton probability $P_{\text{ex}}(t, n)$ with $n = 5$ (top panel) and 10 (bottom panel) calculated by the single D_1 , $D_1^{M=8}$ ansätze and the HEOM method, respectively. Other parameters $J = 0.5, W = 0.5, g = 0.1, \phi = 0$ and $N = 10$ are set.

The propagation patterns of the exciton probability $P_{\text{ex}}(t, n)$ and the phonon displacement $X_{\text{ph}}(t, n)$ obtained with the single D_1 ansatz and the $D_1^{M=4}$ ansatz for diagonal coupling case of $W = 0.5, g = 0.1, J = 0.5$ are depicted in Fig. 4.8. It is found that the exciton gradually

Figure 4.8 The propagation patterns of the exciton probability $P_{\text{ex}}(t, n)$ and phonon displacement $X_{\text{ph}}(t, n)$ calculated by the single D_1 ansatz (left panel) and the $D_1^{M=4}$ ansatz (right panel) are shown in (a)-(d). Other parameters $W = 0.5$, $g = 0.1$, $J = 0.5$ and $\phi = 0$ are set.

converges at the initial excitation site of the molecular ring for the single D_1 ansatz, while it spreads along two opposite directions to the entire ring for the $D_1^{M=4}$ ansatz. Besides, an abnormal intersection of the wavefront of the phonon packet appears at $t \approx 14\pi/\omega_0$ for the single D_1 ansatz, but it disappears for the $D_1^{M=4}$ ansatz. All these findings point out that only the multiple Davydov trial states are capable to capture the accurate dynamics of the exciton-phonon system.

The improvement of the polaron dynamics in the off-diagonal coupling case by the multi- D_2 trial state is shown in Fig. 4.9, which compares the exciton probability $P_{\text{ex}}(t, n)$ calculated by the single D_2 and the $D_2^{M=16}$ ansätze for two cases of $J = 0.1$, $\phi = 0$ and $J = 0.1$, $\phi = 0.1$. It is shown that both trial states exhibit the same dynamics for $\phi = 0$. However, the localization of wavefront of the exciton packet is only correctly described by the $D_2^{M=16}$ ansatz for off-diagonal coupling strength $\phi = 0.1$. In fact, the combined effect of the transfer integral J and

Figure 4.9 The propagation patterns of the exciton probability $P_{\text{ex}}(t, n)$ calculated by the $D_2^{M=16}$ and $D_2^{M=1}$ ansätze are displayed for $J = 0.1, \phi = 0$ (left panel) and $J = 0.1, \phi = 0.1$ (right panel), respectively.

the off-diagonal coupling strength ϕ will confine the exciton to the initial excitation site as can be understood by the analysis of the energy band near the zone center showing that the effective mass in the case of $\phi = 0.1$ is larger than that of $\phi = 0$, which results in a less mobile polaron movement. This further demonstrates that the multiple trial states can accurately capture the polaron dynamics.

4.3 Dynamics of a one-dimensional Holstein polaron with the HEOM

The methodologies used in this section is described in details in Section 3.1.3. We consider one-dimensional ring of 10 sites as our system with initial excitation located at site $n = 0$, i.e., we set the $\rho_{0,\dots,0}(0, 0) = 1$, and all the other matrix elements of $\hat{\rho}_{m_1\pm, m_2\pm, \dots, m_N\pm}$ are set to 0.

Figure 4.10 The propagation profiles of exciton population for (a) $J=0.2$, $W=0.5$, $g=0.1$; (b) $J=0.5$, $W=0.5$, $g=0.1$; (c) $J=1.0$, $W=0.5$, $g=0.1$. We set temperature to zero ($\beta = \infty$)

We first discuss the effect of transfer integral J . The exciton propagation patterns for various values of the transfer integral J at zero temperature are shown in Fig. 4.10. The rest of parameters are $W = 0.5$ and $g = 0.1$. The initial excitation at $n = 0$ creates left- and right-moving wave packets of the exciton that collides at the opposite side of the ring. As a result, the recombined exciton density is high enough to trigger another pair of exciton wave packets. The general feature of the exciton wave packets is that the propagation speed is proportional to the transfer integral J (the velocities of exciton propagation for Figs. 4.10a-4.10c are 2, 5, 10, in units of $\omega_0/2\pi$), which can be easily understood by the fact that the group velocity of the exciton wave packets, expressed as $\partial E_{ex}(k)/\partial k$, is proportional to the exciton transfer integral

J .

Figure 4.11 The propagation profiles of exciton population for (a) $J=0.2$, $W=0.5$, $g=0.2$; (b) $J=0.5$, $W=0.5$, $g=0.2$; (c) $J=1.0$, $W=0.5$, $g=0.2$. We set temperature to zero ($\beta = \infty$)

Fig. 4.11 displays the same time evolution of exciton populations as those exhibited in Fig. 4.10 but at an intermediate exciton-phonon coupling strength of $g = 0.2$. The exciton wavepackets for $g = 0.2$ propagate at a much slower speed as compared to those for $g = 0.1$ at small and intermediate transfer integral J . It is interesting to show that increasing exciton-phonon coupling from $g = 0.1$ to $g = 0.2$ has a minor effect on exciton transport for the case of large transfer integral $J = 1$ thanks to the weak exciton-phonon strength $g = 0.2$, which results in a reorganization energy much smaller than transfer integral J . However, the exciton

density after the first collision event is significantly weakened (compare Figs. 4.11c and 4.10c).

Figure 4.12 Temperature dependent exciton populations for the cases of (a) $J=0.5$, $W=0.5$, $g=0.1$, $\beta = 2$; (b) $J=0.5$, $W=0.5$, $g=0.1$, $\beta = 1.25$.

We then discuss the effect of the temperature. Fig. 4.12 exhibits the time evolution of the exciton population at two temperatures ($\beta = 2$ and $\beta = 1.25$) with a phonon bandwidth of $W = 0.5$ and an exciton-phonon coupling strength of $g = 0.1$. We can clearly see similar V-shaped propagation pattern of the exciton wave packets until they collide at the opposite site of the ring. What is different from that shown in Fig. 4.10b is that the bright spots are largely quenched in Figs. 4.12a and b. This is because high temperature leads to a large dynamical disorder effect that strongly scatters the exciton propagation.

Finally, we study the effect of the off-diagonal exciton-phonon coupling. Fig. 4.13 displays the time evolution of the exciton population for three sets of parameters ($J=0, W=0, g=0$, $\phi = 0.1$, panel (a)), ($J=0.1, W=0, g=0$, $\phi = 0.1$, panel (b)), ($J=-0.1, W=0, g=0$, $\phi = 0.1$, panel (c)) at zero temperature. The initial state for the exciton is that the excitation is located with an equal probability at sites $n = 0$ and $n = 1$. As shown in Fig. 4.13a, the off-diagonal coupling facilitates the exciton transport in the absence of the direct transfer integral. During the first four phonon periods, the exciton is nearly localized at the initial excitation sites, then it starts to spread due to the existence of off-diagonal coupling. Interestingly, the combined effect of transfer integral and off-diagonal coupling as shown in Figs 4.13b and 4.13c exhibit quite different exciton transport behavior as compared to that with only off diagonal coupling (see

Fig. 4.13a), although either the transfer integral or the off-diagonal coupling, on its own, may facilitate the propagation of wave packets. For the case of $J = 0.1$ (see Fig. 4.13b), the exciton prefers to be localized at the sites of exciton creation, while it delocalizes quickly for the case of $J = -0.1$ (see Fig. 4.13c). This quite fascinating phenomenon can be easily understood after analyzing the polaron band structure near the zone center. The calculation reveals that the effective mass in the case of $J = -0.1, \phi = 0.1$ is the smallest, resulting in a more mobile polaron (see Ref. [8]).

Figure 4.13 The propagation profiles of exciton population for the off-diagonal coupling cases of (a) $J=0, W=0, g=0, \phi = 0.1$; (b) $J=0.1, W=0, g=0, \phi = 0.1$. (c) $J=-0.1, W=0, g=0, \phi = 0.1$. We set temperature to zero ($\beta = \infty$)

4.4 Excitonic diffusion in LH2 complexes of purple bacteria

In this section, we utilize the Davydov D_1 ansatz to study the exciton diffusion in a linear chain of chromophores and in a multiple rings of LH2 in purple bacteria. Our study is motivated by a recent experiment showing that biomimetic molecular nanoarray constructed from LH2 antenna complexes from *Rhodobacter sphaeroides* exhibits extremely long-range excitation energy transfer as compared to that in a native bacterial photosynthetic system [9]. Artificial nanoscale devices have been successfully fabricated using natural photosynthetic complexes in the hope of achieving efficient energy transfer or charge separation [9, 10, 11]. Traditional theoretical treatments of exciton diffusion are mostly based on the Förster theory that assumes incoherent hopping between adjacent pigments, while recent experimental findings reveal the important role of quantum coherence in promoting the energy transfer efficiency. Thus, the effect of quantum coherence must be taken into account for reasonable theoretical description of photosynthetic EET dynamics.

In order to simulate quantum mechanically the coherent energy transfer in LH2 rings, we extend the Davydov D_1 ansatz

$$|\Psi_{D_1}(t)\rangle = \sum_n \alpha_n(t) |n\rangle \exp \left\{ \sum_q [\lambda_{nq}(t) b_q^\dagger - H.c.] \right\} |0\rangle. \quad (4.4)$$

to a multi-ring version expressed as

$$|\Psi_{D_1}^r(t)\rangle = \sum_n \alpha_n^r(t) |n\rangle \exp \left\{ \sum_q [\lambda_{nq}^r(t) b_q^\dagger - H.c.] \right\} |0\rangle. \quad (4.5)$$

with $\alpha_n(t)$ ($\alpha_n^r(t)$) and $\lambda_{n,q}(t)$ ($\lambda_{n,q}^r(t)$) representing exciton amplitudes and phonon displacements for a chain (a multiple-ring system). A detailed derivation of equations of motion for variational parameters $\alpha_n(t)$ ($\alpha_n^r(t)$) and $\lambda_{n,q}(t)$ ($\lambda_{n,q}^r(t)$) can be found in Appendix C. It should be noted that the Davydov D_1 ansatz is used in the calculation because the exciton-phonon coupling Hamiltonian is site diagonal form (see Appendix C). The single-exciton density matrix

$\rho_{mn}(t)(\rho_{mn}^{r_1 r_2}(t))$ for the chain (the multiple-ring system) can then be easily obtained by tracing out degrees of freedom of phonon modes, which is written as

$$\rho_{mn}(t) = \alpha_m^*(t)\alpha_n(t)S_{mn}(t), \quad (4.6)$$

$$\rho_{mn}^{r_1 r_2}(t) = \alpha_m^{r_1*}(t)\alpha_n^{r_2}(t)S_{mn}^{r_1 r_2}(t), \quad (4.7)$$

where the Debye-Waller factors $S_{mn}(t)$ and $S_{mn}^{r_1 r_2}(t)$ are defined by Eqs. (C-11) and (C-18), respectively. The mean square displacement (MSD) characterizing the transport properties of the exciton can be formulated for a chain as

$$\langle x^2(t) \rangle = \sum_{n=-N/2+1}^{N/2} (nd)^2 \rho_{nn}(t) \quad (4.8)$$

and for a multiple-ring system as

$$\langle x^2(t) \rangle = \sum_{r=-N_{\text{ring}}/2+1}^{N_{\text{ring}}/2} (rD)^2 \rho_r(t) \quad (4.9)$$

where we have extracted center-to-center distance $d = 9.0 \text{ \AA}$ ($D = 8.0 \text{ nm}$) between two adjacent pigments (LH2 rings) from the structural data of the natural photosynthetic system [12]. $\rho_{nn}(t)(\rho_r(t))$ is the exciton population of the n th pigment (the r th ring) at time t , and N (N_{ring}) is the total number of pigments (rings).

We first discuss the effect of the exciton-phonon coupling strength and the transfer integral on the transport properties of a one-dimensional linear chain. As displayed in Fig. 4.14a, the slopes in the log-log plot of MSD versus t for $S = 0.2, 0.5, 0.8$, and 1.0 are $2.01, 2.12, 2.16$, and 2.16 , respectively, demonstrating the super-diffusion behavior of the exciton transfer dynamics. In contrast, the exciton is found to be less mobile for large $S = 1.5$ and 2.0 . Fig. 4.14b exhibits the log-log plots of MSD versus t for various values of the transfer integral J , and all the curves show a quantum nature of the exciton dynamics. The general trend is that the larger value of J , the faster exciton transfer.

We next investigate the exciton transfer properties in a one-dimensional array of LH2 rings. As shown in Fig. 4.15a, linear fitting of log-log plot of MSD versus t for systems of 9 to 15

LH2 rings results in a slope of approximately 1.5, pointing to the superdiffusive characteristics of the exciton transfer. We also calculate the exciton coherence size L_ρ borrowed from the theory of quantum localization to further elucidate the coherent energy transfer in LH2 rings

Figure 4.14 S (with $J=0.3557$, $W=0.8$, left panel) and J ($S=0.5$, $W=0.8$, right panel) dependent log-log plot of MSD (in units of $\text{\AA}^2$) as a function of time (in units of fs) for a linear chain.

Figure 4.15 (a) Log-log plot of MSD (in units of $\text{\AA}^2$) as a function of time (in units of fs) for different number of LH2 rings. (b) The coherence size L_ρ as a function of time for different number of LH2 rings. We set Huang-Rhys factor $S=0.5$ and phonon bandwidth $W=0.1$.

[13]. It characterizes the extent of excitonic coherence, and can be defined as follows

$$L_\rho(t) = \left(\sum_{r_1 r_2 m n} |\rho_{mn}^{r_1 r_2}(t)| \right)^2 \left[L \sum_{r_1 r_2 m n} |\rho_{mn}^{r_1 r_2}(t)|^2 \right]^{-1} \quad (4.10)$$

where L is the total number of pigments in the LH2 rings. Fig. 4.15b displays the time evolution of coherence size L_ρ for multiple ring systems, and it is found that coherence size L_ρ oscillates between 56 and 88 pigments, i.e., between 3.5 and 5.5 rings with an average of 4.5 rings, demonstrating the coherent energy transfer in LH2 rings.

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Chapter 5*

Quantum dissipative dynamics at a conical intersection

In this chapter, we have utilized the numerically exact HEOM method to study the dissipative dynamics in a minimal model of a conical intersection involving two excited electronic states and two vibrational modes. We first calculated the diabatic (adiabatic) population of electronic states as well as the expectation values of the position and the momentum operator of the tuning mode for different system bath coupling strengths. It is found that this model conical intersection reveals a bimodal electronic relaxation dynamics, i.e., the initial ultrafast decay on a time scale of a few tens of femtoseconds followed by a complete decay to the lower potential energy surface due to the coupling to the environment. In addition, quantum beatings with the tuning mode frequency can be clearly observed in the dynamics behaviors, and this quantum coherence lasts for a longer time in the strong non-Markovian regime. Finally, we have calculated the time dependent probability densities of individual vibrational modes, reduced description of the wave packets, to investigate the ultrafast internal conversion processes. We found that the wave packet propagation patterns follow the shape of the potential energy surface, and the main effect of the bath is to direct the wave packet to the lower adiabatic surface.

