Excitation energy transfer in photosynthetic systems

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NANYANG
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**EXCITATION ENERGY TRANSFER IN
PHOTOSYNTHETIC SYSTEMS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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EXCITATION ENERGY TRANSFER IN PHOTOSYNTHETIC SYSTEMS

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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2017

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

As one of the most significant natural processes providing food and energy for almost all life on the Earth, photosynthesis starts with sunlight absorption by specialized light harvesting complexes (LHCs) and the excitation energy is then transferred with nearly perfect efficiency to reaction centers (RCs). The extraordinary energy transfer efficiency in natural photosynthesis has been attracting increasing attention. Despite that extensive experimental and theoretical efforts have been devoted to studies of the excitation energy transfer in photosynthesis, the mystery of the extremely high energy transfer rate has not yet been well understood. An in-depth understanding of the underlying mechanisms for the energy transfer in photosynthesis can benefit the design of artificial photosynthetic devices. To this end, the current thesis conducts a systematic study of excitation energy transfer in various photosynthetic systems by employing hybrid theoretical methodologies.

Electronic structures and pigment-environment interactions are key factors that determine the energy transfer in photosynthetic complexes. Compared to extensive investigations of such quantities for LHCs, relatively few studies have been proceeded to obtain these properties of RC complexes in which charge separation occurs. In order to fill in this gap, quantum chemistry calculations combined with molecular dynamics simulations are applied in this thesis to evaluate static quantities of the RC complex from purple bacteria *Thermochromatium tepidum*, including excitation energies, excitonic coupling, and spectral densities of the pigments. Effects of protein environments on the electronic structures are taken into account by treating atoms surrounding the pigments as point charges, producing reliable site energies of the RC pigments. In addition to helping interpret asymmetric charge separation pathways in the RCs, comprehensive electronic structures and spectral densities constructed in this thesis can be used in future explorations of dynamical processes in the RCs.

Beyond static property calculations, simulations of energy transfer in different photosynthetic aggregates are then carried out in this thesis. In the preliminary stage, a relatively

small complex, a chlorophyll (Chl) *a* dimer is modeled as the target system to investigate the competitive intra- and inter-chromophore energy transfer by employing the nonadiabatic excited-state molecular dynamics (NA-ESMD). The real time energy relaxation at an atomic level is monitored, and relaxation rates in the Chl*a* dimer are obtained within the NA-ESMD framework. Thanks to the level splitting induced by the excitonic coupling, the overall energy relaxation in the Chl*a* dimer is faster than that in the monomeric Chl*a*. The NA-ESMD trajectories are also utilized to reveal energy relaxation pathways. The electronic transition density is applied to visualize the exciton redistribution on the pigments upon photoexcitation, disclosing detailed intra- and inter-molecular energy transfer mechanisms in natural photosynthetic systems.

In addition to energy transfer in the Chl*a* dimer, exciton diffusion in large-scale artificial B850 nanoarrays is simulated using the Dirac-Frenkel time-dependent variational principle combined with the Davydov trial state, aiming to study the excitation energy transfer in realistic photosynthetic systems typically composed of hundreds of pigments. An efficient program is developed and implemented on the state-of-the-art graphic processor units (GPUs). The excellent scaling properties of GPU architectures facilitate fully quantum mechanical simulations of energy transfer in huge systems. From coherent exciton-phonon dynamics in one-dimensional and two-dimensional nanoarrays, exciton delocalization is scrutinized by analyzing the coherence length and the superradiance enhancement factor. The mean square displacement is measured to characterize the exciton diffusion behavior, and a superdiffusive component is found in the exciton propagation.

In summary, this thesis presents a comprehensive investigation of static as well as dynamics properties in natural and engineered photosynthetic systems by employing various theoretical methodologies, including the combined quantum chemistry calculations and classical molecular dynamics simulations, the mixed quantum-classical dynamics, and the fully quantum mechanical modelling. It is expected that findings obtained in this thesis provide advantageous insights on energy transfer processes in photosynthetic complexes and guiding principles on the design of manufactured photosynthetic devices.

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Abbreviations

1D	one-dimensional
2D	two-dimensional
2DES	two-dimensional electronic spectroscopy
2DEV	two-dimensional electronic-vibrational spectroscopy
Acc. BChl	accessory bacteriochlorophyll
AFA	adaptive fractal analysis
AM1	Austin Model 1
ATP	adenosine triphosphate
BChl	bacteriochlorophyll
BO	Born-Oppenheimer
BPhe	bacteriopheophytin
CEO	collective electron oscillator
Chl	chlorophyll
CIS	configuration interaction singles
CNDO	complete neglect of differential overlap
CRT	carotenoid
CS	charge separation
Cyt	Cytochrome
DOF	degrees of freedom
DFT	density functional theory
EDC	energy-based decoherence correction
EET	excitation energy transfer
EOM	equation of motion
ET	electron transfer
fBm	fractional Brownian motion
fGn	fractional Gaussian noise
FMO	Fenna-Matthews-Olson
FSSH	fewest switches surface hopping
FWHM	full width at half maximum

GPU	Graphic Processor Units
GSMD	ground-state molecular dynamics
HEOM	hierarchical equation of motion
HF	Hartree-Fock
HM	higher monomer
HOMO	highest occupied molecular orbital
ID	instantaneous decoherence
INDO	intermediate neglect of differential overlap
LH1	light-harvesting 1
LH2	light-harvesting 2
LHC	light harvesting complex
LHCII	light-harvesting complex II
LUMO	lowest unoccupied molecular orbital
MD	molecule dynamics
MQ	menaquinone
MSD	mean square displacement
NA	nonadiabatic
NA-ESMD	nonadiabatic excited-state molecular dynamics
NDDO	neglect of diatomic differential overlap
NPQ	non-photochemical quenching
NSED	normalized stationary excitation distribution
OCM	organic conjugated material
PC	point charges
PDA	point dipole approximation
Phe	pheophytin
PM1	Parametric Method 1
PSI	Photosystem I
PSII	Photosystem II
QED	quantum electrodynamics

QHE	quantum heat engines
QM/MM	quantum mechanical/molecular mechanical
<i>Rb. sphaeroides</i>	<i>Rhodobacter sphaeroides</i>
RC	reaction center
<i>Rps. viridis</i>	<i>Rhodopseudomonas viridis</i>
RSMD	root-mean-square deviations
SPX	spirilloxanthin
TD	transition density
TDDFT	time-dependent density functional theory
TrEsp	transition charges from electrostatic potentials
UQ	ubiquinone
ZINDO/S	Zerner intermediate neglect of differential overlap approximation parametrized for spectroscopy

Chapter 1

Introduction

This chapter presents a background of the thesis projects followed by the scope and objectives of this study. Aiming to explore energy transfer mechanisms in photosynthetic complexes and provide insightful principles for the design of artificial photosynthetic apparatuses, this thesis conducts systematic investigations of static properties and dynamic processes of various photosynthetic systems. Employed methodologies include the hybrid quantum mechanical and molecular mechanical method, the mixed quantum-classical approach, and the fully quantum mechanical time-dependent variational principle. Following an overview of the thesis, research outcomes achieved in this study are outlined at the end of this chapter.

1.1 Research Background

As one of the most momentous biological processes, photosynthesis provides energy resources for life on the Earth by harvesting and converting solar energy into biochemical energy. Occurring in various organisms, such as plants, sea algae and photosynthetic bacteria, photosynthesis is initiated with photon caption by light-harvesting complexes (LHCs), and harvested excitation energy eventually flows into reaction centers (RCs), where charge separation takes place with generated electrons picked up by a movable acceptor which transports the electron away from RCs. In contrast to the diversity of photosynthetic systems, a remarkable near-unity efficiency of energy transfer and conversion is commonly seen in natural photosynthetic organisms [1–5]. Considering the increasingly urgent global energy crisis and the inexhaustible solar energy, researchers have been devoting numerous efforts to exploring the mystery of the extraordinary energy transfer efficiency in natural photosynthesis, such that the lessons from nature can be employed to fabricate efficient artificial photosynthetic devices. Plentiful experimental and theoretical investigations have been conducted to achieve a comprehensive understanding of the energy transfer and conversion in natural photosynthesis.

Thanks to the advent of ultrafast spectroscopy and the development of state-of-the-art theoretical frameworks, fruitful progresses have been made in exploring underlying excitation energy transfer (EET) mechanisms in natural photosynthetic systems in the last decade. In 2007, Engel and co-workers measured the two-dimensional electronic spectroscopy (2DES) of the Fenna-Matthews-Olson (FMO) complex at 77 K and discovered long-lived oscillations in the cross peak of the spectra [6]. Lasting for more than 660 fs at 77 K and 300 fs at 277 K, the oscillatory signals were initially interpreted as quantum coherence between electronic states in FMO [6, 7]. The application of the 2DES to studying EET in FMO and the observation of quantum coherence trigger extensive investigations of EET in a variety of photosynthetic systems with the technique of 2DES. Quantum coherence has been observed in the EET process in various LHCs and proposed to be a common property of EET in natural photosynthetic aggregates [8–10]. However, the origin

and functionalities of quantum coherence are still under debate [11–17]. Initially interpreted as electronic coherence, the long-lived oscillations cannot be properly accounted for by dynamics simulations [6, 18–22]. Compared to electronic coherence, coherence between vibrational levels can produce oscillations with similar frequencies but weaker amplitudes [23, 24]. Furthermore, a vibronic characteristic has been assigned to the observed quantum coherence in EET [25], and the persistent oscillations have been reproduced theoretically under this assignment [24–30].

As to the arguments on the roles that quantum coherence plays on EET, considerable attention has been attracted on whether quantum coherence can accelerate the EET in natural photosynthesis. Since the first observation in the 2DES of FMO, quantum coherence was proposed to contribute to the extraordinary energy transfer efficiency in wild photosynthetic complexes [6, 8, 19, 25, 31]. However, it is recently demonstrated that quantum coherence is not essential for efficient EET [12, 13, 13, 14] and electronic coherence cannot promote the EET in FMO from theoretical calculations [13]. Sustained efforts are desired to resolve these fundamental issues concerning photosynthetic EET and to explore energy transfer mechanisms in natural photosynthetic systems.

1.2 Objectives and Scope

In the field of solar energy applications, growing attention has been concentrated on the design and fabrication of novel materials and architectures for more efficient photon absorption, energy transfer and conversion. Natural photosynthesis exhibits remarkable efficiency for excitation energy transfer. Thorough understanding of energy transfer mechanisms in photosynthesis is not only beneficial to studying fundamental physics underlying the energy transfer in noisy environments, but also crucial to making artificial photosynthetic devices. Combining diverse theoretical methodologies, this thesis presents systematic investigations of energy transfer in natural and artificial photosynthetic systems.

Energy transfer in photosynthetic aggregates can be modeled by motion of excitons

coupled to a phonon bath. Consequently, electronic structures and exciton-phonon coupling strengths are two fundamental factors controlling the EET dynamics in photosynthetic complexes. Compared to extensive studies that have been implemented to evaluate the excitation energies, the excitonic coupling, and the exciton-phonon coupling in various LHCs, such as light-harvesting 2 (LH2) and FMO, insufficient efforts are devoted to calculating such quantities in RCs. In order to precisely simulate dynamical processes occurring in RCs, it is imperative to determine the electronic structures and the exciton-phonon coupling strengths of RC pigments. On the basis of a recently reported crystal structure of the RC complex from *Thermochromatium (Tch.) tepidum* [32], systematic investigations are carried out in this thesis to obtain these parameters in the RC by combining molecular dynamics simulations with quantum chemistry calculations. Environmental effects on excitation energies of the RC pigments are investigated by treating surrounding atoms as point charges (PCs) and including the PCs in transition energy calculations. Representing environmental modulations on the site energies of chromophores, excitation energy fluctuations are utilized to evaluate the coupling between electronic transitions and bath modes.

Once the parameters are obtained from static calculations, energy transfer in photosynthetic systems can be simulated with various methods. Many theoretical studies have been conducted on how energy is transferred in diverse LHCs. In the limit of weak excitonic coupling, the Föster theory is suitable to describe the exciton migration by assuming incoherent exciton hopping [33]. If the exciton-phonon coupling strength is weak and can be treated as a perturbation, the Redfield theory is proposed to tackle coherent energy transfer [34]. An accurate description of EET in photosynthetic systems is nontrivial, as the excitonic coupling is comparable to the bath reorganization energy [35–37]. Some nonperturbative approaches, such as the hierarchy equation of motion (HEOM) [38–43] and multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) methods [44–46], have been deployed to study energy transfer in LHCs. However, these approaches are restricted to relatively small systems due to their dramatically increasing computational demands as the system size increases. Although the HEOM algorithm has been adapted to parallel computers and graphic processing units (GPUs) to accelerate calculations, sim-

ulations are still limited to systems with only dozens of pigments, such as the LH2-LH1-RC aggregate [47–53]. However a realistic natural photosynthetic system is composed of hundreds of chromophores. For instance, each LH1 in purple bacteria is surrounded by several LH2 complexes producing a system with more than one hundred bacteriochlorophylls (BChls). In addition to natural photosynthetic complexes, many artificial apparatuses have been fabricated with advanced techniques, such as engineered LH2 nanoarrays [54–56]. Escalante *et al.* measured fluorescence emission spectra to study the energy transfer in one-dimensional (1D) and two-dimensional (2D) nanoarrays composed of hundreds of LH2 complexes. Simulations of energy transfer in such systems are computationally challenging as a result of the huge number of degrees of freedom (DOFs) to be considered. Adequate descriptions of dynamical processes in large-scale natural and manufactured photosynthetic systems raise pressing demand for developing numerically efficient and accurate methods.

It is known that most of the computational expenses of typical numerically exact methods are incurred by quantum mechanical descriptions of the DOFs of the bath. In contrast to the electronic system which is the target of interest and should be treated quantum mechanically, the bath can be depicted classically to improve the computational efficiency in an approximate treatment. Many mixed quantum-classical approaches have been developed to simulate energy and charge transfer in organic systems by propagating the electronic DOFs quantum mechanically while evolving the DOFs of the bath classically. Based on the fewest switches surface hopping (FSSH) algorithm proposed by Tully [57], the nonadiabatic excited-state molecular dynamics (NA-ESMD) approach has been developed to accurately describe excitation energy transfer between coupled excited states of organic molecules [58, 59]. Nonradiative relaxation of high-lying energy excited states to the lowest excited state of pigments occurs in photosynthetic complexes upon photoexcitation. As one of the key processes in photosynthesis, nonradiative relaxation in single chlorophyll (Chl) *a* and Chl *b* molecules has been studied with the NA-ESMD approach. The ratio of simulated relaxation constants in Chl *a* and Chl *b* monomers agrees well with that from ultrafast transient absorption spectroscopy [60]. This approach has also been successfully applied to study ultrafast intramolecular exciton redistribution and energy relaxation in

large-scale organic conjugated molecules. In photosynthesis, intermolecular excitation energy relaxation is critical to energy transfer in photosynthetic systems since an exciton is typically delocalized over several molecules and many pigments participate in global energy flux. A pigment dimer is an ideal model to study the intermolecular energy transfer and the details of internal conversion simultaneously. In this thesis, a Chl a dimer, located at the interface of two subunits of the light-harvesting complex II (LHCII) trimer, is chosen as the target system for NA-ESMD simulations. Depicting intra- and inter-molecule energy transfer on an atomic level, findings from this study can help deepen the comprehension of fundamental energy transfer mechanisms in natural photosynthesis.

Similar to natural photosynthetic systems, artificial light-harvesting apparatuses are composed of hundreds of molecules, and multiple pigments are involved in the energy transfer process. Therefore, in addition to the intra- and inter-chromophore energy transfer in a molecular dimer, EET in large photosynthetic systems is another appealing aspect to be investigated for a comprehensive understanding of the energy transfer mechanisms in photosynthesis. To this end, B850 nanoarrays are constructed in this thesis and used to simulate the EET dynamics in photosynthetic systems with huge size. Complex interactions between the electronic system and the environments are crucial for the EET in the nanoarrays. The system-environment interactions are modeled by coupling the exciton to a phonon bath consisting of a collection of harmonic oscillators. Beyond the mixed quantum-classical methods, numerically efficient fully quantum mechanical approaches are desired to describe both the electronic system and the bath quantum mechanically. Taking advantages of the Davydov *Ansatz*, Zhao *et al.* have applied the Dirac-Frenkel time-dependent variational principle to study the EET in various LHCs, such as a double-LH2 system [61, 62] and chlorosome [63]. In contrast to the reduced density matrix methods, the DOFs of the electronic and bosonic components are explicitly depicted in this method. Implemented into the GPU platforms, this approach has been successfully used to simulate energy transfer dynamics in chlorosome with more than 300 pigments included in the simulations [63]. This formalism exhibits superior accuracy and efficiency, and is suitable to investigate the EET in sizable systems. In current dissertation, this approach is adopted to study exciton

diffusion in 1D and 2D B850 nanoarrays, and fully quantum mechanical simulations are conducted on the GPUs. Exciton diffusion behavior in the nanoarrays is characterized, and the coherence length and the superradiance enhancement factor are calculated to quantify exciton delocalization.

1.3 Dissertation Overview

This thesis addresses static properties and dynamical behaviors in various photosynthetic systems. The combined quantum mechanical/molecular mechanical (QM/MM) method is used to obtain the static properties of the RC pigments, i.e., the site energies, the excitonic coupling, and the exciton-phonon coupling. As to dynamical investigations, a mixed quantum-classical approach is utilized to study the intra- and inter-molecular energy transfer in a Chl a dimer, while a fully quantum mechanical formalism is adopted to simulate the exciton diffusion in large-scale artificial B850 nanoarrays. Insights obtained from this thesis are expected not only to facilitate the comprehension of energy transfer in photosynthesis, but also to provide guiding principles for the design of efficient artificial photosynthetic devices. The structure of the dissertation is shown as follows.

Chapter 1 presents a short introduction to the research background and illuminates motivations for the project with the main objectives of the thesis listed.

Chapter 2 reviews the literature concerning experimental and theoretical investigations on energy transfer and charge separation in photosynthetic systems. Briefly describing various LHCs and RCs, this chapter illustrates findings and puzzles regarding the quantum coherence. Achievements and challenges of theoretical studies on energy transfer are also emphasized in this chapter.

Chapter 3 provides a detailed description of theoretical approaches applied in the thesis, including the QM/MM method used to obtain electronic structures of the RC pigments, the time-dependent variational principle adopted to simulate energy transfer in B850 nanoar-

rays, and the NA-ESMD algorithm employed to investigate energy relaxation in the Chla dimer.

Chapter 4 elaborates electronic structures and pigment-protein interactions of the RC pigments. Within the QM/MM framework, environmental corrections on excitation energies of the RC cofactors are taken into consideration by modeling surrounding atoms as PCs. Excitonic coupling strengths between the RC pigments are estimated with various methods. The significance of these parameters to the unidirectionality of the charge separation in bacterial RC is discussed in this chapter.

Chapter 5 depicts energy relaxation in a Chla dimer by conducting NA-ESMD simulations. Exciton redistribution dynamics, time scales and pathways for energy relaxation are disclosed by analysing the results over an ensemble of trajectories. This study provides an intuitionistic picture of intra- and inter-pigment energy transfer in natural photosynthetic systems.

Chapter 6 shows a fully quantum mechanical description of EET in large-scale B850 nanoarrays by implementing the time-dependent variational principle on advanced GPU architectures. The study not only characterizes the exciton diffusive behavior, but also measures the exciton delocalization size.

Chapter 7 elucidates conclusions of the thesis.

Chapter 8 proposes some potential opportunities for the continuous study in future.

1.4 Findings

This research produces several novel findings by:

1. Constructing comprehensive electronic structures of the pigments in the purple bac-

terial RC with the consideration of dynamical environments, which are found to be crucial for precise determinations of chromophore site energies.

2. Interpreting the unidirectional charge separation in the bacterial RC from a perspective of the electronic structures of the pigments.

3. Disclosing detailed intra- and inter-molecule energy transfer mechanisms in natural photosynthesis on an atomic level.

4. Characterizing the exciton diffusion and estimating the inter-ring transfer rate in large-scale 1D and 2D B850 nanooarrays by implementing fully quantum mechanical simulations with an efficient GPU algorithm.

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Chapter 2

Literature Review

This chapter presents an introduction to photosynthesis and photosynthetic systems from various organisms, and reviews recent experimental and theoretical achievements in the study of excitation energy transfer and charge separation in photosynthetic complexes. In Section 2.1, the light harvesting complexes and the reaction centers are introduced, together with the processes of energy transfer and charge separation in natural photosynthetic systems. Observations, interpretations, and functionalities of quantum coherence are discussed in Section 2.2. Finally, theoretical methodologies for the descriptions of excitation energy transfer are reviewed in Section 2.3, including fully quantum mechanical methods and mixed quantum-classical approaches.

2.1 Overview of Photosynthesis

With the growing energy demand, humankind is faced with an increasing energy crisis, highlighting the urgent need to tap into new energy resources. Solar energy, being clean, inexhaustible, and renewable, is one of the most appealing candidates for further exploitation [1]. In nature, solar energy is transformed to biochemical energy by photosynthesis, which takes place in a variety of organisms, such as plants, sea algae, and photosynthetic bacteria. As one of the most important natural processes, photosynthesis provides food and energy to sustain life on the Earth [2].

Taking the oxygen production as a criterion, natural photosynthesis can be classified into two types: oxygenic and anoxygenic photosynthesis. Assimilating carbon dioxide and producing oxygen, oxygenic photosynthesis occurs in plants, sea algae, and cyanobacteria, with the overall process described by a reaction: $6 \text{CO}_2 + 6 \text{H}_2\text{O} \xrightarrow{\text{sunlight}} \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2$. In contrast, several groups of bacteria, such as purple bacteria and green bacteria carry out anoxygenic photosynthesis without oxygen generation, $\text{CO}_2 + 2 \text{H}_2\text{A} \xrightarrow{\text{sunlight}} (\text{CH}_2\text{O}) + 2\text{A} + \text{H}_2\text{O}$, where H_2A is a reducing compound, such as H_2S [2].

In natural photosynthesis, solar photons are harvested by light-harvesting antennas with generated excitation energy transferred to the RCs, where charge separation (CS) and electron transfer (ET) develop in turn [3], followed by energy stabilization and products synthesis [2]. The excitation energy is eventually converted into chemical energy with nearly 100% quantum efficiency [2, 4, 5], stirring up a boom of investigations of natural photosynthesis and shedding light on the design and the fabrication of efficient artificial photosynthetic systems. A deeper understanding of the efficient energy transfer in natural photosynthesis would be extremely beneficial to the design of photosynthetic devices with high efficiency and robustness.

Figure 2.1 Structure of the light-harvesting complex II (LHCII) from *Spinacia oleracea* [6]. The LHCII is composed of three subunits with each containing 13-15 Chla and Chlb molecules. The chromophores are shown in blue and the proteins are represented by ribbons.

2.1.1 Light-harvesting Complexes

In the primary step of photosynthesis, solar photons are captured by LHCs. Most LHCs are pigment-protein aggregates, such as the LHCII in plants and algae [6, 7], and the light-harvesting 1 and 2 complexes (LH1 and LH2) in purple bacteria [8–11], while the chlorosome complex from green sulfur bacteria has a self-aggregated structure of BChls without protein scaffolds.

LHCII: Acting as the main light-harvesting antenna in green plants, LHCII is the most abundant LHC in nature [6]. As shown in Fig. 2.1, LHCII has a trimer structure and each monomer contains 13-15 Chla and Chlb pigments [6, 7]. Resulting from photon absorption by Chls, the excitation energy is transferred from LHCII to Photosystem II (PSII) the structure of which was first discovered by Barber *et al.* [12]. In addition to increasing the light-harvesting capability of PSII and guiding excitation energy to PSII, LHCII can carry

Figure 2.2 Structures of LH1-RC complexes from (a) *Rhodobacter sphaeroides* [8], (b) *Rhodopseudomonas palustris* [9], and (c) *Thermochromatium (Tch.) tepidum* [10]. The RCs are surrounded by LH1 complexes, which exhibit various structures, such as a S-shaped dimer (a), a ring monomer with a gap (b), and a monomer with a closed ring (c).

out non-photochemical quenching under intense light to dissipate excess excitation energy as heat and protect the photosynthetic systems in plants and algae [6].

LH1: Depending on the species and living environments of the purple bacteria, the LH1 complexes have differing structures [11, 13] and several examples are shown in Fig. 2.2. Typical LH1 complex has a ring shaped structure with a RC complex located at the center of the ring. In contrast to the closed ring shape of the LH1 complex from *Tch. tepidum* [10], the LH1 ring from *Rhodopseudomonas palustris* has a gap, and a W protein is positioned at the gap [9]. The gap in some LH1 complexes is proposed to be the transfer channel for quinones, which carry electrons and neutrons from RC to the cytochrome bc_1 complex in purple bacteria. As shown in Fig. 2.2 (a), an S-shaped LH1 dimer is found in *Rhodobacter (Rb.) sphaeroides* and a PufX polypeptide creates the channel for quinone migration [8].

A typical LH1 complex is composed of 15 or 16 subunits with each containing two BChls, one carotenoid (CRT), and two apoproteins (α - and β -proteins). On the basis of crystal structures [10] and MD simulations [14], the channels on the interface of adjacent subunits are suggested to be the possible pathways for quinone exchange in LH1 complexes with a closed ring [10].

Generally, the long-wavelength absorption band (Q_y band) of LH1 is located at 880 nm, while the LH1 complex from *Tch. tepdium* shows a red-shifted Q_y absorption band at 915 nm. Discovered in the Mammoth Hot Springs of Yellowstone National Park in USA, *Tch. tepdium* lives in an environment with a high temperature ($\sim 50^\circ\text{C}$) and a high value of calcium ions (Ca^{2+}) concentration [10]. In a recently reported crystal structure of the LH1-RC complex from *Tch. tepdium* [10], the LH1 complex is found to contain 16 Ca^{2+} ions which are absent in the LH1 complexes from other purple bacteria. Each Ca^{2+} is positioned between two subunits, and coordinated with five oxygen atoms from the α -protein in one subunit and the β -protein in the neighboring subunit. Niwa *et al.* have carried out a series of experiments and claimed that the calcium ions are responsible for the red-shifted Q_y absorption band at 915 nm [15, 16] and the high thermal stability [17] of the LH1-RC complex from *Tch. tepdium*.

LH2: In photosynthetic systems of purple bacteria, the general ratio of LH1 to RC is 1:1, and accessory LHCs are required to enhance the light-harvesting capability and guarantee the regular operation of the RCs. In most species of purple bacteria, LH2 serves as such peripheral LHCs and the LH2/LH1 ratio depends on living environments of the bacteria, such as the light intensity [18]. As shown in Fig. 2.3, a typical LH2 consists of 8 to 10 subunits with each subunit including two apoproteins (α - and β -proteins), three BChls, and one CRT [3, 19–23]. Two of the three BChls in each subunit form a dimer and all the dimeric BChls are densely packed to form the B850 ring such that it has an absorption peak at 850 nm, while the third BChls in all subunits form the B800 ring, contributing to an absorption peak at 800 nm. Upon excitation, the excitation energy is first transferred from the B800 ring to the B850 ring and then migrates to nearby complexes [24–34].

Figure 2.3 Crystal structure of the light-harvesting 2 (LH2) complex from *Rhodospseudomonas acidophila* [23]. The B800 and B850 pigments are colored in red and green, respectively. The carotenoid (CRT) molecules are depicted in blue.

