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

Natural photo-systems are energy-converting devices which achieved their excellent performance through evolution over billions of years. The electronic energy-transfer mechanisms of natural photo-systems are attracting considerable interest, and researchers wish to know better the processes responsible for efficient energy transfer [1]. A deeper understanding of the energy transfer in photosynthesis is required for implementing its mechanisms in artificial solar cells, which is a promising source of renewable and clean energy for our long-term future.

The multi-step energy-transduction process in natural photo-systems begins with capturing sunlight photons by light-absorbing antenna pigments surrounding a reaction center [1]. The antenna pigments transfer radiation energy to the reaction center directly or through a series of accessory chromophores. The reaction center harnesses the excitation energy 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. But details of energy transduction mechanisms are largely unknown. Recently, two dimensional electronic spectroscopic and theoretical studies revealed that coherences between electronic states play an important role in exciton transfer dynamics [1, 2]. Thus, more precise energy transductions mechanisms have been proposed, but, new questions and controversies have arisen [1, 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 effects of non-Markovian dynamics on the excitation-energy transfer, how to implement efficient coherent electron transfer mechanism in artificial photosynthetic structures. Even though the roles of quantum coherence have not been well understood, it is assumed that quantum coherence makes the exciton-transfer processes directional by creating an energy gradient by forming quantum mechanical superposition states [1]. The reason of the long-lasting electronic coherence, even in presence of the dissipative medium, is not clear yet. Some theoretical calculations show that spatially-correlated environment-induced site-energy fluctuations can considerably increase coherence time. But, so far, all the studies based on a combination of atomistic theories (classical MD calculations and semiempirical quantum chemistry calculations) reveal that bath-induced site-energy fluctuations are uncorrelated [3]. However, the theoretical calculations assuming very slow nuclear relaxation times (i.e., non-Markovian dynamics) and correlated site-energy fluctuations produce the best results to explain experimental findings based on 2D electronic spectroscopy [1-2].

In the fiscal year 2013, we explore intra-ring exciton-transfer dynamics in light harvesting complex 2 (LH2 ) and Fenna – Matthews - Olson (FMO) complexes incorporating of multiple excitons [6]. Mainly, we focus on quantum effects in the multi-exciton dynamics. At weak light intensity, exciton transfer dynamics can be studied based on the assumption of single exciton regime. But, under

increasing light intensity (e.g., spectroscopic studies under intense laser light) multiple chromophores may be excited. Presence of multiple excitons offers a drastically new situation due to an extra relaxation channel for quenching of energy through exciton-exciton annihilation processes.

**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 [4-5] for the details about the method. To calculate several unknown system parameters, like, the transitions energies, coupling energies for internal conversion and excitons fusion for FMO (also B800 ring of LH2) we employ the methods developed in ref. [6]. For calculating the coulomb couplings we use transition density cube method [7].

**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.)*

Multiple excitons dynamics in FMO and LH2 complexes has been explored. We incorporated effect of 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.

Our simulation results show that the energy of the initially-excited antenna chromophores is efficiently funneled to the reaction center in a few picoseconds, with a quantum yield ~ 96% and ~ 60% for the single-exciton and double-exciton cases, respectively. Here we set the parameter regime in such a way that the time scale of EEA processes ($\tau_{EEA}$) is of the order of exciton transfer time ($\tau_e$). When exciton transfer

time is much less than $\tau_{EEA}$, quantum yield in double exciton regime is very high, almost equal to the quantum yield in single excitonic regime. In the opposit limit, $\tau_{EEA} < \tau_e$, quantum yield depress considerably in the double excitonic regime and become less than 50%. Quantum beating between two double excitonic states has been observed in the parameter regime, $\tau_{EEA} \geq \tau_e$, with a decoherence time ~ 400 fs. To capture essential features of energy of transfer mechanism in real system (real parameter space) we still are calculating some unknown systems parameters. Therefore, we do not have sufficient data in our hand to make any conclusion about quantum effects in double excitonic regime in FMO and LH2 complexes.