* This section published substantially as reference [2] shown in the List of Publications

5.1 Introduction

Conical intersection of PE surfaces plays an important role in the ultrafast internal-conversion processes [1]. The methodology development of time-dependent wave packet propagation has enabled detailed investigations of combined electronic and vibrational dynamics in the vicinity of conical intersections, uncovering the mechanisms of ultrafast energy relaxation processes [1, 2]. It is well known that internal conversion through conical intersections involves several active vibrational modes, and the coupling of these active modes to the inactive modes (i.e., environmental modes) results in vibrational energy redistribution in the time scale of picoseconds.

In this chapter, we aim to investigate the mechanisms underlying the vibrational energy redistribution and electronic relaxation processes with special attention given to the possible role of electronic and vibrational coherences played in these processes. In Section 5.2, we introduce the model system, conical intersection of the $S_2[{}^1\mathbf{B}_{2u}(\pi\pi^*)]$ and $S_1[{}^1\mathbf{B}_{3u}(n\pi^*)]$ excited state of pyrazine. We analyze the electronic populations and vibrational coherence as well as vibrational probability densities in Sections 5.3 and 5.4, respectively.

5.2 Characterization of the system

The methodology part have been described in detail in Section 3.2. The model system we considered here is the conical intersection of the $S_2[{}^1\mathbf{B}_{2u}(\pi\pi^*)]$ and $S_1[{}^1\mathbf{B}_{3u}(n\pi^*)]$ excited state of pyrazine, which provides a paradigmatic example of studying the ultrafast electronic relaxation processes [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. Ab Initio calculations have determined that the main coupling and tuning modes are out of plane mode ν_{10a} with B_{1g} symmetry and ring bending ν_{6a} mode, respectively. The value of the parameters, E_1 , E_2 , ω_{6a} , ω_{10a} , κ_1 , κ_2 , λ in the

system Hamiltonian $H^{(S)}$ (3.23) are listed in Table 1 of Ref. [5]. In the following calculations, the temperature is set to 300 K.

Our model system consists of a direct product of a diabatic electronic state and a harmonic-oscillator (HO) state for each mode (see Eq. (3.27)). Numerical convergence tests have revealed that a basis set of 20 HO function for each mode is sufficient, which results in a dimension of 800 for the system Hamiltonian matrix $\mathbf{H}^{(S)}$. It should be noted that numerical integration of the auxiliary matrices with a large dimension in the HEOM formalism requires considerable memory and computational efforts. The emergence of high performance GPU with fast memory bandwidth and several hundred stream processors enables us to tackle this computationally challenging task. Numerical calculations in this chapter are performed on a NVIDIA Tesla M2050 GPU with 448 processors and 2GB ECC-protected on-board memory. Depending on the system-bath coupling strength ($\lambda_j, j = c, t$), we vary truncation number N from 6 to 12 to achieve converged results. Less than 10 hours computing time has been achieved for the time evolution of $\rho(t)$ up to 1000 fs with a time step 0.2 fs on a single GPU by utilizing the efficient GPU algorithms.

The evaluation of the adiabatic population P_n^{ad} (3.42) is simplified by introducing the projector operator on the lower and upper adiabatic electronic states in the diabatic representation (see Ref. [15] for details). We applied the discrete variable representation (DVR) schemes [15], in which an operator is represented in the coordinate space after the transformation between the harmonic oscillator basis and the grid in the coordinate space, to calculate the vibrational probability densities (see Eq. (3.45)).

Figure 5.1 Diabatic (a) and adiabatic (b) population of the S_2 state of pyrazine, assuming instantaneous electronic excitation to the diabatic S_2 state at $t=0$, for different system-bath coupling strengths: $\lambda_c = \lambda_t = 0, 10.6, 53, 106 \text{ cm}^{-1}$, phonon relaxation times are set to be $\gamma_c^{-1} = \gamma_t^{-1} = 50 \text{ fs}$

5.3 Electronic populations and vibrational coherences

In Fig. 5.1, we plot the diabatic $P_2^{\text{di}}(t)$ and the adiabatic population probability $P_2^{\text{ad}}(t)$ of the S_2 state of pyrazine, assuming instantaneous electronic excitation to the diabatic S_2 state at $t=0$, for different system-bath coupling strengths. For zero system-bath coupling ($\lambda_c = \lambda_t = 0$), $P_2^{\text{di}}(t)$ exhibits an initial decay on a timescale of about 50 fs, followed by large fluctuations of the population around its asymptotic value of 0.4. It is found that the inclusion of system bath coupling does not affect the initial fast decay and quantum beatings with the tuning mode frequency dominates the ensuing dynamics. The quantum beatings can last for 1 ps in the weak system-bath coupling case ($\lambda_c = \lambda_t = 10.6 \text{ cm}^{-1}$) reflecting the coherent wave packet motion in the tuning modes. Furthermore, both the duration and the amplitude of the vibronic

beating decreased with the increase of the system bath coupling strength. For strong coupling ($\lambda_c = \lambda_t = 106 \text{ cm}^{-1}$), the vibronic coherence can still persist up to 400 fs, which can not be described by the Redfield theory due to its inherent Markovian and perturbative approximation [3, 4].

The corresponding adiabatic population $P_2^{\text{ad}}(t)$ of isolated conical intersection decays even faster than $P_2^{\text{di}}(t)$ ($\approx 30 \text{ fs}$), and fluctuates around 0.2 as shown in Fig. 5.1b. The higher asymptotic value of P_2^{di} reflects the fact that the admixture of the diabatic S_2 and S_1 states has relaxed to the minimum of the lower adiabatic surface [2, 16]. With the inclusion of system bath coupling, the population $P_2^{\text{ad}}(t)$ further relaxes towards to zero. In general, this model conical intersection exhibits bimodal electronic relaxation dynamics, i.e., the initial ultrafast decay on a time scale of a few tens of femtoseconds followed by a complete decay to the lower adiabatic potential energy surface due to the coupling to the environment.

Figure 5.2 Expectation values of the position and the momentum operator of the tuning mode for different system bath coupling strengths. The parameters are the same as for Fig. 5.1

Fig. 5.2 displays expectation values of the position and the momentum operator of the tun-

ing mode for different system bath coupling strengths. Here, we did not show the expectation values of position and momentum operator of coupling mode as they vanish by symmetry consideration. As shown in Figs. 5.2a and 5.2b, the vibrational coherence decays rapidly on a time scale of 300 fs for zero system-bath coupling (black line). Interestingly, the inclusion of weak system bath coupling ($\lambda_c = \lambda_t = 10.6 \text{ cm}^{-1}$) results in an enhancement of the amplitude of vibrational motion, which can be attributed to the “dedamping” of the vibrational motion of the tuning mode through the effective intrasystem mode coupling between the coupling and the tuning mode [4]. With further increase of system-bath coupling strength ($\lambda_c = \lambda_t = 53, 106 \text{ cm}^{-1}$), the damping of the vibrational motion can be clearly seen.

Figure 5.3 Diabatic (a) and adiabatic (b) population of the S_2 state of pyrazine, assuming instantaneous electronic excitation to the diabatic S_2 state at $t=0$, for different system-bath coupling strengths: $\lambda_c = \lambda_t = 10.6, 53, 106 \text{ cm}^{-1}$, phonon relaxation times are set to be $\gamma_c^{-1} = \gamma_t^{-1} = 166 \text{ fs}$

We also study the effect of the phonon relaxation time on the dynamics behaviors. Fig. 5.3 plots the time-dependent electronic population of the diabatic and adiabatic S_2 state for a longer phonon relaxation time ($\gamma_c^{-1} = \gamma_t^{-1} = 166 \text{ fs}$). The quantum beatings of the diabatic population

are found to last for longer time as shown in Fig. 5.3a, which maybe due to the fact that a longer phonon relaxation time can help maintain the quantum coherence [17]. This strong non-Markovian effect can not be captured by the Redfield theory, which assume infinitely fast fluctuation that can quench quantum coherence quickly [17]. In the meantime, the adiabatic populations of S_2 state exhibit much slower decay as clearly shown in Fig. 5.3b. In Fig. 5.4, we display corresponding expectation values of the position and the momentum operator of the tuning mode for different system bath coupling strengths. It is found that intermediate system bath coupling induces most noticeable quantum coherence for a longer phonon relaxation time as compared to those for fast phonon relaxation time (see Fig. 5.2), reflecting the intricate interplay of the system-bath coupling and the non-Markovian effect.

Figure 5.4 Expectation values of the position and the momentum operator of the tuning mode for different system bath coupling strengths. The parameters are the same as for Fig. 5.3

Finally, we study the influence of a specific bath on the dynamic behaviors by setting only one mode coupled to that bath. The diabatic and adiabatic population probability of the S_2 state for the tuning mode-bath coupling only (black line), the coupling mode-bath coupling only (red line) and both modes-bath coupling (blue line) are shown in Fig. 5.5. It is found that the

diabatic population of S_2 state with only coupling mode-bath coupling exhibits most noticeable quantum beating behaviors, and the order of asymptotic amplitudes of diabatic population is: tuning mode-bath coupling only > coupling mode-bath coupling only > both modes-bath coupling. The asymptotic amplitudes of the adiabatic population of S_2 state present a similar trend (see Fig. 5.5b). In Fig. 5.6, we display the expectation values of the position and the momentum operator of the tuning mode for the cases of tuning mode-bath coupling only (black line), the coupling mode-bath coupling only (red line) and both modes-bath coupling (blue line). Similar to the quantum beating behaviors of the diabatic population of the S_2 state, the vibrational coherence is found to be most pronounced for the coupling mode-bath coupling case.

Figure 5.5 Diabatic (a) and adiabatic (b) population of the S_2 state of pyrazine, assuming instantaneous electronic excitation to the diabatic S_2 state at $t=0$, for different system-bath coupling strengths: $\lambda_c = 0, \lambda_t = 53 \text{ cm}^{-1}$ (black line), $\lambda_c = 53 \text{ cm}^{-1}, \lambda_t = 0$ (red line), $\lambda_c = \lambda_t = 53 \text{ cm}^{-1}$ (blue line), phonon relaxation times are set to be $\gamma_c^{-1} = \gamma_t^{-1} = 50 \text{ fs}$

Figure 5.6 Expectation values of the position and the momentum operator of the tuning mode for different system bath coupling strengths. The parameters are the same as for Fig. 5.5

5.4 Vibrational probability densities

In this section, we provide detailed information on the time-dependent probability densities $P_n^{\text{ad}}(Q_j, t)$ of individual vibrational modes $Q_j (j = c, t)$ in the upper ($n=2$) and lower ($n=1$) adiabatic state in order to elucidate the mechanisms of internal conversion processes. It should be noted that the probability densities $P_n^{\text{ad}}(Q_j, t)$ characterize the reduced description of wave packets.

In Fig. 5.7, we display the time-dependent probability densities of the tuning mode in the upper and lower adiabatic electronic states for zero ($\lambda_c = \lambda_t = 0$) as well as intermediate ($\lambda_c = \lambda_t = 53 \text{ cm}^{-1}$) system-bath coupling strengths. For the isolated conical intersection, the initially prepared wave packet on the S_2 surface propagates to the right because of the gradient of this surface (see Fig. 1b in Ref. [4]). The wave packet then approaches the conical intersec-

tion and transfers to the S_1 state within half of the vibrational period, and the large gradient of this potential energy surface in the opposite direction results in the coherent oscillation of the tuning mode Q_t (see Figs. 5.7a, 5.7c). The ensuing propagation pattern is that the wave packet on the S_1 surface is quasi-periodically created and fed back to the S_2 surface during the transient vibration motion. As shown in the right panel of Fig. 5.7, the main effect of the bath is to suppress the recurrences of the wave packet to the upper adiabatic surface, and as a result, the wave packet exhibits damped quasiperiodic vibrational motion.

Figure 5.7 Time evolution of probability density of the tuning mode in the S_2 (upper frame) and S_1 (lower frame) adiabatic electronic states. Left panel: $\lambda_c = \lambda_t = 0$; Right panel: $\lambda_c = \lambda_t = 53 \text{ cm}^{-1}$. phonon relaxation times are set to be $\gamma_c^{-1} = \gamma_t^{-1} = 50 \text{ fs}$

Contrary to the vibrational probability densities of the tuning mode, the probability den-

Figure 5.8 Time evolution of probability density of the coupling mode in the S_2 (upper frame) and S_1 (lower frame) adiabatic electronic states. The parameters are the same as for Fig. 5.7

sities of the coupling mode display a different pattern as shown in Fig. 5.8. For the isolated conical intersection, the left and right moving wave packets make a quick V-shaped propagation pattern until they reach the outer walls. Once the conical intersection is approached by the motion of the tuning mode, the wave packets transfer immediately to the lower surface, and spreads quickly due to the flatness of this surface (see Fig. 1c in Ref. [4]). The pronounced quantum interference is clearly observed in the ensuing wave packet propagation (see left panel of Fig. 5.8). It should be also noted that $P_n^{\text{ad}}(Q_c, t)$ exhibits a maximum at $Q_c = 0$ for the S_2 surface while a minimum for the S_1 surface due to the symmetry of the system. $P_n^{\text{ad}}(Q_c, t)$ for the intermediate system-bath coupling case ($\lambda_c = \lambda_t = 53 \text{ cm}^{-1}$) displays a similar V-shaped propagation pattern but with oscillation largely damped as shown in Fig. 5.8b. It is also found

that the peaks of the wave packet at $Q_c = 0$ on the S_2 surface disappear due to the symmetry breaking induced by the system-bath coupling. As a result, $P_1^{\text{ad}}(Q_c, t)$ exhibits a maximum at $Q_c = 0$ in the damped system (see lower frame of Fig. 5.8).

Figure 5.9 Time evolution of probability density in the S_2 (upper row) and S_1 (lower row) adiabatic electronic states for bath relaxation times $\gamma_c^{-1} = \gamma_t^{-1} = 50$ fs and system bath coupling $\lambda_c = \lambda_t = 2.1 \text{ cm}^{-1}$. Left column: tuning mode; Right column: coupling mode.

Finally, we discuss the intricate sensitivity of the wave-packet motion at the conical intersection in the presence of a weak system-bath coupling. Fig. 5.9 shows the time-dependent probability densities of the tuning mode $P_n^{\text{ad}}(Q_t, t)$ (left column) and the coupling mode $P_n^{\text{ad}}(Q_c, t)$ (right column) for rather weak system-bath coupling ($\lambda_c = \lambda_t = 2.1 \text{ cm}^{-1}$). It is found that

all erratic features shown on the left column of Fig. 5.7 for the tuning mode and Fig. 5.8 for the coupling mode disappear in Fig. 5.9, indicating a discernable effect of the system-bath coupling. While the weak system-bath coupling with $\lambda_c = \lambda_t = 2.1 \text{ cm}^{-1}$ cannot cause a pronounced vibrational relaxation effect on the time scale of 1000 fs, it produces some wave-packets features visible in the moderately system-bath coupling case but absent in the bath free case. For the bath-free conical intersection, the wave-packet features can be classified into two kinds: regular motion with vibrational frequencies of the coupling and the tuning mode, and numerous erratic oscillatory features which are indicative of chaotic motion. A tiny bath induced perturbation filters the small-amplitude irregular oscillations but has a negligible effect on the stable regular wave packet motion. This finding demonstrates that dissipative conical intersection is quite different from few-mode bath-free conical intersection, as pointed out in Ref. [18].