2.1.2 Reaction Centers

Upon photon absorption, the electronic excitation energy is transferred from the LHCs to the RCs, in which a series of redox reactions take place [35]. Since the first reported X-ray structure of the RC complex from *Rhodospseudomonas (Rps.) viridis* in 1985 [36–38], the structures of RCs from various photosynthetic systems have been determined, such as the RCs in Photosystem I (PSI) [39–41] and PSII [12, 42–46], and the bacterial RCs [10, 47, 48]. RC is a pigment-protein aggregate and the pigments can be excited by photons from sunlight or can accept excitons from surrounding LHCs. Upon excitation of the special pair, which is the primary electron donor, CS occurs and the ejected electron is picked up by a final acceptor after passing through several pigments. According to the properties of electron acceptors, RC complexes are classified into two categories. Type I RCs from PSI, green sulfur bacteria and heliobacteria, use iron sulfur complexes as final electron acceptors, while Type II RCs utilize quinones to transport electrons, and are found in PSII

and purple bacteria. In spite of different electron acceptors, the cofactors in all the RCs are arranged in two quasisymmetric branches.

Type I RC: As an example of the Type I RCs, the RCs in PSI contain six Chl_a molecules and two phyloquinones [49]. Embedded in two proteins, all the cofactors are arranged in two branches, i.e., A and B branches. Two Chl_a pigments comprise the special pair P700 and the lowest energy absorption peak of the pair is located at 700 nm. Two accessory Chl_a molecules are positioned between P700 and the primary electron acceptors. Two phyloquinones act as the secondary electron acceptors by transferring the electron to the terminal iron-sulfur acceptors F_A and F_B via the 4Fe-4S complex.

Type II RC: The RCs in PSII and purple bacteria are typical Type II RCs [12, 42–46]. Shown in Fig. 2.4 is the RC from *Tch. tepidum* with the coordinates extracted from a recently reported crystal structure of LH1-RC complex (PDB ID: 3WMM) [10]. Similar to the RC complex from *Rb. sphaeroides* [50–53], three protein subunits, the so-called L, M and H subunits, and the protein of Cytochrome (Cyt), are included in the RC complex from *Tch. tepidum* [see Fig. 2.4 (a)]. All these RCs also contain the same cofactors [10, 48, 54], namely, four BChls, two bacteriopheophytins (BPhes), one spirilloxanthin (SPX), menaquinone (MQ), ubiquinone (UQ), and four Heme molecules [55] (see Fig. 2.4 (b)). One non-heme iron (assigned to be ferrous ion) located between two quinone molecules, and a calcium ion at the interface of the Cyt and M subunits are also found in the RC complex of *Tch. tepidum* [10]. As shown in Fig. 2.4 (b), Four BChls and two BPhes are arranged in two quasi-symmetric branches, i.e., the L and M branches which are associated to polypeptides L and M, respectively. These pigments are labeled as P_L, P_M, BCh_L, BCh_M, BPh_L and BPh_M with P_L and P_M standing for the two BChls which form the special pair P. BCh_L and BCh_M are called accessory bacteriochlorophylls (Acc. BChls). In contrast to Type I RC, the final electron acceptor in Type II RC is a movable quinone molecule which carries two electrons and two photons away from the RC.

Figure 2.4 Proteins (a) and pigments (b) composing the RC complex from *Tch. tepdium* [98]. Four protein subunits i.e., Cyt, L, M and H proteins are included in the RC complex. Six cofactors, i.e., four BChls (P_L, P_M, BCh_L and BCh_M) and two BPhes (BPh_L and BPh_M) are embedded in the proteins. Two quinones (UQ and MQ), four heme molecules (Heme-1, -2, -3 and -4), one spirilloxanthin (SPX) as well as two ions (Ca²⁺ and Fe²⁺) are also included in the RC complex from *Tch. tepdium*.

CS and ET in RCs: In photosynthetic RCs, an electron is ejected by the excited primary electron donor and passes through several pigments before it is picked up by the terminal electron acceptor. Although all the natural RCs have similar cofactor arrangements, diverse CS and ET mechanisms are found in different types of RCs. For instance, in spite of high transfer efficiency along the branch A, the CS and ET proceed through the two branches in the PSI RC [49, 56, 57]. However, the CS and ET are found to develop exclusively along one branch (denoted as the active branch) in the RCs of PSII and purple bacteria [49, 58–62].

Even with two quasi-symmetric branches, it is found that CS and ET mainly proceed asymmetrically through the L branch in the purple bacterial RCs [49, 58–66]. The primary phase of CS mainly takes place in the special pair P, which is located close to the periplasmic side of the membrane [55, 67]. The excited state of P (labeled as P^*) survives for 3 ps at room temperature while donating one electron to the primary electron acceptor. This primary CS process is faster than the recombination process in which the electron is transferred back to the donor [2]. Based on the cofactor arrangements, the accessory bacteriochlorophyll BCh_L is proposed to be the primary electron acceptor [2], and the electron transfer from P^* to BCh_L produces a state which can be labeled by $P^+BCh_L^-$. In the radical-pair state $P^+BCh_L^-$, the electron is almost localized in BCh_L . Then the electron migrates from BCh_L to BPh_L rapidly (in 1 ps) resulting in the formation of state $P^+BPh_L^-$. As a consequence of the fast transformation from $P^+BCh_L^-$ to $P^+BPh_L^-$, it is difficult to detect $P^+BCh_L^-$ experimentally [68, 69] and an intensive debate is ongoing on the identification of the real primary electron acceptor in this process.

The next step is the secondary electron transfer from BPh_L to quinone in branch L (MQ in Fig. 2.4) which can be completed in 200–300 ps, generating the state P^+MQ^- . Finally, the electron is transferred from MQ to the exchangeable quinone UQ within 100–200 μ s with the oxidation of MQ^- to MQ and the reduction of UQ to semiquinone UQ^- [2]. Simultaneously, the primary donor P is reduced from P^+ by absorbing an electron from the cytochrome c_2 complex. After uptaking another electron through the second round ET process in RC and two protons from cytoplasm, semiquinone UQ^- is fully reduced to quinol $UQ-H_2$. Quinol leaves RC and the site is occupied by a movable quinone which serves as the electron acceptor for the next round ET in RC. Quinol transports electrons and protons to the cytochrome bc_1 complex where electrons and protons are released to the periplasm. The electrons are delivered back to RC via the cytochrome c_2 complex. Concentration gradient of protons between the periplasm and the cytoplasm drives the synthesis of adenosine triphosphate (ATP) [2, 49].

On the basis of quasi-symmetric pigment arrangements and the asymmetric pathway

selection of the two branches, different surroundings of the pigments in the two branches are proposed to underlie the unidirectionality of the CS and ET in RCs from purple bacteria [67, 70]. Compared to the experiments on the bacterial RCs, theoretical investigations of the asymmetric pathway selection remain elusive. The excitonic coupling and the pigment-environment coupling are two fundamental factors affecting the dynamics of excitation energy transfer in photosynthetic complexes [71]. Systematic theoretical studies on excitonic coupling and pigment-environment coupling have not been conducted for the pigments in the bacterial RC complexes.

2.2 Quantum Coherence in Photosynthetic Systems

Aiming to reveal the mysterious energy transfer mechanism in natural LHCs and to provide design principles for manufactured photosynthetic apparatuses, considerable research efforts have been devoted to the studies of EET in native LHCs and massive breakthroughs have been accomplished. Among these remarkable findings, oscillatory beating signals observed in the 2DES of the FMO complex have been attracting extensive attention since 2007 [72]. By analyzing the 2DES data of FMO measured at 77 K, Engel *et al.* reported that the oscillations can persist for more than 660 fs and are interpreted as a signature of electronic coherence between the exciton states of the FMO complex. Subsequently, the coherence in FMO was found to decrease with increasing temperature and to survive for more than 300 fs even at 277 K [73]. Since the successful application of the 2DES to FMO, this technique has been widely adopted to investigate the excitation dynamics in other photosynthetic systems, such as the chlorosome [74–76], LH1 [77–79], LH2 [26, 80–86], LHCII [87–92], RC [5, 93–97], the PE545 and PC645 complexes from sea algae [98–101]. Observed in a variety of photosynthetic complexes, the quantum coherence is claimed to be a universal character of the EET in natural photosynthetic organisms [87, 98, 102].

Although quantum coherence has been widely detected in the energy transfer dynamics of diverse photosynthetic aggregates, several fundamental questions regarding on the quantum coherence still remain unanswered. One question concerns the origin of the co-

herence [103, 104]. The long-lived oscillatory feature was initially interpreted as coherence between electronic states (electronic coherence) [72, 105, 106]. Based on this interpretation, however, theoretically predicted dephasing times of such oscillations (200-300 fs) [106–109] are much shorter than the experimental value which is around 1.2 ps at 77 K [110]. It has also been found that coherence between some vibrational levels (vibrational coherence) can produce such oscillations with similar frequencies as those from electronic coherence in 2DES [111, 112]. The oscillation amplitude from the vibrational coherence is relatively weak compared to those observed [113]. Electronic transitions may couple to selective vibrational modes whose frequencies are resonant with those of electronic energy gaps [95, 104, 113–115]. Consequently, a mixed vibrational-electronic (vibronic) nature was assigned to the quantum coherence in the EET of photosynthetic complexes [112, 113, 116–120]. In order to investigate the origin of the long-lived oscillations in the 2DES of FMO, Mancal and coworkers applied a vibronic exciton model to calculate the 2DES of FMO at 77 K and predicted a dephasing time of 1.3 ps for the oscillations, which is consistent with the experimental observations [113]. The persistent oscillatory feature is proposed to result from the coherence between vibronic exciton states which are localized on the same molecule. In contrast, purely electronic coherence exhibits a fast decay within 200 fs [113]. Simulating the 2DES for a vibronic dimer, Jonas *et al.* also reported persistent quantum coherence in the electronic ground state due to vibronic mixing [112]. In an alternative mechanism, it is proposed by Plenio *et al.* that the electronic coherence can persist for a long time with the assistance of resonant vibrational coherence [116, 118].

Additionally the functionalities of the quantum coherence on the EET are still in contention. Initially the long-lived coherence observed in FMO was argued to accelerate the energy transfer from the chlorosome to the RC in the green sulfur bacteria [72, 106, 113] and other photosynthetic organisms [98, 121]. However, persistent vibronic coherence is found to be generated by vibronic states localized on the same pigment in FMO and thus it may play minor roles on EET which is mainly contributed by inter-pigment energy transfer [113]. With mounting experimental evidence, it is demonstrated that quantum coherence is certainly involved in the EET in photosynthetic systems, whereas coherence is not an

essential ingredient for efficient EET [104]. In recent 2D photon echo spectra of FMO at ambient temperature, the electronic coherence is found to rapidly decay with a time scale of 60 fs and long-lived electronic coherence is not detected [122]. With the Frenkel exciton model for FMO, quantum mechanical methods produce almost the same population dynamics as the approach based on the classical mechanics, indicating that quantum coherence does not contribute to the efficiency of EET in FMO [123]. All these findings and interpretations highlight the compelling need for sustained efforts to understand of the quantum coherence in the EET of photosynthetic complexes.

2.3 Theoretical Description of Energy Transfer in Photosynthetic Systems

Conventionally, excitons in photosynthetic complexes are characterized by the Frenkel exciton model. The site energies of individual pigments and the excitonic coupling between different pigments comprise the Hamiltonian of the excitonic system. The exciton propagation is modulated by the movements of the chromophores and the surrounding proteins. Modeled as a bath, the environment is coupled to the exciton (system of interest) with a system-bath coupling strength. The excitonic coupling and the system-bath coupling are two fundamental ingredients which determine the EET in LHCs.

In the limit of weak excitonic coupling, the Förster theory can be formulated by treating the excitonic coupling perturbatively [124]. In the Förster theory, the exciton is assumed to be localized on individual pigments and energy transfer is achieved by incoherent inter-pigment exciton hopping. Therefore, electronic coherence is neglected and only the excitation probability (population) evolves according to the master equations. The Förster theory fails to explain the oscillating signals in recent 2DES data of photosynthetic systems, which were claimed to be the signatures of quantum coherence [72, 96, 98]. Jang *et al.* proposed a multichromophoric Förster resonance energy transfer theory to describe exciton hopping between weakly coupled molecular groups [125, 126]. This theory has been adopted to study the energy transfer processes of B800 $\rightarrow$ B850 [126, 127] and B850 $\rightarrow$ B850 [128], whereas the coherent dynamics within strongly coupled groups is neglected

in this framework [125].

In the weak system-bath coupling limit, coherent energy transport can be accounted for by the Redfield theory by treating the system-bath interaction perturbatively in the exciton basis [129]. Although the Redfield theory has been widely adopted to investigate the exciton dynamics in many biological aggregates, it is formulated with the Markovian approximation which assumes that the surrounding equilibrates instantly after an electronic transition. In the conventional Redfield theory, all the exciton-phonon coupling elements in a pure exciton basis are considered as perturbations [129–131]. This treatment is invalid if the diagonal exciton-phonon coupling strengths in the exciton basis are strong [131]. To overcome this shortcoming, Zhang *et al.* improved the Redfield theory by describing only the off-diagonal terms perturbatively and depicting the diagonal elements exactly [132]. Multi-phonon effects are included in the modified Redfield theory [130, 133, 134]. It has been found that this theory is valid in broad parameter regimes, and can reduce to the traditional Redfield theory and the Förster theory in the respective limits [130, 135]. However, the modified Redfield theory only describes the population transfer since the coherence dynamics is neglected in the derivations [105, 130, 133, 134, 136].

As the excitonic coupling is comparable to the bath reorganization energy in LHCs [125, 137, 138], accurate descriptions of energy transport dynamics in many light harvesting systems need to go beyond perturbative theory and Markovian approximations [121, 138, 139]. Much progress on non-perturbative and non-Markovian treatments has been made [140–151]. For example, the HEOM approach has been developed to obtain the time-evolution of the reduced density matrix [140–145], while the ML-MCTDH method deals with the wave functions and determines the state via the Dirac-Frenkel variational principle [147–149]. Nevertheless these methods are only applicable to relatively small systems, such as FMO [106, 152–154], due to drastically increased computational demands for large systems. Many efforts have been devoted to extending the applications of the HEOM approach to various photosynthetic complexes with larger system sizes than FMO. Strümpfer *et al.* implemented the HEOM method on parallel computers and simulated

the EET in LH2, LH2-LH2, LH1-LH2 and LH1-RC systems [25, 155–157]. Recently the HEOM algorithm has been adapted to GPUs and utilized to investigate the EET in FMO and LHCII [158–160]. In native photosynthetic systems, such as chlorosome and LH1 surrounded with multiple LH2 complexes, hundreds of pigments participate in the excitation energy propagation. Additionally, many artificial supramolecular structures and nanodevices have been designed and synthesized with advanced fabrication techniques for light-harvesting and energy transfer purposes [1, 115, 161–180]. Escalante *et al.* fabricated LH2 nanoarrays and reported evidence of long-range energy transfer in such systems [176–179]. Numerically efficient methodologies are urgently needed to facilitate precise descriptions of EET in large-scale natural and manufactured photosynthetic systems.

In order to circumvent numerical difficulties that nonperturbative methods encounter with large systems, the Dirac-Frenkel time-dependent variational principle has been adopted by a number of authors to investigate the real time dynamics of exciton [181–185]. Compared to reduced density matrix approaches in which the DOFs of the bath need to be traced out, the variational method can characterize explicitly both the electronic and the bosonic DOFs, making it one of the most promising frameworks to study many-body boson-electronic systems where boson dynamics deserves to be depicted explicitly. Taking advantage of the variational method with the Davydov *Ansatz*, Zhao *et al.* investigated the inter-B850 exciton dynamics [186, 187] focusing on the exciton diffusion in the chlorosome with GPUs [188]. Great performance of this approach in simulating exciton dynamics in the chlorosome of more than 300 pigments gives strong evidence of the applicability of this method to large systems, such as B850 nanoarrays.

In addition to the efficient time-dependent variational approach, some mixed quantum-classical methods have been developed to study the exciton dynamics in large systems by treating the DOFs of the bath classically to facilitate fast computation. Examples include the mean-field treatment and the surface hopping algorithm. The mean-field approximation is valid in the adiabatic limit and leads to unreliable dynamics when the coupling between adiabatic states is strong, while the surface hopping approach is suitable to describe the

nonadiabatic dynamics with transitions between multiple coupled states. The original surface hopping method was put forth by Tully in 1990 [189], and was initially called the FSSH algorithm. A basic approach for the calculation of surface hopping wave functions or propagators involves selecting an initial position and momentum for a trajectory followed by integration of the trajectory one step forward in time on the initial state adiabatic energy surface. Probabilities for the system to evolve on the initial surface or hop to a different adiabatic surface are evaluated during this trajectory step. A decision to hop or not during this step is arrived at by comparing the hopping probabilities with a random number. The trajectory propagates on an appropriate energy surface, according to the decision made at each time-step. The wave function amplitude for each excited state is obtained by averaging over the contributions from all the trajectories ending in that state.

The FSSH algorithm is proved very advantageous due to the ease with which it can be generalized to any number of states. This approach enables calculation of many physical and chemical quantities, such as the hopping rate derived from the expansion coefficient. Although in Tully’s seminal work, three tests of the algorithm were provided for various systems, there exists a drastic gap from the algorithmic perspective to bridge its application to realistic systems. According to specific problems to be solved, many modifications and improvements of this method have been reported. Recently, the surface hopping approach has been used to model the charge transport in organic crystals, revealing a crossover from hopping to band-like transport behavior with increased electron-phonon coupling [190]. The 2DES of the dimer system simulated by the FSSH algorithm [191] nicely agree with the results from HEOM.

The Tretiak group and Sebastian Fernandez-Alberti have developed the NA-ESMD methodology [192, 193] over past few years. NA-ESMD is capable to launch direct nonadiabatic molecular dynamics simulations of photoinduced dynamics in large organic conjugated molecules involving multiple coupled electronic excited states. Such simulations are carried out by combining the FSSH scheme with “on the fly” analytical calculations of excited state energies, gradients, and non-adiabatic coupling terms [194–202]. This

is possible using the collective electron oscillator (CEO) method [203–206] at the AM1 semiempirical level in combination with the configuration interaction singles (CIS) formalism to characterize correlated excited states. Decoherence has been included in this approach to ensure internal consistency. This methodology, via extensive evaluations, has been proposed to be an adequate approach to extend the applications of generalized FSSH frameworks. It has been developed and tested for small or model systems, as well as for larger polyatomic systems containing many excited states and multiple unavoids potential energy surfaces crossings [207]. It provides a computationally efficient and accurate description of photoinduced dynamics in extended conjugated molecular systems.

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Chapter 3

Overview of Theoretical Methodologies

*This chapter documents a review of various theoretical approaches, which are applied to investigate static and dynamical properties of photosynthetic systems. A brief introduction of the quantum mechanics / molecular mechanics (QM/MM) approach and its applications to photosynthesis research is presented in Section 3.1. The QM/MM method is adopted to probe electronic structures and pigment-environment interactions in the bacterial RC from *Tch. tepidum*. The nonadiabatic excited-state molecular dynamics (NA-ESMD) algorithm is explained in detail in Section 3.2, including the fewest switches surface hopping method. The NA-ESMD approach is employed to simulate energy relaxation in a realistic Chla dimer system. Finally, Section 3.3 gives an overview of the Holstien molecular crystal model describing exciton motion in the presence of lattice scattering in molecular crystals. An introduction is also given for the Dirac-Frenkel time-dependent variational principle with the Davydov Ansätze. Implementation of this variational methodology on GPU architectures is elaborated as an efficient description of the exciton diffusion in large-scale B850 nanoarrays.*

3.1 Hybrid Quantum Mechanics / Molecular Mechanics Approach

As illuminated in Chapter 2, theoretical simulations of dynamical processes in photosynthetic systems require preliminary knowledge of electronic properties of the target systems, such as the excitation energies of the pigments, the excitonic coupling between the pigments, and the system-environment interactions. These quantities are calculated on the basis of the conformations extracted from the trajectories of molecular dynamics (MD) simulations. The electronic structures are affected by molecular vibrations and environmental fluctuations, and thus a sufficiently large number of arrangements are necessary. For any given molecular configurations, static quantum chemistry calculations are carried out to obtain the site energies of the chromophores. Reliable excitation energies and excitonic coupling are evaluated from the ensemble average over all the snapshots. The system-environment interactions are characterized by the spectral densities, which are calculated from the site energy fluctuations.

The QM/MM approach incorporates quantum mechanical calculations with MD simulations, making it a powerful tool to study various processes in natural and artificial systems at an atomic level. This method has found various applications in many research fields, such as physical chemistry, biochemistry, medicine and pharmacology. In this dissertation, the QM/MM method is employed to explore the electronic structures of the pigments in bacterial RC. The excitation energy fluctuations obtained are further utilized to evaluate the pigment-environment interactions.

3.1.1 Molecular Dynamics Simulation

Proposed by Alder and Wainwright in the late 1950s [1], MD simulations have been broadly adopted to study the dynamical processes of various molecules and aggregates. In the MD simulations, the movements of all the atoms are determined by the Newton's law of motion

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i \quad (3.1)$$

where m_i and $\mathbf{r}_i$ are the mass and coordinates of atom i , respectively. The force acting on this atom, $\mathbf{F}_i$, can be obtained from the potential energy $\mathcal{U}(\mathbf{r})$ according to the relation

$$\mathbf{F}_i = -\frac{\partial}{\partial \mathbf{r}_i} \mathcal{U}(\mathbf{r}). \quad (3.2)$$

In order to solve Eq. (3.1), the potential energy $\mathcal{U}(\mathbf{r})$ is first calculated from which $\mathbf{F}_i$ is derived using Eq. (3.2). For each atom, the potential energy is determined by its interactions with the surrounding atoms. In MD simulations, the interactions between all the atoms are approximately described by the force field. Force fields contain the information regarding the bonded terms like bond strengths, angles and torsion strains, and also give the energies corresponding to non-bonded terms such as Coulomb and Van der waals interactions. Many force fields, such as CHARMM, AMBER, and GROMOS, have been developed and widely used in the MD simulations of diverse systems.

With the initial atomic coordinates extracted from experimentally reported structures, the target system is placed into a water box with specific ions added to neutralize the whole box or to construct a certain environment for the system. Periodic boundary conditions are usually applied to the simulation box, making it possible to consider the mirror images of the original box in all directions. After sufficient steps of energy minimization at zero temperature, the whole box is ready for MD simulations under certain ensemble, i.e., NPT, NVT, or NVE (N, P, V, T, and E represent constant number of particles, pressure, volume, temperature and energy, respectively). In order to mimic realistic experimental conditions, the NPT and NVT ensemble are widely used in MD simulations. Typically, the system is gradually heated up to the desired temperature under NVT, and then long-time production simulations are developed using NPT until the equilibration is achieved. The structures at equilibrium are used in the analysis of the conformational details of the system and in further quantum chemistry calculations for the electronic properties [2, 3].

Using state-of-the-art computer hardwares and efficient integrated packages, it is possible to conduct MD simulations for enormous systems composed of millions of atoms. In this study, the CHARMM force field [4] is combined with the NAMD package [5] to do

advanced MD simulations of the RC complex from purple bacteria *Tch. tepidum*. This provides a series of configurations used in the quantum chemistry calculations for the excitation energies.

3.1.2 Quantum Mechanical Calculation

The distinct advantage of MD is its ability to simulate huge systems and provide detailed dynamic picture for numerous atoms. However, electronic structure calculations are beyond the scope of this method, as MD is based on the classical mechanics. Quantum mechanical approaches are thus developed to determine desired physical and chemical characteristics of various molecules and aggregates. The first attempt at solving for the electronic structure was the Hartree-Fock (HF) theory which expresses the molecular orbitals as a linear combination of atomic orbitals [6]. The HF theory also assumes that the electrons move faster than the nuclei due to the relative mass difference, i.e. it adopts the Born-Oppenheimer (BO) approximation. Since each electron is assumed to move in the average potential due to the nucleus and the other electrons, the HF theory cannot give an accurate description of the electron repulsion energies. In order to adequately describe the electron correlation, the density functional theory (DFT) [7] and the time-dependent density functional theory (TDDFT) [8] have been invented to study the ground and the excited state properties, respectively. Due to intensive demand on computational resources, the aforementioned approaches are only applicable to systems with relatively small sizes.

Since solving for large molecules is extremely taxing computationally, semi-empirical methods have been developed to tackle these problems. These methods incorporate approximations such as the “neglect of diatomic differential overlap” (NDDO) [9], the “intermediate neglect of differential overlap” (INDO) [10], and the “complete neglect of differential overlap” (CNDO) [11]. Among these methods, the INDO approach exhibits the best performance for excitation energy calculations [3, 12]. An improved method, the “Zerner’s intermediate neglect of differential overlap approximation parameterized for spectroscopy” (ZINDO/S) [12], was then proposed to predict accurately the $n \rightarrow \pi^*$ transitions in a vari-

ety of molecules, including the chlorophylls [13]. The ZINDO/S method is used in current study to calculate the excitation energies of the chromophores in the bacterial RC because of its superior computational efficiency and successful applications [14–33].

3.1.3 QM/MM Approach

The electronic structure of a molecule is affected by its surroundings. However, it is challenging to treat the whole system (molecule + environments) fully quantum mechanically. Thus, the environment is simulated using molecular mechanics while the molecules of interest are treated quantum mechanically. This forms the basis of the QM/MM approach [34, 35]. Since the final excitation energies from QM calculations are averaged over all snapshots, various small environmental changes present are all taken into account. Thus, more realistic excitation energies are obtained compared to that of an isolated molecule.

In this thesis, the QM/MM approach is applied to accurately depict the electronic structure of the bacterial RC with its associated environment. The computational procedure of the QM/MM approach is illustrated in Fig. 3.1. Sufficient snapshots of the equilibrium crystal structure are extracted from classical MD simulations. The molecular configurations in each frame are used to calculate the excitation energies using the ZINDO/S method. Atoms surrounding the molecules are treated as point charges and included for the site energy calculations. With the excitation energies for all the frames, not only can the average site energy be obtained, but also the pigment-environment coupling strength can be evaluated by calculating auto-correlation functions of excitation energy fluctuations.

3.2 Nonadiabatic Excited-state Molecular Dynamics Algorithm

Organic conjugated materials (OCMs) have received significant attention due to their remarkable chemical and physical properties [36]. They have both prominent electronic correlation and strong electron-phonon coupling strength [37–39]. This allows them to exhibit

Figure 3.1 Procedure followed for the QM/MM approach.

intricate electronic structures and multiple excited states which are involved in excitation dynamics. Unfortunately, precise descriptions of the nonadiabatic dynamics developing in the excited states are beyond the scope of the BO approximation. Thus, new theoretical frameworks need to be developed for these problems. It has been proposed that mixed quantum-classical methods can tackle the NA dynamics by propagating the electron DOFs quantum mechanically while simulating the phonon DOFs classically. The quantum and classical subsystems are evolved simultaneously, and the interactions between them are treated in a self-consistent manner. Among mixed quantum-classical methods, the FSSH approach has been applied to study the NA dynamics in various systems, owing to its excellent accuracy and high efficiency [40].

Figure 3.2 Sketch of the nonadiabatic dynamics between coupled adiabatic excited states. The potential energy surfaces (PESs) of the ground state (S_0) and the excited states (S_1 and S_2) are illustrated as quadratic functions of the nuclear coordinates $\mathbf{R}$. Upon excitation from S_0 to S_2 , the nuclear trajectory is propagated on the PES of the adiabatic state S_2 and the nonadiabatic transition from S_2 to S_1 is allowed.

