RICC Usage Report for Fiscal Year 2012

Project Title:

Theoretical Modeling of Photosynthesis

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A. Charge and energy transfer dynamics in natural and artificial photosynthetic structures

1. Background and purpose

The energy-transduction process in photosynthesis begins with absorbing sunlight photons by a large number of photo-sensitive pigment-protein complexes (antenna) surrounding reaction centers (RC) [1]. The light harvesting complexes around the RC transfer their electronic excitation energy to the reaction center directly or through a series of accessory chromophores. In the next stage, the electronic excitation energy is used to create a stable charge-separated state. This is the general pathway of energy transduction in the primary stage of photosynthesis and has been well-known for a long time. Recently, two dimensional electronic spectroscopic and theoretical studies reveal that coherences between electronic states play an important role in exciton-transfer dynamics [2]. Thus, more precise energy-transductions mechanisms have been proposed, but, new questions and controversies have arisen [2]. Open issues include: the quantitative impacts of quantum coherence in the efficiency of energy transfer, the role of the surrounding protein medium and environment-induced correlated fluctuations in long-lasting quantum coherence, the multiple exciton dynamics and effects of exciton-exciton annihilation processes in exciton relaxation mechanisms, etc.

In last couple of years, we explored both charge and electronic energy transduction dynamics in some artificial photosynthetic structures, which are functional mimicry of the natural photo-system [3, 4, and 5]. To be specific, two types of artificial photo-systems we studied: (a) photo-systems based on molecular triads (comprised of three basic components: a donor, an acceptor and a photosensitive component) [3], (b) a wheel-shaped antenna-RC complex containing six light absorbing pigments and an electron acceptor [4, 5]. For the first system [3], we studied energy conversion mechanism in the molecular triads to find out maximum efficiency conditions in terms of the controllable system-parameters. Examples include reorganization energies, energy spacings, coupling energies, and topological arrangements of antenna chromophores around RC. The main focus of these studies was on electron- and energy-transfer dynamics in the time scale from hundreds of picoseconds to nanoseconds and the effects of quantum coherence have been ignored. We studied the second system (the wheel-shaped antenna-RC complex [4, 5]) to explore the fundamental issue, whether excitons and electrons transfer via incoherent hopping motion or by wave-like coherent motion. Our results [5] showed that at short time regimes, not only excitons but also electron transfer takes place via wake-like coherent motion. So, the coherent movement of exciton is not only observed at natural photosynthetic structures, but also in the artificial structures which have a completely different surrounding environment.

In the last year, we studied intra-ring exciton-transfer dynamics in LH2 (light harvesting complex 2) and FMO (Fenna – Matthews - Olson) complex incorporating of multiple excitons [6]. Most of the earlier studies concentrate on the

energy transfer dynamics in the single exciton regime. The single excitonic regime is justified at weak light intensity. However, under increasing light intensity (e.g., spectroscopic studies under intense laser light) multiple chromophores may be excited. The multiple-excitonic condition opens a new relaxation channel due to quenching of energy through exciton-exciton annihilation processes. In this regime, two types of superposition states (superposition between 1st excited states as well as between higher-cited states) are formed.

2. Methods:

(The following method has been employed for studying the multi-excitonic dynamics in presence of the exciton-exciton annihilation processes).

We exploit reduced density matrix method to examine electronic excitation energy transfer mechanisms in presence of exciton-exciton annihilation processes. We introduce creation/annihilation operators to characterize electrons in the adiabatic electronic states. We assume each electron state can be occupied by a single electron as the spin degrees of freedom are neglected. We choose 32 basis states to describe time evolution of electron density at 14 adiabatic electronic states (seven for 1st excited states and another seven for fused states) of FMO complex. Similarly, 54 basis states have been chosen to describe double exciton dynamics in B800 ring of LH2 complex. We derived coupled matrix equations (32 × 32 for FMO complex and 54 × 54 for B800 ring of LH2) including the coherence of the density matrix. To capture the features of electrons and excitons transfer in presence of the exciton-exciton annihilation processes, we estimate time evolution of the elements of density matrix by numerical integration of the coupled 1st order differential equations. We refer [5] for the details about the method. As there are several unknown system parameters, we explored the entire parameter space for the better understanding the role of the extra relaxation channel in the energy transfer dynamics.

3. Results and conclusions:

(The following are the outcomes of our studies on the multi-excitonic dynamics in presence of the exciton-exciton annihilation processes.)