It is noted that one can also consider the full diabatic and adiabatic electronic coherences $P_{12}^{\text{di}}(t) = \text{tr}_S\{|\varphi_1\rangle\langle\varphi_2|\rho(t)\}$ and $P_{12}^{\text{ad}}(t) = \text{tr}_S\{|\tilde{\varphi}_1\rangle\langle\tilde{\varphi}_2|\rho(t)\}$ as well as the electronic coherence wave packets $\rho_{12}^{\text{di}}(Q_c, Q_t; Q'_c, Q'_t; t)$ and $\rho_{12}^{\text{ad}}(Q_c, Q_t; Q'_c, Q'_t; t)$ (see Eq. (3.44)). The symmetry of the initial wave-packet preparation and the system itself dictate that all those quantities are zero. However, this does not mean that electronic coherences are zero at the conical intersection, for example, the quantities $\text{tr}_S\{|\varphi_1\rangle\langle\varphi_2|x_c\rho(t)\}$ and $\text{tr}_S\{|\tilde{\varphi}_1\rangle\langle\tilde{\varphi}_2|x_c\rho(t)\}$ are non-zero. It is the interplay of multiple transfers between the electronic populations and coherences of the reduced density matrix $\rho(t)$ that dominates the wave-packet motions as shown in Figs. 5.7 and 5.8.

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Chapter 6*

Theory of femtosecond coherent double pump single molecule spectroscopy: Application to light harvesting complexes

In this chapter, we have developed a first principles method of dealing with femtosecond double-pump single-molecule signals of molecular aggregates by including vibrational modes with significant exciton-phonon coupling into the system Hamiltonian, and treating remaining intra- and inter-molecule vibrational modes as a bath. By taking the advantage of parallel architecture of GPU, we have efficiently implemented the algorithm on a GPU cluster. The application of our theory to the simulation of the single molecule signals of LHCII reveals that the oscillations in the signals are of vibronic origin, and the period of these oscillations depends significantly on the exciton-phonon coupling.

* This section published substantially as reference [11] shown in the List of Publications

6.1 Introduction

Femtosecond four wave mixing techniques have dramatically advanced our understanding of dynamics of complex molecular systems as compared to the traditional linear spectroscopy techniques [1]. Yet the signals measured in the ensemble experiments comprise of an incoherent sum of $\sim 10^{23}$ transients coming from individual molecule and are thus subject to the inhomogeneous broadening and dephasing which obscure the underlying (possibly coherent) individual evolution. The situation has changed since the advent of the single molecule spectroscopy through which we can gain invaluable insight into the structure and functioning of the photosynthetic pigment-protein complexes [2, 3, 4, 5, 6, 7]. In particular, recent fluorescence-detection single molecule spectroscopy experiments have permitted researchers to investigate long-lived electronic coherence in single LH2 complex [8]. This new fluorescence-detection single molecule spectroscopy has reached a temporal resolution of ~ 10 fs [9], and permits us to record in real time not only electronic populations and vibrational wavepackets, but also electronic coherences of the density matrices of individual molecules.

The simulation and the interpretation of femtosecond single molecule experiments imposes stringent requirements on the level of theoretical descriptions and necessitates a nonperturbative treatment of the exciton-exciton, exciton-phonon, or system-bath coupling. There exists several numerical methods in the literature: the HEOM approach [10, 11], the hierarchical approximation of the bath spectral density [12, 13], multiconfigurational time-depedent Hartree (MCTDH) methods [14, 15], the numerical renormalization group approach [16]. Yet, these numerically “exact” methods are extremely time consuming when applied to the simulation of single molecule spectroscopy of light harvesting systems with strong exciton-exciton and exciton-phonon coupling. A promising, computationally efficient approach to the description of dynamics of molecular aggregates with strong exciton-exciton and exciton-phonon coupling is based on the application of the Dirac-Frenkel time-dependent variational method to

the construction of the Davydov ansätze [17, 18, 19, 20]. In this chapter, we utilized the theoretical framework described in Section 3.3 to calculate the single molecule signals of LHCII. Specifically, all singly excited electronic states and vibrational modes with significant exciton-phonon coupling are incorporated into a system Hamiltonian and the ensuing system dynamics is treated using the Davydov D_1 ansatz. The remaining intra- and inter-molecular vibrational modes are treated as a heat bath and their effect is accounted for by lineshape functions. In Section 6.2, we described the parameters used in the construction of the model Hamiltonian matrix as well as exciton-phonon coupling strengths. We then discuss the response function $R(t)$ defined by Eq. (3.68), characterizing the coherent dynamics in the singly excited excitonic manifold in Section 6.3. In Section 6.4, the effects of the phonon bath, different polarizations of the pump pulses as well as static disorder on the single molecule signals of LHCII are investigated in detail.

6.2 Parameterization of the Hamiltonian and computational details

LHCII possesses a trimeric structure with each monomer containing eight Chla and six Chlb molecules [21]. In this chapter, we utilize a full 42×42 one exciton Hamiltonian with corresponding transition energies ϵ_m and J_{nm} taken from Ref. [22]. We explicitly consider 48 high frequency modes with frequencies ω_q and coupling strengths $\lambda_q = S_q \omega_q$ obtained from the best fitting of the experimental linear spectra [23, 24]. It should be noted that these represent some characteristic values, while the values used in the single molecule spectra should satisfy a certain distribution.

We set the transition dipole moment $\boldsymbol{\mu}_m$ according to the crystal structures (PDB ID: 1RWT [21]), and the best fit of the linear spectra yields the absolute values of transition dipole moments for Chla and Chlb to be 4.0 and 3.8 Debye, respectively.

The overdamped Brownian oscillator model accounts for the impact of the heat bath and is thus responsible for the temperature effects (dynamic disorder). According to Ref. [24], its spectral density (see Eq. (3.53)) is taken in the Drude form

$$D(\omega) = 2\lambda_0 \frac{\omega\gamma_0}{\omega^2 + \gamma^2} \quad (6.1)$$

with the parameters $\hbar\lambda_0 = 37 \text{ cm}^{-1}$ and $\hbar\gamma_0 = 30 \text{ cm}^{-1}$. Correspondingly, the lineshape function defined in Eq. (3.69) can be calculated analytically [1]

$$g(t) = \frac{\lambda_0}{\gamma_0} \{e^{-\gamma_0 t} + \gamma_0 t - 1\} \left(\cot\left(\frac{\hbar\gamma_0\beta}{2}\right) - i \right) + \frac{4\lambda_0\gamma_0}{\hbar\beta} \sum_{k=1}^{\infty} \frac{e^{-\nu_k t} + \nu_k t - 1}{\nu_k(\nu_k^2 - \gamma_0^2)} \quad (6.2)$$

where $\nu_k = \frac{2\pi}{\hbar\beta}k$ are the Matsubara frequencies. It is noted that the bath parameters were optimized to reproduce the temperature effects in ensemble measurements. Yet there is no guarantee that the same values of the bath parameters yield a good approximation to the single molecule bath spectral density, since the very notion of the temperature is questionable for a single molecule. We will therefore consider two models for the overdamped mode: one with the ensemble experiment parameters indicated above and the other one with no system-bath coupling.

We assume Gaussian envelopes for the pulses

$$E(t) = \exp\{-\Gamma^2 t^2\} \quad (6.3)$$

where $\Gamma = 2\sqrt{\ln 2}/\tau_p$, and the pulse duration τ_p is set to 15 fs in accordance with the experiment of Ref. [8]. Then the integration over t in Eq. (3.64) can be done analytically, with the result

$$S(\tau) \sim \text{Re} \int_0^\infty dt_1 A(\tau, t_1) R(t_1) \quad (6.4)$$

where

$$\begin{aligned} A(\tau, t_1) = & e^{-\Gamma^2 t_1^2/2} (e^{i\omega_1 t_1 + i\omega_2 t_1}) + e^{-\omega^2/(2\Gamma^2)} e^{i\Omega t_1} \times \\ & (e^{-\Gamma^2(\tau-t_1)^2/2} e^{-i(\phi-\omega\tau)} + e^{-\Gamma^2(\tau+t_1)^2/2} e^{i(\phi-\omega\tau)}) \end{aligned} \quad (6.5)$$

and

$$\Omega = (\omega_1 + \omega_2)/2, \quad \omega = (\omega_2 - \omega_1)/2. \quad (6.6)$$

where the frequencies of the two pump pulses ω_1, ω_2 are set to $\omega_1 = 15375 \text{ cm}^{-1}, \omega_2 = 14800 \text{ cm}^{-1}$, in accordance with the Chlb and Chla bands of the linear absorption spectra of LHCII.

The numerical evaluation of the single molecule signal necessitates the solution of thousands of differential equations (see Eq. (3.75)). We take the advantage of the parallel GPU architecture, and efficiently integrate the equation of motion for the variational parameters on a NVIDIA Tesla M2050 GPU with 448 processors and 2GB ECC-protected on-board memory. The memory and computational limitations can be circumvented by our newly developed algorithm, and the computation time for the time evolution of $S(\tau)$ up to 400 fs on a single GPU decreases to about 1 h.

6.3 Single molecule response functions

We first discuss the response function $R(t)$ defined in Eq. (3.68). It is composed of contributions from the term $e^{-g(t)}$, which accounts for the bath induced relaxation, and contributions from the coherent system dynamics. For the system part, we explicitly consider 42 singly excitonic states and 48 vibrational modes. The influence of exciton phonon coupling on the system dynamics can be explained as a polaron effect (see appendix E).

Fig. 6.1 displays the response function $R(t)$ and its power spectra $|R(\omega)|^2$ calculated for pure system Hamiltonian H_S . Panels (a), (b), (c) correspond to the cases of the exciton-phonon coupling strength S_q from [23, 24], $S_q/2$, and $S_q = 0$, respectively. While the peaks in the power spectra of panel (a), (b) characterize the electron-vibrational eigenvalues of H_S with

Figure 6.1 Response function $R(\tau)$ (left column) and its fourier transform $|R(\omega)|^2$ (right column) at zero system-bath coupling $\lambda = 0$ and for pump pulse polarization $\mathbf{e} \parallel \mathbf{Z}$. Panels (a)-(c) correspond to electron-phonon coupling strengths S_q [23, 24], $S_q/2$, and $S_q = 0$, respectively.

favorable Franck-Condon factors, those presented in panel (c) exhibit pure electronic eigenvalues. Comparisons of peak structures of $|R(\omega)|^2$ shown in panels (a-c) reveal no qualitative difference. It is thus conjectured that the peaks are of electronic origin, and the main effect of exciton-phonon coupling is to shift their positions and changes their shapes. The strongest

peaks of $|R(\omega)|^2$ in panel (a) are found to be located at 14820 and 15410 cm^{-1} , corresponding to the absorption maxima of Chla and Chlb band of LHCII.

Figure 6.2 Response function $R(\tau)$ (left column) and its fourier transform $|R(\omega)|^2$ (right column) for a heat bath with temperature 77 K and under pump pulse polarization $\mathbf{e} \parallel \mathbf{Z}$. Panels (a)-(c) correspond to electron-phonon coupling strengths S_q [23, 24], $S_q/2$, and $S_q = 0$, respectively.

The response function $R(t)$ in the left column of Fig. 6.1 exhibits fast oscillations with a period of ~ 2 fs superimposed with slower beatings on the timescale of several dozens of

femtoseconds and longer. These beating frequencies can be read out from the multi-frequency structure of $|R(\omega)|^2$: the three strongest peaks are positioned at 14640, 14820, and 15410 cm^{-1} (full exciton-phonon coupling S_q , panel (a)); 14860, 15000, and 15730 cm^{-1} ($S_q/2$, panel (b)); and 14920, 15100, and 15830 cm^{-1} ($S_q = 0$, panel (c)). The differences of the frequencies of the third and second peaks yield periods of 56, 46, and 46 fs, corresponding to the first maxima of $R(t)$: 53 fs (a), 47fs (b), and 44 fs (c). The second recurrence of $R(t)$, with an oscillation frequency around 250 fs correlating with the differences of the frequencies of the first and second peaks of $|R(\omega)|^2$, have smaller amplitudes.

We then study the bath effect on the response function $R(t)$. The response function $R(t)$ and its power spectra $|R(\omega)|^2$ computed at bath temperature 77 K are shown in Fig. 6.2. As presented in the right column of Fig. 6.2, the main effect of the bath is to broaden and shift the vibronic peaks of $|R(\omega)|^2$. $|R(\omega)|^2$ has three peaks, and they are located at 14640, 14800, and 15390 cm^{-1} (a); 14840, 15000, and 15710 cm^{-1} (b); and 14920, 15060, and 15810 cm^{-1} (c). The corresponding response functions exhibit damped oscillation on a time scale of ~ 300 fs. The positions of the first maxima of $R(t)$ are related to the frequency differences between the two largest peaks in $|R(\omega)|^2$, i.e., 57 fs and 590 cm^{-1} (a), 47 fs and 710 cm^{-1} (b), and 44fs and 750 cm^{-1} .

Fig. 6.3 displays the response function $R(t)$ and its power spectra $|R(\omega)|^2$ calculated at bath temperature 300 K. The general behavior of the response function is similar to that shown in Fig. 6.2, but with even shorter oscillation time scale of ~ 100 fs. $|R(\omega)|^2$ exhibits two broadened peaks at 14800 and 15360 cm^{-1} (a), 15000 and 15670 cm^{-1} (b), and 15060 and 15790 cm^{-1} (c). The frequency differences between the two peaks of $|R(\omega)|^2$ correspond to 60 (a), 50 (b), and 46 fs (c), in consistent with the position of the first hump of $R(t)$.

To summarize, this section presents the general behavior of the response function for the parameters retrieved from the ensemble experiments.

Figure 6.3 Response function $R(\tau)$ (left column) and its fourier transform $|R(\omega)|^2$ (right column) for a heat bath with temperature 300 K and under pump pulse polarization $e \parallel Z$. Panels (a)-(c) correspond to electron-phonon coupling strengths S_q [23, 24], $S_q/2$, and $S_q = 0$, respectively.

6.4 Single molecule signals

The simple expression in Eq. (6.5) tells us that the signal consists of the τ independent background and the τ dependent contribution with the latter delivering useful information on the

single molecule dynamics. In addition, the signal exhibits a cosine-like pattern when the relative phase ϕ of the two pump pulses is varied from 0 to 2π for any fixed τ . This means that the dependence of the signal on ϕ is trivial, and we thus set $\phi = 0$ in the simulation, resulting in $S(\tau) = S(-\tau)$.

The values of the parameters specifying the LHCII Hamiltonian have been optimized for the simultaneous interpretation of a number of ensemble experiments. As explained in Section 6.2, the parameters give some characteristic values, which should be sampled to generate specific single molecule signal. In the following part, we discuss how different realizations of the site energies, the electron-phonon coupling, the system-bath coupling, and the direction of the transition dipole moment, affect the single molecule signal.

Fig. 6.4 plots the single molecule signal $S(\tau)$ for different exciton-phonon coupling strengths. Panels (a), (b), and (c) correspond to cases of the Huang-Rhys factors S_q retrieved from Refs. [23, 24], $S_q/2$, and $S_q = 0$. The bath is specified by the lineshape function of Eq. (6.2) for $T = 77$ K (left column) and $T = 300$ K (right column). We assume that pump pulses are polarized along the Z axis of the laboratory frame.