On the basis of the FSSH algorithm, the NA-ESMD approach has been developed by the Tretiak group and Sebastian Fernandez-Alberti to simulate photoinduced dynamical processes within the excited states of large-scale OCMs [41–49]. In this methodology, excited state gradients and nonadiabatic coupling terms are calculated analytically by applying the CEO method with the CIS formalism to a semiempirical Hamiltonian. Thanks to comprehensive optimizations and systematic tests for various systems, the NA-ESMD algorithm exhibits high computational efficiency and accuracy, making it a promising approach to study excited state dynamics in realistic organic systems with multiple electronic excited states. Aiming to achieve an in-depth understanding of the intra- and inter-pigment ener-

gy transfer in natural photosynthetic systems, the NA-ESMD methodology is employed to investigate detailed energy relaxation mechanisms in a Chl*a* dimer. In this thesis both the relaxation rates and the energy transfer pathways in the dimer are obtained by analysing an ensemble of independent trajectories.

In addition to an introduction of the FSSH principle, the detailed procedure of the NA-ESMD methodology is presented in this section.

3.2.1 The FSSH Method

In order to adequately describe the molecular dynamics with quantum transitions, Tully developed the FSSH framework, in which electrons are propagated quantum mechanically while nuclei are simulated classically [40]. In the FSSH approach, the wave function $\psi(\mathbf{r}, \mathbf{R}, t)$ of electronic state at time t can be expanded with the electronic basis functions $\phi_\alpha(\mathbf{r}; \mathbf{R}(t))$

$$\psi(\mathbf{r}, \mathbf{R}, t) = \sum_{\alpha} c_{\alpha}(t) \phi_{\alpha}(\mathbf{r}; \mathbf{R}(t)) \quad (3.3)$$

where c_{α} is the expansion coefficient, $\mathbf{r}$ and $\mathbf{R}$ are the coordinates of electrons and nuclei, respectively. Substituting Eq. (3.3) into the time-dependent Schrödinger equation, the equation of motion of c_{α} can be expressed as

$$i\hbar \dot{c}_{\alpha}(t) = \sum_{\beta} c_{\beta}(t) (V_{\alpha\beta} - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{\alpha\beta}) \quad (3.4)$$

where $V_{\alpha\beta}$ is the matrix element of the electronic Hamiltonian and $\mathbf{d}_{\alpha\beta}(\mathbf{R}) = \langle \phi_{\alpha}(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}} \phi_{\beta}(\mathbf{r}; \mathbf{R}) \rangle$ is the nonadiabatic coupling vector. On the basis of Eq. (3.4), the equation of motion for density matrix element $\rho_{\alpha\beta} = c_{\alpha}c_{\beta}^*$ is written as

$$i\hbar \dot{\rho}_{\alpha\beta} = \sum_{\kappa} [\rho_{\kappa\beta} (V_{\alpha\kappa} - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{\alpha\kappa}) - \rho_{\alpha\kappa} (V_{\kappa\beta} - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{\kappa\beta})]. \quad (3.5)$$

The quantum population $\rho_{\alpha\alpha}$ on electronic state α satisfies

$$\dot{\rho}_{\alpha\alpha} = \sum_{\beta \neq \alpha} b_{\alpha\beta} \quad (3.6)$$

where

$$b_{\alpha\beta} = 2\hbar^{-1}\text{Im}(\rho_{\alpha\beta}^* V_{\alpha\beta}) - 2\text{Re}(\rho_{\alpha\beta}^* \mathbf{R} \cdot \mathbf{d}_{\alpha\beta}) \quad (3.7)$$

and $b_{\alpha\alpha} = 0$. The transition probability from current electronic state α to another state β during the time interval Δt is given as

$$g_{\alpha\beta} = \Delta t \frac{b_{\beta\alpha}}{\rho_{\alpha\alpha}}. \quad (3.8)$$

If $g_{\alpha\beta}$ is negative, it is set to be zero since negative transition probability is unphysical. When implemented into a stochastic switching formalism, transition probabilities are used in following judgements to determine the quantum transitions between coupled excited states.

At each time interval Δt , a random number $\xi \sim U(0, 1)$ is generated to compare with the transition probabilities and determine whether a quantum transition will occur or not. A hop from state α to state β takes place successfully when

$$\sum_{\kappa=1}^{\beta} g_{\alpha\kappa} < \xi \leq \sum_{\kappa=1}^{\beta+1} g_{\alpha\kappa}. \quad (3.9)$$

After hopping, the system will evolve on the potential energy surface (PES) of the new state β and certain adjustments are required for the energy conservation, such as the rescaling of nuclear velocities. If $\sum_{\kappa=1}^N g_{\alpha\kappa} < \xi < 1$ where N is the total number of excited states, the transition is rejected and the system continues to propagate on the PES of state α . For a hop tending to a higher energy state, the nuclear kinetic energy must be large enough to compensate the energy gap between the electronic states, otherwise the transition is classically forbidden.

Multiple trajectories are launched to obtain observables with desired precision from ensemble averages. In addition to the population dynamics of all the excited states, the pathways and time-scales of energy transfer are obtained by analysing simulated trajectories.

3.2.2 Initial Condition Preparation

Preliminary calculations are needed to prepare initial conditions for the NA-ESMD simulations. For each trajectory, a set of initial expansion coefficients c_α is assigned to the electronic excited states to simulate electron dynamics quantum mechanically, while a collection of nuclear coordinates $\mathbf{R}$ and velocities $\dot{\mathbf{R}}$ is required to propagate the nuclear motion classically.

Initial molecular structures can be manually constructed using commercial software or obtained from databases. Ground-state molecular dynamics (GSMD) simulations are then carried out according to the constant temperature Langevin equation. Several hundred snapshots are extracted from equilibrated GSMD simulations. Since the snapshots contain all the atomic geometries and velocities, each conformation is used to initiate a single NA-ESMD trajectory.

Prior to the assignments of initial values to the excited state coefficients, energies and oscillator strengths of the excited states of the target system need to be evaluated for each initial configuration by implementing the CEO method with the CIS theory to a semiempirical Hamiltonian, such as the Austin Model 1 (AM1), and the Parametric Method 1 (PM1). Then the linear absorption spectra are calculated by analysing the electronic structures for all the conformations. The contribution of each excited state to the overall spectra also is evaluated. To model the photoexcitation, a Gaussian laser pulse is adopted to initially populate the excited states for each configuration according to the Franck-Condon window

$$\chi_\alpha(\mathbf{r}, \mathbf{R}) = (f_\alpha/\Omega_\alpha^2) \exp[-\Gamma^2(E_{\text{laser}} - \Omega_\alpha)^2]. \quad (3.10)$$

Here f_α is the normalized oscillator strength of state α with a transition energy of Ω_α , E_{laser} is the laser energy, and Γ is the standard deviation of the laser pulse [38, 39].

3.2.3 Time Evolution of the Electronic and Nuclear DOFs

For an individual molecular configuration, a NA-ESMD trajectory is launched with the initial coefficients calculated for the electronic excited states and the nuclear coordinates and velocities extracted from the snapshots. Upon initial excitation, the nuclear DOFs evolve along the PES $E_\alpha(\mathbf{R})$ of excited-state α following the constant temperature Langevin equation

$$M_i \ddot{R}_i(t) = -\nabla E_\alpha(\mathbf{R}(t)) - \gamma M_i \dot{R}_i(t) + \mathbf{A}(t) \quad (3.11)$$

where M_i , $\ddot{R}_i$, and $\dot{R}_i$ denote the mass, the acceleration, and the velocity of nucleus i , respectively. The first term on the right hand side is the excited-state gradient $\nabla E_\alpha(\mathbf{R}) \equiv (\partial E_\alpha)/(\partial \mathbf{R})$. It is analytically calculated from the excited-state PES E_α which is obtained by the CEO approach. The third term is the stochastic force $\mathbf{A}$, which depends on the temperature T and the friction coefficient γ .

The quantum transitions between adiabatic excited states are described with the FSSH method, as demonstrated in Sec. 3.2.1. On the adiabatic basis, temporal evolution of the excited-state expansion coefficient c_α is simplified to

$$i\hbar \dot{c}_\alpha(t) = c_\alpha E_\alpha(\mathbf{R}) - i\hbar \sum_\beta c_\beta(t) \dot{\mathbf{R}} \cdot \mathbf{d}_{\alpha\beta}. \quad (3.12)$$

In the NA-ESMD algorithm, the nonadiabatic coupling vector $\mathbf{d}_{\alpha\beta}$ is computed with analytical techniques, which greatly reduce computational consumptions and make the NA-ESMD methodology applicable to simulating the excited state dynamics in large-scale organic molecules. In order to numerically solve Eq. (3.12), the expansion coefficient is expressed as a production of its real and imaginary parts $c_\alpha = \sigma_\alpha e^{i\theta_\alpha}$, producing following equations [38]

$$\dot{\sigma}_\alpha = - \sum_\beta \sigma_\beta \cos(\theta_\alpha + \theta_\beta) \dot{\mathbf{R}} \cdot \mathbf{d}_{\alpha\beta} \quad (3.13)$$

and

$$\hbar \sigma_\alpha \dot{\theta}_\alpha = -\sigma_\alpha E_\alpha - \hbar \sum_\beta \sigma_\beta \sin(\theta_\beta - \theta_\alpha) \dot{\mathbf{R}} \cdot \mathbf{d}_{\alpha\beta}. \quad (3.14)$$

With an initial electronic and nuclear configuration, Eqs. (3.11), (3.13) and (3.14) are solved simultaneously for a single trajectory. The classical DOFs are propagated according to Eq. (3.11) with a time step of Δt , while a smaller time step $\delta t \leq \Delta t$ is required for the evolution of the quantum expansion coefficients. Assuming a classical interval Δt is divided into $N_q = \Delta t / \delta t$ quantum steps, the transition probability $g_{\alpha\beta}$ measured at each classical time step Δt is computed as

$$g_{\alpha\beta} = \frac{\sum_{i=1}^{N_q} b_{\beta\alpha}(i) \delta t}{\rho_{\alpha\alpha}}. \quad (3.15)$$

Here $\rho_{\alpha\alpha}$ is the quantum population on the adiabatic state α . On the adiabatic basis, $b_{\beta\alpha} = -2\text{Re}(\rho_{\alpha\beta}^* \mathbf{R} \cdot \mathbf{d}_{\alpha\beta})$ and this quantity is evaluated at each quantum step.

3.2.4 Decoherence Correction

In the original FSSH formulism proposed by Tully, a bunch of independent trajectories is launched and the excited state coefficients are propagated coherently along each trajectory [40]. In a phase space where the nonadiabatic coupling is strong, a wavepacket initially localized on a certain excited state spreads among the strongly coupled states, generating considerable quantum amplitudes on multiple states. Within a short time after the quantum transition from an initial state to a final state, subpackets on the initial and final states are evolved coherently, due to the strong coupling between these states. However, these wavepackets should undergo independent evolutions when they are adequately detached in the phase space. This mechanism is known as decoherence, which can be induced by various environmental factors, such as the temperature and nuclear vibrations [50]. Therefore, a proper treatment of decoherence is crucial to an accurate description of nonadiabatic dynamics.

Decoherence was not considered in the standard FSSH approach [40], resulting in a violation of the “internal consistency” which ensures the equivalence between the classical and the quantum population on a certain quantum state. The classical probability on each state is obtained by calculating the fraction of the classical trajectories propagating

Figure 3.3 Schematic representation of various treatments of decoherence [50], (a) coherent evolution of the excited state coefficients in the original FSSH algorithm without decoherence correction, (b) instantaneous decoherence correction approach, and (c) energy-based decoherence correction method.

on that state. The quantum population on state α is the average of the quantum probability $\rho_{\alpha\alpha} = c_{\alpha}c_{\alpha}^*$ over all the trajectories. The internal inconsistency of the FSSH algorithm is shown in Fig. 3.3 (a). Initiated with a pure state, the electronic wavepacket is coherently evolved and the classical trajectory gradually hops to lower energy excited states. Although being broadened, the quantum wavepacket is still centered at the initial higher energy state and only a minor fraction of population is transferred to the excited states with lower energies. In contrast, the classical system continuously relaxes to lower states via a series of hops. Therefore, the time evolution of the quantum wave function falls behind the transitions between the excited states. In order to achieve internal consistency and improve the simulation accuracy, appropriate decoherence corrections should be incorporated into the

original FSSH method.

Various methods have been proposed to implement decoherence effects into the surface hopping algorithm. A straightforward scheme is to reset the quantum coefficients and remove the quantum coherence. After a hop, for instance, the quantum coefficient of the current state can be assigned with a value of unity. That is, the wavepacket collapses to the current state and is fully localized on this state. As illustrated in Fig. 3.3 (b), this method is denoted as instantaneous decoherence (ID) correction and has been successfully adopted to simulate nonadiabatic dynamics in systems with two states [50].

Another approach for decoherence correction is based on energies of the excited states. Instead of completely resetting the current-state coefficient to unity, Granucci *et al.* proposed the energy-based decoherence correction (EDC) method to rescale the quantum coefficients and narrow the wavepacket after each classical step Δt [50–52], as sketched in Fig. 3.3 (c). Before a hopping assessment, a trajectory was evolved along the PES of a current state β with a coefficient $c_\beta(t)$. Upon the judgement for the transition, a hop from state β to state α occurs and the trajectory starts to propagate on the PES of the updated current state α with an initial coefficient $c'_\alpha(t)$, which is obtained by rescaling the coefficients before transition through the relationship [50–52]

$$c'_\alpha(t) = c_\alpha(t) \left[\frac{1 - \sum_{\beta \neq \alpha} |c'_\beta(t)|^2}{|c_\alpha(t)|^2} \right]^{1/2}. \quad (3.16)$$

Here, $c_\alpha(t)$ is the coefficient of state α before the transition and $c'_\beta(t)$ is the rescaled coefficient of state β after the transition. For state β , $c'_\beta(t)$ is the initial coefficient for its evolution in the next classical time step Δt and is obtained via

$$c'_\beta(t) = c_\beta(t) e^{-\Delta t / \tau_{\beta\alpha}} \quad (3.17)$$

where $\tau_{\beta\alpha}$ is the so-called decoherence time.

Within the EDC scheme developed by Granucci *et al.* (G-EDC), the decoherence time

is formulated as

$$\tau_{\beta\alpha}(t) = \frac{\hbar}{|E_{\beta}(t) - E_{\alpha}(t)|} \left(C + \frac{E_0}{E_{kin}(t)} \right) \quad (3.18)$$

where $|E_{\beta}(t) - E_{\alpha}(t)|$ is the energy gap between current state α and state β , $E_{kin}(t)$ is the nuclear kinetic energy, C is a dimensionless parameter ($C \geq 1$), and E_0 has the same unit as energy ($E_0 > 0$). Above expression for the decoherence time is simplified from the formula

$$\tau_{\beta\alpha}(t) = \frac{\hbar}{|E_{\beta}(t) - E_{\alpha}(t)|} \left(C + \frac{E_0}{(\mathbf{P} \cdot \hat{\mathbf{s}})^2 / 2\mu} \right), \quad (3.19)$$

which was proposed by Truhlar and coworkers. Here, $\hat{\mathbf{s}}$ is the unit vector along the decoherent direction, $\mathbf{P}$ and μ are the momentum and the reduced mass of the nuclei, respectively [50, 53, 54].

Above methods for the decoherence correction have been implemented into the NA-ESMD algorithm and the performance has been extensively tested by simulating the photoinduced dynamics in various organic molecules [50]. With proper considerations of the decoherence, the NA-ESMD framework exhibits excellent internal consistency and improved accuracy.

3.2.5 Analysis of Simulation Results

As shown in Fig. 3.4 and described above, a swarm of independent NA-ESMD trajectories are launched and desired observables are evaluated from ensemble averages over all the trajectories. In order to obtain energy relaxation rates, the time evolution of the population on the excited states is one of the most significant quantities to be calculated from the NA-ESMD simulations. Within the mixed quantum-classical framework, both the classical and quantum population can be obtained from a bunch of NA-ESMD trajectories. The classical population on state α is defined as

$$P_{\alpha}^C(t) = \frac{N_{\alpha}(t)}{N_{\text{traj}}} \quad (3.20)$$

where $N_{\alpha}(t)$ is the number of trajectories propagating on state α at time t and N_{traj} is the total number of independent NA-ESMD trajectories. In contrast, the quantum population

Figure 3.4 Detailed procedure of the NA-ESMD methodology.

$P_{\alpha}^Q(t)$ is calculated as an ensemble average of the norm of the quantum coefficients

$$P_{\alpha}^Q(t) = \frac{\sum_i^{N_{\text{traj}}} |c_{\alpha}^i(t)|^2}{N_{\text{traj}}}. \quad (3.21)$$

Here $c_{\alpha}^i(t)$ is the quantum expansion coefficient of state α along the i th trajectory. The internal consistency requires that $P_{\alpha}^C(t) = P_{\alpha}^Q(t)$. The detailed energy relaxation process

can be investigated by monitoring the population dynamics, while the relaxation rates can be estimated by fitting simulated results with energy transfer models.

In addition to the population, the electronic transition density (TD) is another crucial observable from the NA-ESMD simulations and can be used to intuitively visualize the exciton transfer during the energy relaxation. On the basis of the AM1/CIS adiabatic states, the TD from ground state $\phi_g(\mathbf{r}; \mathbf{R}(t))$ to state $\phi_\alpha(\mathbf{r}; \mathbf{R}(t))$ is defined as

$$(\rho^{g\alpha})_{nm} \equiv \langle \phi_\alpha(\mathbf{r}; \mathbf{R}(t)) | c_m^\dagger c_n | \phi_g(\mathbf{r}; \mathbf{R}(t)) \rangle \quad (3.22)$$

where n and m are indices of atomic orbital basis functions. Diagonal elements $(\rho^{g\alpha})_{nn}$ denote the change of the electronic density induced by the g to α transition and obey the normalization relation $\sum_n (\rho^{g\alpha})_{nn}^2 = 1$. The TD fraction on a molecular group can be obtained by making a summation of the TD fraction on the atoms comprising this group.

3.3 Describing Exciton Dynamics with Time-dependent Variational Method

As demonstrated in Chapter 2, large-scale systems cannot be efficiently treated fully quantum mechanically. The huge number of DOFs that are included make it an extremely challenging numerical problem. Exhibiting balanced accuracy and efficiency, the Dirac-Frenkel time-dependent variational principle combined with the Davydov trial states has been employed to study the polaron dynamics in coupled exciton-phonon systems. Both the exciton and the phonon DOFs are treated explicitly in this approach. Implemented on the advanced GPU architectures, this formalism is adopted to simulate the coherent exciton dynamics in 1D and 2D B850 nanoarrays in this thesis. The exciton in the nanoarrays is modeled with the Holstein model and the time-dependent wave function is characterized with the Davydov D_1 *Ansatz*. The Dirac-Frenkel variational principle is utilized to evaluate the variational parameters, which determine the time-dependent wave function of the system.

3.3.1 The Holstein Hamiltonian

In 1950s, Holstein proposed a theoretical model to describe the polaron in organic crystals and pioneered the research of polaron dynamics in a variety of systems [55, 56]. Dressing the exciton with a phonon cloud, the Holstein model depicts a polaron system with a Hamiltonian composed of three terms

$$\hat{H} = \hat{H}_{\text{ex}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{ex-ph}} \quad (3.23)$$

where $\hat{H}_{\text{ex}}$, $\hat{H}_{\text{ph}}$, and $\hat{H}_{\text{ex-ph}}$ are the Hamiltonian for the exciton, the phonon bath, and the exciton-phonon interaction, respectively. The exciton part is expressed as electronically coupled two-level systems

$$\hat{H}_{\text{ex}} = \sum_{n=1}^N \epsilon_n \hat{a}_n^\dagger \hat{a}_n + \sum_{m \neq n} J_{mn} \hat{a}_m^\dagger \hat{a}_n \quad (3.24)$$

where $\hat{a}_n^\dagger$ ($\hat{a}_n$) is the exciton creation (annihilation) operator on site n with an excitation energy of ϵ_n , and J_{mn} represents the excitonic coupling strength between sites m and n . N is the totally number of sites in the system. Conventionally the boson bath is written as a collection of harmonic oscillators

$$\hat{H}_{\text{ph}} = \sum_q \omega_q \hat{b}_q^\dagger \hat{b}_q \quad (3.25)$$

with $\hat{b}_q^\dagger$ ($\hat{b}_q$) being the creation (annihilation) operator of a phonon with frequency ω_q and momentum $q = 2\pi n_q/N$ where $n_q = -\frac{N}{2} + 1, \dots, \frac{N}{2} - 1, \frac{N}{2}$. The exciton-phonon interaction Hamiltonian consists of diagonal and off-diagonal components

$$\hat{H}_{\text{ex-ph}} = \hat{H}_{\text{ex-ph}}^{\text{diag}} + \hat{H}_{\text{ex-ph}}^{\text{o.d.}} \quad (3.26)$$

where

$$\hat{H}_{\text{ex-ph}}^{\text{diag}} = -\frac{g}{\sqrt{N}} \sum_{nq} \omega_q \hat{a}_n^\dagger \hat{a}_n (e^{iqn} \hat{b}_q + e^{-iqn} \hat{b}_q^\dagger) \quad (3.27)$$

and

$$\hat{H}_{\text{ex-ph}}^{\text{o.d.}} = \frac{\phi}{2\sqrt{N}} \sum_{nq} \omega_q \left\{ \hat{a}_n^\dagger \hat{a}_{n+1} [e^{iqn} (e^{iq} - 1) \hat{b}_q + \text{H.c.}] + \hat{a}_n^\dagger \hat{a}_{n-1} [e^{iqn} (1 - e^{-iq}) \hat{b}_q + \text{H.c.}] \right\} \quad (3.28)$$

with $g(\phi)$ quantifying the diagonal (off-diagonal) coupling strength and H.c. representing the Hermitian conjugate.

As explained above, it is the site energy, the excitonic coupling and the exciton-phonon coupling that determine the polaron dynamics in the Holstein model. All these parameters can be obtained from the QM/MM approach, as presented in Section 3.1. A linear phonon dispersion, $\omega_q = \omega_0[1 + W(2|q|/\pi - 1)]$, is typically adopted to characterize the phonon modes with W and ω_0 standing for the phonon bandwidth and the characteristic phonon frequency, respectively. When only the diagonal coupling is considered, the Huang-Rhys factor S is used to parameterize g through the relation $\frac{1}{N} \sum_q g^2 \omega_q = S\omega_0$.

3.3.2 The Davydov *Ansätze*

In order to explicitly describe the exciton and phonon DOFs in the Holstein model, a series of Davydov trial states, i.e., the Davydov D_2 , $\tilde{D}$, and D_1 *Ansätze*, are adopted. The time-dependent variational calculations with these *Ansätze* show superior computational efficiency, validity in broad parameter regimes and capability to deal with the off-diagonal exciton-phonon coupling [57, 58]. The *Ansätze* have been successfully used to study the energy transfer in LH2 [59, 60]. The Davydov D_1 and D_2 trial states can be expressed as

$$|D_1(t)\rangle = \sum_n \psi_n(t) \hat{a}_n^\dagger |0\rangle_{\text{ex}} \otimes \exp \left\{ \sum_n [\lambda_{nq}(t) \hat{b}_q^\dagger - \text{H.c.}] \right\} |0\rangle_{\text{ph}} \quad (3.29)$$

and

$$|D_2(t)\rangle = \sum_n \psi_n(t) \hat{a}_n^\dagger |0\rangle_{\text{ex}} \otimes \exp \left\{ \sum_n [\lambda_q(t) \hat{b}_q^\dagger - \text{H.c.}] \right\} |0\rangle_{\text{ph}} \quad (3.30)$$

where $\psi_n(t)$ and $\lambda_{nq}(t)$ ($\lambda_q(t)$) are the time-dependent variational parameters for the exciton amplitudes and the phonon displacements, respectively. Equations of motion (EOMs) for the variational parameters can be derived by using the time-dependent Dirac-Frenkel variational principle. Accuracy of obtained trial states is determined by the amplitude of the “deviation vector”, which quantifies how faithfully a trial state obeys the Schrödinger equation.

The D_1 *Ansatz* is suitable to simulate the dynamical processes in which only the diagonal exciton-phonon coupling is considered. Compared to the D_1 *Ansatz*, the D_2 trial state is simplified and the phonon displacements $\lambda_q(t)$ are independent of the exciton sites. However, the D_2 *Ansatz* exhibits better performance than D_1 in the presence of off-diagonal coupling. Recently, it is shown that the variational method with the single D_2 *Ansatz* is equivalent to the semiclassical Ehrenfest method [61]. This approach has been recently extended to include multiple Davydov trial states [61–66], producing numerically exact results in a broad parameter regime. Denoting the number of the single Davydov *Ansatz* included as the multiplicity M , the multiple D_1 and D_2 *Ansätze* can be written as

$$|D_1^M(t)\rangle = \sum_i^M \sum_n^N \psi_{in}(t) \hat{a}_n^\dagger |0\rangle_{\text{ex}} \otimes \exp \left\{ \sum_q [\lambda_{iq}(t) \hat{b}_q^\dagger - \text{H.c.}] \right\} |0\rangle_{\text{ph}} \quad (3.31)$$

and

$$|D_2^M(t)\rangle = \sum_i^M \sum_n^N \psi_{in}(t) \hat{a}_n^\dagger |0\rangle_{\text{ex}} \otimes \exp \left\{ \sum_q [\lambda_{iq}(t) \hat{b}_q^\dagger - \text{H.c.}] \right\} |0\rangle_{\text{ph}}, \quad (3.32)$$

respectively. Here N stands for the total number of exciton sites. Applications have been made to simulate various dynamical processes, such as the dynamics of the Holstein polaron and the spin-boson model [57, 58, 61–67], energy transfer in photosynthetic systems [59, 60, 68–72], singlet fission dynamics [73–75], the Landau-Zener transition [76], and the qubit and photon dynamics in circuit QED system [75].

3.3.3 The Dirac-Frenkel Time-dependent Variational Principle

The time-dependent variational parameters are evaluated using the Dirac-Frenkel time-dependent variational principle [77–80]. Within this framework, the Lagrangian L is first constructed as

$$L = \langle \Phi(t) | \frac{i\hbar}{2} \left(\frac{\overrightarrow{\partial}}{\partial t} - \frac{\overleftarrow{\partial}}{\partial t} \right) - \hat{H} | \Phi(t) \rangle. \quad (3.33)$$

EOMs of the variational parameters $u_n(t)$ of the trial state $|\Phi(t)\rangle$ can be obtained from the Dirac-Frenkel time-dependent variational formula

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{u}_n^*} \right) - \frac{\partial L}{\partial u_n^*} = 0 \quad (3.34)$$

where $\dot{u}_n^*$ is the time derivative of u_n^* . For the Davydov *Ansätze* adopted in this thesis, variational parameter u_n represents the exciton amplitude or the phonon displacement. After solving the EOMs for all the variational parameters, one can obtain the explicit form of the time-dependent wave function with all the exciton and phonon DOFs depicted individually. Rich information regarding the polaron dynamics can thus be extracted from the time-dependent wave function. Both the exciton and phonon DOFs can be well treated on an equal footing by the time-dependent variational principle with the Davydov *ansätze* [57, 58, 78–82].

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Chapter 4***Electronic Structure of the Bacterial Reaction Center**

This chapter documents a systematic study of the electronic structures and the pigment-surrounding interactions of pigments in the bacterial RC by applying the hybrid QM/MM approach. The environmental effects are found to be essential for electronic structure determination. With transition charges obtained by fitting electrostatic potentials, excitonic coupling strengths are evaluated accurately. These findings help to interpret the directional charge separation in RC, and can be used in future simulations of dynamical processes occurring in RC.