We studied the dynamics of multiple excitons in aggregates of chromophores, incorporating exciton-exciton annihilation processes (EEA). The EEA is a two step process: first, two excitons move to close together and combine to create a higher excited state, also known as a fused state. In the second step, a very fast internal conversion mechanism brings the system back to the first excited state. To incorporate exciton-exciton annihilation processes, three adiabatic electronic states (the ground state, the first excited state and a higher excited) for every chromophores have been considered. To describe the quantum dynamics of multiple excitons on a femto-second time scale, we derive a set of exact non-Markovian equations for the Heisenberg operators for the electronic states of chromophores in contact with a Gaussian heat bath. With these equations, we can analyze the regime of strong system-bath interactions, where reorganization energies are of the order of the inter-site exciton couplings. At the same time these equations are valid in the regime when the nuclear reorganization time is of the order of the exciton transfer time. To be specific, our study focuses on the FMO complex and the B800 ring of LH2, which have seven and nine chromophores, respectively. We show that the energy of the initially-excited antenna chromophores is efficiently funneled to the reaction center (trap) in a few picoseconds, with a quantum yield ~ 96% and ~ 46% for the single-exciton and double-exciton cases, respectively. In the absence of EEA processes (or even in the presence of EEA, but when the exciton

transfer time scale is of the order of the internal conversion processes) we observe apparent quantum beatings of energy between two double excitonic states with a decoherence time of ~ 400 fs. Again, a conspicuous presence of wave-like oscillatory behavior of electron population in higher excited (fused) states confirms the formation of a quantum mechanical superposition of the combined states (i.e., fused states, with two excitons). Thus, the energy-transduction dynamics in the multi-exciton regime, for both the FMO and LH2 complexes, is dominated by wave-like coherent motion over incoherent hopping. Besides the inclusion of EEA processes, a coupling to a monochromatic continuous light source has been incorporated, in order to explore the effects of the light intensity in multi-exciton dynamics. Specifically, we find the regimes where multi-excitons are formed and hence the EEA mechanism becomes operational.

4. Future plan

Many parameters of the FMO and the B800 ring of LH2 complexes are unknown. For example, transitions energies (e.g., from the first excited state to higher excited states), coupling energies (for both internal conversions and excitons fusion), are unknown. Therefore, we have numerically calculated [6] the time evolution of electron populations in the adiabatic electronic states for the various regimes of the time scales of exciton transfer, exciton-exciton annihilation and internal conversion processes. Our studies show that the underlying mechanisms and efficiency of the energy-transduction processes depend on the relative time scales of these relaxation processes. Therefore, to capture the exact features of the energy-transduction mechanism in the FMO complex and the B800 ring our goals for next fiscal year will be as follows:

(a) The transitions energies, coupling energies for internal conversion and excitons fusion for FMO (also B800 ring of LH2) will be calculated using the methods developed in ref. [7]. For calculating the coulomb couplings we planned to use transition density cube method [7]. Energy of the higher excited states will be calculated using the configuration interaction method.

(b) To make our outcome testable in future experiments, we will numerically calculate the third optical response of the FMO complex, but now incorporating the exciton-annihilation mechanism. For this purpose, the density matrix method with reduced-hierarchy equations [8] will be exploited. Here, a large number of coupled 1st order differential equations will be solved numerically. For details about simulation method we refer [8]

References:

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In addition to the above items I used RICC for simulation of Brownian dynamics in confined geometries.

B. Diffusion of Brownian particles in confined geometries.

1. Background and purpose

The effective control of mass and charge transport in artificial micro- and nanostructures requires a deep understanding for the diffusive mechanisms involving small objects in confined geometries. Such situations are typically encountered when studying the transport of particles in, e.g., biological cells and zeolites, catalytic reactions occurring either on templates or in porous media, chromatography or, more generally, separation techniques of size-dispersed particles on micro or even nano-scales [1, 2]. In many respects these transport phenomena can be regarded as diverse manifestations of geometrically constrained Brownian dynamics in one or higher dimensions.

In the past three years our concentration was on exploring unique features in confined diffusion processes. We got some very interesting results which stimulate further research activity on diffusion in confined geometries. The most important outcome of our studies on confined diffusion is geometric stochastic resonance (SR). We developed a new scheme of stochastic resonance in confined system by adopting sharp constriction. The most important feature of geometric SR is that it does not require the entropic or energetic barrier [3]. We also extended the scheme of the geometric-SR for a system of interacting particles and show that it is possible to amplify signal by tuning particle density instead of noise strength [4].

We also investigated the transport of a suspended overdamped Brownian particle which is driven through a two-dimensional rectangular array of circular obstacles with finite radius [5]. We found prominent transport features, like negative differential mobilities, excess diffusion peaks, and unconventional asymptotic behaviors. These results are potentially important for controlling mobility and diffusivity in electrophoresis processes.

In the last year I have paid most of my effort, to find a mechanism for producing position dependent diffusion by tuning geometry of the system. Our main purpose here is to find out a technique to localized particle or direct to a particular direction without breaking detailed balanced of the system.

2.Methods:

(The following method has been employed for studying the diffusion problems in confined systems).