The signals presented in Fig. 6.4 exhibit a single-frequency beatings, in a qualitative agreement with Ref. [8]. The oscillation period of ~ 58 fs in panel (a) correlates with frequencies differences of the pump pulses $\omega_1 - \omega_2$. Due to the decrease in the exciton-phonon coupling, the oscillation period also decreases: ~ 36 fs (panel (b)) and ~ 28 fs (panel (c)). In fact, the frequency of the oscillations of $S(\tau)$ can be easily determined by the difference between $\omega_2 = 14800 \text{ cm}^{-1}$ and the frequency of the rightmost peak of $|R(\omega)|^2$ in Figs. 6.2 and 6.3, as revealed by Eq. (6.4) which shows that the single molecule signal $S(\tau)$ is proportional to $R(\tau)e^{i\omega_2\tau}$. As shown in Fig. 6.4, the high frequency vibrational modes affect the signals significantly, and the beatings are of the mixed electronic-vibrational (vibronic) origin. It should be noted that recent 2D spectroscopic experiments on light harvesting systems also reveal that

Figure 6.4 Single molecule signal $S(\tau)$ for heat bath with temperatures 77 K (left column) and 300 K (right column). The pump pulse polarization is $e \parallel Z$. Panels (a)-(c) correspond to the electron-phonon coupling strengths S_q [23, 24], $S_q/2$ and $S_q = 0$, respectively.

the quantum coherences are of vibronic origin (see Refs. [25, 26]). In addition, the coherent oscillations in the single molecule signals last for ~ 300 fs at 77 K but only for ~ 100 fs at 300

K.

Figure 6.5 Single molecule signal $S(\tau)$ at system-bath coupling $\lambda = 0$. The pump pulse polarization is $e \parallel Z$. Panels (a)-(c) correspond to the electron-phonon coupling strengths S_q [23, 24], $S_q/2$ and $S_q = 0$, respectively.

It should be noted that the signals reported in Ref. [8] exhibit no visible damping on a time scale of ~ 400 fs. In order to address these differences, Fig. 6.5 shows the signals similar to those presented in Fig. 6.4, but calculated for zero system-bath coupling. It is found that the signals exhibit fast underdamped oscillations superimposed with the slower beatings, and oscillation periods of the slower beatings decrease with the decrease of the exciton-phonon coupling: ~ 250 fs (panel (a)), ~ 150 fs (panel (b)), ~ 120 fs (panel (c)). It is noted that experimental single molecule signals of LH2 (see Ref. [8]) exhibit the same undamped oscillations on the time scale of several hundreds of femtoseconds. We thus tentatively conclude that single molecule signals are almost not subject to bath induced relaxations on the femtosecond time

scale and thus reflect coherent system dynamics. Furthermore, the actual system-bath coupling should be significantly weaker, while the static disorder may have a more pronounced effect on the single molecule spectra.

Figure 6.6 Single molecule signal $S(\tau)$ for different pump pulse polarizations, the other system and bath parameters are the same as Fig. 6.4a

Next we consider the effect of the orientation of transition dipole moments. Fig. 6.6 shows $S(\tau)$ calculated at $T = 77$ K (a) and $T = 300$ K (b) for pump pulses polarized along the axis X, Y, and Z of the laboratory frame (with legends XX, YY, and ZZ, respectively) as well as the averaged signal. In general, the signals calculated for different polarizations as well as the averaged one exhibit similar oscillatory pattern, but with different amplitudes of the peaks. The fact that the signals are not sensitive to the specific molecular orientation can be explained as follows: the layout of transition dipole moments in LHCII has an isotropic pattern, while LH2, on the other hand, has a double-ring structure. As a result, LHCII has a low polarization sensitivity, while the single-molecule signals of LH2 should exhibit strong anisotropy (see Ref. [8]).

Finally, we analyze the effect of static disorder (spread in the site energies) on the single molecule signals. Static disorder is induced by the slow fluctuations in pigment structures and their protein environments, and contributes to the inhomogeneous broadening in ensemble experiments. A single molecule signal involves a specific realization of the site energies.

Figure 6.7 (a) Three representative single molecule signals $S(\tau)$ for heat bath with temperature 77 K. (b) Distribution of the oscillation period T for 200 samplings. The other parameters are the same as Fig. 6.4a.

Fig. 6.7a shows three representative single molecule signals $S(\tau)$ of LHCII at 77 K. The samples correspond to random realizations of the uncorrelated diagonal Gaussian disorder for the site energies (standard deviation of 80 cm^{-1} for Chls a and 104 cm^{-1} for Chls b). All three signals exhibit similar oscillatory patterns, but with different oscillation periods. To characterize these differences, we have retrieved the oscillations periods from 200 samplings of $S(\tau)$. The resulting histogram shown in Fig. 6.7b presents a broad distribution of oscillation periods ranging from $\sim 40 \text{ fs}$ to $\sim 90 \text{ fs}$ with a maximum near 58 fs. This broad spread in the oscillation period reflects a large structural and electronic disorder that is caused by heterogenous local protein environment (see Refs. [27, 28]). It is noted that the spread of periods reported in Ref. [8] is even broader.

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Chapter 7*

Theory of two dimensional electronic spectroscopy and its application to the study of energy transfer processes in LHCII

In this chapter, we have developed a novel theoretical framework to calculate non-linear four wave-mixing signals. Simulated 2D spectra of model J aggregates show that a single peak structure resembling that of a two level system dominates the general 2D patterns for weak diagonal (off-diagonal) exciton phonon coupling. While a multi-peak vibronic structure accompanied by the population relaxation from high to low energy regions emerges in the presence of large diagonal (off-diagonal) exciton phonon coupling. In addition, the main effect of the temperature is to broaden the peaks. As an application of our theory to the energy relaxation and dephasing in realistic systems, we study the energy transfer processes in the LHCII complex through the calculation of 2D spectra by using the Davydov D_1 trial state. In general, we reproduce the diagonal peaks and cross-peaks as well as measured lineshapes. We also found a long lived intermediate state which is observed in the experimental 2D spectra. Furthermore, the oscillatory behavior of the cross peak as a function of population time reveals the existence of coherent energy transport between different excitonic states within Chlb and Chla bands.

* This section published partially as reference [5] shown in the List of Publications

7.1 Introduction

The emergence of 2DES techniques with femtosecond resolution has dramatically broaden our knowledge of complicated energy and charge transport processes in a variety of multichromophoric complexes and aggregates. The experimental 2DES setup involves three broad-band pulses separated by two time delays, and the measured signal after interacting with system provides direct information about the exciton states as well as the energy relaxation between these states. In order to facilitate the analysis of the 2D spectra, various theoretical frameworks have been proposed. The theoretical description of 2D spectra involves the treatment of the third order polarization $P^{(3)}(t)$, which can be expressed as a triple time integral involving the third order response functions by treating the field-matter interactions perturbatively.

We have developed a new approach using the Davydov trial states that can efficiently handle the 2D spectra calculation [1, 2]. Conceptually, our approach for describing and analyzing the optical response of a molecular aggregate is to include high frequency intramolecular phonons into the system Hamiltonian, while other nuclear degrees of freedom of the environment which are responsible for phenomenological relaxation rates are treated as a heat bath. In addition, this theory can cover broad parameter regimes, from intermediate to strong electron-phonon and electron-electron coupling strengths. In Section 7.2, we will utilize the theoretical framework introduced in Appendix F to systematically study the 2D spectra of a one dimensional aggregate characterized by the Holstein model with various control parameters. Specifically, 2D spectra of a J aggregate in the presence of simultaneous diagonal/off-diagonal exciton-phonon coupling will be calculated via the multi- D_2 ansatz as it provides a reliable and computationally efficient description of polaron dynamics for all the parameter regimes (see discussion in Section 4.2.1). As a comparison, we will present benchmark calculations of 2D spectra by applying the numerically exact HEOM method in Section 7.3. Finally, as an example, we will investigate the energy transfer processes in LHCII through 2D electronic spectra calcu-

lated by the theory described in Section 3.4. As the exciton-phonon coupling Hamiltonian is site-diagonal form, the Davydov D_1 ansatz is used in the calculation.

7.2 Simulation of 2D spectra by Multi- D_2 Ansatz

The procedure for simulation of 2D spectra via the Multi- D_2 ansätze has been described in detail in Section 3.4 and Appendix F. In this section, we study the effect of various physics parameters (the transfer integral J , phonon bandwidth W , diagonal and off-diagonal exciton-phonon coupling strength g and ϕ) on the 2D spectra of a molecular ring of 10 sites calculated by the Multi- D_2 ansätze. The model system is a J aggregate with the tangential (head-to-tail) configuration for the transition dipoles. For the secondary bath describing the excitonic relaxation and dephasing effect, its spectral density as defined in Eq. (3.53) is taken to be the Drude form

$$D(\omega) = 2\eta \frac{\gamma\omega}{\omega^2 + \gamma^2} \quad (7.1)$$

The corresponding lineshape function (Eq. (3.69)) can be expressed as

$$g(t) = \frac{\eta}{\gamma} \cot \frac{\gamma\beta}{2} [e^{-\gamma t} + \gamma t - 1] - i \frac{\eta}{\gamma} [e^{-\gamma t} + \gamma t - 1] + \frac{4\eta\gamma}{\beta} \sum_{n=1}^{\infty} \frac{e^{-\nu_n t} + \nu_n t - 1}{\nu_n(\nu_n^2 - \gamma^2)} \quad (7.2)$$

where $\nu_n = 2\pi n/\beta$ are the Matsubara frequencies. The parameters $\eta = 0.1$, $\beta = 5$, and $\gamma = 0.02$ are set in our calculation.

We first present calculated 2D spectra of the molecular ring for the diagonal exciton-phonon coupling case. Fig. 7.1 displays the 2D spectra for diagonal coupling strength $g = 0.2$ at several population times $T = 0, 20, 40$. Among other parameters are the transfer integral $J = 0.5$, the bandwidth $W = 0.5$, the off diagonal coupling strength $\phi = 0$, and the inverse temperature $\beta = 5$. At $T = 0$, the signal exhibits a single diagonal peak located at $\omega_\tau = \omega_t = -1.04$, resembling that of a two level system as the diagonal coupling is weak. In addition, the shape

is elliptical and elongated along the diagonal direction. With the increase of T , the axis of the ellipse rotates clockwise and the shape of the peak becomes more rounded. Due to the energy relaxation process, the splitting of the absorption and the emission peak is also clearly observed (see the shift of the strongest peak down from the diagonal at population time $T = 40$).

Figure 7.1 2D spectra of a molecular ring with 10 sites for diagonal coupling strength $g = 0.2$ at population times $T=0, 20, 40$, respectively. Other parameters are $J=0.5$, $W=0.5$, $\phi = 0$ and $\beta = 5$

Fig. 7.2 depicts the 2D spectra of the molecular ring calculated with the intermediate diagonal coupling strength $g = 0.5$. As shown in Fig. 7.2, there appears a vibronic multi-peaks structure due to the strong exciton-phonon coupling. With the increase of the population time, the shape as well as the intensity of diagonal and cross-peaks changed. At $T = 0$, the strongest

absorption and emission peaks are located at $\omega_\tau = \omega_t = -2.68$. The population relaxation from high to low energy regions with lower ω_t for larger values of T can be clearly observed (compare $T = 0, 20, 40$ cases).

Figure 7.2 2D spectra of a molecular ring with 10 sites for intermediate diagonal coupling strength $g = 0.5$ at population times $T=0, 20, 40$, respectively. Other parameters are $J=0.5$, $W=0.5$, $\phi = 0$ and $\beta = 5$

We also study the effect of temperature on 2D spectra of molecular ring. Fig. 7.3 shows the 2D spectra of the molecular ring at population time $T = 20$ and diagonal coupling strength $g = 0.5$ for several bath temperature $\beta = 50, 20, 5, 2$, respectively. The other parameters $J=0.5$, $W=0.5$, $\phi = 0$, and $N=10$ are set. It is found that the main effect of temperature is to broaden the peak shapes, and with the increase of the temperature the individual vibronic state cannot be resolved due to the large spectral overlap.

Figure 7.3 2D spectra of a molecular ring with 10 sites for diagonal coupling strength $g = 0.5$ at a population time $T=20$ for several bath temperatures $\beta = 50, 20, 5, 2$, respectively. Other parameters are $J=0.5$, $W=0.5$ and $\phi = 0$

Finally, we also calculate the 2D spectra of the molecular ring for the off-diagonal coupling case. 2D spectra of the 10-site ring are shown in Fig. 7.4 for the case of $\phi = 0.1$ (left panel) and $\phi = 0.4$ (right panel). For simplicity, other parameters $J = g = W = 0$ and $\beta = 5$ are set. We first study the weak off diagonal coupling case $\phi = 0.1$. The 2D spectra are shown in panels (a-c) of Fig. 7.4, corresponding to the population times $T = 0, 20$, and 40 , respectively. Similar to the diagonal coupling case, the signal exhibits a single diagonal peak located at $\omega_\tau = \omega_t = -0.08$, and is elongated along the diagonal direction. The peak becomes more rounded with the increase of the population time. We then consider the strong off-diagonal coupling case $\phi = 0.4$, as displayed in the right panel of Fig. 7.4 for several population times $T = 0, 20$, and 40 . In general, a pronounced vibronic multi-peak structure appears in the 2D

Figure 7.4 2D spectra of a molecular ring with 10 sites for off-diagonal coupling cases: $\phi = 0.1$ (left column) and $\phi = 0.4$ (right column). The population times are $T = 0, 20, 40$, respectively. We set other parameters $g = W = J = 0, \beta = 5$.

spectra due to the strong exciton phonon coupling. It is also found that the shapes and strengths of the peaks change with the population time, and the population relaxes from the high to low energy regions with lower ω_t for larger values of T , as demonstrated in Figs. 7.4d, 7.4e, and 7.4f.

7.3 Simulation of 2D spectra by the HEOM method

Figure 7.5 2D spectra of a molecular ring with 5 sites obtained by HEOM method for off-diagonal coupling strength $\phi = 0.1$ at population times $T=0, 20, 40$, respectively. Other parameters $g = W = J = 0, \beta = 5$ are set.

The simulation of 2D spectra with the HEOM method is described in Appendix G. As benchmark calculations, here we only present the 2D spectra of a molecular ring of 5 sites

for an off-diagonal exciton-phonon coupling case. Fig. 7.5 shows the 2D spectra for rather weak off-diagonal coupling strength $\phi = 0.1$ at three population times $T = 0, 20, 40$. Other parameters are $g = W = J = 0$, $\beta = 5$ and $N = 5$. As usual, the signal has a peak structure similar to that of the two level system. With the increase of population time T , a slight Stokes shift due to the population relaxation can be observed. Fig. 7.6 displays the 2D spectra calculated at stronger off-diagonal coupling strength $\phi = 0.3$. The multiple vibronic peaks can be clearly seen, and population relaxation from high energy states to low energy states is also demonstrated for a long population time $T=40$.

Figure 7.6 2D spectra of a molecular ring with 5 sites obtained by HEOM method for off-diagonal coupling strength $\phi = 0.3$ at population times $T=0, 20, 40$, respectively. Other parameters $g = W = J = 0, \beta = 5$ are set.

Figure 7.7 Simulated and experimental [3] absorption spectra of LHCII at room temperature.