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4.1 Introduction

In natural photosynthesis, the excitation energy generated by light absorption in LHCs is transferred to RCs, in which the CS process takes place. In contrast to two quasi-symmetric molecular branches in RCs, CS mainly develops along one active branch. Revelations of electronic structures of RC pigments can provide valuable insights into directional CS. Surrounding proteins should be taken into account to arrive at reliable electronic structures. Induced by molecular vibrations and protein modulations, site energy fluctuations can be used to evaluate the exciton-phonon coupling. As demonstrated in Chapter 3, the QM/MM approach is suitable to investigate the electronic structures of molecular systems with the consideration of environmental effects. The QM/MM approach has been widely employed to elucidate the surrounding influences on the preferential selection of energy transfer pathways in different photosynthetic systems [1–7]. For instance, Gao *et al.* [1] employed the QM/MM method to find that the pigment-environment coupling plays an important role in determining excitation energy transfer pathways in FMO. Zhang *et al.* [2] constructed an exciton model via extensive QM/MM calculations to investigate the environmental effects on the preferential selection of the CS and ET pathways of the RCs from PSII.

In this chapter, a combination of classical MD simulations and semiempirical quantum chemistry methods is applied to study influences of the environment on the electronic structures of the pigments in the RC from *Tch. tepidum*. The pigment-environment coupling is also calculated on the basis of excitation energy fluctuations. The determination of the environmental effects on the unidirectionality of the CS and ET will be discussed for the RC from *Tch. tepidum*. Section 4.2 describes the details of computational methods employed in this work. Excitation energies of the pigments are presented in Section 4.3 and the environmental effects on electronic structures are also discussed in this part. The excitonic coupling is collected in Section 4.4, and is used to explain the unidirectivity of the CS. Quantifying the exciton-phonon coupling, the spectral densities of all the cofactors in the RC from *Tch. tepidum* are calculated and discussed in Section 4.5.

4.2 Computational Details

Figure 4.1 Crystal structure of the RC from *Tch. tepidum* [8]. Different protein subunits are labeled and distinguished by different colours, i.e., Cyt in blue, L in pink, M in green and H in red. Six cofactors, i.e., two BChls composing the special pair (P_L and P_M , red), two accessory BChls (BCh_L and BCh_M , royal) and two BPhes (BPh_L and BPh_M , green) are embeded in the proteins. Two quinones (UQ and MQ, purple), four heme molecules (Heme-1, -2, -3 and -4, gray), one spirilloxanthin (SPX, orange) as well as two ions (Ca^{2+} and Fe^{2+}) are also included in the simulations.

Structure of the RC complex used in this work is extracted from the crystal structure of LH1-RC complex of *Tch. tepidum* (PDB ID: 3WMM) at 3.0 Å resolution [8]. As is shown in Fig. 4.1, three protein subunits in RC, i.e., the L, M and H subunits, and the protein of Cyt are included in our system as well as all the cofactors, i.e., four BChls, two BPhes, one CRT, two quinones (MQ and UQ) and four Heme molecules. One calcium ion and one non-heme iron are also included in the simulation. The system is neutralized by adding five chloride ions and solvated into a water box composed of TIP3P water molecules with 15 Å

from the boundaries of the complex to the edges of the box. The size of the simulation box is $125.0 \text{ \AA} \times 106.5 \text{ \AA} \times 153.0 \text{ \AA}$ with 190989 atoms in total. All simulations are done with the NAMD package with the CHARMM27 force field [9–11] for the protein and the ions. The force field parameters for the cofactors (BChl, BPhe and Heme) and UQ molecule are from the literature [12]. The parameters for MQ and CRT molecules are obtained from the CGenFF program [13, 14].

After 20000 steps of energy minimization, the system is gradually heated up from 30 K to 270 K in 90 ps and equilibrated at 300 K for 200 ps in an NVT ensemble, followed by two separate simulations for 300 K and 77 K, respectively. As to the simulation at 300 K, a 6 ns NPT run ($T=300 \text{ K}$, $P=1 \text{ bar}$) is launched directly, while for the 77 K case, the system is first simulated in another NVT ensemble at 77 K for 200 ps followed by 6 ns simulation under NPT ensemble ($T=77 \text{ K}$, $P=1 \text{ bar}$). A time step of 2 fs is applied for all MD simulations. Calculated root-mean-square deviations (RMSDs) of the protein backbones and the cofactors are used to verify system equilibration.

The energy gaps between the ground states and the first excited states of the cofactors are calculated individually. The ZINDO/S [15, 16] combined with the Configuration Interaction Singles (ZINDO/S-CIS) method (implemented in ORCA program version 2.8 [17, 18]) is adopted to calculate the excitation energies. An active space spanned by the 10 highest occupied and the 10 lowest unoccupied orbitals is applied to describe the configuration interaction. Configurations extracted from the equilibrated trajectories are utilized to prepare input files for the excitation energies calculations. Besides numerous applications of this method to site energy calculations of various photosynthetic pigments [1–3, 5–7, 16, 19–27], the ZINDO method has also been successfully applied to establish the electronic structure of the special pair from the bacterial RCs [28–31]. In this study, the ZINDO/S-CIS method is applied to calculate the excited state energies of the special pair in the RC of *Tch. tepidum*.

To investigate the influence of the environment on the excitation energies of the cofac-

tors, two sets of excitation energy calculations are carried out. The excitation energies for the cofactors with different configurations without the consideration of the environment. Another set of calculations is done by modeling the surrounding atoms of the target cofactor (within a cutoff radius) as atomic point charges (PCs). This treatment has been widely applied to obtain the electronic structure of the pigments in various photosynthetic systems, such as LH2, FMO and PSII [1–3, 26, 27]. The effect of the cutoff radii on the electronic structure was investigated recently [3] and a cutoff radius of 20 Å was adopted to calculate the excitation energies of the LH2 pigments. In order to determine if a cutoff radius is sufficiently large for calculations in this work, excitation energy calculations of P_L are conducted with larger cutoff radii. Only minor changes in the average excitation energy are found when the cutoff radius is larger than 20 Å, and therefore, a cutoff radius of 20 Å is also applied in this chapter.

Fully dynamic PCs which are updated for every snapshot are selected and used for the calculations in this work. The calculations for all snapshots can also be launched with the same PCs which are selected from a certain snapshot and called “frozen PCs” [19]. Even though the “frozen PCs” can take the surrounding environment of the pigments into consideration, the same PCs for all the snapshots represent a “frozen” environment and the fluctuations of the excitation energy are mainly induced by the different configurations of the pigments. In contrast to the “frozen PCs”, both the total number and the coordinates of the PCs in our calculations are distinct for each snapshot. As a result, calculated excitation energies in this chapter have larger fluctuations compared to those obtained with “frozen PCs”. Dynamic PCs are used in all calculations to subject the cofactors to a realistically fluctuating environment.

4.3 Excitation Energies

From the two sets of 6 ns NPT simulations at 77 and 300 K, 2000 snapshots are extracted from the trajectories of the last 4 ns with one snapshot recorded every 2 ps. Excitation energies of the cofactors are obtained as the average of results calculated for all the snapshots.

Figure 4.2 Excitation energies of the cofactors in the RC with (magenta) and without (cyan) the consideration of surrounding environment at 77 and 300 K. For the separated pigments, i.e., P_L, P_M, BCh_L, BCh_M, BPh_L and BPh_M, the excitation energies are the energies of the first excited states. For the special pair (P), the excitation energies for P₁ and P₂ are energies of the first and second excited states of P, respectively. All the results are averaged over 2000 configurations extracted from 4 ns production simulations with the blue lines being the standard deviations.

Calculations are firstly done for the site energies of all the individual cofactors, i.e., P_L, P_M, BCh_L, BCh_M, BPh_L and BPh_M, at 77 and 300 K. In Fig. 4.2, the site energies for these cofactors in vacuum (without considering the surrounding environment) are depicted. It is found that the site energy differences between the L branch cofactors and their M branch counterparts are originated in different protein environments and different configurations of the pigments. For the vacuum case, the cofactors in the L branch have similar site energies to their counterparts in the M branch. This indicates that the fluctuations in the pigment configurations in the two branches have similar influences on the pigment excitation energies. Compared to Acc. BChls, BPhes have lower site energies in the vacuum case at both 77 and 300 K. However, the BPhes have a shorter wavelength absorption band (755 nm) than Acc. BChls (800 nm) in the RC according to measured absorption spectra [32]. Therefore, it is essential to include environmental effects in electronic structures calculations of the RC complex.

Taking into account the surrounding atoms within 20 Å of the cofactors, the site energies for most of the cofactors show obvious corrections compared to those calculated in the vacuum case, except for the two Acc. BChls. For P_L and P_M which compose the special pair, PCs surrounding them contribute to an increase of their site energies by 47 and 104 meV at 300 K, and by 28 and 63 meV at 77 K, respectively. An increase of the site energies induced by the PCs is also found for BPh_L and BPh_M with the values of 33 meV and 87 meV at 300 K, and 21 meV and 91 meV at 77 K. Except for the slightly lower site energy of BPh_L at 77 K, both BPh_L and BPh_M have larger site energies than BCh_L and BCh_M in most cases which is consistent with the published experimental and theoretical results [32, 33].

The special pair in the RC from *Tch. tepidum* serves as the primary electron donor, and the BChls of the special pair have the longest absorption wavelength (885 nm) according to the measured spectra [32]. Contradictorily, the two BChls composing the special pair, i.e., P_L and P_M , have higher site energies than two Acc. BChls at both 77 and 300 K when the surrounding PCs are included in the calculations and the pigments are treated as separate units (see Fig. 4.2). Digging into the crystal structure of the RC complex, it is possible to explore the special arrangements of P_L and P_M . These two BChls are relatively near to each other with a distance of 7.7 Å between the magnesium atoms of the two molecules. The porphyrin rings of these two BChls are nearly parallel. On the basis of the configurations of the special pair, one can expect not only strong resonance coupling leading to a loss of individuality of the two molecules, but also a non-negligible orbital overlap between the two molecules. It is therefore more natural to calculate the excitation energy of the special pair by treating P_L and P_M as one aggregate P. Because of the strong excitonic coupling within the two monomers of the special pair, the first excited states of P_L and P_M will split into two energy levels of P [34], denoted as, P_1 and P_2 . The same calculation method as introduced above has been applied to obtain the excitation energies for the first two excited states of P. At both 77 and 300 K, excitation energies calculations of P with and without the consideration of surrounding PCs have been conducted for 2000 snapshots and the averaged results are shown in Fig. 4.2. As the first excited state, P_1 has the lowest energy

of all pigments, responsible for the longest wavelength absorption band in the absorption spectrum of the RC complex [32, 33]. The excitation energies of P_1 , 1.427 ± 0.124 eV at 300 K and 1.426 ± 0.056 eV at 77 K, show excellent agreement with that from the measurements (1.40 eV). The red shift of the excitation energy of P_1 and the blue shift of P_2 with respect to P_L and P_M are attributed to strong excitonic coupling and energy level splitting.

As shown in Fig. 4.2, BCh_L and BCh_M have very similar site energies even when the surrounding PCs are included in the calculations, and the differences are only 0.6 meV at 77 K and 4.3 meV at 300 K. This indicates that the environment-induced site energy difference between BCh_L and BCh_M is negligible. In contrast, the site energies of BPh_L and BPh_M show large differences with the consideration of their environments. BPh_L has lower site energies than BPh_M with a gap of 60.7 meV at 77 K and 44.6 meV at 300 K. This means that the surrounding environments of BPh_L and BPh_M have totally different influences on these two pigments. The asymmetric electronic structure of BPh_L and BPh_M will contribute to the asymmetry of the two branches. On the basis of our calculated results, it is conjectured that the two BPhes play a crucial role in the determination of pathways for CS and ET in the RC complex of *Tch. tepdium* as the asymmetric environment of BPh_L and BPh_M will most likely affect the charge-transfer states.

As to the influences of the temperature on the site energies of the cofactors, it is found that higher temperature leads to larger fluctuations in the results. For the special pair P, the aggregate has more atoms and more PCs surrounding it, such that flexibilities are included in the calculations, which produces a larger standard derivation of the excitation energy than in case of other cofactors.

4.4 Excitonic Coupling

In addition to the site energies of the RC cofactors, electronic interactions between the cofactors are also evaluated. Because of a sufficiently large interpigment distance and a lack of orbital overlaps, excitonic coupling between pigments in photosynthetic systems

Table 4.1 Excitonic coupling (Unit: cm^{-1}) with both PDA and TrEsp methods, center-to-center distances (Unit: Å) and angles between the transition dipole moments (Unit: $^\circ$) of the separated pigments in the RC at 300 K and 77 K.

	300 K				77 K			
	V_{mn}^{TrEsp}	V_{mn}^{PDA}	R_{mn}	Angle	V_{mn}^{TrEsp}	V_{mn}^{PDA}	R_{mn}	Angle
P_L - P_M	339.65	535.31	7.69	137.76	308.13	635.54	7.33	136.82
P_L - BCh_L	-50.64	-13.65	11.35	135.18	-67.82	-23.68	10.68	131.72
P_L - BCh_M	-152.2	-85.83	13.34	7.25	-144.8	-81.96	13.48	8.41
P_L - BPh_L	-15.74	-6.04	16.41	96.18	-11.19	-3.80	16.41	94.60
P_L - BPh_M	41.97	20.12	19.82	129.20	42.42	20.05	20.20	134.46
P_M - BCh_L	-144.7	-73.84	13.84	11.63	-171.6	-94.39	12.88	10.54
P_M - BCh_M	-66.89	-15.48	10.40	141.67	-53.38	-6.58	10.73	142.29
P_M - BPh_L	39.63	19.33	19.51	120.96	39.97	19.33	19.23	121.30
P_M - BPh_M	-13.51	-8.72	16.48	87.56	-15.86	-8.65	16.86	83.76
BCh_L - BCh_M	18.11	11.03	22.39	140.23	18.49	11.77	21.81	138.53
BCh_L - BPh_L	162.72	112.04	10.37	116.13	184.25	125.78	10.51	118.26
BCh_L - BPh_M	-10.16	-5.34	25.24	93.78	-11.47	-6.12	24.83	91.66
BCh_M - BPh_L	-8.97	-5.08	24.50	94.67	-7.84	-4.45	24.42	92.77
BCh_M - BPh_M	174.7	131.23	10.40	122.99	143.37	118.08	10.63	126.29
BPh_L - BPh_M	7.64	3.49	23.84	64.68	6.85	2.82	23.87	70.83

can be often calculated with the point dipole approximation (PDA) as

$$V_{mn}^{\text{PDA}} = \frac{f_{mn}}{4\pi\epsilon_0} \frac{\mu_m \mu_n}{R_{mn}^3} [\hat{e}_m \cdot \hat{e}_n - 3(\hat{e}_m \cdot \hat{e}_{mn})(\hat{e}_n \cdot \hat{e}_{mn})], \quad (4.1)$$

where μ_m (μ_n) is the magnitude of the Q_y transition dipole moment of pigment m (n) with the unit vector $\hat{e}_m$ ($\hat{e}_n$), R_{mn} is the center to center distance of pigments m and n with the unit vector $\hat{e}_{mn}$, ε_0 is the dielectric constant, and f_{mn} is a factor to account for the influence of the solvent on the excitonic coupling. This method has been widely applied to calculate excitonic coupling of pigments from various photosynthetic systems, such as LH1 [35], LH2 [20–22], FMO [1, 36–38] and RC [36] complexes. However, the method is only valid for pigments with large intermolecular distances [39], and it overestimates the excitonic coupling for the pigments arranged densely [36], such as P_L and P_M . To increase the accuracy in the region of small intermolecular distances, Renger and co-workers calculated the excitonic coupling with the transition charges from electrostatic potentials (TrEsp) method [36, 40], where the excitonic coupling is written as:

$$V_{mn}^{\text{TrEsp}} = \frac{f_{mn}}{4\pi\varepsilon_0} \sum_{I,J} \frac{q_I^m \cdot q_J^n}{|\mathbf{R}_I^m - \mathbf{R}_J^n|}. \quad (4.2)$$

Here, q_I^m (q_J^n) and $\mathbf{R}_I^m$ ($\mathbf{R}_J^n$) are the transition charges and coordinates of atom I (J) in pigment m (n), respectively. The transition charges are obtained by fitting the electrostatic potentials of the transition densities [36].

Quantum chemistry calculations are applied to obtain the transition charges of BChl and BPhe molecules in this study. The molecule geometry is first optimized by the DFT method with the B3LYP functional and the 6-31G** basis set [2, 36]. The CHELPG program [41] is then employed to obtain the transition charges based on the excitation transition density of the molecule calculated with the TDDFT on the optimized molecular structure. All DFT calculations are done with the GAUSSIAN 09 package [42]. In the calculations of transition charges, the phytol tail is replaced with a CH_3 group and the transition charges of the hydrogen atoms are added to the bonded carbon, oxygen and nitrogen atoms. The transition charges for BChl and BPhe are shown in Tables A.1 and A.2 of the Appendix A, respectively. The measured magnitudes of the Q_y transition dipole moments for the calculations of V_{mn}^{PDA} are 6.40 D and 6.25 D for BChl and BPhe molecules, respectively [43]. In this work, the calculated magnitude of BChl Q_y transition dipole moment is 7.23 D which agrees well with other published results [44]. For the BPhe molecule, the magnitude

of the dipole moment associated with the Q_y transition is 6.68 D. To match the experimental values, the transition charges for BChl and BPhe are rescaled with factors of 0.885 and 0.936, respectively [2, 12, 36].

The screening factor f_{mn} has been reported to be dependent on the center to center distance R_{mn} between two molecules as $f_{mn} = 2.68 \times \exp(-0.27 \cdot R_{mn}) + 0.54$ [45]. The center of the pigment is assigned to the coordinate of magnesium atom for BChl and the center of mass of two nitrogen atoms [N_2 and N_4 atoms in Figure A.1 (b) in the Appendix A] for BPhe. The center of the magnesium atoms of P_L and P_M is treated as the center of the special pair P.

Excitonic coupling calculations have been carried out on the same 2000 configurations used for the site energy calculations and final results are averaged along the trajectories. Both the PDA and the TrEsp methods are used to calculate the excitonic coupling between six individual pigments at 300 K and 77 K with the results shown in Table 4.1. At both 300 K and 77 K, P_L and P_M have the strongest excitonic coupling, consistent with the analysis in the previous section. The excitonic coupling between P_L and P_M calculated with the TrEsp method is comparable with those reported by other authors [33, 46]. Compared with the TrEsp method, the PDA method produces stronger excitonic coupling for P_L and P_M at both temperatures which is also consistent with the assertion that the PDA method overestimates the excitonic coupling for the pigments separated by short distance [36]. For the other pigments, the results from the PDA method are weaker than those from the TrEsp method. The excitonic coupling of BCh_L - BPh_L and BCh_M - BPh_M obtained with the TrEsp method is in excellent agreement with the experimental value of $\sim 170 \pm 30 \text{ cm}^{-1}$ [47] which leads support to the validity of the TrEsp method [48].

Separation and orientations of the transition dipoles are main factors that influence the coupling strength between two pigments. V_{mn}^{PDA} is determined by the coordinates of three atoms [Mg_1 , N_3 and N_5 atoms] and is more sensitive to the interpigment distance than V_{mn}^{TrEsp} . The short inter-molecular distance between P_L and P_M contributes to its strong ex-

citonic coupling. There are other four relatively strong excitonic coupling as shown with bold numbers in Table 4.1. Taking for example the results at 300 K, smaller angles between the transition dipole moments for P_L -BCh_M and P_M -BCh_L lead to stronger coupling than the pair of P_L -BCh_L and P_M -BCh_M (although the inter-molecular distances are larger than those of P_L -BCh_L and P_M -BCh_M). Similar to P_L - P_M , short pigment distances of BCh_L-BPh_L and BCh_M-BPh_M give rise to relatively strong coupling. Large center-to-center distance and nearly perpendicular transition dipole moments produce relatively weak excitonic coupling for BCh_L-BPh_M and BCh_M-BPh_L. Among all the pigments, BPh_L and BPh_M have the weakest excitonic coupling which results from the large inter-pigment distance, an unfavorable angle between the two transition dipole moments, and a smaller transition dipole moment of BPh_L and BPh_M molecules than the BCh_L and BCh_M molecules. P_M presents stronger excitonic coupling with the pigments in the L branch, i.e., BCh_L and BPh_L comparing to the values with the M branch pigments. Strong excitonic coupling between P_M and the L branch pigments will contribute to the directionality of the CS and ET process along the L branch as there is a charge transfer characteristic of the first excited state of the special pair from P_L to P_M which will be discussed below.

The excitonic coupling between P and other four pigments (BCh_L, BCh_M, BPh_L and BPh_M) are also evaluated. An excitonic Hamiltonian is constructed as

$$H_P = \begin{pmatrix} E_{P_L} & V_{P_L P_M} \\ V_{P_M P_L} & E_{P_M} \end{pmatrix} \quad (4.3)$$

for the special pair with E_{P_L} (E_{P_M}) being the site energy of P_L (P_M) including the consideration of PCs as obtained in the previous section. $V_{P_L P_M}$ is the excitonic coupling between P_L and P_M which is shown in Table 4.1. The two exciton states P_- and P_+ can be obtained by diagonalization of H_P with a transformation matrix

$$S = \begin{pmatrix} \alpha & \beta \\ -\beta & \alpha \end{pmatrix}, \quad (4.4)$$

yielding exciton state energies ϵ_{P_-} and ϵ_{P_+} .

Three methods will be applied in this section to the calculation of excitonic coupling

Table 4.2 Excitonic coupling (Unit:cm⁻¹) from the methods of SP-PDA, PDH-PDA, PDH-TrEsp and SP-TrEsp between the special pair and the other pigments in the RC at 300 K and 77 K.

	300 K				77 K			
	$V_{mn}^{\text{SP-PDA}}$	$V_{mn}^{\text{PDH-PDA}}$	$V_{mn}^{\text{PDH-TrEsp}}$	$V_{mn}^{\text{SP-TrEsp}}$	$V_{mn}^{\text{SP-PDA}}$	$V_{mn}^{\text{PDH-PDA}}$	$V_{mn}^{\text{PDH-TrEsp}}$	$V_{mn}^{\text{SP-TrEsp}}$
P ₋ -BCh _L	78.47	30.61	27.32	66.66	98.87	43.35	46.06	75.09
P ₋ -BCh _M	-122.1	-61.94	-99.27	-36.46	-112.4	-58.01	-85.68	-42.49
P ₋ -BPh _L	-21.26	-15.94	-33.23	-43.26	-20.04	-15.45	-32.56	-39.74
P ₋ -BPh _M	28.13	21.52	43.14	39.33	27.32	20.86	43.63	41.77
P ₊ -BCh _L	-38.13	-68.52	-150.9	-145.1	-38.43	-87.12	-178.7	-178.8
P ₊ -BCh _M	15.09	-61.44	-133.1	-176.4	1.26	-58.27	-128.3	-159.1
P ₊ -BPh _L	12.92	12.49	26.73	16.17	10.68	12.22	25.74	20.04
P ₊ -BPh _M	-0.73	4.24	8.91	24.88	2.89	6.46	12.12	23.91

between the special pair and the other pigments. The excitonic coupling between the P₋ state and the other pigments is computed as well as that between the P₊ state and the other pigments.

In the first method, the transition dipole moments for the two exciton states of the special pair are constructed and utilized to compute the excitonic coupling with the P-DA method. With the coefficients α and β obtained from the diagonalization of H_P , the transition dipole moments for P₋ and P₊ can be expressed as $\vec{\mu}_{P_-} = \alpha\vec{\mu}_{P_L} - \beta\vec{\mu}_{P_M}$ and $\vec{\mu}_{P_+} = \beta\vec{\mu}_{P_L} + \alpha\vec{\mu}_{P_M}$ where $\vec{\mu}_{P_L}$ ($\vec{\mu}_{P_M}$) is the transition dipole moment of P_L (P_M) and $\alpha^2 + \beta^2 = 1$ [46, 49–53]. The PDA method is then applied to calculate the excitonic coupling between the special pair and the other pigments. $V_{P_L P_M}^{\text{TrEsp}}$ is chosen as the excitonic coupling between P_L and P_M in the diagonalization of H_P . The values for α and β are 0.8690 and 0.4948 at 300 K (0.8082 and 0.5889 at 77 K), respectively. This method is

abbreviated as SP-PDA in the rest of this chapter.

The second method is based on the partial diagonalization of the complete excitonic Hamiltonian (PDH) for the RC system comprising six pigments. Similar to H_P , the excitonic Hamiltonian for the system of P_L - P_M - BCh_L - BCh_M - BPh_L - BPh_M is constructed as

$$H = \sum_m E_m |m\rangle\langle m| + \sum_{m \neq n} V_{mn} |m\rangle\langle n| \quad (4.5)$$

where E_m is the averaged excitation energy of the state $|m\rangle$ localized on cofactor m with the consideration of the surrounding environment, and V_{mn} is the excitonic coupling between $|m\rangle$ and $|n\rangle$. H_P is included in H as a 2×2 block. In order to obtain the two exciton states of the special pair, the H_P block in the complete excitonic Hamiltonian is diagonalized within the framework of an expanded transformation matrix

$$S' = \begin{pmatrix} S & 0 \\ 0 & \mathbf{I} \end{pmatrix} \quad (4.6)$$

where $\mathbf{I}$ is a 4×4 identity matrix and S is the transformation matrix to diagonalize H_P . The partially diagonalized complete exciton Hamiltonian can then be written as

$$H' = S'^{-1} H S'. \quad (4.7)$$

The excitonic coupling between the special pair and the other pigments is included in the first two rows (columns) in H' , and the excitonic coupling between any pair of the other four pigments remains unchanged from the values in H . Both the TrEsp and the PDA methods can be applied to compute the excitonic coupling V_{mn} in Eq. (4.5). The method is denoted as PDH-TrEsp (PDH-PDA) with V_{mn} obtained from the TrEsp (PDA) method.

Quantum chemistry calculations are carried out to obtain the transition charges for the first two exciton states of the special pair. The transition charges are then utilized to estimate the excitonic coupling with the TrEsp method. This method is denoted as SP-TrEsp. The transition charges for the first two excited states of the special pair are obtained with the CHELPG algorithm and the excitation transition density is calculated by the TDDFT

with the wB97XD functional and the 6-31G** basis set to account for the charge transfer characteristics of the excited states. The transition charges for the first two excited states of P are shown Table A.1 of the Appendix A. The transition charges are rescaled with the same factor (0.885) as that used for the single BChl.

Table 4.3 Exciton energies (eV) and coefficients of P₋-P₊-BCh_L-BCh_M-BPh_L-BPh_M system at 300 K and 77 K.