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 self-propelled Brownian particles in confined geometries.**

**1. Background and purpose**

Self-propulsion is the ability of a particle or living organisms to move, in the absence of any external forcing, thanks to an "engine" of their own [1]. Self-propulsion of micro- and nano-particles (artificial micro-swimmers) poses a challenge with respect to their unusual non-equilibrium diffusion properties as well as their applications to nanotechnology[2-5]. Recently, a new type of micro-swimmers has been synthesized, where self-propulsion takes advantage of the local gradients that asymmetric particles can generate in the presence of an external energy source (self-phoretic effect). Such particles, called Janus particles [5], consist of two distinct "faces," only one of which is chemically or physically active. Such two-faced objects can induce either concentration gradients, by catalyzing some chemical reaction on their active surface[6-7] , or thermal gradients, by inhomogeneous light absorption (self-thermophoresis) [8] or magnetic excitation (magnetically induced self-thermophoresis [9]. Moreover, experiments demonstrated the ability of Janus micro-swimmers to perform guided motions through periodic arrays and separate colloidal mixtures, due to their selective interaction with the constituents of the mixture[8].

We are carrying out research on diffusion in confined geometries since a couple of years back. We have explored several interesting issues[10-11], like: scheme for geometric stochastic resonance, controlling mechanisms of Brownian transport in compartmentalized channel and stochastic resonance mechanisms of interacting particles in a confined system. The most important feature of geometric SR is that it does not require the energetic barrier [10]. 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 [11]. In the last year I have paid most of my effort, to find

a mechanism for extraction of direction motions of Janus particles in confined geometry. Directional motion of the Janus particle might be useful for some medical application, particularly in drag delivery.

**2.Methods:**

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

We use the Langevin description for modeling diffusion of Janus 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 [12] implementing as well the appropriate boundary conditions, depending on the shape of Janus 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 or self-propulstion velocity have to be incorporated into the Langevin description. Again, translational motion is coupled to the rotational motion due self-propulsive force. 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:**

We numerically studied Brownian transport of self-propelled overdamped microswimmers (like Janus particles) in a two-dimensional periodically compartmentalized channel for different compartment geometries, boundary collisional dynamics, and particle rotational diffusion. The resulting time-correlated active Brownian motion is subject to rectification in the presence of spatial asymmetry. We prove that ratcheting of Janus particles can be orders of magnitude stronger than for ordinary thermal potential ratchets and thus experimentally accessible. In particular, autonomous pumping of a large mixture of passive particles can be induced by just adding a small fraction of Janus particles.

**4. Future plan:**

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

To use self-propelled particles in nano-mechanics and medical science (e.g., eliminating pollutant in aquatic media, removing toxic chemical from biological channels, delivery of drags at targeted locations etc) we need a clear understanding of the diffusion mechanism of it. Moreover, self-propelled Janus particles can be used to demonstrate various noise-induced non-equilibrium phenomena. Followings are details about our future research plan on self-propelled Janus particles.

(a) Noise-induced phenomena in self-propelled Janus particles: Noise-induced phenomena like ratchet effects, stochastic resonance, noise-induced localization etc. have been focus of concerted effort, both conceptual and technological. These phenomena provide mechanisms for manipulating noise or non-equilibrium fluctuations for doing constructive works. Despite their conceptual interest, practical uses are limited. This is due to the fact that in practical situation it is difficult to meet with the essential ingredients needed for noise-induced phenomena. Self-propelling Janus particles can act as a color noise-driven diffusive tracer and offer the possibility of a direct demonstration of striking noise-induced phenomena. We have already explored thermal ratchet effect using self-propelled Janus particles [4] . We plan to extend this idea to explore schemes for demonstrating other more challenging non-induced phenomena like, absolute negative mobility, stochastic resonance and stochastic localization which require more subtle conditions.

(b) Role of the shape of diffusing self-propelled particles: The shape of both the self-propelled particles and the confining walls determine the course of interactions between them and hence the boundary conditions. Thus, the shape of the confining wall and self-propeller (e.g., Janus particle) are important factors in controlling diffusive transport through artificial nano-pores or in biological channels. We intend to explore the geometric effects of both boundary walls and the finite-size diffusing particles on transport.

To address the above issues we shall numerically solve the Langevin equations with appropriate boundary conditions to account for the shape of the Brownian particles and the structure of the confining walls. Inertial and hydrodynamics effects will be taken into account when they are relevant.

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 2015) in the same user category.

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**Fiscal Year 2013 List of Publications Resulting from the Use of RICC**

**[Publication]**

Self-propelled Janus Particles in a Ratchet: Numerical simulations, P. K. Ghosh, V. R. Misko , F. Marchesoni and F. Nori, Physical Review Letters 110, 268301 (2013).

**[Proceedings, etc.]**

None

**[Oral presentation at an international symposium]**

Invited speaker: Symposium on quantum simulation at Indian Institute of Science, Bangalore, September 2-3, 2013.

Title of talk: *Quantum effect in charge and energy transfer mechanism in photosynthesis.*