7.4 Energy transfer processes in LHCII studied by 2D electronic spectra

As a simple test of our approach, we start by the calculation of the LHCII absorption spectrum, which is given by the real part of the Fourier transformation of the linear response function $R(t)$ of Eq. (3.68) with an averaged geometrical factor (see Appendix D for the site energies, electronic couplings, Huang-Rhys factors, and transition dipole moments for LHCII complexes). Additionally, we account for the static disorder (site inhomogeneity), which is modeled as an uncorrelated diagonal Gaussian disorder (standard deviation of 80 cm^{-1} for Chls a and 104 cm^{-1} for Chls b). Fig. 7.7 shows the simulated and experimental [3] absorption spectra of the

Q_y band of LHCII at room temperature. The simulated spectrum exhibits two peaks corresponding to the absorption maxima of the Chla ($\sim 14800 \text{ cm}^{-1}$) and Chlb ($\sim 15375 \text{ cm}^{-1}$) bands and agrees reasonably well with recently and previously [4, 5, 6] measured spectra.

Figure 7.8 Simulated 2D spectra (absorptive part) of the LHCII complex calculated using Davydov D_1 trial state for the population times 0 fs, 300 fs, 600 fs, and 2500 fs, respectively, at temperature 298 K

Next we turn to the calculation of 2D spectra of the LHCII complex using the Davydov D_1 trial state. Fig. 7.8 shows simulated 2D spectra (absorptive part) of the LHCII complex for several population times at temperature 298 K. We divide the raw data by a constant to restrict the amplitude to be on 0-1 range for the ease of comparison. All 2D spectra exhibit two main features. Firstly, diagonal peaks correspond to the Chlb and Chla bands in the absorption spectra. Secondly, the amplitude of off-diagonal peak ($\omega_\tau = 15375 \text{ cm}^{-1}$, $\omega_t = 14800 \text{ cm}^{-1}$) oscillates

with population times, indicating the coherent energy transfer from the Chlb band to the Chla band. In a typical 2D spectrum, a cross peak appearing at the intersection of pump frequency ω_τ and probe frequency ω_t can be interpreted as the indication of energy transfer from the state with resonant frequency ω_τ to the state with resonant frequency ω_t . In addition, the amplitude changes of the cross peak denote the population change of an acceptor state in an EET process. Although individual exciton state can not be resolved due to the homogenous broadening, the simulated 2D spectra as a whole reproduce the diagonal and the cross peaks as well as the shapes of the measured ones [3]. It should be noted that diagonal peaks as well as quantum coherences are missing in the Chla band region in the experimental 2D spectra (See Ref. [3]) because the first two pump pulses do not spectrally cover the Chla bands. It is also found that the cross peak becomes narrower and more rounded at a longer population time, which is again consistent with the measurement. In particular, let us concentrate on the 2D spectra at population time $T = 300$ fs. As is shown, there is a relatively high intensity at intersection $(\omega_\tau, \omega_t) = (15300, 15000)$, while it is much weaker at intersection $(\omega_\tau, \omega_t) = (15500, 15000)$, indicating that an exciton state at 15000 cm^{-1} is populated from state corresponding to 15300 cm^{-1} at a time scale of 300 fs. It is also found that the 15000 cm^{-1} state exists even at $T = 2.5$ ps showing its long life time feature, which is also observed in the experimental 2D spectra.

The signature of the coherent EET process can be traced by the observed oscillation of off-diagonal peaks in the 2D spectra of LHCII complex [7]. Fig. 7.9 displays the amplitude of the cross peak as a function of the population time. When we calculate the peak amplitude, we average over a circle of radius $\Delta\omega = 5 \text{ cm}^{-1}$ with the center at intersection $(\omega_\tau, \omega_t) = (15375, 14800)$ and normalize data with respect to the value at $T = 0$ fs. As is shown in Fig. 7.9, the cross peak oscillates with a frequency of approximately 50 fs, in reasonable agreement with a frequency 58fs corresponding to the difference between the Chlb and the Chla band, indicating the coherent energy transfer between different excitonic states within the Chlb and Chla bands.

Figure 7.9 Amplitude of the cross peak of the 2D spectra for the LHCII complex as a function of population time

Finally, we study the effect of the bath temperature on the calculated 2D spectra. Fig. 7.10 shows the 2D spectra of the LHCII complex for the population time $T = 300$ fs at several bath temperatures, 25 K, 77 K, 150 K, 298 K. At low temperature, we can clearly see multiple peaks corresponding to the different excitonic states within the Chlb and Chla band. With the increase of temperature, the multiple peaks are broadened due to the large spectral overlap as expected.

Figure 7.10 Simulated 2D spectra of LHCII complex for several bath temperatures at population time $T=300$ fs

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Chapter 8

Conclusions

In summary, this thesis seeks to provide a thorough investigation of energy transfer processes in light harvesting systems and to corroborate spectroscopic measurements as reported in the literature. By undertaking a comprehensive computational studies ranging from model Hamiltonian to realistic systems, we have accurately described the polaron dynamics in the simultaneous presence of diagonal and off-diagonal exciton-phonon coupling, uncovered the intricate nonadiabatic wave-packet dynamics at a conical intersection, reproduced the pronounced oscillations of vibronic origin in measured femtosecond single molecule spectra as well as revealed the coherent energy transfer between excitonic states within Chlb and Chla bands in LHCII.

Understanding photosynthesis, one of the most essential biological processes in nature, has been a long term pursuit of mankind as solar energy provides a large-scale, carbon-neutral source of power. Some organisms have evolved over millions of years to develop the apparatus to efficiently harvest sunlight. However, the underlying mechanisms for the intricate processes starting from the light absorption, excitation energy transfer, to charge separation remain unknown. It is generally conjectured that the intricate excitonic interference allows the system to search among various pathways the optimal channel to direct the excitation energy to the RCs. In this thesis, we have extensively elucidated the molecular level understanding of factors affecting the energy transfer in light harvesting systems. A number of state-of-the-art numerical techniques and fast algorithms have been developed forming a formidable arsenal to attack the difficult, unresolved problems of energy transfer in light harvesting systems.

Starting with the one-dimensional Holstein polaron with simultaneous diagonal and off-diagonal exciton-phonon coupling, we have developed a general theory of treating polaron dynamics using the time-dependent multiple Davydov trial states, i.e., a superposition of the D_1 or the D_2 ansätze, referred to the multi- D_1 or multi- D_2 ansätze. Our goal is to provide an efficient and accurate description of polaron dynamics in the Holstein molecular crystal model, and to shed insight on the complex interplay between the exciton (electron) and its surrounding phonon cloud, and their intricate role on the energy transfer behaviors. By quantifying how faithfully the multiple Davydov trial states follow the Schrödinger equation, it is found that the accuracy of simulated dynamics obtained with the multi- D_1 and multi- D_2 ansätze has been dramatically enhanced compared to that with the usual single D_1 and D_2 trial states. With the increase of the multiplicity, the multi- D_1 and multi- D_2 ansätze can provide a nearly exact description of the underlying many-body dynamics for a broad parameter regimes. We have also formulated a novel HEOM formalism, expressed in terms of discretized phonon modes instead of the Matsubara expansion, that is capable of treating exciton-phonon coupling in a nonperturbative way and valid at any temperatures. Our simulations show that strong exciton-phonon coupling tends to localize the exciton, while the transfer integral leads to the acceler-

ation of exciton transport. Interestingly, an abnormal self trapping of exciton appears with the increase of off-diagonal coupling strength, indicating the complicated interplay of transfer integral and off-diagonal coupling. The application of the Davydov D_1 ansatz to engineered 1D LH2 nano-arrays reveals superdiffusive characteristics of exciton transport, which is consistent with fluorescence measurements.

Through a comprehensive study of electronic and vibrational dynamics of a two state two-mode conical intersection in pyrazine which is bilinearly coupled to a bath of harmonic oscillators, we uncovered many intriguing facets of nonadiabatic wave-packet dynamics at a conical intersection. We solved the equation of motion for the reduced density matrix of the system with HEOM method by using the GPU technology, which provides a numerically exact description of system dynamics for arbitrary system-bath coupling strengths and bath memory relaxation times. The simulation results show that even weak coupling to the bath will effectively quench the chaotic features of the intrinsic dynamics of an isolated two-mode conical intersection. While the population of upper adiabatic excited state completely decays to the lower potential energy surface on sub-picosecond time scales due to the coupling to the environment, the population of the diabatic upper state exhibits long-lived quantum beating induced by the coherent motion of the tuning mode. Interestingly, a counterintuitive enhancement of the amplitude of vibrational motion of the tuning mode is observed for certain values of the system-bath coupling, which reflects the exceptionally pronounced nonseparability of vibrational motions of the coupling and tuning modes of the conical intersection that leads to the dedamping of vibrational motion of the tuning mode. Furthermore, the time-dependent probability density of individual vibrational mode exhibits propagation patterns following the shape of the potential energy surface, which is funneled to the lower adiabatic surface through the conical intersection. The present study will shed light on the future first-principles simulations of femtosecond time-resolved four-wave mixing spectra, for example, pump-probe and photo-echo spectroscopy, 2DES or femtosecond resonant Raman spectroscopy.

Single molecule spectroscopy provides responses which are free of inhomogeneous (ensemble) averaging and broadening effects. Inspired by recent experiments of the van Hulst group in which the femtosecond time-resolved double-pump single molecule technique has been extended to investigate the long-lived coherences in individual LH2 light-harvesting complex, we have developed a theoretical framework for the interpretation and computational simulation of femtosecond single molecule spectra. As an example, we have applied the theoretical formalism to simulate femtosecond double-pump signals of single LHCII complex. The LHCII complex was chosen because an empirical parametrized model Hamiltonian is available for this complex. The explicitly treated system is described by a Frenkel exciton model involving 42 electronic states and 48 high-frequency vibrational modes. Effects of the low frequency vibrational modes and of the solvent environment are phenomenologically described in the Brownian oscillator model with a Drude spectral function. The dynamics of the system is treated variationally with the Davydov D_1 ansatz. The numerical simulations, which are the first for femtosecond single molecule spectra, reproduce pronounced oscillations of vibronic origin in qualitative agreement with the experimental observations for LH2. Our results indicate that the microscopic models derived from the analysis of ensemble experiments are insufficient to reproduce the wealth of data obtained in single molecule experiments. It seems that the existing models overestimate the strength of system-bath coupling (homogeneous broadening) and underestimate, on the other hand, the effects of quasi-static disorder (inhomogeneous broadening). The single molecule spectra measured in the van Hulst group involves weak laser pulses, which provides instantaneous information on the electronic coherences of the system density matrix. The use of strong laser pulses can simultaneously detect the electronic coherences and populations. The development of a general theory of femtosecond single molecule spectroscopy thus requires a nonperturbative treatment of the field-matter interactions.

Recent technological advances have enabled the 2DES technique to be a convenient tool to study the energy transfer processes in light harvesting complexes. We have developed a novel theoretical framework to calculate 2DES, which integrates the Davydov trial states into

nonlinear response function formalisms. Specifically, we incorporate vibrational modes that are strongly coupled to the exciton into the system Hamiltonian, and the rest of intramolecular and environmental modes are treated as a bath. While the former is described by the Davydov ansatz, the latter is taken into account through nonlinear response function theory. The application of our theory to the simulation of 2DES of a model J aggregate shows that the 2D signal exhibits single peak features similar to that of a two level system for weak diagonal (off-diagonal) exciton-phonon coupling, while a multi-peak vibronic structure appears in 2DES with accompanying cascading energy relaxation as a function of waiting time for large diagonal (off-diagonal) exciton-phonon coupling. For the first time, we utilize the theory to study the energy relaxation and dephasing process in a realistic light harvesting system (LHCII) with a model system Hamiltonian comprising of 42 electronic states and 48 high-frequency vibrational modes. In general, measured diagonal and cross-peaks as well as their shapes are reproduced by this theory. Furthermore, the coherent energy transfer between different excitonic states within Chlb and Chla bands is revealed from the oscillation of cross peak as a function of waiting time.

Chapter 9

Recommendations for future work

In this thesis, we have systematically studied the energy transfer processes in light harvesting systems by applying fully quantum mechanical models of great sophistication and the state-of-the-art GPU acceleration technology. Here, we will comment on possible areas of improvement on the present theoretical studies and suggest some likely directions for future expanded research.

9.1 Nonequilibrium dynamics of the Holstein polaron driven by an external electric field

In OSC, photoinduced excitons migrate to the donor-acceptor interface, where under strong electric field, they further dissociate into charge carriers to be transported to respective electrodes. We thus plan to study nonequilibrium dynamics of the Holstein polaron driven by an external electric field in order to provide a microscopic description of charge transport in OSC. Theoretical studies of the polaron motion in a strong but constant electric field started with the seminal work by Thornber and Feynman, who, using a path-integral approach, discovered that the electron acquires a constant velocity due to the emission of phonons [1]. It is recently suggested by some theoretical studies that an accurate treatment of quantum effects is essential to obtain proper electric field dependence of the drift velocity in the presence of large electric fields. Moreover, Bloch oscillations (BO) represent a fundamental physical phenomenon, which states that a single particle exhibits coherent oscillation with Bloch time when exposed to a uniform external electric field and a periodic potential. A full quantum mechanical description of the BO damping in the presence of a dissipative medium is still elusive in the literature. By choosing the Holstein Hamiltonian as one of the simplest model systems capable to capture the complex interplay between the electron and the accompany phonon cloud, we plan to investigate field-induced acceleration of a polaron with energy dissipation induced by inelastic phonon scattering using the multiple Davydov trial states and the HEOM methods. Special attention will be paid to the effect of electron-phonon coupling and the external field on the steady-state current as well as the time evolution of the traveling polaron.

9.2 Probing charge transfer processes by means of 2DES

With recent technological advances, the technique of 2DES has been frequently employed to probe electron and charge transfer processes in organic solar cells as well as biological photo-

synthetic light harvesting complexes. The advantages of 2DES are twofold. First, it detects not only populations but also the coherences of the density matrix. Second, it allows the selective measurements of excitation pathways based on the phase matching conditions. In this part, we plan to extend the theoretical framework based on the Davydov ansätze (see Section 7.1) to include the contribution of excited state absorption. The newly developed theory as well as the HEOM method will be applied to calculate the 2DES in model systems related to the charge transfer processes. Starting with the simplest model that is often applied to study charge transfer processes, i.e., one in which the electronic states are coupled to a primary intramolecular vibrational mode which is in turn coupled to secondary bath modes, we will investigate the role the underdamped intramolecular vibrational mode plays in the charge transfer process, as well as the effect of secondary bath modes on the dephasing and relaxation processes. Subsequently, we will extend the methodologies to account for multiple underdamped vibrational modes and apply our theory to charge transfer processes in realistic light harvesting systems with environments involving overdamped Drude and underdamped Brownian modes as obtained by molecular dynamics simulations.

9.3 Molecular level mechanistic study on the NPQ process in green plant

As one of the most important photo-protective mechanisms, NPQ plays a central role in tuning the photosynthesis process in green plants. Despite considerable experimental and theoretical efforts have devoted to the molecular level understanding of the NPQ process, the unanimous consensus regarding its fundamental mechanisms is still missing. The first step of elucidating the mechanisms of NPQ involves the determination of quenching sites and their specific roles in quenching the fluorescence. Our hypothesis assumes that the most likely site of quenching is composed of either closely spaced chlorophyll molecules of the LHCII or hetero-dimers/trimers of chlorophyll and carotenoid molecules [2, 3, 4]. Formation of such quenching species may be a result of the reorganization of PSII in high light. The possibility of

formation of such dimers/trimers of chlorophyll molecules either within single LHCII trimers or at the interface between different LHCII trimers upon the speculated aggregation and its role in quenching the fluorescence will thus be probed in detail. In addition, it is found that charge transfer states acting as quenchers may also be formed by chlorophyll dimers/trimers [5, 6]. As a result, detailed quantum chemistry calculations will be performed to accurately characterize their role in comparison with excitonic states. Given the complexity of the system and presently wide range of potential mechanisms, we plan to adopt a step-by-step multiscale approach with increasing sophistication. We start with a simple model to be subjected to MC simulations for studying the excitation energy decay in trimeric LHCII systems, both in isolated and in crystalline forms, along different possible pathways such as fluorescence, energy transfer, and non-radiative decay. This model will further pave the way to the development of a more complex framework of hybrid coarse-grained and fine-grained model to mimic the in vivo dynamics of PS-II supercomplexes, under NPQ conditions. By building up sophisticated models starting from simple systems to the most complicated in vivo supercomplexes, we plan to achieve a full description of the fluorescence lifetime dynamics and thus corroborate/rationalize the experimental fluorescence NPQ data reported in the literature.