T (K)	exciton level	exciton energies	P ₋	P ₊	BCh _L	BCh _M	BPh _L	BPh _M
300	1	1.425	0.988	-0.003	-0.109	0.065	0.076	-0.044
	2	1.499	-0.085	-0.207	-0.708	-0.416	0.512	0.122
	3	1.502	-0.127	0.113	-0.341	0.834	0.295	-0.269
	4	1.541	0.008	0.109	0.583	-0.051	0.804	0.024
	5	1.578	-0.021	-0.082	0.030	-0.287	-0.001	0.954
	6	1.619	0.003	-0.962	0.176	0.205	0.015	0.026
77	1	1.424	-0.985	0.006	0.119	-0.064	-0.102	0.047
	2	1.486	0.150	0.080	0.523	0.008	-0.836	0.004
	3	1.513	0.074	-0.138	-0.041	-0.924	-0.032	0.344
	4	1.535	-0.051	-0.127	-0.828	0.055	-0.539	-0.041
	5	1.568	-0.020	-0.038	0.028	-0.346	0.003	-0.937
	6	1.665	-0.003	0.978	-0.156	-0.137	-0.006	0.007

The excitonic coupling between the special pair and the other pigments calculated by the above methods at both 77 K and 300 K is shown in Table 4.2. From the results of the SP-PDA, PDH-PDA and PDH-TrEsp methods it can be found that P₋-BCh_M and P₊-BCh_L have relatively stronger coupling than P₋-BCh_L and P₊-BCh_M, respectively. The reason

is that all these three methods are based on the coefficients obtained from the diagonalization of H_P in which P_L has lower site energy than P_M , so P_- has larger distribution on P_L and P_+ is contributed from P_M with larger portion. As shown in Table 4.1, both P_L -BCh_M and P_M -BCh_L have relatively stronger excitonic coupling compared to P_L -BCh_L and P_M -BCh_M which in turn produce stronger coupling for P_- -BCh_M and P_+ -BCh_L than P_- -BCh_L and P_+ -BCh_M, respectively. Compared to the SP-PDA and PDH-PDA methods, the PDH-TrEsp and SP-TrEsp methods lead to stronger coupling between the P_+ state and the other pigments. This effect is due to the nearly antiparallel arrangement of transition dipole moments of P_L and P_M . In the SP-PDA method, the excitonic coupling between the special pair and the other pigments is directly computed with the PDA method based on the transition dipole moments of the special pair. It is a crude approximation to construct the dipole moments of the excited states of the special pair from the transition dipole moments of single molecules (P_L and P_M), as the local excitation is assumed and the charge transfer characteristic cannot be captured. Additionally, the transition dipole for the P_+ state is very small, and leads to underestimation of coupling between the P_+ state and the other pigments. Another drawback induced by the small value of transition dipole of the P_+ state is that its sign is very sensitive to the configuration fluctuations of individual molecules. A small configuration change of BChls of the special pair may flip the direction of the transition dipole moment of the P_+ state. So the excitonic coupling between the P_+ state and the other pigments calculated with the SP-PDA method is not as accurate as those obtained with the other three methods (PDH-PDA, PDH-TrEsp and SP-TrEsp). The sign of the excitonic coupling may also be at variance with those from the other methods as a result of the small transition dipole moment of the P_+ state which may flip its direction for different configurations. The results of the SP-TrEsp method is not affected by the biased site energies of P_L and P_M , and the constructions of the transition dipole moments for the two exciton states of the special pair (P_- and P_+). The SP-TrEsp method gives stronger excitonic coupling for P_- -BCh_L than P_- -BCh_M. The stronger excitonic coupling between P_- and BCh_L will favor the CS along the L branch from the excited special pair. The excitonic coupling between the special pair and the other pigments calculated with the SP-TrEsp method will be applied for the further calculations below.

The system of $P_-P_+-BCh_L-BCh_M-BPh_L-BPh_M$ can be described with the partially diagonalized Hamiltonian H' in which the coupling between P_- and P_+ is zero. The site energies in H' (diagonal entries) have been obtained in the previous section with the effects of the environments included (see the magenta columns in Fig. 4.2). The excitonic coupling between two individual pigments is calculated with the TrEsp method (shown in Table 4.1), and the SP-TrEsp method is applied to compute the excitonic coupling between the special pair and the other pigments (shown in Table 4.2). Diagonalizing the Hamiltonian H' one can obtain the eigenvalues ε_M and corresponding eigenvectors $\xi_m^{(M)}$ as shown in Table 4.3. Eigenvalue ε_M is the energy of the delocalized exciton state $|M\rangle$ and $\xi_m^{(M)}$ is the coefficient that represents the contribution of the localized excited state on cofactor m to the exciton state $|M\rangle$.

As shown in Table 4.3, the lowest and highest exciton states are mainly localized on the P_- and P_+ states, respectively. Both the second and the fourth exciton states are delocalized on BCh_L and BPh_L . In contrast, the third and the fifth exciton states are mostly localized on BCh_M and BPh_M , respectively.

With the exciton energy ε_M and expansion coefficient $\xi_m^{(M)}$, one can calculate the excitation probability of the localized excited state on cofactor m which is defined as [2]:

$$P_m = \sum_M f(M) |\xi_m^{(M)}|^2 \quad (4.8)$$

where $f(M)$ is the Boltzmann factor for the exciton state $|M\rangle$ with energy of ε_M . The excitation probabilities of all the cofactors in the RC are plotted in Fig. 4.3 at both 300 K and 77 K. Compared with the Acc. BChs and BPhes, the P_- state exhibits the highest probability to be excited at 300 K ($P_{P_-} \approx 87\%$) and 77 K ($P_{P_-} \approx 97\%$) and is the most probable site for initial excitation. As a result of the highest excitation energy, P_+ state has very low probability to be excited at both 77 K and 300 K.

As the primary electron donor in the bacterial RCs, the special pair has been one of the hot spots for the investigations of asymmetric CS and ET in the RCs. Tremendous

Figure 4.3 Excitation probabilities of the cofactors in the RC at 300 K and 77 K.

experimental [54–67] and theoretical [28, 51, 68–81] efforts have been devoted to construct the electronic structures of P and attempted to explain the directionality of CS and ET. Asymmetric charge density distributions on the two halves of P have been proposed as the intrinsic characteristic of P [28, 71, 73], and observed for both ground and the excited state of P [54, 55, 57–59, 62–65, 69, 70, 72–75, 79] as well as the cation radical of P [66, 67, 70, 71]. The symmetry breaking of the charge density distribution on P_L and P_M could result from various factors, *e.g.*, different orientations of the side groups of two pigments [59, 70, 71, 73] and the tuning effects of the surrounding protein residues [57, 58, 69, 71, 74]. For the RCs from *Rb. sphaeroides*, P_L has higher electron density when P is in the ground state while excited P has more electron density localized on P_M . The asymmetric charge distribution on P then gives rise to the $P_L^+P_M^-$ CT characteristics for the excited state of P.

In addition to the transition charges, the transition densities of the first two excited s-

Figure 4.4 Transition density (left column) for the first two excited state of the special pair in the bacterial RC and the contributions to these excited states from the transitions between different orbital pairs (right column). HOMO and LUMO stand for the highest occupied molecular orbital and lowest unoccupied molecular orbital for the special pair, respectively. In the dimer, the left monomer is P_L and the right one is P_M .

tates of the special pair are obtained with quantum chemistry calculations. As illustrated in Fig. 4.4, the plots of the transition densities for P_- and P_+ agree well with the analytical predictions. As discussed in the previous section, the P_- state is the antisymmetric com-

combination of the localized excited states on P_L and P_M with a transition dipole moment of $\vec{\mu}_{P_-} = \alpha\vec{\mu}_{P_L} - \beta\vec{\mu}_{P_M}$, while the P_+ state is a symmetric combination with a transition dipole moment of $\vec{\mu}_{P_+} = \beta\vec{\mu}_{P_L} + \alpha\vec{\mu}_{P_M}$. From the transition densities shown in Fig. 4.4, one can find that the P_L has an ordinary Q_y excitation in the two states. P_M presents a transition dipole opposite (parallel) to the Q_y direction in the P_- (P_+) state.

In order to investigate the transition characteristics of the first two excited states of the special pair, contributions from the orbital transitions to these two excited states are calculated, and the results are shown in the right column in Fig. 4.4. The excitations to P_- and P_+ are mainly attributed to the transitions among the four molecular orbitals (as shown in Fig. 4.4) including the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The states of P_- and P_+ are mainly composed of two transitions of HOMO-1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1, and both transitions are local. The P_- state also has a transition of HOMO $\rightarrow$ LUMO which possesses an inter-molecular charge transfer component from P_L to P_M . Most of the excited states of the special pair, including the P_+ state, have CT characteristics. Not listed in Fig. 4.4 are transitions with a CT component and less than 10% contribution to the P_+ state. The CT characteristics of the P_- state and the strong excitonic coupling of P_M -BCh_L favor the CS along the active (L) branch in the RC from *Tch. tepidum*.

4.5 Spectral Densities

A key quantity in the description of system-bath coupling is the spectral density. In this section, our focus is the spectral density in the RC, which quantifies the pigment-protein coupling for all cofactors, using the combined QM/MM approach. Kleinekathöfer and co-workers have calculated the spectral densities for the pigments in LH2 [12], FMO [23] and PE545 [19] from the fluctuations of the excitation energies of the pigments obtained from the quantum chemistry calculations. Renger *et al.* proposed a charge density coupling (CDC) method [37, 40, 82, 83] to obtain the excitation energy fluctuations, which has been applied to calculate the spectral densities for the pigments in FMO [84, 85] and RC [24]

from *Rb. sphaeroides*. In this work, the site energies are calculated for the pigments in the RC based on the trajectories from MD simulations, and site energy fluctuations are utilized for spectral density estimation for all cofactors in the RC. The excitation energy fluctuation $\delta E_m(t_i)$ for cofactor m is defined as

$$\delta E_m(t_i) = E_m(t_i) - \bar{E}_m, \quad (4.9)$$

where $E_m(t_i)$ is the site energy at time t_i , and $\bar{E}_m$ is the averaged site energy of cofactor m with the consideration of the protein environments. The autocorrelation function of the excitation energy fluctuation for cofactor m is defined as [12]

$$\begin{aligned} C_m(t_i) &= \langle \delta E_m(t_i) \delta E_m(t_0) \rangle \\ &= \frac{1}{N-i} \sum_{k=1}^{N-i} \delta E_m(t_i + t_k) \delta E_m(t_k), \end{aligned} \quad (4.10)$$

where the summation is over the N configurations extracted from the trajectories of the MD simulation. Then the spectral density $J_m(\omega)$ can be written as [19, 25, 86, 87]

$$J_m(\omega) = \frac{\beta\omega}{\pi} \int_0^\infty dt C_m(t) \cos(\omega t) \quad (4.11)$$

where $\beta = 1/(k_B T)$ is the inverse temperature.

A total of 50000 configurations are extracted from the 100 ps NPT production simulation at 300 K and used for the excitation energy calculation with a time step of 2 fs between adjacent snapshots. Time windows of 4 ps are prepared to calculate the correlation functions with a spacing of 400 fs between adjacent time windows. There are 241 4-ps-long time windows along a trajectory of 100 ps and the final correlation functions are averaged over the correlation functions calculated for all the time windows.

Calculated spectral densities for all cofactors in the RC are shown in Fig. 4.5. For the two pigments P_L and P_M which compose the special pair, the spectral densities have similar shapes while the coupling to the surrounding environment of P_M is slightly stronger than that of P_L . As a result of the short distance between P_L and P_M , a large number of surrounding atoms of the two pigments are the same, which leads to similar coupling of

Figure 4.5 Spectral densities of the cofactors in the RC based on the MD simulations at 300 K. The excitation energy for the first excited state of P is used to calculate the spectral density for P.

the two molecules to nuclear modes. The spectral density for the first excited state of the special pair P is also calculated and shown as the solid red line in Fig. 4.5 (a). Besides the modes of the intramolecular vibration of BChls, the intermolecular modes between P_L and P_M also contribute to the spectral density of P. As an aggregate of P_L and P_M , the special pair P has more surrounding atoms included in the site energy calculations than individual pigments (P_L and P_M), which produces larger fluctuations of its site energy. Both factors give rise to larger amplitudes of the spectral density of P for most frequencies than those of single P_L and P_M . Among the cofactors, Acc. BChls have the minimal spectral density amplitudes. The position and the amplitudes of the peaks of the spectral density for BCh_L are similar to those of BCh_M , indicating that BCh_L and BCh_M are coupled to similar environmental modes with similar strengths. This is in agreement with the results

from site energy calculations, from which it is found that the surrounding environments of BCh_L and BCh_M have nearly the same influences on the two pigments. Comparing the spectral densities of BPhes in Fig. 4.5 (c) to those of all the other cofactors, one can find that BPhes have the strongest pigment-protein coupling strengths of all the cofactors in the RC. BPh_M is coupled to its surrounding more strongly than BPh_L, and differences in amplitude between the spectral densities of the two BPhes are larger than those for Acc. BChls. The strong pigment-protein coupling of BPhes is consistent with the large fluctuations of the site energies of these two pigments. BPh_L and BPh_M are coupled to their respective protein environments with different coupling strengths, a finding that also leads to differing environmental effects on the site energies of BPh_L and BPh_M (see Fig. 4.2) and the branch selectivity of the CS and ET in the RC. Corresponding coupling strengths to a specific vibration mode for all the cofactors can be extracted from the calculated spectral densities and made use of in theoretical modeling of the CS and ET dynamics including full details on the nuclear degrees of freedom in these processes.

In principle spectral densities should be independent of temperature and this issue has been discussed in details in some recent literature [85, 86]. The spectral densities for all the cofactors are also calculated on the basis of the MD simulations at 77 K and the results are shown in Fig. 4.6. The overall shape of the spectral densities is temperature independent. Only for a few pigments, magnitudes of spectral densities show minor difference between different temperatures. In a recent study on the spectral densities of the FMO pigments [6], obvious variations of the magnitudes are found for the spectral densities calculated from the ZINDO calculations at different temperatures. The spectral densities from ZINDO calculations are also shown to be dependent on the initial conditions for the production run in MD simulations. In current work, the deviations of magnitudes of the spectral densities at different temperatures may rise from the fact that the production trajectories in MD simulations are initialized from different configurations at 300 and 77 K.

In summary, the excitation energies, electronic coupling, and spectral densities of the pigments in the RC complex from *Tch. tepidum* are obtained in this study by performing

Figure 4.6 Spectral densities of the cofactors in the RC based on the MD simulations at 77 K. The excitation energy for the first excited state of P is used to calculate the spectral density for P.

extensive QM/MM simulations. All these parameters can be adopted in future simulations for dynamical processes in the RC, such as the energy transfer, charge separation and electron migration. The linear and nonlinear optical spectra of the RC system also can be investigated on the basis of the information presented here, deepening our understanding of the static and dynamic properties in the RC complex.

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Chapter 5*

Energy Relaxation in Chla Dimer

The nonadiabatic excited-state molecular dynamics algorithm is applied in this chapter to investigate excitation energy transfer and exciton localization dynamics in a Chla dimer system located at the interface of two subunits of the LHCII trimer. Energy relaxation pathways in the Chla dimer are revealed with their rates calculated. With both intra- and intermolecular components, the relaxation from the B band to the Q_y band in the Chla dimer is faster than that in the Chla monomer, thanks to level splitting induced by intermolecular excitonic coupling. Exciton redistribution upon photoexcitation is also investigated by recording transition density dynamics.

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5.1 Introduction

In LHCII, solar energy can be absorbed by both Chla and Chlb, and resulting excitation energy is transferred between pigments. In addition to intermolecular energy transfer, the relaxation process that funnels energy from high-lying excited states to the lowest excited state is another crucial step of excitation energy transfer in photosynthetic systems. Extensive efforts have been applied to study the internal conversion process in various photosynthetic pigments, such as Chla [1–5], Chlb [1], BChla and mutants of BChla [6–8]. However, only the internal conversion in an individual pigment has been elucidated in these investigations [1–8]. On the basis of successful applications of the NA-ESMD approach to the internal conversion in Chla and Chlb monomers, it makes sense to extend the NA-ESMD simulations to systems with multiple pigments, where intermolecular energy transfer and internal conversion can be investigated simultaneously.

A Chla dimer in LHCII, shown in Fig. 5.1, is chosen as the target system for NA-ESMD simulations in this chapter. Located in the interface of two subunits of LHCII trimer, the Chla dimer is an ideal model to study inter-pigment energy transfer in natural photosynthetic systems. Computational details are described in Section 5.2, covering ground state MD simulations and initial configuration preparations. Presented in Section 5.3 is the population dynamics which is fitted with an energy transfer model to yield the relaxation rates. The energy transfer pathways are discussed in Section 5.4. In order to reveal inter- and intra-monomer energy transfer mechanisms in the Chla dimer, the transition density for the excited states is calculated and analyzed in Section 5.5.

5.2 Computational Details

The crystal structure of the LHCII complex in *Spinacia oleracea* [9] (PDB ID: 1RWT) is adopted for our simulation. Two Chla molecules (residues 613 and 614 in chain B of 1RWT) are selected in this work to simulate excited-state dynamics in the Chla dimer

Figure 5.1 (a) Crystal structure of light-harvesting complex II (LHCII) from *Spinacia oleracea* [9] (PDB ID: 1RWT). (b) System simulated in this chapter, chlorophylla (Chla) dimer in the LHCII complex. (c) Molecular structure of Chla. Carbon (gray) atoms are labeled according to the IUPAC convention for porphyrins, with the standard x- and y- axes of Gouterman's four-orbital theory shown. The nitrogen and magnesium atoms are in blue and yellow, respectively. Chlorophyll phytyl tails (R) are replaced by a methyl group in the simulations. The total carbon macrocycle is defined as the carbon atoms comprising the porphyrin ring structure (carbon atoms 1 - 20 including atoms C13¹ and C13²), whereas the "inner macrocycle" (atoms between two red dashed lines excluding the N atoms) consists of atoms C1, C4, C5, C6, C9, C10, C11, C14, C15, C16, C19, and C20, and the "outer macrocycle" is comprised of carbon atoms from the total carbon macrocycle minus those in the inner macrocycle.

system, and the orientation of the two pigments in the dimer is shown in Fig. 5.1 (b).

First, ground state MD simulations for the Chla dimer are developed from the initial

structure for 520 ps at 300 K with a time step of 0.5 fs. Four nitrogen atoms of Chla molecules are fixed during the simulation to stabilize the relative molecular configurations in the absence of protein environment. The constant-temperature Langevin equation is adopted to describe the evolution of the nuclear degrees of freedom with a friction coefficient of 2.0 ps^{-1} . 500 snapshots from the last 500 ps simulation are extracted with a space of 1 ps, and every snapshot is then used to initialize another set of ground state MD simulation for 200 fs after releasing the constraints on the nitrogen atoms. The final configurations are used to compute absorption spectra and to simulate the NA-ESMD of the Chla dimer.

Figure 5.2 Absorption spectra of Chla dimer. The red solid line is the integral absorption spectra obtained from the sampling results containing 500 molecular configurations. The colored profiles are the contributions of the first 20 excited states considered in the calculations to the final absorption spectra. The contributions of $S_{11} - S_{20}$ are represented with gray profiles.

The absorption spectra are calculated for 500 configurations with 20 excited states considered. Shown in Fig. 5.2 are the entire absorption spectra and contributions from all the excited states to the spectra. The first absorption band of Chla dimer is around 1.69 eV which is redshifted with respect to the first excited state (Q_y) of Chla monomer (1.88 eV)

due to inter-chromophore coupling. The second peak is at about 2.53 eV, and the third, at 2.91 eV close to the Soret band of the Chla monomer. As it has been pointed out previously [1], although the absolute excitation energies produced by semiempirical methods deviate from measurements, energy gaps between excited states agree with experimental findings. This agreement allows simulations to predict the overall time scales of nonradiative relaxation from the high-energy excited states in the *B* band to the lowest excited state Q_y in the Chla monomer, in agreement with transient absorption pump-probe measurements [1].

A Gaussian-shaped laser pulse is chosen to simulate photoexcitation on the configurations obtained from the ground state MD. Excited state α is initially populated according to a Frank-Condon window defined by $g_\alpha(\mathbf{r}; \mathbf{R}) = (f_\alpha/\Omega_\alpha^2) \exp[-T^2(E_{\text{laser}} - \Omega_\alpha)^2]$ where f_α is the normalized oscillator strength of state α with a frequency of Ω_α , $\mathbf{r}$ ($\mathbf{R}$) is the electronic (nuclear) coordinate, and E_{laser} is the laser energy. In this study, the Gaussian-shaped laser pulse is centered at 2.93 eV (423 nm) with a standard deviation of 42.5 fs corresponding to a full width at half maximum (FWHM) of 100 fs. A total of 500 independent excited state trajectories are calculated for 1 ps at 300 K, with a classical time-step of $\Delta t = 0.1$ fs and $N_q = 4$ quantum time steps per classical step to simultaneously propagate the coefficients of the electronic states. During the excited state dynamics, the 10 lowest excited states are taken into account for each trajectory.

5.3 Population Dynamics

To investigate internal conversion dynamics in the Chla dimer, the average classical populations of the electronic states are calculated from an ensemble of 500 trajectories. The average populations for the first six excited states are shown in Fig. 5.3. Here it can be clearly seen that nearly 90% of the excitation relaxes to the lowest excited states within 600 fs.

According to the simulated absorption spectra of the Chla dimer, the first ten excited states in the simulations are categorized into three bands, i.e., Q_y , Q_x and *B* bands. The

S_1 and S_2 states yield the Q_y band while the S_3 and S_4 states contribute to the Q_x band. The B band is composed of excited states $S_5 - S_{10}$. The average populations for these three bands are computed by summing the average populations of corresponding electronic states which belong to the bands.

Figure 5.3 Calculated time evolution of classical population for (a) the lowest six electronic states and (b) three bands of Chla dimer system. The results are averaged over 500 trajectories. Dashed lines in (b) are the fitting curves of the band populations with the fitting parameters in Table 5.1.

To quantify the internal conversion rates in the Chla dimer, a first-order monodirectional

Table 5.1 Comparison of internal conversion rates obtained from a first-order irreversible population model for $B \rightarrow Q_x$, $Q_x \rightarrow Q_y$, and $B \rightarrow Q_y$ pathways for Chla dimer and monomer [1] systems. Populations of specific excited states are averaged from 500 trajectories for Chla dimer and 500 trajectories for Chla monomer [1] in the NA-ESMD simulations.

System	$B \rightarrow Q_x$		$Q_x \rightarrow Q_y$		$B \rightarrow Q_y$
	k_1 (fs ⁻¹)	τ_1 (fs)	k_2 (fs ⁻¹)	τ_2 (fs)	τ_{tot} (fs)
Monomer	0.0101	99.2±1.1	0.00781	128±2	227±3
Dimer	0.00924	108.2±1.1	0.02952	33.9±0.7	142±2

transfer model is adopted to describe the energy transfer from B to Q_x and from Q_x to Q_y with rate constants k_1 and k_2 , respectively. This yields the sequential transfer pathway $B \xrightarrow{k_1} Q_x \xrightarrow{k_2} Q_y$, to fit the average populations of these three bands.

The population of each band can then be given as

$$B(t) = B_0 e^{-k_1 t} \quad (5.1)$$

$$X(t) = \frac{k_1 B_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) + X_0 e^{-k_2 t} \quad (5.2)$$

$$Y(t) = B_0 + X_0 + Y_0 - B(t) - X(t) \quad (5.3)$$

where B_0 , X_0 , and Y_0 represent the initial ($t = 0$) populations of the B , Q_x , and Q_y bands, respectively. The fitting is conducted through a least-squares regression analysis. The rate constants and the corresponding time constants ($\tau_1 = k_1^{-1}$, $\tau_2 = k_2^{-1}$) are presented in Table 5.1 in comparison to the respective parameters obtained for the Chla monomer [1]. Shown in Fig. 5.3 (b) are the simulated population on the bands and the fitting results using modeled rate constants. The coefficients of determination (R^2) for the population curve fittings are 0.9958, 0.9192, and 0.9985 for $B(t)$, $X(t)$, and $Y(t)$, respectively.

As shown in Table 5.1, the $B \rightarrow Q_x$ relaxation is marginally slower in the Chla dimer than that in the Chla monomer. In stark contrast, the dimer system has much faster $Q_x \rightarrow Q_y$ transfer rate compared to the Chla monomer. Consequently, the overall relaxation from

B to Q_y in the Chla dimer (142 fs) is faster than that in the Chla monomer (227 fs). For the Chla dimer, each of the three energy bands is mainly composed of two electronic states as shown in Fig. 5.2. As a result of the intermolecular excitonic coupling and the configurational differences between the two monomers, there is a level splitting between the two electronic states (the so-called Davydov's pair) comprising the energy band of the Chla dimer. The level splitting reduces the effective energy gaps between the absorption peaks of the Chla dimer and enhances the relaxation efficiency between these energy bands.

Once the molecular system reaches the lowest Q_y band, there is a final relaxation step within the band. The population transfer from S_2 to S_1 exhibits contributions from two distinguished energy transfer regimes. As shown in Fig. 5.3 (a), more than 95% of population transfer to the Q_y band occurs within 400 fs. In this time interval, the population of S_1 increases quickly as the electronic energy flows into the Q_y band. From 400 fs on, the energy of S_2 is transferred to S_1 slowly and leads to a gradual increase of the population on S_1 . In order to reveal the fast and slow transfer components from S_2 to S_1 , the population of S_1 is fitted using the above model with the transfer rate from S_2 to S_1 being k_{S21} . It is assumed that in the transfer pathway $B \xrightarrow{k_1} Q_x \xrightarrow{k_2} S_2 \xrightarrow{k_{S21}} S_1$, the energy of the Q_x band is first transferred to S_2 then from S_2 to S_1 . This assumption is based on the fact that only a few hops to S_1 are observed from S_5 (6) and S_3 (29), which are negligible compared to an enormous number of hops from S_2 (3690) to S_1 . Here, the population of S_2 can be fitted by the equation

$$S_2(t) = ae^{-k_1 t} + be^{-k_2 t} + ce^{-k_{S21} t} + S_{20}e^{-k_{S21} t} \quad (5.4)$$

with

$$a = -\frac{B_0 k_1 k_2}{(k_1 - k_2)(k_{S21} - k_1)},$$

$$b = \frac{B_0 k_1 k_2 + k_1 k_2 X_0 - k_2^2 X_0}{(k_1 - k_2)(k_{S21} - k_2)},$$

and

$$c = \frac{B_0 k_1 k_2 - k_2 k_{S21} X_0 + k_1 k_2 X_0}{(k_{S21} - k_1)(k_{S21} - k_2)}.$$

Figure 5.4 Population of S_1 averaged from 500 trajectories and fitting results with Eq. (5.5) for fast (a) and slow (b) regimes.

Subsequently, the population of S_1 is

$$\begin{aligned}
 S_1(t) &= B_0 + X_0 + S_2(0) + S_1(0) \\
 &- B(t) - X(t) - S_2(t)
 \end{aligned}
 \tag{5.5}$$

The population of S_1 in these two time intervals are fitted with Eq. (5.5) and the results are shown in Fig. 5.4. By fitting the first 400 fs and subsequent 400-600 fs time-intervals of relaxation dynamics, the fast $k_{s21} = 0.0237 \text{ fs}^{-1}$ ($\tau_{s21} = k_{s21}^{-1} = 42.19 \text{ fs}$) and slow $k'_{s21} = 0.00716 \text{ fs}^{-1}$ ($\tau'_{s21} = 139.66 \text{ fs}$) transfer rates can be evaluated respectively.

5.4 Energy Relaxation Pathways

Subsequent to photoexcitation, the Chla dimer experiences an efficient B band $\rightarrow Q_y$ band transition. According to the FSSH algorithm [10] implemented in our NA-ESMD simulations, electronic transitions are described as hops from one initial electronic state S_i to another S_f final state. The relative probabilities of effective $S_i \rightarrow S_f$ transitions during all the NA-ESMD simulations are summarized in Table 5.2. An effective $S_i \rightarrow S_f$ transition refers as $S_i \rightarrow S_f$ hops for which no back-hopping $S_f \rightarrow S_i$ occurs along the rest time of this NA-ESMD trajectory. The relative probabilities have been normalized for hops corresponding to the same S_i state.