We use the Langevin description for modeling diffusion Brownian particles in confined systems. An exact analytical solution of Langevin equations is typically never possible. We numerically solve the Langevin equations using a Milstein algorithm [7] implementing as well the appropriate boundary conditions, depending on the shape of Brownian particles and the shape of the confining walls. In addition to the thermal noise and the frictional force, remaining physical force terms arise either due to hydrodynamic interactions or due to intrinsic and externally applied forces have to be incorporated into the Langevin description. To solve the Langevin equation we have to use very small time step for numerical integration to minimize numerical error. Moreover, there is a noise term in the Langevin equations. So the estimated quantities need to be averaged over at least 10,000 trajectories.

3. Results and conclusions:

Equilibrium energy harvesting

Specifying the diffusion rate as a function of position is not enough to characterize the behavior

of a system, even assuming the absence of external forces. We propose an alternative framework for modelling diffusive dynamics in which both the diffusion rate and equilibrium probability density for the position of the particle are specified. As a consequence the diffusing particle may be subjected to a drift term even for situations when the net current is set to zero. The apparent paradox is investigated in the context of Brownian motion rectification under equilibrium conditions. For this purpose, we simulate Brownian dynamics in both smoothly corrugated and sharply corrugated 2D-channels. We assume that there are some gradient in pore size of the channels. We numerically estimated the mean exit time and probability to exit towards both directions assuming initially particles are in the middle of the channels. Our simulation results show geometry depend asymmetry in both exit time and accumulation of the particles, as well as a drift even when net current is zero.

4. Future plan:

Diffusion mechanism in a system of interacting Brownian particles in confined geometries.

In the FY2013, we will concentrate on self-driven micro-swimmer induced transport properties of passive particles in confined spaces. Our earlier studies [3-6] show that due to confinement, some interesting features are observed in diffusivity and mobility (like negative differential mobilities, excess diffusion peaks, and unconventional asymptotic behaviors). These properties may useful to enhance amplification of weak signal (via SR mechanism), particles separation efficiency and rectification of energy from non-equilibrium fluctuations in micro-swimmer driven system. I intend to complete the following tasks.

(i) We will study the effects of the confinement in separation of particles according to theirs masses, charge and size. For this purpose we will consider mixtures of two types of interacting passive particles and micro-swimmers. The micro-swimmers can be driven by applying light [8]. Mainly, two classes of confinement will be considered: (a) smoothly corrugated channels, (b) sharply corrugated channels with both tri-angular and rectangular shapes. We will numerically calculate diffusivity and direction velocity of all the passive particles and micro-summer considering various types of repulsive interactions. Particles are separated according to their diffusivity and mobility.

(ii) We also plan to investigate stochastic resonance phenomenon in self-propelled micro-swimmer in the confined geometries. Micro-swimmers exhibits stochastic motion under action of light with randomly changing directions. Our main intention here to explore weather micro-swimmer dynamics in absence of back-ground noise exhibit SR or not. In SR experiment, heating the entire system to increase noise strength creates several problems. Therefore, it would be desirable to develop a scheme of SR without thermal noises.

To address the objectives of confined diffusions we shall use the Langevin description as described in the previous section.

Currently, I have a “Quick Use” user account and I would like to get extension of computation facilities for next usage term (up to 31st March 2014) in the same user category and the same research topic.

References:

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Fiscal Year 2012 List of Publications Resulting from the Use of RICC

[Publication]

(1) Title: Effects of exciton-exciton annihilation processes on energy transduction mechanisms in FMO and LH2 complexes.
Authors: P. K. Ghosh, A. Yu. Smirnov and F. Nori
Manuscript under preparation.

(2) Title: Equilibrium energy harvesting
Authors: P. K. Ghosh, F. Marchesoni and F. Nori,
Manuscript under preparation.

[Proceedings, etc.]

None

[Oral presentation at an international symposium]

None

[Others]

Poster presentation:

Title: Quantum effects in energy and charge transfer in a wheel-shaped artificial photosynthetic complex.
Name of the symposium: The Principle and Applications of Control in Quantum Systems
Date: 2012/09/13
Venue: Tokyo, Japan

Oral presentations (but not in symposium):

- Speaker: Raman Research Institute, Bangalore, India, On 6th August, 2012.
  Title of talk: Charge and energy transfer mechanism in an artificial antenna-reaction center complex.

- Speaker: Indian Institute of Science Education and Research, Mohali, India, On 8th August, 2012.
  Title of talk: Quantum dynamics in charge and energy transfer mechanism in an artificial antenna-reaction center complex.

- Speaker: IISER Pune, India, On 21st January, 2013.
  Title of talk: Quantum dynamics in charge and energy transfer mechanism in an artificial antenna-reaction center complex.