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Appendices

Appendix A The multi-D₁ trial state

The individual energy term can be calculated as follows

$$\langle D_1^M(t) | H_{ex} | D_1^M(t) \rangle = -J \sum_{i,j} \sum_n^M \psi_{j,n}^*(t) [\psi_{i,n+1}(t) S_{j,n;i,n+1} + \psi_{i,n-1}(t) S_{j,n;i,n-1}], \quad (\text{A-1})$$

$$\langle D_1^M(t) | H_{ph} | D_1^M(t) \rangle = \sum_{i,j} \sum_n^M \psi_{jn}^* \psi_{in} \sum_q \omega_q \lambda_{jnq}^* \lambda_{inq} S_{ji}, \quad (\text{A-2})$$

$$\langle D_1^M(t) | H_{ex-ph}^{diag} | D_1^M(t) \rangle = -g \sum_{i,j} \sum_n^M \psi_{jn}^* \psi_{in} \sum_q \omega_q (e^{iqn} \lambda_{inq} + e^{-iqn} \lambda_{jnq}^*) S_{ji}, \quad (\text{A-3})$$

$$\begin{aligned} & \langle D_1^M(t) | H_{ex-ph}^{o.d.} | D_1^M(t) \rangle \\ &= \frac{1}{2} \phi \sum_{n,q} \sum_{i,j}^M \omega_q S_{j,n;i,n+1} \psi_{j,n}^*(t) \psi_{i,n+1}(t) [e^{iqn} (e^{iq} - 1) \lambda_{i,n+1,q}(t) + e^{-iqn} (e^{-iq} - 1) \lambda_{jnq}^*(t)] \\ &+ \frac{1}{2} \phi \sum_{n,q} \sum_{i,j}^M \omega_q S_{j,n;i,n-1} \psi_{j,n}^*(t) \psi_{i,n-1}(t) [e^{iqn} (1 - e^{-iq}) \lambda_{i,n-1,q}(t) + e^{-iqn} (1 - e^{iq}) \lambda_{jnq}^*(t)], \end{aligned} \quad (\text{A-4})$$

where the Debye-Waller factor is formulated as

$$\begin{aligned}
 S_{ij} &= \exp \left\{ \sum_q \lambda_{iq}^* \lambda_{jq} - \frac{1}{2} (|\lambda_{iq}|^2 + |\lambda_{jq}|^2) \right\}, \\
 S_{j,n;i,n+1} &= \exp \left\{ \sum_q \lambda_{jnq}^* \lambda_{i,n+1,q} - \frac{1}{2} (|\lambda_{jnq}|^2 + |\lambda_{i,n+1,q}|^2) \right\}, \quad (\text{A-5})
 \end{aligned}$$

The Dirac-Frenkel variational principle leads to equations of motion including the first equation of motion

$$\begin{aligned}
 & -i \sum_i^M \dot{\psi}_{in} S_{ki} - \frac{i}{2} \sum_i^M \psi_{in} \sum_q \left(2\lambda_{knq}^* \dot{\lambda}_{inq} - \dot{\lambda}_{inq} \lambda_{knq}^* - \lambda_{inq} \dot{\lambda}_{knq}^* \right) S_{k,i} \\
 & = J \sum_i^M (\psi_{i,n+1} S_{k,n;i,n+1} + \psi_{i,n-1} S_{k,n;i,n-1}) - \sum_i^M \psi_{in} \sum_q \omega_q \lambda_{knq}^* \lambda_{inq} S_{ki} \\
 & + g \sum_i^M \psi_{in} \sum_q \omega_q (e^{iqn} \lambda_{inq} + e^{-iqn} \lambda_{knq}^*) S_{ki} \quad (\text{A-6}) \\
 & - \frac{1}{2} \phi \sum_i^M \sum_q \omega_q \psi_{i,n+1}(t) [e^{iqn} (e^{iq} - 1) \lambda_{i,n+1,q}(t) + e^{-iqn} (e^{-iq} - 1) \lambda_{knq}^*(t)] S_{k,n;i,n+1} \\
 & - \frac{1}{2} \phi \sum_i^M \sum_q \omega_q \psi_{i,n-1}(t) [e^{iqn} (1 - e^{-iq}) \lambda_{i,n-1,q}(t) + e^{-iqn} (1 - e^{iq}) \lambda_{knq}^*] S_{k,n;i,n-1},
 \end{aligned}$$

and the second equation of motion

$$\begin{aligned}
 & -i \sum_i^M \psi_{kn}^* \psi_{in} \lambda_{inq} S_{ki} - i \sum_i^M \psi_{kn}^* \psi_{in} \dot{\lambda}_{inq} S_{ki} - \frac{i}{2} \sum_i^M \psi_{kn}^* \psi_{in} \lambda_{inq} S_{k,i} \\
 & \sum_p \left(2\lambda_{knp}^* \dot{\lambda}_{inp} - \dot{\lambda}_{inp} \lambda_{knp}^* - \lambda_{inp} \dot{\lambda}_{knp}^* \right) = J \sum_i^M \psi_{k,n}^* (\psi_{i,n+1} \lambda_{i,n+1,q} S_{k,n;i,n+1} + \psi_{i,n-1} \lambda_{i,n-1,q} S_{k,n;i,n-1}) \\
 & - \sum_i^M \psi_{kn}^* \psi_{in} \lambda_{inq} S_{ki} \left(\omega_q + \sum_p \omega_p \lambda_{knp}^* \lambda_{inp} \right) + g \sum_i^M \psi_{kn}^* \psi_{in} \omega_q e^{-iqn} S_{ki} \\
 & + g \sum_i^M \psi_{kn}^* \psi_{in} \lambda_{inq} \sum_p \omega_p (e^{ipn} \lambda_{inp} + e^{-ipn} \lambda_{knp}^*) S_{k,i} \\
 & - \frac{1}{2} \phi \sum_i^M \omega_q \psi_{kn}^* [\psi_{i,n+1} e^{-iqn} (e^{-iq} - 1) S_{k,n;i,n+1} + \psi_{i,n-1} e^{-iqn} (1 - e^{iq}) S_{k,n;i,n-1}] \\
 & - \frac{1}{2} \phi \sum_p \sum_i^M \omega_p \psi_{k,n}^* \psi_{i,n+1} [e^{ipn} (e^{ip} - 1) \lambda_{i,n+1,p} + e^{-ipn} (e^{-ip} - 1) \lambda_{knp}^*] \lambda_{i,n+1,q} S_{k,n;i,n+1} \\
 & - \frac{1}{2} \phi \sum_p \sum_i^M \omega_p \psi_{k,n}^* \psi_{i,n-1} [e^{ipn} (1 - e^{-ip}) \lambda_{i,n-1,p} + e^{-ipn} (1 - e^{ip}) \lambda_{knp}^*] \lambda_{i,n-1,q} S_{k,n;i,n-1},
 \end{aligned} \tag{A-7}$$

Appendix B The multi-D₂ trial state

The individual energy term can be calculated by multi-D₂ as follows:

$$\begin{aligned}
 E_{\text{ex}} &= \langle D_2^M | \hat{H}_{\text{ex}} | D_2^M \rangle = -J \sum_{i,j} \sum_n^M \psi_{j,n}^* (\psi_{i,n+1} + \psi_{i,n-1}) S_{j,i}, \\
 E_{\text{ph}} &= \langle D_2^M | \hat{H}_{\text{ph}} | D_2^M \rangle = \sum_{i,j} \sum_n^M \psi_{j,n}^* \psi_{i,n} \sum_q \omega_q \lambda_{j,q}^* \lambda_{i,q} S_{j,i}, \\
 E_{\text{diag}} &= \langle D_2^M | \hat{H}_{\text{ex-ph}}^{\text{diag}} | D_2^M \rangle \\
 &= -g \sum_{i,j} \sum_n^M \psi_{j,n}^* \psi_{i,n} + \sum_q \omega_q (e^{iqn} \lambda_{i,q} + e^{-iqn} \lambda_{j,q}^*) S_{j,i}, \\
 E_{\text{off}} &= \langle D_2^M | \hat{H}_{\text{ex-ph}}^{\text{o.d.}} | D_2^M \rangle = \frac{1}{2} \phi \sum_{i,j} \sum_n^M \omega_q S_{j,i} \\
 &\quad \left\{ \psi_{j,n}^* \psi_{i,n+1} [e^{iqn} (e^{iq} - 1) \lambda_{i,q} + \text{H.c.}] + \psi_{j,n}^* \psi_{i,n-1} [e^{iqn} (1 - e^{-iq}) \lambda_{i,q} + \text{H.c.}] \right\},
 \end{aligned} \tag{B-1}$$

where $S_{j,i}$ is the Debye-Waller factor defined as

$$S_{j,i} = \exp \left\{ \sum_q \lambda_{j,q}^* \lambda_{i,q} - \frac{1}{2} (|\lambda_{i,q}|^2 + |\lambda_{j,q}|^2) \right\}. \tag{B-2}$$

The Dirac-Frenkel variational principle leads to equations of motion

$$\begin{aligned}
 & -i \sum_i^M \dot{\psi}_{in} S_{ki} - \frac{i}{2} \sum_i^M \psi_{in} \sum_q \left(2\lambda_{kq}^* \dot{\lambda}_{iq} - \dot{\lambda}_{iq} \lambda_{kq}^* - \lambda_{iq} \dot{\lambda}_{kq}^* \right) S_{k,i} \\
 = & J \sum_i^M (\psi_{i,n+1} + \psi_{i,n-1}) S_{ki} - \sum_i^M \psi_{in} \sum_q \omega_q \lambda_{kq}^* \lambda_{iq} S_{ki} + g \sum_i^M \psi_{in} \sum_q \omega_q (e^{iqn} \lambda_{iq} + e^{-iqn} \lambda_{kq}^*) S_{ki} \\
 & - \frac{1}{2} \phi \sum_i^M \sum_q \omega_q \psi_{i,n+1} [e^{iqn} (e^{iq} - 1) \lambda_{iq} + e^{-iqn} (e^{-iq} - 1) \lambda_{kq}^*] S_{ki} \\
 & - \frac{1}{2} \phi \sum_i^M \sum_q \omega_q \psi_{i,n-1} [e^{iqn} (1 - e^{-iq}) \lambda_{iq} + e^{-iqn} (1 - e^{iq}) \lambda_{kq}^*] S_{ki},
 \end{aligned} \tag{B-3}$$

and

$$\begin{aligned}
 & -i \sum_i \sum_n^M \psi_{kn}^* \dot{\psi}_{in} \lambda_{iq} S_{ki} - i \sum_i \sum_n^M \psi_{kn}^* \dot{\psi}_{in} \dot{\lambda}_{iq} S_{ki} - \frac{i}{2} \sum_i \sum_n^M \psi_{kn}^* \dot{\psi}_{in} \lambda_{iq} S_{k,i} \\
 & \sum_p \left(2\lambda_{kp}^* \dot{\lambda}_{ip} - \dot{\lambda}_{ip} \lambda_{kp}^* - \lambda_{ip} \dot{\lambda}_{kp}^* \right) = J \sum_i \sum_n^M \psi_{kn}^* (\psi_{i,n+1} + \psi_{i,n-1}) \lambda_{iq} S_{k,i} \\
 & - \sum_i \sum_n^M \psi_{kn}^* \psi_{in} \left(\omega_q + \sum_p \omega_p \lambda_{kp}^* \lambda_{ip} \right) \lambda_{iq} S_{ki} + g \sum_i \sum_n^M \psi_{kn}^* \psi_{in} \omega_q e^{-iqn} S_{ki} \\
 & + g \sum_i \sum_n^M \psi_{kn}^* \psi_{in} \lambda_{iq} \sum_p \omega_p (e^{ipn} \lambda_{ip} + e^{-ipn} \lambda_{kp}^*) S_{k,i} \tag{B-4} \\
 & - \frac{1}{2} \phi \sum_n \sum_i^M \omega_q \psi_{kn}^* [\psi_{i,n+1} e^{-iqn} (e^{-iq} - 1) + \psi_{i,n-1} e^{-iqn} (1 - e^{iq})] S_{ki} \\
 & - \frac{1}{2} \phi \sum_n \sum_i^M (\psi_{k,n+1}^* \psi_{i,n} + \psi_{kn}^* \psi_{i,n+1}) \lambda_{iq} \sum_p \omega_p [e^{ipn} (e^{ip} - 1) \lambda_{ip} + e^{-ipn} (e^{-ip} - 1) \lambda_{kp}^*] S_{k,i},
 \end{aligned}$$

where $S_{k,i}$ is the Debye-Waller factor defined in Eq. (B-2).

Appendix C Frenkel exciton model and exciton dynamics for one dimensional chain and the LH2 complexes

The one-dimensional Holstein model which describes exciton coupled to phonon cloud can be written as [1, 2, 3]

$$\hat{H} = \hat{H}_{\text{ex}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{ex-ph}} \tag{C-1}$$

with

$$\hat{H}_{\text{ex}} = -J \sum_n \hat{a}_n^\dagger (\hat{a}_{n+1} + \hat{a}_{n-1}) \tag{C-2}$$

$$\hat{H}_{\text{ph}} = \sum_q \omega_q \hat{b}_q^\dagger \hat{b}_q \tag{C-3}$$

$$\hat{H}_{\text{ex-ph}} = -\frac{1}{\sqrt{N}} \sum_n \sum_q g_q \omega_q \hat{a}_n^\dagger \hat{a}_n (\hat{b}_q e^{iqn} + H.c.) \tag{C-4}$$

Here $\hat{a}_n^\dagger(\hat{a}_n)$ is the creation (annihilation) operator for an exciton at site n , J is the inter-chromophore coupling. $\hat{b}_q^\dagger(\hat{b}_q)$ is the creation (annihilation) operator of a phonon with frequency ω_q . g_q is the exciton phonon coupling constant as determined by $\sum_q g_q^2 \omega_q = S\omega_0$, where S is the Huang-Rhys factor and ω_0 is central frequency of phonon band (we set $\omega_0=1$). A linear phonon dispersion represented by $\omega_q = \omega_0[1 + W(2|q|/\pi - 1)]$ with phonon bandwidth W is assumed.