Table 5.2 Fraction of effective transitions from S_i to S_f ($S_i > S_f$)

$S_f \backslash S_i$	S_6	S_5	S_4	S_3	S_2
S_5	0.97	-	-	-	-
S_4	0.02	0.78	-	-	-
S_3	0.01	0.21	1.0	-	-
S_2	0	0	0	0.95	-
S_1	0	0.01	0	0.05	1.0

It can be clearly seen from the data in Table 5.2 that the relaxation mainly takes place along the sequential pathway $S_6 \rightarrow S_5 \rightarrow S_4 \rightarrow S_3 \rightarrow S_2 \rightarrow S_1$ in the Chla dimer. Transitions from S_6 to S_5 , S_4 and S_3 occur with relative probabilities of 0.97, 0.02 and 0.01, respectively. According to the ambiguous initial localization of this state (see Figs. 5.5 and 5.6) these initial relaxation steps involve both intra- and inter- monomer energy transfer events. In the case of effective hops from S_5 , the sequential pathway to S_4 takes up 78% of its energy transfer flux and, according to Figs. 5.5 and 5.6, it involves mainly an inter-monomer energy transfer. The intra-monomer $S_5 \rightarrow S_3$ channel accounts for the remainder 21%. In contrast, effective hops from S_4 mostly develop only through the inter-monomer channel to S_3 . The inter-monomer channel of $S_3 \rightarrow S_2$ occupies 95% of the relaxation

Figure 5.5 Schematic illustration of the overall relaxation pathway in the Chla dimer upon excitation from the ground state S_0 to high excited states. From the transition densities of the excited states, it can be seen that almost all the excited states are localized on individual pigments.

from S_3 while the intra-monomer channel holds a minor 5% contribution, followed by a final inter-monomer $S_2 \rightarrow S_1$ relaxation.

In order to intuitively depict the energy transfer pathways in the Chla dimer, the transition densities of the lowest six excited states are calculated by applying the CEO approach with the CIS formalism to the AM1 Hamiltonian. As shown in Fig. 5.5, transition densities of excited states $S_1 - S_6$ show that these states are almost localized on individual

pigments. S_1 , S_3 and S_5 are localized on CLA 613, while S_2 , S_4 and S_6 are localized on the other monomer. Therefore, the energy relaxation in the dimer is mainly contributed from inter-molecular transitions and the overall relaxation pathway is sketched in Fig. 5.5. A small portion of the transition density of S_6 (S_5) is on CLA 613 (614), indicating that intra-pigment transition is also involved in the energy relaxation the Chla dimer.

5.5 Electronic Transition Density Analysis

To study exciton delocalization over the Chla dimer, the electronic transition density (TD) is calculated as

$$(\rho^{g\alpha})_{nm} \equiv \langle \phi_\alpha(\mathbf{r}; \mathbf{R}(t)) | c_m^\dagger c_n | \phi_g(\mathbf{r}; \mathbf{R}(t)) \rangle \quad (5.6)$$

where $\phi_g(\mathbf{r}; \mathbf{R}(t))$ ($\phi_\alpha(\mathbf{r}; \mathbf{R}(t))$) is the wave function of the AM1/CIS adiabatic ground (excited) state, $c_m^\dagger$ (c_n) are the creation (annihilation) operators, and indices n and m refer to the atomic orbital basis functions. The diagonal elements $(\rho^{g\alpha})_{nn}$ represent the net change of the electronic density resulting from excitation from the ground state g to an electronic excited state α [11]. The normalization condition $\sum_n (\rho^{g\alpha})_{nn}^2 = 1$ is valid within the CIS approximation [12]. The fraction of the TD localized on different Chla monomers, or arbitrary groups of atoms in the pigment can be obtained by summing up the atomic contributions belonging to each of them as

$$(\rho^{g\alpha})_X^2 = \sum_{n_A} (\rho^{g\alpha})_{n_A, n_A}^2 + \frac{1}{2} \sum_{n_B} (\rho^{g\alpha})_{n_B, n_B}^2 \quad (5.7)$$

where A is the index of atoms localized in the X-group, and the index B labels the atoms located at the interface of group X and another group.

5.5.1 Initial Exciton Localization

On the basis of the NA-ESMD simulations, one can analyze exciton localization of various electronic excited states at the moment of Frank-Condon photoexcitation from ground state configurations equilibrated at 300 K. Static calculations are carried out for each configuration, producing the TDs of all the excited states. Each state has specific TD distributions on

Figure 5.6 Distribution of the transition density for the electronic states on the higher monomer (HM) of S_1 at initial time (500 configurations).

two pigments. If the TD fraction of state α on monomer CLA 613 is close to one, this state is almost completely localized on CLA 613. If every monomer has nearly half of the TD fraction of state α , the state is delocalized over two molecules. In order to illustrate the TD distributions of all the excited states, a pigment is chosen as the reference monomer and denoted as the higher monomer (HM) of S_1 for a configuration if the TD fraction of S_1 on this molecule is greater than 0.5, i.e., $(\rho^{01})_{\text{HM}}^2 > 0.5$. The TD fractions of the other excited states ($S_2 - S_6$) on the reference monomer can be obtained for individual configurations. As a result of molecular vibrations, different conformations may have different reference monomers. Roughly, half of the total configurations (i.e., 243 out of 500 configurations) have monomer CLA 613 as their HM of S_1 . As shown in Fig. 5.6, histograms of the TD fractions of all the excited states on the HM of S_1 are constructed by analyzing the TDs of all the snapshots.

The initial distribution of all the states on the HM of S_1 is shown in Fig. 5.6. It is clearly seen that S_1 is strongly localized on its HM. The TD of all other electronic states are distributed near 0 and 1 which indicates persistent localization on a single monomer for all cases. As expected, for most configurations, S_1 and S_3 are initially localized on the same monomer while S_2 and S_4 are localized on the other monomer. High-lying energy states S_5 and S_6 seem to be ambiguously localized on any chromophore. Thus, in spite of significant excitonic coupling between monomers, which splits the electronic states, thermal fluctuations at room temperature essentially localize the excited state wave function initially to a single Chla in a dimer configuration.

5.5.2 Transient Electronic Transition Density Redistribution

Summarizing the above observations, the $B \rightarrow Q_y$ internal conversion process after photoexcitation of the Chla dimer takes place mainly through a sequential cascade mechanism involving multiple exciton exchanges between monomers. Notably, a localization pattern shown in Fig. 5.6 is getting significantly perturbed by the dynamics, i.e., the wave function should not necessarily remain localized on a single Chla, which is subject to analysis in this section. Namely, the time evolution of the photoinduced inter- and intra- monomer electronic transition can be tracked by TD redistribution in the Chla dimer. Thus, complementary studies of the exciton spatial localization in the trajectory ensemble depict a comprehensive picture on the interplay of concomitant inter- and intra- monomer relaxation processes.

Inter-monomer Exciton Exchange

The Chla dimer considered in this study is composed of CLA 613 and CLA 614 residues from the chain B of the crystal structure 1RWT of LHCII. The laser excitation leads to nearly equivalent probabilities for the two residues to become excited initially. The time

Figure 5.7 Fraction of electronic transition density localized on (a) the monomer CLA 613 and (b) the higher monomer (HM*) being averaged over all trajectories.

evolution of the average fraction of TD on CLA 613 ($(\rho^{0\alpha})_{\text{CLA 613}}^2$) is shown in Fig. 5.7 (a). Its value fluctuates around 0.6, indicating a slightly higher tendency of the exciton to get trapped on it.

Figure 5.8 Time evolution of the participation number of Chla dimer taken as an average over all trajectories.

Assuming that the system is on current state α upon initial excitation of a configuration, the TD fractions on the two monomers can be calculated at the initial time. In order to further investigate signatures of exciton delocalization between the two monomers during the energy relaxation, the higher monomer (HM*) for a trajectory is defined as the monomer with a higher TD fraction of state α initially, $(\rho^{0\alpha})_{\text{HM}^*}^2(t=0) > 0.5$. It is important to stress that, according with the given definition, HM* can be either CLA 613 or CLA 614 residues and it should be chosen individually for each NA-ESMD trajectory. Once the HM* has been selected at $t=0$ for each trajectory, it remains the same throughout this NA-ESMD simulation. The time evolution of the average over all trajectories of $(\rho^{0\alpha})_{\text{HM}^*}^2$ is depicted in Fig. 5.7 (b). HM* corresponds to CLA 613 for 53.6% of trajectories. As a result of an ultrafast effective inter-monomer exciton exchange, the value of $(\rho^{0\alpha})_{\text{HM}^*}^2$ experiences an ultrafast decrease during the first ~ 100 fs. Its final value of ~ 0.5 may

follow from two possible scenarios. In one scenario, a true delocalized electronic state can be equally shared by two monomers, and in the second, it can result from localized states that hop between monomers. In order to distinguish between these scenarios, one needs to further analyze the participation number which is defined as

$$P = \left[((\rho^{0\alpha})_{\text{CLA } 613}^2)^2 + ((\rho^{0\alpha})_{\text{CLA } 614}^2)^2 \right]^{-1} \quad (5.8)$$

where $(\rho^{0\alpha})_{\text{CLA } 613}^2$ $((\rho^{0\alpha})_{\text{CLA } 614}^2)$ is the fraction of TD localized on monomer CLA 613 (614). The value of P varies in the interval between 1 and 2 as each monomer is treated as a unit. If $P \approx 1$, it means that the TD is almost completely localized on a single Chla monomer, while $P \approx 2$ means that the TD is delocalized over the two Chla monomers. The time evolution of the average value of P during the NA-ESMD simulation is shown in Fig. 5.8. As can be seen, the initial excitation effectively generates a weakly delocalized state between the two monomers. Thereafter, the excited state dynamics leads to an almost complete localization of the TD to one monomer within ~ 100 fs.

The inter-monomer exciton exchanges throughout the NA-ESMD simulations can be further analyzed by events with significant changes of $(\rho^{0\alpha})_{\text{monomer}}^2$. Figure 5.9 (a) displays the time dependence of the relative probability of exciton-exchange events between monomers. An event of significant TD exchange between monomers is considered when $\Delta(\rho^{0\alpha})_{\text{monomer}}^2 > 0.5$. Despite larger probabilities at earlier times, the inter-monomer energy exchange persists throughout the simulations, highlighting the main role of the inter-monomer pathway during the internal conversion process of the Chla dimer. Therefore, the average number of exciton hops between monomers per NA-ESMD simulation is relatively high (~ 38) (see Fig. 5.9 (b)).

Energy relaxation through localized states on the individual chromophores can be explained by analyzing coupling between states belonging to each band, that is, S_1 and S_2 for Q_y , S_3 and S_4 for Q_x , and S_5 to S_{10} for B band. The coupling is computed as half of the energy splitting between two excited states of the Chla dimer, and both the Förster and the Dexter contributions to the coupling can be included [13, 14]. This method has been

Figure 5.9 (a) Relative probability of exciton exchange between monomers as a function of time. (b) Histogram of the number of TD localization changes between the monomers during the NA-ESMD simulations.

successfully applied to estimate the excitonic coupling between the pigments in LH2 (e.g., Ref. [14]). Our calculations on all 500 initial configurations, obtained from the equilibrated ground state MD simulation, are shown in Table 5.3. Considering coupling as half of the energy splitting between states, one can obtain average values of 224 cm^{-1} and 398 cm^{-1} for Q_y and Q_x bands, respectively. On the basis of the four-orbital model for porphyrins [15, 16], the B band of chlorophylls are composed of two bands, namely, the B_x and B_y bands [17, 18]. For the Chla dimer studied in this work, S_5 and S_6 comprise the B_x band, and S_7 and S_8 are assigned to the B_y band, respectively. Then a coupling strength of 360 cm^{-1} (250 cm^{-1}) between the states in B_x (B_y) band is evaluated. The $Q_y - Q_y$ and $B_x - B_x$ coupling strengths computed here agree well with previous results obtained for the LH2 pigments [14]. Compare to the $Q_y - Q_y$ coupling estimated by the dipole-dipole interaction approximation [19] and the Poisson-TrEsp method [20], a relatively stronger $Q_y - Q_y$ coupling is obtained in this work as a result of excluding protein environments. As can be seen, the strength of the thermal fluctuations (FWHM of the excitation energy distribution) do exceed the coupling which leads to localized states on individual chro-

Table 5.3 Average excitation energy and Full width at half maximum (FWHM) extracted from the Gaussian fitting of the excitation energy distribution from 500 configurations.

band	excited state	average excitation energy (eV)	FWHM (eV)
Q_y	1	1.669	0.104
	2	1.725	0.101
Q_x	3	2.478	0.177
	4	2.577	0.173
B	5	2.889	0.116
	6	2.978	0.120
	7	3.094	0.136
	8	3.156	0.111
	9	3.207	0.114
	10	3.252	0.117

mophores. Excited state dynamics then separates the states even further due to vibrational relaxation. However, in the phase space domains where electronic states are strongly coupled, states become nearly degenerate promoting delocalization as a Frenkel exciton and facilitating thus efficient inter-chromophore energy transfer.

Intra-monomer Exciton Redistribution

During the internal conversion process of the Chla dimer, each monomer experiences an intramolecular wave function redistribution. It is possible to monitor the fractions of TD localized on specific atoms, functional groups, and regions of each Chla monomer. The structure of the Chla molecule is depicted in Fig. 5.1 (c). Following our previous work

Figure 5.10 Time evolution of the averaged TD localized on the (a) Mg atom, (b) N atoms, (c) inner macrocycle, and (d) outer macrocycle for higher monomer (HM*) and lower monomer (LM*). (e) Schematic representation for the predominant transition density redistribution on a chlorophyll *a* monomer during the conversion from *B* to Q_y . Background areas with blue and red colors represent the transition density for the *B* and Q_y bands, respectively.

on the Chla monomer [2], the porphyrin ring of the molecule is fragmented into following groups, i.e., atom Mg, atoms N, the inner and the outer macrocycle. The total carbon macrocycle contains the carbon atoms comprising the porphyrin ring structure (carbon

atoms 1 - 20 including atoms C13¹ and C13²). The “inner macrocycle” (atoms between two red dashed lines excluding the N atoms in Fig. 5.1 (c)) is comprised of atoms C1, C4, C5, C6, C9, C10, C11, C14, C15, C16, C19, and C20. The “outer macrocycle” consists of carbon atoms in the total carbon macrocycle excluding those in the inner macrocycle.

For each trajectory, the HM* (LM*) denotes the monomer which has higher (lower) fraction of TD in the current excited state initially. The time evolution of the averaged TD localized on each partition of the porphyrin ring of either HM* and LM* is depicted in Fig. 5.10 (a)-(d). Within ~ 100 fs, the fractions of TD on specific atoms (Mg and N atoms), and regions (inner and outer carbon macrocycles) of LM* approach those of HM*. The overall TD redistribution on a monomer during the conversion from B to Q_y is analyzed and depicted in Fig. 5.10 (e). The intramolecular exciton redistribution within each monomer of the Chla dimer reproduces results previously found in individual Chla molecules [2]. That is, the overall $B \rightarrow Q_y$ energy relaxation process implies the transfer of localized TD from the N atoms and the outer carbon macrocycle to the inner carbon macrocycle, and the central Mg atoms play minor roles in the exciton relocation.

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Chapter 6

Excitation Energy Transfer in B850 Nanoarrays

This chapter documents a study of exciton diffusion in large 1D and 2D B850 nanoarrays by employing the Dirac-Frenkel time-dependent variational principle and the classical master equation approach. Quantum mechanical calculations are conducted on the GPU architecture and a superdiffusive component is found in the exciton dynamics in B850 nanoarrays. The coherence length and the superradiance enhancement factor are evaluated to quantify exciton delocalization. A fractal analysis is done for the first time on exciton dynamics in photosynthetic systems. From both quantum and classical simulations, energy transfer is found to be more efficient in 2D nanoarrays than in linear B850 chains, owing to multiple channels for the energy transfer in the 2D arrangement.

6.1 Introduction

By measuring fluorescence emission spectra, Escalante and co-workers reported evidence of long range energy transfer in engineered nanoarrays constructed with LH2 antenna complexes from *Rb. sphaeroides* [1–4]. However, long-range energy transport in native light harvesting systems is rarely achieved as LH2 complexes have a disorderly configuration surrounded with a complex environment [5, 6]. Regarding the anomalous energy migration behavior observed in fabricated LH2 nanoarrays, some fundamental issues remain unresolved, such as the origin of the extremely long transfer distance as claimed in Ref. [5]. More efforts should be devoted to investigations of the underlying energy transfer mechanisms in artificial LH2 nanoarrays. An in-depth understanding of energy transport in LH2 nanoarrays may provide guiding principles on the design of artificial light harvesting devices for sustainable energy production.

In contrast to experimental work in which photosynthetic systems are typically composed of multiple LH2 complexes, theoretical investigations are mostly conducted on a single LH2 complex [7–12]. Strümpfer and Schulten applied the HEOM approach to two B850 rings using a parallel computational architecture [13]. Taking advantage of time-dependent variation with the Davydov *Ansatz*, Zhao *et al.* investigated inter-B850 exciton dynamics [14, 15] and exciton diffusion in chlorosome with GPU architectures [16]. Excellent performance of this approach in simulating exciton dynamics in a chlorosome of more than 300 pigments points to applicability the method to much larger systems, such as B850 nanoarrays.

In this chapter, exciton propagation in engineered B850 assemblies is investigated using both time-dependent variational and classical master equation approaches, and results are summarized in this chapter. The theoretical framework of the Dirac-Frenkel time-dependent variational approach and the classical master equation method are outlined in Section 6.2, where structures of the nanoarrays are also described. Numerical results from the quantum description are discussed in Section 6.3. With efficient GPU simulations, ex-

citon dynamics in B850 nanoarrays is obtained and a superdiffusive component for short times is found. The superradiance enhancement factor is recorded to quantify exciton delocalization. For the first time fractal analysis is carried out on the exciton dynamics. Section 6.4 presents the application of the classical master equation to the exciton diffusion in B850 nanoarrays. Both the quantum and the classical simulations show that the energy transfer in 2D arrays is more efficient than that in LH2 chains.

6.2 Model of B850 Nanoarrays and Methodologies

6.2.1 B850 Nanoarrays

Typical LH2 has a ring-shaped structure and contains 8-10 subunits. Each subunit is composed of two apoproteins (α - and β -proteins), one carotenoid, and three BChls. Within each subunit, two pigments form a BChl dimer and the third molecule is positioned relatively far from the dimer with its porphyrin plane nearly perpendicular to those of the dimeric BChls. For instance, in the LH2 complex from *Rhodospirillum Rubrum* [17], 8 BChl dimers comprise the B850 ring (see Fig. 6.1 (c)), which is named after its absorption peak at 850 nm. The third BChls in all subunits form the B800 ring. Coordinated with the apoproteins, the B850 ring is dimerized with two types of pigments, i.e., α - and β -BChls, which are colored blue and red in Fig. 6.1 (c), respectively. Within a single LH2 complex, the excitation energy is transferred from the B800 ring to the B850 ring. Inter-LH2 energy transfer takes place between neighboring B850 rings.

As shown in Fig. 6.1, two kinds of B850 nanoarrays, i.e., 1D and 2D nanoarrays are constructed to study excitation energy transfer in this chapter. For 2D nanoarrays shown in Fig. 6.1 (a), each ring is surrounded by six others. Two nearest B850 rings are separated by a distance of 8.0 nm for both 1D and 2D nanoarrays.

Figure 6.1 Schematic representation of the B850 nanoarrays used in this work to investigate the excitation energy migration: (a) two-dimensional (2D) and (b) one-dimensional (1D) B850 nanoarrays. The center-center distance between adjacent B850 rings is 8 nm and each B850 ring is surrounded with six rings in the 2D nanoarray (as illustrated with the yellow hexagon in (a)). The arrangements of the bacteriochlorophyll *a* (BChla) molecules in the B850 ring are illustrated in (c) with the proteins represented by ribbons. The coordinates are extracted from the crystal structure of the LH2 complex (PDB ID: 1LGH) [17]. The α and β pigments are colored blue and red, respectively.

6.2.2 Quantum Coherent Exciton Transfer

The B850 pigments are densely packed, and strong inter-pigment excitonic interactions give rise to delocalized exciton over several chromophores [18]. The excitation energy transfer in B850 nanoarrays is modeled with the Holstein Hamiltonian [19, 20]:

$$\hat{H} = \hat{H}_{\text{ex}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{ex-ph}}. \quad (6.1)$$

Here

$$\hat{H}_{\text{ex}} = \sum_{r_1 r_2} \sum_{mn} J_{mn}^{r_1 r_2} \hat{a}_m^{r_1 \dagger} \hat{a}_n^{r_2} \quad (6.2)$$

is the Frenkel-exciton Hamiltonian, and $\hat{a}_n^{r\dagger}$ ($\hat{a}_n^r$) is the exciton creation (annihilation) operator on the n^{th} site (with a total number of $N_s = 16$ sites in one B850 ring) of the r^{th} ring

Figure 6.2 Interpigment excitonic coupling in a B850 ring. The α and β pigments are colored in blue and gray, respectively. The coupling strengthes are given in units of cm^{-1} and are reported in Ref. [11].

(with a total number of N_r B850 rings). $J_{mn}^{r_1 r_2}$ is the excitonic coupling between pigment m on the r_1^{th} B850 ring and pigment n on the r_2^{th} B850 ring [21]. The diagonal elements in the exciton Hamiltonian J are the site energies of the B850 pigments. Each B850 ring is composed of 8 BChla dimers. Two pigments within in each dimer are labeled as BChla α and BChla β , respectively. The site energy of BChla α (BChla β) is 12050 cm^{-1} (11970 cm^{-1}) [11]. The off-diagonal elements in J are the excitonic coupling strengths between different pigments. Several strong coupling constants are shown in Fig. 6.2. The intra-dimer coupling strength is 205 cm^{-1} and the coupling strength between BChla α and BChla β in adjacent dimer is 144 cm^{-1} . The excitonic coupling strength between the BChla α (BChla β) molecules in two neighboring dimers is -52 cm^{-1} (-31 cm^{-1}) [11]. The coupling strengths between the other pairs of pigments are estimated with the transition charges from the electrostatic potentials method [22–24].

The exciton dynamics in B850 complexes is affected by environmental vibrations, such as the conformational changes of the pigments and the proteins. In the Holstein model, the surrounding of the exciton is represented by a phonon bath, which is expressed as a set of

harmonic oscillators

$$\hat{H}_{\text{ph}} = \sum_r \sum_q \omega_q^r \hat{b}_q^{r\dagger} \hat{b}_q^r. \quad (6.3)$$

where $\hat{b}_q^{r\dagger}$ ($\hat{b}_q^r$) is the phonon creation (annihilation) operator with momentum $q = 2\pi n_q/N_s$ ($n_q = -7, -6, \dots, 7, 8$) and frequency ω_q^r in the r^{th} ring. The exciton is coupled to the phonon bath via the exciton-phonon interaction Hamiltonian

$$\hat{H}_{\text{ex-ph}} = -\frac{1}{\sqrt{N_s}} \sum_r \sum_n \sum_q g_q^r \omega_q^r \hat{a}_n^{r\dagger} \hat{a}_n^r (e^{iqn} \hat{b}_q^r + e^{-iqn} \hat{b}_q^{r\dagger}). \quad (6.4)$$

Here g_q^r is the exciton-phonon coupling strength and the Planck's constant $\hbar$ is set to unity. A linear phonon dispersion $\omega_q^r = \omega_0[1 + W(2|q|/\pi - 1)]$ with $W = 0.1$ is adopted in this work. The exciton-phonon coupling strength is parameterized from the Huang-Rhys factor S with the relation $\frac{1}{N_s} \sum_q (g_q^r)^2 \omega_q^r = S\omega_0$ where $\omega_0 = 1670 \text{ cm}^{-1}$ is the characteristic phonon frequency [25]. A fixed Huang-Rhys factor $S = 0.5$ is used throughout the chapter.

A fully quantum mechanical description of both the exciton and the phonons can be afforded by the Davydov D_1 *Ansatz*

$$|\Psi_{D_1}(t)\rangle = \sum_r \sum_n \alpha_n^r(t) \hat{a}_n^{r\dagger} \hat{U}_n^{r\dagger}(t) |0\rangle_{\text{ex}} |0\rangle_{\text{ph}}, \quad (6.5)$$

where

$$\hat{U}_n^{r\dagger}(t) = \exp \left\{ \sum_q [\lambda_{nq}^r(t) \hat{b}_q^{r\dagger} - \lambda_{nq}^{r*}(t) \hat{b}_q^r] \right\}$$

is the Glauber coherent operator and $\alpha_n^r(t)$ ($\lambda_{nq}^r(t)$) are the variational parameters representing exciton amplitudes (phonon displacements).

In order to capture detailed exciton dynamics among the chromophores, the Dirac-Frenkel time-dependent variational approach is employed to investigate excitation energy transfer in both 1D and 2D B850 nanoarrays from a fully quantum perspective. The Lagrangian formalism of the Dirac-Frenkel time-dependent variational principle is applied to obtain the equations of motion for the variational parameters [26–29], and detailed derivations are shown in Appendix B.

Many observables can be calculated on the basis of the evaluated time-dependent wave function. The electronic population and coherence are included in the reduced single-exciton density matrix $\rho_{mn}^{r_1 r_2}(t)$ which is obtained from a trace over the phonon bath

$$\begin{aligned}\rho_{mn}^{r_1 r_2}(t) &= \text{Tr}_b \left[|\Psi_{D_1}(t)\rangle \langle \Psi_{D_1}(t)| \hat{a}_m^{r_1 \dagger} \hat{a}_n^{r_2} \right] \\ &= \alpha_m^{r_1*}(t) \alpha_n^{r_2}(t) S_{mn}^{r_1 r_2}(t),\end{aligned}\quad (6.6)$$

where the Debye-Waller factor $S_{mn}^{r_1 r_2}(t)$ is

$$S_{mn}^{r_1 r_2}(t) = \exp \left\{ \sum_q \left[\lambda_{mq}^{r_1*}(t) \lambda_{nq}^{r_2}(t) \delta_{r_1 r_2} - \frac{1}{2} |\lambda_{mq}^{r_1}(t)|^2 - \frac{1}{2} |\lambda_{nq}^{r_2}(t)|^2 \right] \right\}. \quad (6.7)$$

The exciton population on the r^{th} B850 ring can be obtained by tracing $\rho_{mn}^{r_1 r_2}(t)$ over pigments comprising this complex

$$\rho_r(t) = \sum_{m=1}^{N_s} \rho_{mm}^{rr}(t). \quad (6.8)$$

For an exciton propagation, the mean square displacement (MSD) can be measured as

$$\langle x^2(t) \rangle = \sum_{r=1}^{N_r} (d_r)^2 \rho_r(t) \quad (6.9)$$

with d_r being the distance between the r^{th} B850 ring and the complex on which the exciton is initially localized. Usually, the MSD exhibits a power-law relation with time, i.e., $\langle x^2(t) \rangle \propto t^\gamma$. The exponent γ determines the characteristics of diffusion processes. If $\gamma = 1$, the process is the Fickian diffusion. $0 < \gamma < 1$ and $\gamma > 1$ correspond to the subdiffusion and superdiffusion, respectively. In this work, the time evolution of the MSD is measured in order to characterize the exciton diffusion process in B850 nanoarrays.