We have extended one-dimensional Holstein model to multiple-rings version

$$\hat{H} = \hat{H}_{\text{ex}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{ex-ph}} \quad (\text{C-5})$$

with

$$\hat{H}_{\text{ex}} = - \sum_{r_1 \neq r_2} \sum_{nm} J_{nm}^{r_1 r_2} \hat{a}_n^{r_1 \dagger} \hat{a}_m^{r_2} - \sum_r \sum_{nm} J_{nm}^r \hat{a}_n^{r \dagger} \hat{a}_m^r \quad (\text{C-6})$$

$$\hat{H}_{\text{ph}} = \sum_r \sum_q \omega_q^r \hat{b}_q^{r \dagger} \hat{b}_q^r \quad (\text{C-7})$$

$$\hat{H}_{\text{ex-ph}} = -\frac{1}{\sqrt{N}} \sum_r \sum_n \sum_q g_q^r \omega_q^r \hat{a}_n^{r \dagger} \hat{a}_n^r (e^{iqn} \hat{b}_q^r + H.c.) \quad (\text{C-8})$$

Here $r_1 = 1 \dots N_{\text{ring}}$ and $r_2 = 1 \dots N_{\text{ring}}$ is a pair of rings. $J_{nm}^{r_1 r_2}$ is the exciton transfer integral between two pigments on different LH2 rings with value calculated by point dipole approximation, and J_{nm}^r is exciton transfer integral between pigments m and n inside one LH2 ring with value extracted from Ref. [4]. Similar to the single-ring case, the Huang-Rhys factor S is obtained from $\sum_q (g_q^r)^2 \omega_q^r = S\omega_0$ with characteristic phonon frequency $\omega_0=1670 \text{ cm}^{-1}$ [5]

Following Dirac-Frenkel variational principle, we obtain the equations of motion for the time-dependent variational parameters $\alpha_n(t)$, $\lambda_{nq}(t)$

$$\begin{aligned} -i\dot{\alpha}_n(t) &= \frac{i}{2} N^{-1} \alpha_n \sum_q [\dot{\lambda}_{nq} \lambda_{nq}^* - H.c.] + J \alpha_{n+1} S_{n,n+1} + J \alpha_{n-1} S_{n,n-1} \\ &\quad - N^{-1/2} \alpha_n \sum_q g_q \omega_q [\lambda_{nq} e^{iqn} + H.c.] - N^{-1} \alpha_n \sum_q \omega_q |\lambda_{nq}|^2 \end{aligned} \quad (\text{C-9})$$

$$\begin{aligned}
 -iN^{-1}|\alpha_n|^2\dot{\lambda}_{nq}(t) &= N^{-1}J\alpha_n^*\alpha_{n+1}(\lambda_{n+1,q} - \lambda_{nq})S_{n,n+1} \\
 &\quad + N^{-1}J\alpha_n^*\alpha_{n-1}(\lambda_{n-1,q} - \lambda_{nq})S_{n,n-1} \\
 &\quad - N^{-1}|\alpha_n|^2\omega_q\lambda_{nq} - N^{-1/2}|\alpha_n|^2g_q\omega_q e^{-iqn}
 \end{aligned} \tag{C-10}$$

with Debye-Waller factor $S_{nm}(t)$ given by

$$S_{nm}(t) = \exp\left\{\sum_q [\lambda_{nq}^*(t)\lambda_{mq}(t) - \frac{1}{2}|\lambda_{nq}(t)|^2 - \frac{1}{2}|\lambda_{mq}(t)|^2]\right\} \tag{C-11}$$

The equations of motions for the time-dependent variational parameters $\alpha_n^r(t)$ and $\lambda_{nq}^r(t)$ can be derived in a similar way as

$$\dot{\alpha}_n^r(t) = i[T_n^r(t) + \alpha_n^r(t)R_n^r(t)] \tag{C-12}$$

and

$$\dot{\lambda}_{nq}^r(t) = i\left[\frac{\Omega_{nq}^r(t)}{\alpha_n^r(t)} + \frac{g_q^r}{\sqrt{N}}\omega_q^r e^{-iqn} - \omega_q^r\lambda_{nq}^r(t)\right] \tag{C-13}$$

Auxiliary functions in Eqs. (C-12) and (C-13) are given as

$$\varpi_{nq}^r(t) = i\dot{\lambda}_{nq}^r(t) + \frac{g_q^r}{\sqrt{N}}\omega_q^r e^{-iqn} - \omega_q^r\lambda_{nq}^r(t) \tag{C-14}$$

$$R_n^r(t) = \text{Re} \sum_q [\varpi_{nq}^r(t) + \frac{g_q^r}{\sqrt{N}}\omega_q^r e^{-iqn}] \lambda_{nq}^{r*}(t) \tag{C-15}$$

$$T_n^{r_1}(t) = - \sum_{r_2} \sum_m J_{nm}^{r_1 r_2} \alpha_m^{r_2}(t) S_{nm}^{r_1 r_2}(t) \tag{C-16}$$

$$\Omega_{nq}^{r_1}(t) = - \sum_{r_2} \sum_m J_{nm}^{r_1 r_2} \alpha_m^{r_2}(t) S_{nm}^{r_1 r_2}(t) [\lambda_{mq}^{r_2}(t) \delta_{r_1 r_2} - \lambda_{nq}^{r_1}(t)] \tag{C-17}$$

with Debye-Waller factor $S_{nm}^{r_1 r_2}(t)$ given by

$$S_{nm}^{r_1 r_2}(t) = \exp\left\{\sum_q [\lambda_{nq}^{r_1*}(t)\lambda_{mq}^{r_2}(t)\delta_{r_1 r_2} - \frac{1}{2}|\lambda_{nq}^{r_1}(t)|^2 - \frac{1}{2}|\lambda_{mq}^{r_2}(t)|^2]\right\} \tag{C-18}$$

Table D-1 Site energies $E_1-E_{14}(\text{cm}^{-1})$ for the LHCII complex

pigments	b601	a602	a603	a604	b605	b606	b607	b608	b609	a610	a611	a612	a613	a614
Energies	15854	15103	15222	15410	15674	15796	15677	15728	15686	15038	15100	15082	15140	15249

Table D-2 Interaction energies $J_{nm}(\text{cm}^{-1})$ for the trimeric LHCII complex. The effective transition dipoles for Chla and Chlb are taken to be 4 and 3.8 debye, respectively

	b601	a602	a603	a604	b605	b606	b607	b608	b609	a610	a611	a612	a613	a614
b601	0	49.9	-6.2	-2.5	0.78	-1.9	-2.5	2.84	3.87	-6	26	9.18	-10.9	3.7
a602	49.9	0	38	6.4	-0.7	5.66	7.2	-5.9	-19.4	-11.4	9.66	15.8	-4.95	0.7
a603	-6.18	38	0	-3.27	1.14	-9	1.25	6.78	97.52	12.93	-2.7	-0.76	2.67	-6.68
a604	-2.5	6.41	-3.27	0	3.38	105.43	36.24	-2.8	-7.35	-4.17	-3.8	4.65	2.12	-3.41
b605	0.8	-0.72	1.14	3.38	0	30.33	-4.57	-5.24	-0.8	1.63	1.35	-2.88	-1.42	0.37
b606	-1.93	5.66	-8.97	105.43	30.33	0	60.64	-5.10	-0.17	-3.32	-2.55	3.13	1.5	-2.18
b607	-2.52	7.2	1.25	36.25	-4.57	60.64	0	-4.52	-12.3	-0.15	-2.8	3.1	2.22	-3.3
b608	2.85	-5.9	6.78	-2.8	-5.24	-5.1	-4.52	0	36.83	62.5	4.4	-1.09	-2.03	1.31
b609	3.87	-19.4	97.52	-7.35	-0.8	-0.17	-12.2	36.83	0	3.9	4.34	-2.6	-2.95	2.36
a610	-6	-11.4	12.93	-4.17	1.63	-3.32	-0.15	62.5	3.9	0	-24.9	23	7.2	-1.55
a611	26	9.66	-2.7	-3.8	1.35	-2.55	-2.8	4.4	4.34	-24.9	0	126.54	-6.13	4.54
a612	9.18	15.78	-0.76	4.66	-2.88	3.13	3.10	-1.1	-2.6	23	126.54	0	-0.47	-0.18
a613	-10.9	-4.95	2.67	2.12	-1.42	1.48	2.22	-2.03	-2.94	7.2	-6.13	-0.47	0	-50.1
a614	3.68	0.7	-6.68	-3.41	0.37	-2.18	-3.28	1.31	2.35	-1.55	4.54	-0.18	-50.1	0

Appendix D The site energies, electronic couplings, Huang-Rhys factors, and transition dipole moments for the LHCII trimeric complex

Appendix E A pedestrian analysis of polaron effect

In a first approximation, the exciton-phonon coupling renormalizes the site energies and electronic couplings in the excitonic Hamiltonian as follows (see Ref. [6])

$$\bar{\epsilon}_m = \epsilon_m + r_m \quad (\text{E-1})$$

$$\bar{J}_{nm} = J_{nm}\theta_n\theta_m \quad (\text{E-2})$$

	b601	a602	a603	a604	b605	b606	b607	b608	b609	a610	a611	a612	a613	a614
b601'	-0.46	-0.36	-0.72	2.72	-2.31	2.77	0.31	5.94	38.95	-4.24	-0.89	1.43	0.91	0.17
a602'	0.25	1.11	8.11	-0.9	0.67	-0.83	0.54	0.08	-10.76	2.94	0.55	-0.69	-1.2	-0.86
a603'	-1.5	5.2	-6.5	2.56	-0.27	2.83	3.21	-0.55	0.24	-0.92	-1.22	1.3	-0.48	-0.91
a604'	-0.26	1.15	-0.51	0.87	-0.5	1.08	1.35	-0.6	-0.27	-0.19	-0.3	-0.01	-0.25	-0.68
b605'	0.17	-0.34	0.51	-0.3	0.07	-0.21	-0.21	0.05	-0.24	0.23	0.17	-0.05	-0.22	0.12
b606'	-0.34	1.19	-0.41	0.82	-0.25	0.85	0.9	-0.43	-0.12	-0.23	-0.37	0.1	-0.24	-0.67
b607'	-0.6	1.84	-0.98	1.23	-0.35	1.23	1.55	-0.48	0	-0.44	-0.56	0.20	0.22	-0.69
b608'	0.46	-1.17	1.34	-0.72	0.23	-0.68	-0.68	0.42	-0.24	0.5	0.45	-0.12	-0.18	0.39
b609'	0.91	-2.35	2.36	-1.06	0.18	-1.02	-0.96	0.43	-0.35	0.69	0.72	-0.42	-0.18	0.43
a610'	-0.37	0.76	-2.04	0.54	0.06	0.26	-0.2	0.55	2.27	-0.68	-0.36	0.52	0.07	-0.01
a611'	-0.12	-0.51	-0.16	0.27	-0.33	-0.79	-0.87	2.73	4.67	-1.13	-0.25	0.57	0.45	0.3
a612'	0.37	-0.51	2.4	-0.68	0.49	-0.37	-0.44	-0.62	-3.23	1.14	0.42	-0.3	-0.67	-0.07
a613'	0.26	-0.45	-4.35	-1.08	-0.99	-0.9	8.26	0.39	5.29	-1.19	0.23	-0.93	2	0.97
a614'	0.74	-2.51	4.14	-3.9	3.47	-5.68	0.74	0.75	-4.6	0.7	0.8	-0.76	0.49	1.11
	b601	a602	a603	a604	b605	b606	b607	b608	b609	a610	a611	a612	a613	a614
b601''	-0.47	0.23	-1.47	-0.26	0.17	-0.36	-0.61	0.47	0.92	-0.35	-0.1	0.36	0.24	0.74
a602''	-0.24	1.06	5.15	1.11	-0.34	1.19	1.82	-1.16	-2.38	0.74	-0.54	-0.51	-0.42	-2.52
a603''	-0.91	7.82	-6.93	-0.51	0.51	-0.47	-1	1.35	2.36	-2	0	2.36	-4.37	4.24
a604''	2.69	-0.84	2.53	0.86	-0.29	0.82	1.22	-0.71	-1.08	0.52	0.22	-0.65	-1.05	-3.91
b605''	-2.264	0.63	-0.28	-0.51	0.07	-0.25	-0.35	0.23	0.19	0.08	-0.25	0.45	-0.9	3.6
b606''	2.89	-0.81	2.81	1.07	-0.21	0.85	1.23	-0.69	-1.05	0.25	-0.81	-0.37	-0.85	-5.78
b607''	0.48	0.53	2.89	1.31	-0.19	0.85	1.43	-0.65	-0.92	-0.27	-0.89	-0.43	8.96	1.13
b608''	5.87	0.06	-0.55	-0.6	0.05	-0.42	-0.48	0.41	0.45	0.57	2.77	-0.63	0.41	0.76
b609''	39.21	-10.62	0.45	-0.26	-0.25	-0.08	0.03	-0.26	-0.34	2.28	4.57	-3.19	5.28	-4.66
a610''	-4.25	2.88	-0.98	-0.2	0.23	-0.26	-0.45	0.51	0.69	-0.66	-1.07	1.12	-1.18	0.73
a611''	-0.92	0.55	-1.21	-0.29	0.17	-0.37	-0.56	0.44	0.72	-0.35	-0.23	0.42	0.22	0.81
a612''	1.45	-0.68	1.32	0	-0.05	0.13	0.23	-0.14	-0.45	0.52	0.56	-0.3	-0.92	-0.8
a613''	0.91	-1.2	-0.43	-0.24	-0.23	-0.22	0.21	-0.17	-0.14	0.07	0.43	-0.66	2.03	0.5
a614''	0.15	-0.85	-0.84	-0.67	0.12	-0.66	-0.69	0.39	0.46	0	0.3	-0.07	0.95	1.1

Table D-3 Frequencies $\omega_j(\text{cm}^{-1})$, and Huang-Rhys factors S_j for nuclear modes $j = 1 - 48$

ω_j	S_j	ω_j	S_j	ω_j	S_j	ω_j	S_j
97	0.02396	604	0.00194	1143	0.04094	1354	0.00576
138	0.02881	700	0.00197	1181	0.01759	1382	0.00667
213	0.03002	722	0.00394	1190	0.00667	1439	0.00667
260	0.02669	752	0.02578	1208	0.01759	1524	0.00636
298	0.02669	752	0.02578	1216	0.01759	1524	0.00636
342	0.06035	795	0.00485	1235	0.00697	1537	0.02183
388	0.02487	916	0.02123	1252	0.00636	1553	0.00909
425	0.01486	986	0.01031	1260	0.00636	1573	0.00454
518	0.03942	995	0.02274	1286	0.00454	1580	0.00454
546	0.00269	1052	0.01213	1304	0.00576	1612	0.00454
573	0.00849	1069	0.00636	1322	0.03032	1645	0.00363
585	0.00303	1110	0.01122	1338	0.00394	1673	0.00097

where

$$r_m = - \sum_q |\chi_{qm}|^2 \quad (\text{E-3})$$

$$\theta_m = e^{-\frac{1}{2} \sum_q \coth(\frac{\hbar\omega_q}{2k_B T}) |\chi_{qm}|^2} \quad (\text{E-4})$$

Equations (E-1) and (E-3) reveal that the exciton-phonon coupling decreases the site energies. If we further assume the coupling is site-independent, then all $\bar{\epsilon}_m$ decrease by the same value $r_m = r$. Thus, the k th eigenvalues $\bar{\epsilon}_k$ of the renormalized excitonic Hamiltonian $\bar{H}_{ex}$ are red-shifted as compared to the k th eigenvalues ϵ_k of the purely excitonic Hamiltonian H_{ex} .