To study the effects of coherence on exciton diffusion in B850 nanoarrays, the coherence size L_ρ is defined as [30, 31]

$$L_\rho(t) = \left(\sum_{r_1 r_2} \sum_{mn} |\rho_{mn}^{r_1 r_2}(t)| \right)^2 \left[N \sum_{r_1 r_2} \sum_{mn} |\rho_{mn}^{r_1 r_2}(t)|^2 \right]^{-1} \quad (6.10)$$

where $N = N_s \times N_r$ is the total number of pigments in the system. The coherence size L_ρ has been used as the exciton delocalization length in various photosynthetic systems,

such as the LH2 [11, 13, 25, 30, 32–35] and the chlorosome [16]. L_ρ quantifies the length scale over which $\rho_{mn}^{r_1 r_2}$ decays along the anti-diagonal direction [30, 33]. This quantity is related to the superradiance enhancement factor L_s which is the ratio of radiative decay rate of a molecular aggregate to that of a monomer of the same type [30, 31, 33]. In a doorway-window representation, L_s can be written as [30, 33]

$$L_s(t) = \sum_{r_1 r_2} \sum_{mn} M_{mn}^{r_1 r_2} \rho_{mn}^{r_1 r_2}(t) \quad (6.11)$$

where $M_{mn}^{r_1 r_2} = \mathbf{d}_m^{r_1} \cdot \mathbf{d}_n^{r_2}$ contains all the relevant geometric information of the system with $\mathbf{d}_m^{r_1}$ being the unit vector of the transition dipole moment of pigment m on the r_1^{th} B850 ring.

6.2.3 Incoherent Inter-B850 Exciton Hopping

Ignoring energy transfer within a B850 ring and modeling the B850 complex as one single aggregate, one can apply the Förster theory to describe the excitation energy propagation in large B850 nanoarrays by treating inter-aggregate energy transfer as incoherent hopping of exciton. This model is used to investigate excitation energy transfer in both 1D and 2D B850 nanoarrays.

The exciton dynamics in 1D nanoarrays composed of B850 rings can be described with the classical master equation

$$\frac{dp_i}{dt} = r_a A_i - (K_i + \sum_j k_{ij}) p_i + \sum_j k_{ji} p_j, \quad (6.12)$$

where the ring index i runs from 1 to N_r , p_i is the unnormalized probability that ring i is excited, K_i is the rate of local dissipation for ring i , k_{ij} is the exciton transfer rate from ring i to j , A_i is the profile of excitation laser, and r_a is the rate of energy absorption by the B850 ring from the laser.

Assuming that the exciton transfer only occurs between two neighboring complexes with an inter-complex transfer rate k and that the dissipation rate is the same for all com-

plexes $K = K_i$, the master equation Eq. (6.12) is reduced to

$$\frac{dp_i}{dt} = r_a A_i - (K + 2k)p_i + kp_{i-1} + kp_{i+1}. \quad (6.13)$$

For the stationary case of $dp_i/dt = 0$, Eq. (6.13) has an analytical solution [36]

$$p_i = \frac{1}{k} \sum_{j=1}^{N_r} \left[\left(\cosh [(N_r + 1 - |j - i|)\lambda] - \cosh [(N_r + 1 - i - j)\lambda] \right) / \left(2 \sinh \lambda \sinh [(N_r + 1)\lambda] \right) \right] r_a A_j \quad (6.14)$$

where $\lambda = \text{arccosh}[(K + 2k)/2k]$. In order to compare with the laser profile, the normalized excitation probability $\tilde{p}_i$ is calculated as

$$\tilde{p}_i = \frac{p_i}{p_{i_0}}. \quad (6.15)$$

It is clear that $\tilde{p}_{i_0} = 1$, and r_a has no effects on $\tilde{p}_i$, which is set to be unity in the rest of this chapter. Eqs. (6.14) and (6.15) indicate that $\tilde{p}_i$ only depends on the ratio K/k and the excitation laser.

In a 2D B850 nanoarray, each complex is surrounded with six neighboring complexes. The master equation is written as

$$\begin{aligned} \frac{dp_{ij}}{dt} = & r_a A_{ij} - (K + 6k)p_{ij} + k(p_{i-1,j} + p_{i+1,j} \\ & + p_{i,j-1} + p_{i,j+1} + p_{i-1,j+1} + p_{i+1,j-1}), \end{aligned} \quad (6.16)$$

where (i, j) is the B850 index in 2D nanoarray model. Stationary excitation probability distribution can be obtained by solving Eq. (6.16) numerically with the constraint of $dp_{ij}/dt = 0$.

In addition, analytical solutions can be obtained for exciton dynamics with laser produced initial conditions. For a B850 chain in the absence of a laser field ($A_i = 0$), the excitation dynamics governed by Eq. (6.13) has an analytical solution [37, 38]

$$p_i(t) = e^{-(K+2k)t} \sum_{m=-\infty}^{\infty} p_m(0) I_{i-m}(2kt), \quad (6.17)$$

where $I_n(x) = i^{-n} J_n(ix)$ is the modified Bessel function of the first kind. For the 2D B850 nanoarray, a similar solution can be derived from Eq. (6.16) with $A_{ij} = 0$,

$$p_{ij}(t) = e^{-(K+6k)t} \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} p_{lm}(0) I_{i-n-l}(2kt) I_{j+n-m}(2kt) I_n(2kt). \quad (6.18)$$

The initial condition $p_m(0)$ [$p_{lm}(0)$] for the 1D (2D) nanoarray can be prepared by turning on the laser field and then switching it off immediately. Then the excitation probability dynamics of a given complex can be obtained using Eq. (6.17) [Eq. (6.18)] for the 1D (2D) model.

6.3 Quantum Coherent Exciton Transfer in B850 Nanoarrays

With the advent of ultrafast spectroscopy, many breakthroughs in understanding efficient energy transfer in natural photosynthetic systems have been achieved. For example, observation of the long-lived beating in the 2DES of the FMO complex [39] stirs a boom of 2DES probes of excitation dynamics in various photosynthetic systems, including LH2 complexes [40–48]. The oscillatory behavior is attributed by a number of authors to quantum coherence, the origin of which is still under debate [18, 49, 50]. In the B850 ring of the LH2 complex, neighbouring BChls are closely packed and the porphyrin rings of these molecules are nearly parallel [17], producing strong excitonic coupling between two adjacent pigments which leads to exciton delocalization [11, 18, 51]. Therefore, a quantum description is essential to understand energy transfer in systems composed of B850 rings.

The environment is modeled as a phonon bath composed of high energy optical modes with a characteristic frequency of $\omega_0 = 1670 \text{ cm}^{-1}$. Room temperature is considered to be a very low temperature compared to ω_0 . Therefore, it is reasonable to describe the phonon bath at zero-temperature with a quantum mechanical treatment. To this end, the phonon field is initiated from a vacuum state with $\lambda_{nq}^r(0) = 0, \forall r, n, q$. Combined with the Dirac-Frenkel time-dependent variational principle, the Davydov D_1 *Ansatz* has been successfully applied to investigate zero-temperature exciton-phonon dynamics in various photosynthetic systems, such as the chlorosome [16], the single and double B850 complexes [14, 15, 52].

The extraordinary numerical efficiency and accuracy of this approach make it a promising methodology to study the exciton diffusion in large B850 nanoarrays.

A simplified trial state, the Davydov D_2 *Ansatz*, had been used previously to study finite temperature exciton dynamics in a single B850 complex [53]. However, time-dependent variation with this trial wave function is shown to be equivalent to the semi-classical Ehrenfest approach [54]. It is found that the variational method with the single Davydov D_2 *Ansatz* is only accurate when the exciton-phonon coupling is sufficiently strong and the temperature is high [55]. In order to precisely describe the polaron dynamics in wider parameter regimes, a variational framework with the multiple Davydov states has been developed recently [56]. It has been reported that a high multiplicity (~ 32) is required for the multiple- D_2 trial state to acquire comparable accuracy of a single Davydov D_1 *Ansatz* in the strong electronic coupling regime [54, 56]. Parameterizing the initial phonon states with temperature-dependent phonon displacements, one can apply the time-dependent variational principle with the multiple Davydov states to produce accurate system dynamics at finite temperatures in a broad range of various parameters, such as the system-bath coupling, and the electronic coupling [54, 57]. The time-dependent variation of the multiple Davydov states can be adopted to simulate the finite temperature exciton dynamics in photosynthetic systems in future studies.

In realistic photosynthetic systems, the excitation energies and the electronic coupling strengths are modulated by surrounding fluctuations, such as protein vibrations and structural deformations of pigments. Slow environmental fluctuations lead to random noises in electronic structures over long timescales, inducing the static disorder. Fast modulations of the electronic parameters are realized by the exciton-phonon interactions, producing the dynamic disorder [18]. Both types of disorder are believed to exist in the LH2 complex [58–60] and the effects of disorder have been studied from various perspectives. For instance, Novoderezhkin *et al.* simulated the pump-dump-probe response of the B850 complex and found that the realization of the disorder has crucial influences on the relaxation rates [61]. The disorder parameters are recently proposed to be temperature dependent from

2DES calculations for the LH2 complex with the considerations of the static and dynamic disorder [62]. Stross and co-workers reproduced the experimental anisotropy pump-probe signals of LH2 by incorporating the static disorder with the exciton model [63]. Recently, disorder induced effects on the exciton dynamics in a B850 ring have been probed using the time-dependent variational principle combined with the Davydov D_1 Ansatz [52]. Aforementioned theoretical studies of disorder only focus on a single LH2 or B850 complex. In simulations, the static disorder is mimicked by adding random noises (usually in Gaussian) to the site energies, generating many excitonic Hamiltonian containing disordered diagonal elements. Every excitonic Hamiltonian is then utilized to initiate an individual simulation trajectory. Desired observables are evaluated from the ensemble average over all the realizations. Conventionally several thousand trajectories need to be launched to achieve convergent results. It is computationally challenging to develop thousands of dynamical trajectories for large systems, such as the B850 nanoarrays. Therefore, the static disorder is neglected in the simulations of excitation energy transfer in B850 nanoarrays.

6.3.1 Computational Advantage of GPU

A fully quantum mechanical description of the exciton-phonon dynamics in a multiple-chromophore system is a computational challenge because a huge number of DOFs in the Hilbert space are involved in calculations. To tackle this problem, a numerically efficient algorithm is implemented here on the architecture of GPUs. To compare the computational efficiency between the CPU and GPU architecture, calculations for various B850 chains are done on CPU and GPU to obtain a 1 ps-long trajectory for each nanoarray. Computational times are compared in Fig. 6.3 between CPU and GPU. The CPU computational time is found to increase with system size N obeying a power law ($\propto N^{1.6}$). The GPU architecture exhibits great advantages over CPU especially for larger system sizes, as the GPU computational time is a logarithmic function of system size [$\propto \ln(N + 129)$]. With the efficient GPU algorithm, one can calculate the exciton dynamics in B850 chains composed of more than 100 B850 rings (more than 1600 sites). All quantum mechanical calculations in this work are carried out on the GPU platform.

Figure 6.3 CPU and GPU computational times for different size of systems. The blue line is the power law fitting for the CPU time and the red line is the logarithmic fitting of the GPU time. The fitting parameters are shown in the legend with N being the total number of sites in the system.

6.3.2 Effect of Initial Excitation Conditions

Exciton dynamics is first simulated in a B850 chain with three rings. The initial excitation is located on the central B850. Three initial excitation conditions are employed. In Cases I and II, the lowest and second lowest exciton state of the central ring are initially populated, respectively. In Case III, only one pigment on the central B850 is excited. For the third case, 16 trajectories are simulated and each trajectory is started from an individual pigment on the central complex. Results for three cases are shown in Fig. 6.4. For Case III, averaged results from 16 trajectories are depicted in comparison with those from a single trajectory.

Shown in Fig. 6.4 is the population dynamics of the central complex (a), the time evo-

Figure 6.4 The exciton population on the central complex (a), the superradiance enhancement factor (b), the mean square displacement (c), and the coherence size (d) for the exciton diffusion in a B850 chain with three B850 complexes. Calculations are conducted with three initial excitation conditions, i.e., the lowest (Case I) and the second lowest (Case II) exciton states, and an individual pigment (Case III) of the central complex. For comparison, the results from a single trajectory (blue curves) of Case III are shown with the averaged results over 16 trajectories (red curves).

lution of the superradiance enhancement factor (b), the logarithmic plot of the mean square displacement versus simulation time (c), and the temporal dependence of the coherence size (d). As illustrated in Fig. 6.4 (a), the exciton is localized on the ring of initial excitation for a long time if the central ring is initialized to be in its lowest exciton state (Case I), an optically dark state considering the transition dipole configurations of the B850 pigments. In contrast, the excitation energy transfer is most efficient in Case II where the exciton starts to propagate from the second lowest exciton state of the central complex. As the optically bright state which contributes to the absorption peak of the B850 ring, the second lowest exciton state is pairwise degenerate and exhibits the largest transition dipole moment a-

among all the exciton states of the B850 aggregate, producing the most efficient excitation energy transfer. This finding is consistent with a previous finding that an exciton state of the B850 ring with a larger transition dipole moment produces more efficient excitation energy transfer [64]. Comparing the exciton localization on the initial complex in Case I and the efficient energy transfer in Case II, one can safely draw the conclusion that the excitation energy is most likely transferred from the second lowest exciton state of a B850 ring to the neighboring complexes. Therefore, the second lowest exciton state of the central B850 ring is chosen as the initial conditions for the quantum mechanical calculations hereafter.

The log-log plots of the MSDs for three cases versus time are shown in Fig. 6.4 (c), and linear relations with slopes ~ 1.6 have been extracted indicating the superdiffusion behavior. In Case II, superdiffusion seems to last for about 600 fs in contrast to the time of 300 fs in Case I. Based on the averaged results from the 16 trajectories of Case III, the superdiffusive behavior of exciton holds for about 400 fs. This superdiffusive behavior is found for all the simulations irrespective of initial conditions, and is proposed to be an intrinsic property of exciton propagation in B850 nanoarrays.

6.3.3 Exciton Delocalization

Two quantities, i.e., the superradiance enhancement factor L_s and the coherence size L_ρ are recorded during the simulations to characterize the exciton delocalization in B850 nanoarrays. As can be seen from its definition Eq. (6.11), L_s is dependent on the state and the transition dipole configuration of the system, quantifying the ratio of the radiative decay rate of the system to that of a single pigment [30, 31]. In contrast, L_ρ only contains the information of the reduced density matrix.

As illustrated in Fig. 6.4 (b), the superradiance enhancement factor L_s in Case II has an initial value of 8. The large value of L_s results from the initial state of this trajectory, i.e., the second lowest exciton state of the B850 aggregate which is one of the superradiant states of B850 [30]. For Case I in which exciton initiates propagation from the optically

dark state ($L_s(0) = 0$), the superradiance enhancement factor L_s oscillates below 1.0 with the characteristic phonon frequency (20 fs) until the exciton starts to escape from the initial complex. As the oscillator strength of the initial dark state is almost zero, cooperative spontaneous emission of the whole system is nonexistent. For Case III where the exciton starts to propagate from an individual pigment, a superradiance enhancement factor oscillates around 1.0.

Compared to the superradiance enhancement factor L_s , the coherence size L_ρ presents a different picture as shown in Fig. 6.4 (d). At initial time, Case I has the largest coherence size because of nearly uniform excitation for the pigments in the central ring. With temporal evolution, L_ρ oscillates around the value of 5 for Case I. Cases II and III exhibit larger coherence sizes which cover more than 10 pigments. Special attention should be paid to the out-of-phase oscillations in the L_s and the L_ρ for Case II. The total transition dipole moment of the B850 complex is very small due to the nearly opposite orientations of the transition dipole moments of adjacent pigments. In this situation, the emission is induced by the loss of coherence. Therefore, the superradiance enhancement factor L_s increases with the decrease of L_ρ [30].

To demonstrate the difference between L_s and L_ρ , the exciton dynamics in several B850 chains with different system sizes is simulated and the initial excitation is localized on the central ring for all the simulations. The sizes of the chains vary from 11 to 101 B850 rings and the time evolution of the coherence sizes for these systems are shown in Fig. 6.5 (a). Before the exciton arrives the boundary of the shortest chain ($N_r = 11$), the exciton propagation in various chains is very similar, so the differences in L_ρ are induced by the system size N in the denominator of Eq. (6.10). As shown in Fig. 6.5 (a), larger systems have smaller coherence sizes within 3 ps. At long times, the coherence sizes oscillate around an equilibrium value which is about half of the system size. In contrast to L_ρ , the superradiance enhancement factor L_s is independent on the system size. The temporal evolution of L_s for different B850 chains is depicted in Fig. 6.5 (b). In the first 3 ps, all the systems exhibit the same behavior of L_s . Subsequently, the superradiance

Figure 6.5 Time evolution of the coherence size L_p (a) and the superradiance enhancement factor L_s (b) for various B850 chains with the system size varying from 11 to 101 rings. Initially the central ring of the B850 chain is excited to its second lowest exciton state.

enhancement factor L_s in the chain with 11 rings shows some visible deviations from those in other systems. It stems from the fact that the wave function spreads to the boundary of the 11-ring chain by 3 ps. The gradual decrease of L_s is induced by the phonon induced decoherence. At long times, L_s oscillates around 2 and agrees with the measured radiative rate of LH2 [51].

6.3.4 Fractal Analysis of Exciton Dynamics

Fractal dynamics governs many physiological and behavioral processes with measured signals exhibiting self-similarity and scaling [65, 66]. Self-similarity refers to that the fluctua-

tion patterns at faster time scales imitate those at slower time scales. Scaling means that the pattern measurements depend on the resolution or the time scale at which the measurements are conducted [65, 66]. Many methods for fractal analysis have been proposed and applied to study the scaling rules in the signals from various processes [67]. A recently developed method by Gao and coworkers, called adaptive fractal analysis (AFA), has been widely adopted to establish the scaling rules of many signals [66, 68–72]. Optimally combining local linear or polynomial fitting, the AFA method can obtain a globally smooth trend and mitigate the discontinuities between adjacent data fragments, making it suitable to deal with arbitrary strong nonlinear trends [66]. The latter is especially pertinent to analyzing simulated signals here, as they all show strong oscillatory trends.

In the AFA algorithm, a global trend, $\nu(i), i = 1, 2, \dots, N_f$, is firstly determined by partitioning original data $u(i)$ into windows of length $w = 2n + 1$ and fitting the data in each window with polynomial of order M ($M = 1$ in this work). Two neighboring windows overlap with $n + 1$ points. The fit to the overlapping points is achieved by a weighted combination of the fitting polynomials of two adjacent fragments. Then the variance $F(w)$ of the fitting residual $u(i) - \nu(i)$ is computed to yield the Hurst parameter H with the scaling equation

$$F(w) = \left[\frac{1}{N_f} \sum_{i=1}^{N_f} (u(i) - \nu(i))^2 \right]^{1/2} \sim w^H. \quad (6.19)$$

In the fractional Brownian motion (fBm) and the fractional Gaussian noise (fGn) processes, the value of H falls within the interval of $[0, 1]$. $0 < H < 1/2$, $H = 1/2$ and $1/2 < H < 1$ correspond to the processes with anti-persistent correlation, short-range correlation, and persistent long-range correlation, respectively. Beyond the fBm-fGn framework, a variety of processes have $H > 1$, such as the center of pressure signals, the on-off intermittent and the Lévy walk processes [66, 71–73]. These are the superdiffusive processes in physics and chemistry.

In this work, the AFA method is applied to analyze the population dynamics during

Figure 6.6 (a) Results of the adaptive fractal analysis for the population dynamics of site 8 in different B850 rings. The dashed lines in (a) are the linear fitting curves with the slopes (Hurst parameter H) shown in the legend. (b) Exciton populations on site 8 in four rings (rings 3, 4, 5, and 6). The simulation is carried out for a B850 chain containing 11 rings and initially the central ring (ring 6) is excited to its second lowest exciton state. The insert in (b) is the enlarged plot of the population on site 8 in rings 3, 4, and 5.

the exciton diffusion in B850 nanoarrays and the curves of $\log_2 F(w)$ vs. $\log_2 w$ are shown in Fig. 6.6 (a). A simulation for a B850 chain containing 11 rings is conducted with the second lowest exciton state of the central ring (ring 6) initially populated. Shown in Fig. 6.6 (b), the populations on site 8 in four rings (rings 3, 4, 5, and 6) are extracted and used as the

Figure 6.7 Bilogarithmic plot of the mean square displacement as a function of time for the exciton diffusion in a B850 chain containing 11 rings. The open circles are the results from the simulation which is initiated from the second lowest exciton state of the central ring (ring 6). The red (green) line is the linear fitting curve for the short (long) time regime. The fitting slopes are shown in the legend.

source data for the AFA. Both high and low frequency oscillations are present in the exciton populations. The fast oscillating patterns resemble those with low oscillation frequencies, indicating the temporal self-similarity of the exciton populations. Fitting the data points with linear functions, one can obtain the Hurst parameters H from fitting slopes, which are shown in the legend of Fig. 6.6 (a). In the short time regime, i.e., $w < 2^8 = 256$ fs, the Hurst parameters larger than 1 indicate superdiffusion in the exciton dynamics in B850 nanoarrays. From the bilogarithmic plot of the MSD versus time shown in Fig. 6.7, a superdiffusion component is found to last for about 600 fs with a $\gamma \approx 1.789$. Persisting for about 250 fs, the scaling regime with $H > 1$ is nearly half of the duration of superdiffusion and this phenomenon is consistent with the fact that the fractal scaling usually only extends to half of the period of the signal [68]. Once the window size w exceeds $2^8 + 1 = 257$ fs, the slopes exhibit obvious decreases compared with those in short times. Determined by

the fluctuation amplitudes of the population, $F(w)$ for the site 8 in ring 6 has the largest absolute value among all cases. The Hurst parameter for ring 6 is found to be the smallest due to phonon induced decoherence.

6.3.5 Exciton Diffusion in 2D B850 Nanoarray

Figure 6.8 Exciton diffusion in a 2D nanoarray composed of 7 B850 rings. (a)-(d) Four snapshots of the excitation probability distribution. The radii of the color bubbles represent the excitation probabilities on individual pigments. (e) Population dynamics for all B850 rings. (f) Time evolution of the superradiance enhancement factor L_s . (g) log-log plot of the mean square displacement as a function of time.

In addition to the B850 chains, the exciton diffusion in 2D nanoarrays of B850 rings is also studied in this chapter. As shown in Fig. 6.8 (a), one central ring (ring 4) is surrounded by six rings, and the initial excitation is on the central ring. With the evolution of time, the

excitation energy is gradually transferred to the surrounding rings. Three snapshots of the excitation probability distribution on all the pigments during the dynamics are shown in Fig. 6.8 (b)-(d). The time-dependent populations in all B850 rings are depicted in Fig. 6.8 (e). By comparing the central-ring populations for the 1D (Case II in Fig. 6.4 (a)) and the 2D (Ring 4 in Fig. 6.8 (e)) B850 nanoarrays, more efficient exciton transfer is found in the 2D nanoarray, because of more energy-transfer channels in the 2D nanoarray than the B850 chain. Similar to the 1D case, extremely efficient energy transfer occurs in the first 600 fs with about half of the excitation energy migrates out from the central ring to the adjacent rings in the 2D nanoarray. During this time interval, the exciton propagates with superdiffusive behavior, which can be seen from Fig. 6.8 (g) where $\langle x^2 \rangle \propto t^{1.66}$ within 600 fs. Recently, anomalous triplet exciton diffusion for short times is also observed in the single tetracene crystals [74]. Similar to the scenario in the B850 chain, the exciton is delocalized over about 4 pigments in the 2D nanoarray as indicated by the superradiance enhancement factor L_s in Fig. 6.8 (f). This means that the exciton delocalization size is invariant with respect to the system dimension, while the excitation energy transfer is more efficient in the 2D nanoarrays than that in the B850 chains.

6.4 Incoherent Exciton Hopping in B850 Nanoarrays

In natural photosynthetic systems, energy transfer in an array of LH2 complexes is affected by various environmental fluctuations, which may destroy coherence and induce dissipation. In addition, the inter-ring excitonic coupling is weaker than the intra-ring coupling. Ignoring quantum coherence and intra-ring energy transfer in this section, an incoherent hopping model is devised to describe the inter-ring energy transfer in B850 nanoarrays.

As described above, the excitonic superdiffusive behavior only persists for about 500 fs, and the exciton is only transferred over a short distance from the initial ring of excitation within this time interval (see the MSD shown in Fig. 6.4 (c) and Fig. 6.8 (g)). Therefore, this short-time superdiffusion is ignored in this section, and the classical master equation is applied to simulate exciton diffusion in B850 nanoarrays. In this model, the excitation

Figure 6.9 Normalized stationary excitation distribution in a B850 chain with different decay rates K and transfer rates k . Parameter configurations are given in brackets (K, k) . Both K and k are in units of ps^{-1} . Represented by the solid red line, the excitation laser profile is centered at $x = 0$ and has a full width of half maximum (FWHM) of 400 nm.

energy transfer in B850 nanoarrays is determined by a few control parameters, i.e., the decay rate K , the inter-ring transfer rate k , the distance a between adjacent B850 rings, and the parameters of the excitation laser. In this study, a fixed inter-ring distance $a = 8$ nm is chosen and the effects of all the other parameters on the exciton diffusion in B850 nanoarrays will be investigated in this section.

For native LH2 complexes, the inter-complex excitation energy transfer rate k is estimated to 0.1 ps^{-1} [75–77]. The decay rate K is chosen as the inverse of the fluorescence life time of the singlet excited state of BChla, $K \approx 10^{-3} \text{ ps}^{-1}$ [51, 76, 78–81]. Firstly, the influences of the decay rate K and the transfer rate k on the normalized stationary excitation distribution (NSED) in a B850 chain are investigated and the results are shown in

Fig. 6.9. A Gaussian laser profile $A_i = A_0 e^{-[(i-i_0)a]^2/2\sigma^2}$ is adopted with a standard deviation (SD) $\sigma = 169.86$ nm, which leads to a FWHM of 400 nm. The laser is centered at complex i_0 which locates at $x = 0$, and A_0 is set to unity throughout this study. The B850 chain contains 4001 rings to mimic a system of an infinite size and to ensure that the stationary distribution is achieved before the exciton reaches the system boundary.

As shown in Fig. 6.9, the excitation energy transfer is accelerated (decelerated) by increasing the transfer rate k (the decay rate K). As expected, the NSED only depends on the ratio of K/k for a fixed laser profile. This phenomenon can be clearly seen from comparing the solid and dashed lines of the same color in Fig. 6.9. With a fixed K/k ratio, various sets of (K, k) can produce the same NSED. It can be concluded that the energy transfer in the 1D B850 nanoarray is determined by K/k . In order to demonstrate the dependence of the excitation energy transfer on K/k , the exciton diffusion length $L_d = \sqrt{\sigma_s - \sigma}$ is calculated, where σ_s (σ) is the SD of the stationary excitation probability distribution (the laser profile) [74, 82]. As shown in Fig. 6.10, there is an obvious increase in the exciton diffusion length with a decrease in K/k . As K/k steadily decreases, L_d tends to infinity. If K is comparable with k , the exciton diffusion length is relatively short. This dependence of the energy transfer length on K/k is important to design of artificial photosynthetic devices. Comparing to the exciton diffusion distance in native light-harvesting systems which is less than 50 nm [6], a longer exciton diffusion length of 100 nm is obtained with the parameters of $K = 10^{-3} \text{ ps}^{-1}$ and $k = 0.1 \text{ ps}^{-1}$, as disorder is neglected in the calculations.