Equations (E-2) and (E-4) show that the exciton-phonon coupling also decreases the effective electronic coupling. We further argue that the exciton-phonon coupling should decrease the energy differences between different eigenvalues of the excitonic Hamiltonian, i.e.,

$$|\bar{\epsilon}_k - \bar{\epsilon}_{k'}| < |\epsilon_k - \epsilon_{k'}| \quad (\text{E-5})$$

Table D-4 Transition dipole moments for 42 pigments in LHCII trimeric complex

pigments	X	Y	Z	pigments	X	Y	Z	pigments	X	Y	Z
b601	-1.924	-0.262	2.791	b601'	-1.924	-0.262	2.791	b601''	-1.924	-0.262	2.791
a602	2.832	-2.298	-1.644	a602'	2.832	-2.298	-1.644	a602''	2.832	-2.298	-1.643
a603	-3.459	-0.944	1.773	a603'	-3.459	-0.944	1.773	a603''	-3.459	-0.944	1.773
a604	2.641	1.165	2.769	a604'	2.641	1.165	2.769	a604''	2.641	1.165	2.769
b605	0.683	-3.147	-1.090	b605'	0.683	-3.147	-1.090	b605''	0.683	-3.147	-1.090
b606	0.2537	1.212	3.167	b606'	0.253	1.212	3.167	b606''	0.253	1.212	3.166
b607	-0.205	2.518	2.275	b607'	-0.205	2.518	2.275	b607''	-0.205	2.518	2.275
b608	1.128	-0.763	-3.115	b608'	1.128	-0.763	-3.115	b608''	1.128	-0.762	-3.115
b609	2.679	-0.764	-1.948	b609'	2.679	-0.764	-1.948	b609''	2.679	-0.764	-1.948
a610	-3.834	-0.414	1.063	a610'	-3.834	-0.414	1.063	a610''	-3.834	-0.414	1.063
a611	-3.309	0.309	2.226	a611'	-3.309	0.309	2.226	a611''	-3.309	0.309	2.226
a612	1.655	-2.199	-2.902	a612'	1.655	-2.199	-2.902	a612''	1.655	-2.199	-2.902
a613	-0.450	3.816	-1.111	a613'	-0.450	3.816	-1.111	a613''	-0.450	3.816	-1.111
a614	-3.788	0.049	-1.284	a614'	-3.788	0.049	-1.284	a614''	-3.788	0.049	-1.284

We cannot prove Eq. (E-5) in full generality, but we demonstrate its validity in two particular cases. The first case involves a dimer with the electronic coupling J_{12} . Then given $r_1 = r_2 = r$, we have

$$|\bar{\epsilon}_2 - \bar{\epsilon}_1| = \sqrt{(\epsilon_1 - \epsilon_2)^2 + 4\bar{J}_{12}^2} \quad (\text{E-6})$$

which proves Eq. (E-5). The second case considers a molecular ring comprising N sites with only constant nearest-neighbor coupling J and same site energy $\epsilon_n = \epsilon$, we have (see Ref. [7])

$$|\bar{\epsilon}_k - \bar{\epsilon}_{k'}| = 2\bar{J} \left| \cos\left(\frac{2\pi k}{N}\right) - \cos\left(\frac{2\pi k'}{N}\right) \right| \quad (\text{E-7})$$

with $k, k' = -, 1, \dots, N - 1$. Thus, Eq. (E-5) holds.

Appendix F Model 2D spectra calculations using multi-D₂

The general theory follows the descriptions presented in Section 3.4, except that the system Hamiltonian we considered is Holstein Hamiltonian with simultaneous diagonal and off-diagonal exciton phonon couplings (see Eq. (3.3)). We then approximate the propagator in terms of the multiple D₂ ansätze, i.e.,

$$e^{-iH_{st}}|n\rangle|0\rangle_{ph} = \sum_i^M \sum_n^N \psi_{i,n} \hat{a}_n^\dagger |0\rangle_{ex} \exp \left\{ \sum_q \left[\lambda_{iq} \hat{b}_q^\dagger - \lambda_{iq}^* \hat{b}_q \right] \right\} |0\rangle_{ph} \quad (\text{F-1})$$

Thus, the third order response function (see Eq. (3.82)) can be easily calculated as

$$\begin{aligned}
 R_1(t, T, \tau) &= F_1(t, T, \tau) \sum_{n, n', n'', n'''} C_{n, n', n'', n'''} \sum_{i, j=1}^M \psi_{jn'}^{n*}(T) \psi_{in''}^{n'''}(\tau + T + t) e^{-\frac{1}{2} \sum_q (|\lambda_{jq}^n(T)|^2 + |\lambda_{iq}^{n'''}(\tau + T + t)|^2)} \\
 &\quad e^{\sum_q \lambda_{jq}^{n*}(T) \lambda_{iq}^{n'''}(\tau + T + t) e^{i\omega_q t}} \\
 R_2(t, T, \tau) &= F_2(t, T, \tau) \sum_{n, n', n'', n'''} C_{n, n', n'', n'''} \sum_{i, j=1}^M \psi_{jn'}^{n*}(T + \tau) \psi_{in''}^{n'''}(T + t) e^{-\frac{1}{2} \sum_q (|\lambda_{jq}^n(T + \tau)|^2 + |\lambda_{iq}^{n'''}(T + t)|^2)} \\
 &\quad e^{\sum_q \lambda_{jq}^{n*}(T + \tau) \lambda_{iq}^{n'''}(T + t) e^{i\omega_q t}} \\
 R_3(t, T, \tau) &= F_3(t, T, \tau) \sum_{n, n', n'', n'''} C_{n, n', n'', n'''} \sum_{i, j=1}^M \psi_{jn'}^{n*}(\tau) \psi_{in''}^{n'''}(t) e^{-\frac{1}{2} \sum_q (|\lambda_{jq}^n(\tau)|^2 + |\lambda_{iq}^{n'''}(t)|^2)} \\
 &\quad e^{\sum_q \lambda_{jq}^{n*}(\tau) \lambda_{iq}^{n'''}(t) e^{i\omega_q(t+T)}} \\
 R_4(t, T, \tau) &= F_4(t, T, \tau) \sum_{n, n', n'', n'''} C_{n, n', n'', n'''} \sum_{i, j=1}^M \psi_{jn'}^{n*}(-t) \psi_{in''}^{n'''}(\tau) e^{-\frac{1}{2} \sum_q (|\lambda_{jq}^n(-t)|^2 + |\lambda_{iq}^{n'''}(\tau)|^2)} \\
 &\quad e^{\sum_q \lambda_{jq}^{n*}(-t) \lambda_{iq}^{n'''}(\tau) e^{-i\omega_q T}}
 \end{aligned} \tag{F-2}$$

The time evolution of equations of motion for the variational parameters $\psi_{i,n}$ and λ_{iq} is discussed in Appendix B.

Appendix G Model 2D spectra calculations using HEOM method

The model system Hamiltonian (H_S) is again Holstein model with simultaneous diagonal and off-diagonal exciton phonon couplings (see Eq. (3.3)). In order to account for the population decays and dephasings, we add an additional term $H_B + H_{SB}$ (see Eqs. (3.51) and (3.52)) to the original Holstein Hamiltonian (H_S). The polarization operator closely related to the optical spectra can be defined as

$$\hat{P} = \sum_{m=1}^N [\boldsymbol{\mu}_m |m\rangle \langle g| + \boldsymbol{\mu}_m^* |g\rangle \langle m|] \tag{G-1}$$

If the electric field is weak, we can expand the field-matter interaction perturbatively, thus various linear and nonlinear signals can be expressed as optical response function in terms of

dipole correlation function [8]. The absorption spectra can be calculated as

$$I(\omega) \propto \frac{1}{2\pi} \int_0^\infty dt e^{i\omega t} \langle \mathbf{P}(t) \mathbf{P}(0) \rangle_g e^{-g(t)} \quad (\text{G-2})$$

Here, the subscript g denotes that the trace is taken at ground electronic state and equilibrium state for the phonon modes, i.e., $\rho_g = |g\rangle\langle g| \otimes e^{-\beta H_{ph}} / \text{Tr} e^{-\beta H_{ph}}$ ($\beta = 1/k_B T$ is the inverse temperature). The factor $e^{-g(t)}$ is responsible for the second bath induced relaxation.

The 2D spectra can be retrieved from the third order response function $R^{(3)}(t_3, t_2, t_1)$, which is defined as

$$R^{(3)}(t_3, t_2, t_1) = \langle [[[\mathbf{P}(t_3 + t_2 + t_1), \mathbf{P}(t_2 + t_1)], \mathbf{P}(t_1)], \mathbf{P}(0)] \rho_0 \rangle \quad (\text{G-3})$$

where ρ_0 is the equilibrium system+second bath operator, and $\mathbf{P}(t) = e^{i(H_S + H_B + H_{SB})t} \mathbf{P} e^{-i(H_S + H_B + H_{SB})t}$. Following the same reasoning as discussed in Section 3.4, i.e., $[H_S, H_B + H_{SB}] = 0$, the contributions to the nonlinear response function can be separated into system and bath parts. The former can be dealt with the HEOM method, while the latter is accounted for through lineshape function. Finally, we arrived at the formulas for the nonlinear response function

$$\begin{aligned} R_1(t_3, t_2, t_1) &= \langle \mathbf{P}_-^\leftarrow e^{-i\mathcal{L}_S t_3} \mathbf{P}_+^\rightarrow e^{-i\mathcal{L}_t t_2} \mathbf{P}_-^\rightarrow e^{-i\mathcal{L}_t t_1} \mathbf{P}_+^\leftarrow \rho_g \rangle F_1(t_3, t_2, t_1) \\ R_2(t_3, t_2, t_1) &= \langle \mathbf{P}_-^\leftarrow e^{-i\mathcal{L}_S t_3} \mathbf{P}_+^\rightarrow e^{-i\mathcal{L}_t t_2} \mathbf{P}_+^\leftarrow e^{-i\mathcal{L}_t t_1} \mathbf{P}_-^\rightarrow \rho_g \rangle F_2(t_3, t_2, t_1) \\ R_3(t_3, t_2, t_1) &= \langle \mathbf{P}_-^\leftarrow e^{-i\mathcal{L}_S t_3} \mathbf{P}_+^\leftarrow e^{-i\mathcal{L}_t t_2} \mathbf{P}_+^\rightarrow e^{-i\mathcal{L}_t t_3} \mathbf{P}_-^\rightarrow \rho_g \rangle F_3(t_3, t_2, t_1) \\ R_4(t_3, t_2, t_1) &= \langle \mathbf{P}_-^\leftarrow e^{-i\mathcal{L}_S t_3} \mathbf{P}_+^\leftarrow e^{-i\mathcal{L}_t t_2} \mathbf{P}_-^\leftarrow e^{-i\mathcal{L}_t t_3} \mathbf{P}_+^\leftarrow \rho_g \rangle F_4(t_3, t_2, t_1) \end{aligned} \quad (\text{G-4})$$

Here we have defined notations $\mathbf{P}_- = \sum_{m=1}^N \boldsymbol{\mu}_m |m\rangle\langle g|$ and $\mathbf{P}_+ = \sum_{m=1}^N \boldsymbol{\mu}_m^* |g\rangle\langle m|$, and abbreviations of $\mathbf{P}_\pm^\leftarrow A = \mathbf{P}_\pm A$, and $\mathbf{P}_\pm^\rightarrow A = A \mathbf{P}_\pm$ for any operator A . $\mathcal{L}_S$ is the Liouville operator corresponding to the system Hamiltonian H_S with time evolution of propagator $e^{-i\mathcal{L}_t}$ treated by utilizing HEOM method. F_i , where i goes from 1 to 4 are lineshape factors defined in Eq. (3.85).

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List of Publications

1. **L. P. Chen**, J. Lu, G. K. Long, F. L. Zheng, J. P. Zhang, and Y. Zhao. "Optical and transport properties of single crystal rubrene: a theoretical study" *Chemical Physics*, 2016, doi:10.1016/j.chemphys.2016.05.012
2. **L. P. Chen**, M. F. Gelin, V. Y. Chernyak, W. Domcke, and Y. Zhao. "Dissipative dynamics at conical intersections: Simulations with the hierarchy equations of motion method" *Faraday Discusssions*, 2016, doi:10.1039/C6FD00088F
3. F. Grossman, M. Werther, **L. P. Chen**, and Y. Zhao. "Generalization of the Davydov ansatz by squeezing" *Chemical Physics*, 2016, doi:10.1016/j.chemphys.2016.04.019
4. T. R. Deng, Y. Y. Yan, **L. P. Chen**, and Y. Zhao. "Dynamics of the two spin spin boson model with a common bath" *The Journal of Chemical Physics*, **144**, 144102 (2016).
5. N. J. Zhou, **L. P. Chen**, Z. K. Huang, K. W. Sun, Y. Tanimura and Y. Zhao, "Fast, Accurate Simulation of Polaron Dynamics and Multidimensional Spectroscopy by Multiple Davydov Trial States" *The Journal of Physical Chemistry A*, **120**, 1562 (2016).
6. R. A. Molina, E. B. Matias, A. Somoza, **L. P. Chen** and Y. Zhao, "Superradiance at the localization-delocalization crossover in tubular chlorosomes" *Physics Review E*, **93**, 022414 (2016).

7. L. Wang, **L. P. Chen**, N. J. Zhou and Y. Zhao, "Variational dynamics of the sub-Ohmic spin boson model on the basis of multiple Davydov D1 states" *The Journal of Chemical Physics*, **144**, 024101 (2016).
8. S. M. Alejandro, **L. P. Chen**, K. W. Sun and Y. Zhao, "Probing ultrafast excitation energy transfer of the Chlorosome with exciton-phonon variational dynamics" *Physical Chemistry Chemical Physics*, (2016), doi:10.1039/C5CP06491K.
9. **L. P. Chen**, P. M. Shenai, F. L. Zheng, A. Somoza and Y. Zhao, "Optimal energy transfer in light harvesting systems" *Molecules*, **20**, 15224 (2015).
10. **L. P. Chen**, Y. Zhao, and Y. Tanimura, "Dynamics of a one dimensional Holstein polaron with the hierarchical equations of motion approach" *The Journal of Physical Chemistry Letters*, **6**, 3110 (2015).
11. **L. P. Chen**, M. F. Gelin, W. Domcke, and Y. Zhao, "Theory of femtosecond coherent double pump single molecule spectroscopy: Application to light harvesting complexes" *The Journal of Chemical Physics*, **142**, 164106 (2015).
12. N. J. Zhou, **L. P. Chen**, D. Z. Xu, V. Chernyak, and Y. Zhao, "Symmetry and the critical phase of the two bath spin boson model: Ground state properties" *Physical Review B*, **91**, 195129 (2015).
13. J. Lu, Y. Yao, P. M. Shenai, **L. P. Chen**, Y. Zhao, "Elucidating the enhancement in the optical properties of low band gap polymers by tuning the structure of alkyl side chains" *Physical Chemistry Chemical Physics*, **17**, 9541 (2015).
14. N. J. Zhou, **L. P. Chen**, Y. Zhao, D. Mozyrsky, V. Chernyak and Y. Zhao, "Ground state properties of sub-Ohmic spin boson model with simultaneous diagonal and off-diagonal coupling" *Physical Review B*, **90**, 155135 (2014).
15. S. J. Xiong, **L. P. Chen**, Y. Zhao, "Dephasing and dissipation in a source-drain model of light harvesting systems", *ChemPhysChem*, **15**, 2859 (2014).