In addition to the stationary excitation probability distribution, the time-dependent excitation probability in both 1D and 2D B850 nanoarrays is further investigated in this section. The 1D and 2D systems contain 501 and 2601 B850 rings, respectively. The initial excitation is prepared with a Gaussian laser profile with $\sigma = 33.97$ nm and placed at the center of the nanoarrays, i.e., an initial condition of $p_m(0) = c_1 \exp[-d_m^2/2\sigma^2]$ ($p_{lm}(0) = c_2 \exp[-d_{lm}^2/2\sigma^2]$) for the 1D (2D) sample. c_1 (c_2) is the normalization constant for the initial excitation probability and d_m (d_{lm}) is the distance between the central ring and ring m [(l, m)] in the 1D (2D) nanoarray. In the calculations, the decay rate K and the

Figure 6.10 The influence of the ratio K/k on the exciton diffusion length in a 1D B850 nanoarray. The center of the laser profile is located at $x = 0$, and the FWHM of the laser is 400 nm.

transfer rate k are 0.001 ps^{-1} and 0.1 ps^{-1} , respectively.

To investigate the influence of nanoarray structures on the excitation energy transfer in B850 nanoarrays, one can compare the time evolution of the excitation probability of B850 rings in 1D and 2D nanoarrays with the results shown in Fig. 6.11. The excitation probabilities of five rings in the 1D nanoarray (solid lines) are compared with those in the 2D nanoarray (dashed lines). The distance between ring m and ring 0 in the B850 chain is equivalent to that between ring $(m, 0)$ and ring $(0, 0)$ in the 2D nanoarray. For ring m in 1D array and ring $(m, 0)$ in 2D array, the results are displayed with the same color. The excitation probability of ring $(m, 0)$ in the 2D model is scaled to produce an initial excitation probability identical to that of ring m in the 1D system.

Figure 6.11 The time-dependent excitation probability for B850 rings in 1D (solid lines) and 2D nanoarrays (dashed lines). The 1D and 2D models contain 501 and 2601 B850 rings, respectively. The initial excitation is at the center of the nanoarrays. Prepared initial conditions are $p_m(0) = c_1 \exp[-d_m^2/2\sigma^2]$ for the 1D sample and $p_{lm}(0) = c_2 \exp[-d_{lm}^2/2\sigma^2]$ for the 2D sample with $\sigma = 33.97$ nm. Constant c_1 (c_2) is used to normalize the initial excitation probability, and d_m (d_{lm}) is the distance between ring m [(l, m)] and the central ring in the 1D (2D) system. The decay rate $K = 0.001$ ps $^{-1}$ and the transfer rate $k = 0.1$ ps $^{-1}$.

As shown in Fig. 6.11, the excitation probability decreases monotonically with time if the ring is close to the center of the initial excitation profile, i.e., ring 0 [ring (0, 0)] in the 1D (2D) nanoarray. For a ring located far away from the laser profile center, the probability first increases for short times and then decreases steadily. The short-time increase of the excitation probability is mainly due to the incoming excitation energy transferred from the ones next to the center of the laser profile. The probability decrease at long times stems from energy migration to other distant rings. Direct evidence of the energy transfer is the delayed maximum excitation probability for rings located further from the center

of the initial excitation profile. Due to the irreversible decay of the excitation energy, the maximum probability decreases with the increased distance between the ring and the center of the laser profile. The excitation probabilities for the rings in the 2D system change more rapidly than that for the 1D sample. In addition, the maximum probabilities in the 2D case is lower than that in the 1D case, a result stemmed from the fact that there are more available channels for energy transfer in the 2D nanoarray.

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Chapter 7

Conclusions

*In summary, this dissertation conducts a comprehensive study of excitation energy transfer in photosynthetic systems from a theoretical perspective. MD simulations and quantum chemistry calculations are combined to systematically examine electronic structures and evaluate exciton-phonon coupling strengths of RC pigments from purple bacteria *Tch. tepidum*. Parameters obtained in this study can be used not only to interpret the directional charge separation in bacterial RCs, but also to implement dynamics simulations of the RCs. Beyond static property calculations, various dynamic processes are also investigated with diverse methodologies in this thesis. The NA-ESMD algorithm, a mixed quantum-classical approach with superior accuracy and efficiency, is applied to simulate excitation energy relaxation in a *Chla* dimer. Detailed intra- and inter-molecular energy transfer mechanisms in natural photosynthetic systems are simultaneously revealed from the simulations. Furthermore, excitation energy transfer investigations are extended to engineered large-scale B850 nanoarrays by employing the numerically efficient time-dependent variational principle. A state-of-the-art GPU algorithm is implemented to simulate exciton diffusion in 1D and 2D nanoarrays fully quantum mechanically. This study sheds bright light on energy transfer simulations in natural and artificial photosynthetic systems with fully quantum mechanical treatments.*

Efficient sunlight capture and excitation energy transfer are among the most challenging issues faced by the modern world with energy crisis looming. Having evolved for millions of years, some organisms have developed complex mechanisms for light-harvesting and energy transfer with a nearly perfect efficiency. However, a fundamental understanding of the extremely efficient energy transfer in various photosynthetic systems still remains elusive. By applying comprehensive theoretical methodologies ranging from MD simulations, quantum chemistry calculations, mixed quantum-classical computations, to quantum mechanical modeling, this thesis documents a systematic study of the static and dynamical properties in various photosynthetic systems. Findings and conclusions of this thesis are summarized as follows.

Excitation energy transfer in photosynthetic systems is determined by some key parameters, such as the site energy, the excitonic coupling, and the exciton-phonon coupling. Precise evaluation of these parameters is crucial to reliable dynamics simulations. To this end, electronic structures and pigment-environment interactions of the RC complex from purple bacteria *Tch. tepidum* are studied in this work by combining extensive MD simulations and static quantum chemistry calculations. It is found that environments are essential for reliable site energies of the RC pigments by comparing excitation energies obtained with and without the consideration of surrounding atoms. Excited states of the bacterial special pair P are disclosed for the first time by treating the pair as an aggregate. Excitonic coupling strengths between cofactors are evaluated with the TrEsp method on the basis of transition charges. Directional charge separation along the L branch in the bacterial RCs is interpreted from the findings of this study. Firstly, the excitonic coupling between P_M and the pigments in the L branch is stronger than that between P_M and the M branch pigments. Meanwhile, there is a charge transfer component (from P_L to P_M) in the first excited state of the special pair (P_*). Secondly, stronger excitonic coupling between P_* and BCh_L is found comparing with that between P_* and BCh_M . These results favor the asymmetric charge separation along the L branch. Quantifying the pigment-protein interactions, spectral densities for all cofactors are calculated by analyzing site energy fluctuations. It is shown that two BPhe molecules are more strongly coupled to their surroundings than other cofactors. Re-

spective environments of BPh_L and BPh_M have different influences on the target pigments. It is thus predicted that BPhes also play a crucial role in the determination of charge separation pathways. I hope that parameters obtained in this study will find their applications in the simulation of CS and ET dynamics as well as in the determination of vibrational influences on directionalities of these processes in the RC of *Tch. tepidum*.

Beyond static property calculations for the RC pigments, simulations of energy transfer in diverse photosynthetic systems have also been carried out in this study. Regarding dynamics simulations, the energy relaxation in a Chl_a dimer system is investigated as a preliminary step. Previously, the internal conversion process in a Chl_a monomer has been studied by Zhao and co-workers. In addition to intramolecular energy relaxation, intermolecular energy transfer is of great significance in natural and artificial photosynthetic systems. A molecular dimer is an ideal model to simulate intra- and inter-pigment energy transfer on an equal footing. Through extensive NA-ESMD simulations on the Chl_a dimer, detailed energy relaxation mechanisms in natural photosynthetic molecules are revealed and energy transfer pathways are depicted on an atomic level in this study. The overall Soret to Q_y internal conversion in the Chl_a dimer is found to be faster than that in an isolated Chl_a monomer, due to energy level splitting induced by dimerization. The internal conversion process is found to develop mainly via a sequential pathway $S_6 \rightarrow S_5 \rightarrow S_4 \rightarrow S_3 \rightarrow S_2 \rightarrow S_1$, involving frequent inter-monomer exciton transfer. It is also found that as the system arrives at the Q_y band composed of two excited states S_2 and S_1 , the $S_2 \rightarrow S_1$ relaxation includes a fast and a slow component. Findings from this study greatly facilitate our understanding of intra- and inter-molecule energy transfer in realistic photosynthetic systems.

Natural photosynthetic systems contain many LHCs and numerous pigments are involved in the overall energy transfer process. In addition to the fundamental energy transfer behavior in a pigment dimer, the EET dynamics in large-scale photosynthetic aggregates should also be investigated to construct a comprehensive picture of energy transfer in photosynthesis. To this end, B850 nanoarrays are constructed and used for extended EET

simulations in this dissertation. The Dirac-Frenkel variational principle with the Davydov *Ansatz* is adopted in this study, and a numerically efficient algorithm is implemented on the GPU architecture to arrive at a fully quantum mechanical description of the exciton dynamics in both 1D and 2D B850 nanoarrays. With this advanced GPU algorithm, the computational time is greatly reduced relative to the conventional CPU computation, making feasible quantum dynamics simulations of EET in nanoarrays containing more than one hundred B850 rings (more than 1600 sites). It is found that initially populating the second lowest exciton state (optically bright) of the B850 ring leads to more efficient inter-ring energy transfer than other initial excitation patterns, thanks to the large transition dipole moment of the optically bright state. The superradiance enhancement factor is calculated indicating exciton delocalization over 2 to 3 BChls. For the first time, a fractal analysis is carried out on exciton dynamics in photosynthetic systems, and a superdiffusive component is found to persist for about 500 fs. Due to weak inter-ring coupling and decoherence, the exciton diffusion in B850 nanoarrays can also be described with the classical master equation by treating each B850 ring as an aggregate. Analytical expressions of the time-dependent excitation probability in both 1D and 2D nanoarrays are obtained in this study. From both quantum and classical calculations, exciton transfer in 2D B850 nanoarrays is found to be more efficient than that in B850 chains, owing to multiple channels involved in the energy transfer in the 2D configuration.

This thesis summarizes a comprehensive study on static and dynamic properties of various photosynthetic systems. Electronic structures of the bacterial RC obtained here can facilitate our understanding of directional CS in RC and provide much-needed parameters for future dynamics simulations. A unified framework of energy transfer in LHCs has been constructed via simulating EET processes in natural Chl a dimer and engineered B850 nanoarrays.

Chapter 8

Recommendations for Future Work

*Combining QM/MM calculations, mixed quantum-classical simulations and fully quantum mechanical modeling, this thesis presents a comprehensive study of excitation energy transfer in various natural and artificial photosynthetic systems. Based on the studies and findings documented in current thesis, some potential subjects for future research are given in this chapter. The QM/MM approach is capable to investigate the redshifted Q_y band and the high thermal stability of the LH1-RC complex from *Tch. tepidum*. Functionalities of quantum coherence on the charge separation in bacterial RC can be studied by using fully quantum mechanical methods. Modeled as a quantum heat engine, the RC complex provides a platform to reveal the environmental effects on the operation of the quantum heat engines.*

Figure 8.1 (a) Top view of the arrangement of cofactors of LH1-RC complex from *Tch. tepidum* [1]. (b) Possible binding sites for calcium ion in LH1 complex [1].

8.1 Functionalities of Ca^{2+} in the LH1-RC Complex from *Tch. tepidum*

As discussed in Chapter 2, natural LH1 complexes have diverse structures that depend on the species and living environments of the bacteria. Examples include a monomer with a closed ring [1], a ring-shaped monomer with a gap [2], and an S shaped dimer [3]. For most species of purple bacteria, the Q_y absorption band of the LH1-RC complexes is typically located at 880 nm. However, the LH1-RC complex from *Tch. tepidum* [see Fig. 8.1 (a)] exhibits a redshifted Q_y band at 915 nm. Another interesting property of this LH1-RC complex is its high thermal stability. The living environment of *Tch. tepidum* has a temperature around 50°C and is enriched with calcium ions (Ca^{2+}). A series of experiments have been carried out on the LH1-RC complex from *Tch. tepidum*, and it is found that the calcium ions lead to the redshifted Q_y band [4, 5] and high thermal stability [6]. Experiments show that the native LH1-RC complexes (with Ca^{2+}) are very stable at 50°C, and have the 915 nm Q_y band. After terminating the calcium ions, the Q_y band is found to peak at 880 nm. Surprisingly, the influence of calcium ions on the location of Q_y band is reversible, i.e., after adding calcium ions to the sample solution where calcium ions have been depleted,

the Q_y band is found again at 915 nm.

Theoretical investigations of the redshifted Q_y band and the high thermal stability of the LH1-RC complex from *Tch. tepidum* are lagging behind due to a lack of high-resolution structural data of this aggregate. Fortunately, the structure of this LH1-RC complex at 3 Å resolution was reported recently by Niwa and co-workers [1]. As shown in Fig. 8.1 (a), the LH1 complex with an elliptical closed ring shape is composed of 16 $\alpha\beta$ -heterodimer subunits, and each subunit contains two BChla molecules, one CRT molecule, one calcium ion and two apoproteins, i.e., α and β -apoproteins. The calcium ions are coordinated between the n th α -apoprotein and the $(n + 1)$ th β -apoprotein, as illustrated in Fig. 8.1 (b). Five Oxygen atoms from the C-terminals of two apoproteins can be possible binding sites for the calcium ions. The calcium ions have been proposed to enhance thermal stability by strengthening interactions of the coordinated apoproteins [6]. Wang and co-workers found that the redshifted Q_y band is originated from configurational modifications of the pigments induced by the calcium ions [4, 5].

With the high resolution structural data available, a sequence of theoretical investigations can be conducted to reveal functionalities of the calcium ions. Supposing that the calcium ions can modify molecular arrangements in LH1, such conformational changes can be detected by comparing the structures of native LH1 and the mutant LH1 with the calcium ions removed. As stated above, the crystal structure of native LH1-RC complex containing Ca^{2+} has been reported, while the configuration of the LH1-RC complex without calcium ions is unknown. On the basis of the structural data of native LH1-RC complex, MD simulations can be launched to obtain a stable structure of this aggregate. Then calcium ions are removed to initiate a new MD trajectory. A stable configuration of the modified complex can be obtained from a sufficiently long production run. Configurational modifications on the pigments induced by Ca^{2+} can be identified by structural comparisons between the native and the modified LH1-RC complexes. In order to study the effects of the Ca^{2+} on the Q_y shift, semiempirical methods can be applied to calculate absorption spectra of these aggregates.

As to the influence of Ca^{2+} on the thermal stability of the LH1-RC complex, MD simulations of the two systems, i.e., the native complex with Ca^{2+} and the modified complex without Ca^{2+} , can be carried out at a certain temperature to compare stabilities of the two aggregates. Additionally, electronic structures, such as the site energy and the excitonic coupling, of the pigments in the LH1-RC complex can be obtained by the QM/MM approach with considerations of protein environments. Effects of Ca^{2+} on the electronic structures of the LH1 pigments can be detected. Parameters obtained can be used in future dynamical simulations of excitation energy transfer in the LH1-RC complex.

8.2 Influences of Quantum Coherence on the Charge Separation

In addition to the quantum coherence observed from the energy transfer in various light-harvesting systems, vibronic coherence has been detected from the 2DES measurements on the PSII RC [7]. The presence of specific nuclear modes was claimed to enhance the CS efficiency in this system [7]. The origin and the effects of the coherence on the CS in RC can be studied from a theoretical perspective by quantum mechanical modeling and nonlinear spectroscopy calculations. In order to probe the role of quantum coherence in CS, it is essential to choose an approach that can describe DOFs of both the system and bath modes quantum mechanically. As demonstrated in Chapter 2, the Dirac-Frenkel time dependent variational principle combined with the Davydov trial states is an accurate, numerically efficient formalism to simulate energy transfer in photosynthetic systems. In addition, this methodology has been successfully utilized to calculate nonlinear spectroscopic signals of molecular aggregates [8–10].

Thanks to its high accuracy and efficiency, this approach can be applied to study charge separation in the RC with considerations of vibrational modes obtained from quantum chemistry calculations. Fully quantum mechanical models can be used to systematically characterize the nature of quantum coherence. Effects of the coherence on charge separation and functionalities of the vibrational modes can be investigated. The time dependent variational method cooperating with Davydov *Ansatz* can also be used to simulate the

two-dimensional electronic-vibrational spectroscopy (2DEV) [11] for the charge separation process in the RC. Useful information can be extracted from 2DEV, such as the time scale of charge separation. These findings will not only provide explanations for existing experimental results, but also give guidelines for further studies of dynamical processes in the RC.

8.3 Modeling the RC as Quantum Heat Engine

The 2016 Nobel Prize in Chemistry has been awarded to the design and synthesis of nanomachines, pointing to the importance of nanoscale heat engines. With the advent of nanotechnology, the size of power generating devices has reached the molecular level, making their operations susceptible to quantum and thermal fluctuations. Among these apparatuses, light harvesting devices, such as solar cells are relevant examples of quantum heat engines (QHEs) [12]. Various quantum effects have been observed in thermodynamic properties of such small systems [13]. Influences of quantum coherence are especially important as they may significantly affect the operation cycle of QHEs. Therefore, instruments of classical thermodynamics should be revisited, and quantum mechanical descriptions should be contemplated. The RC complex is one ideal candidate for QHEs [14]. Recently, Dorfman and coworkers investigated the possible role of quantum coherence on the steady-state and transient behavior of various QHE models, including photovoltaic cells [15, 16] and PSII reaction centers [14]. It is shown that the maximum power of a QHE that converts incoherent thermal energy into coherent cavity photons could be enhanced by manipulating quantum coherences [15].

Coherent and incoherent energy transfer has long been studied in molecular crystals and aggregates. It is well established that the interplay between excitonic coupling and energetic disorder controls the extent of exciton delocalization, which in turn determines the nature of transport. Coherence may play a more prominent role as excitons become more delocalized. Recent femtosecond spectroscopic measurements in certain photosynthetic complexes have revived the interest in such issues. Oscillatory temporal features in

2DES have been initially attributed to electronic coherence but growing evidence indicates that this could be due as well to strongly coupled vibrational motions [17]. Dorfman *et al.* have recently showed that this oscillatory behavior arises from the population-coherence coupling term [14]. Furthermore, the same term is responsible for the enhancement of the yield of various QHEs [13]. Interestingly, this type of quantum coherence has been recently predicted to be important for photo-carrier generation dynamics at polymeric semiconductor heterojunctions [18]. Simple kinetic models have been applied to study the steady state and time-dependent behavior of various QHE models [13, 14].

In future study, the bacterial RC complex from *Tch. tepidum* can be modeled as a QHE with the electronic structures and the exciton-phonon coupling strengthes established in Chapter 4. Fully quantum mechanical calculations can be implemented with the consideration of system-bath interactions. It is accomplishable to explore the dependence of the QHE performance on various environmental factors, including the system-bath coupling, the temperature and the disorder. Effects of quantum coherence on static and dynamical properties of the QHE also can be revealed.

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APPENDIX

Appendix A Transition Charges for the Pigments in Bacterial Reaction Center

The molecular structures for the BChl *a* and BPhe *a* pigments in the RC of *Tch. tepidum* are illustrated in Fig. A.1. The hydrogen atoms are not included in the structures apparently and the phytyl tail has been replaced with a methyl (CH₃).

Figure A.1 Molecular structures of the BChl *a* and BPhe *a* with the phytyl tail replaced with a methyl (CH₃). The atoms of carbon (C), nitrogen (N), magnesium (Mg) and oxygen (O) are represented with gray, blue, yellow and red balls, respectively. The hydrogen atoms are not included in the structures apparently in order to show the labels of the heavy atoms clearly.

Transition charges in atomic unit for the heavy atoms of BChl *a* and BPhe *a* pigments in the RC from *Tch. tepidum* are listed in Tab. A.1 and Tab. A.2, respectively. The phytyl tails are replaced with a methyl (CH₃) and the transition charges of the hydrogen atoms are added to the connected heavy atoms. The atomic labels are consistent with that shown in Fig. A.1. All the transition charges are obtained with CHELPG algorithm by fitting the electrostatic potentials calculated with the Time-Dependent Density Functional Theory (TDDFT) by the Gaussian 09 package. The TDDFT calculations for single BChl and BPhe

molecules are done with the B3LYP functional on the 6-31G** basis set. The wb97XD functional with the 6-31G** basis set is applied to the TDDFT calculations for the excited states of the special pair (P_- and P_+) in order to capture the charge transfer characteristic of the P_- and P_+ states.

Table A.1 Transition charges in atomic unit for the heavy atoms of BChl *a* pigments in the RC from *Tch. tepidum*.

Label	Atom Type	Transition Charges				
		single BChl	P_-		P_+	
			P_L	P_M	P_L	P_M
1	Mg	-0.007049	-0.017094	0.008274	0.021499	0.001193
2	N	-0.006835	0.000788	-0.003102	-0.025207	-0.010292
3	N	-0.05526	-0.064436	0.068061	-0.092151	-0.067604
4	N	0.002103	0.012788	-0.009196	-0.005596	0.011301
5	N	0.06506	0.066544	-0.074498	0.064561	0.052800
6	C	-0.103652	-0.101403	0.108021	-0.097684	-0.082784
7	C	0.10204	0.099097	-0.099689	0.095620	0.071922
8	C	-0.090413	-0.076632	0.094985	-0.085795	-0.073626
9	C	0.102974	0.087329	-0.101903	0.131139	0.107737
10	C	-0.065812	-0.057141	0.073217	-0.101339	-0.078433
11	C	0.124896	0.110059	-0.119858	0.123662	0.108400
12	C	0.107623	0.097908	-0.102069	0.098567	0.057566
13	C	-0.06373	-0.088321	0.066611	-0.054384	-0.047649
14	C	0.064202	0.098016	-0.083913	0.059331	0.066853
15	C	-0.096355	-0.093112	0.095145	-0.106224	-0.087782
16	C	0.062249	0.064028	-0.063151	0.079390	0.061732
17	C	-0.115476	-0.109278	0.121563	-0.104137	-0.090440
18	C	-0.022407	-0.011021	0.035751	-0.053111	-0.026831
19	C	0.007727	0.020218	-0.031730	0.019740	0.003586
20	C	0.016772	0.013748	-0.020882	0.042340	0.020422
21	C	0.002278	-0.006718	0.003349	0.001192	0.005830
22	C	0.048694	0.039585	-0.053658	0.017686	0.021527
23	C	0.022321	0.012678	-0.006603	0.015689	0.017036
24	C	0.032008	0.002535	-0.009781	0.054676	0.019087
25	C	0.002436	0.004312	-0.012375	-0.023179	-0.017164
26	C	0.00953	0.002242	-0.001432	0.022151	0.027150
27	O	0.038012	0.005236	-0.000202	0.039878	0.020311
28	C	0.018828	0.007826	-0.020455	0.040108	0.055771
29	C	-0.003333	-0.003409	0.009326	-0.001465	0.003320
30	C	-0.023634	-0.022393	0.025685	-0.052145	-0.058419
31	C	0.012752	0.017357	-0.021906	0.021865	0.010144
32	C	-0.011171	-0.014888	0.018555	-0.009140	-0.000030

Continued on next page

Table A.1 – Continued from previous page

Label	Atom Type	Transition Charges				
		single BChl	P _−		P ₊	
			P _L	P _M	P _L	P _M
33	C	-0.062227	-0.041460	0.056145	-0.049479	-0.042666
34	C	-0.017031	-0.015045	0.015286	-0.011732	-0.009870
35	C	-0.007501	-0.016020	0.009703	-0.011231	-0.005612
36	C	-0.005466	0.007043	-0.007375	-0.002915	-0.004622
37	O	-0.029918	-0.026435	0.030605	-0.024009	-0.019377
38	C	-0.045085	-0.042526	0.043185	-0.037300	-0.025185
39	C	0.024119	0.016028	-0.024582	0.024463	0.015883
40	O	-0.016339	-0.011088	0.012691	-0.012845	-0.007740
41	O	-0.000094	0.001066	0.004863	-0.001938	0.003967
42	C	-0.010758	-0.008791	0.007276	-0.007240	-0.007499
43	C	-0.003659	-0.019500	0.019602	-0.001434	0.005677
44	C	-0.005666	0.008279	-0.001751	-0.002510	-0.009289
45	O	-0.002523	-0.006134	0.004056	-0.002450	0.000120
46	O	0.005857	-0.000411	-0.001702	0.001197	0.003872
47	C	-0.001087	-0.003274	0.001678	0.001230	0.000358

Table A.2 Transition charges in atomic unit for the heavy atoms of BPhe *a* pigments in the RC from *Tch. tepidum*.

Label	Atom Type	Transition Charges	Label	Atom Type	Transition Charges	Label	Atom Type	Transition Charges
1	N	0.002342	17	C	-0.019616	33	C	-0.010627
2	N	-0.041265	18	C	0.003691	34	C	-0.01538
3	N	-0.012439	19	C	0.020479	35	C	-0.004785
4	N	0.039053	20	C	0.000237	36	O	-0.028531
5	C	-0.080233	21	C	0.064431	37	C	-0.042659
6	C	0.067463	22	C	0.01691	38	C	0.024752
7	C	-0.038159	23	C	0.038264	39	O	-0.015175
8	C	0.049824	24	C	-0.001152	40	O	-0.000431
9	C	-0.02525	25	C	0.008827	41	C	-0.010135
10	C	0.087537	26	O	0.037849	42	C	0.001069
11	C	0.086321	27	C	0.028623	43	C	-0.004019
12	C	-0.040099	28	C	-0.007856	44	O	0.002338
13	C	0.021735	29	C	-0.035951	45	O	-0.000642
14	C	-0.047716	30	C	0.014296	46	C	-0.00046
15	C	0.029959	31	C	-0.009422			
16	C	-0.081592	32	C	-0.072404			

Appendix B Derivation of Polaron Dynamics in B850 Nanoarrays

In the framework of the Dirac-Frenkel time-dependent variational principle [1], the Lagrangian L is written as

$$L = \langle \Psi_{D1}(t) | \frac{i\hbar}{2} \left(\frac{\overrightarrow{\partial}}{\partial t} - \frac{\overleftarrow{\partial}}{\partial t} \right) - \hat{H} | \Psi_{D1}(t) \rangle. \quad (\text{B.1})$$

Applying the Lagrangian L to the Euler-Lagrange equations

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\alpha}_m^{r*}} \right) - \frac{\partial L}{\partial \alpha_m^{r*}} = 0 \quad (\text{B.2})$$

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\lambda}_{mq}^{r*}} \right) - \frac{\partial L}{\partial \lambda_{mq}^{r*}} = 0, \quad (\text{B.3})$$

one can obtain the equations of motions for the time-dependent variational parameters $\alpha_m^r(t)$ and $\lambda_{mq}^r(t)$:

$$\dot{\alpha}_m^r(t) = i[T_m^r(t) + \alpha_m^r(t)R_m^r(t)], \quad (\text{B.4})$$

$$\dot{\lambda}_{mq}^r(t) = i \left[\frac{\Omega_{mq}^r(t)}{\alpha_m^r(t)} + \frac{g_q^r}{\sqrt{N}} \omega_q^r e^{-iqm} - \omega_q^r \lambda_{mq}^r(t) \right], \quad (\text{B.5})$$

with

$$T_m^r(t) = - \sum_{r'} \sum_n J_{mn}^{rr'} \alpha_n^{r'}(t) S_{mn}^{rr'}(t), \quad (\text{B.6})$$

$$R_m^r(t) = \text{Re} \sum_q \left[- \frac{\Omega_{mq}^r(t)}{\alpha_m^r(t)} + \frac{g_q^r}{\sqrt{N}} \omega_q^r e^{-iqm} \right] \lambda_{mq}^{r*}(t), \quad (\text{B.7})$$

and

$$\Omega_{mq}^r(t) = - \sum_{r'} \sum_n J_{mn}^{rr'} \alpha_n^{r'}(t) S_{mn}^{rr'}(t) [\lambda_{nq}^{r'}(t) \delta_{rr'} - \lambda_{mq}^r(t)]. \quad (\text{B.8})$$

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