Project Title:

Theoretical Modeling of Photosynthesis

Name: Pulak Kumar Ghosh
Laboratory at RIKEN:
    Digital Materials Team, Single Quantum Dynamics Research Group,
    Emergent Materials Department, RIKEN Advanced Science Institute, RIKEN Wako Institute

Description of the project

1. Background and purpose

Past three years our attention mainly focused on charge and energy transduction dynamics in several artificial photosynthetic structures [1]. The artificially synthesized systems, which we have studied, are functional mimicry of the natural photosynthetic structures. These photo-systems are comprised of three basic components: donors, acceptors and photosensitive moieties for capturing light energy. We studied primary processes of multi-step energy transduction to the goal of finding out a sophisticated mechanism for conversion of light energy into a usable form, like electricity, fuel (chemical energy) mimicking natural photosynthesis. These studies focused, mainly, on electron- and energy-transfer dynamics in the time scale from hundreds of picoseconds to nanoseconds, ignoring effects of quantum coherence. In spite of this, these studies provide interesting insights for direct conversion of light energy into proton motive force or electricity.

Last year, we have studied energy and charge transfer kinetics in a wheel-shaped artificial antenna-reaction complex to explore the effects of quantum coherence in sub-picoseconds time scale. This complex has been synthesized and experimentally investigated in Ref. [2]. It has four antennas two bis(pheny -lethynyl)anthracene (BPEA) molecules and two borondipyrromethene (BDPY) chromophores, as well as two zinc porphyrins (ZnPy). These six light-absorbing chromophores are attached to a central hexaphenylbenzene core. In addition to the antenna components, the photo-system contains a fullerene

derivative (F) containing two pyridyl groups, acting as an electron acceptor. The fullerene derivative F is attached to the both ZnPy chromophores via the coordination of the pyridyl nitrogens with the zinc atoms. Each component absorbs energy at the different region of the solar energy spectra and delivers their excitation energy to adjacent component. The excitation energy rapidly moves to the reaction center where a charge separated state is setup. We have examined these energy transduction process based on the modified Redfield like equations taking into account the time evolution of the off diagonal elements of the density matrix.

Beside this, we have been studying intra-ring exciton-transfer dynamics in both LH I and LH II, with special emphasis on the multiple-exciton dynamics, this aspect has not been addressed so far. Mainly, we intend to explore how the excitation-energy transfer efficiency is affected by multiple excitons, and its impact on the wave-like coherent dynamics in the short-time regime.

2. Methods

Energy and charge transfer dynamics in an artificial wheel-shaped antenna-reaction complex:

Our studies are based on the methods of quantum transport theory. The electron and exciton are described characterized Fermi operators. We assume each electron state can be occupied by a single electron as the spin degrees of freedom are neglected. We choose 160 basis states to describe time evolution of electron density at 13 electron sites (six chromophores having 12 sites and one site on electron acceptor F). We derive 160 X 160 coupled

matrix equations (including the coherence of the density matrix) to estimate evolutions of the electron density at each chromophore. To analyzed features of electrons and energy transfer in the wheel-shaped antenna-reaction center complex we estimate time evolution of the elements of density matrix (160 X 160) by numerical integration. We refer [3] for the details about the method.

Also, for the other part of the project relating exciton-transfer dynamics in LH I and LH II, we are using similar method.

3. Result and conclusions:

We demonstrated that, in agreement with the experiments performed in Ref. [2], the excitation energy of the BPEA antenna chromophores is efficiently funneled to porphyrins (ZnPy). The excited ZnPy molecules rapidly donate an electron to the fullerene electron acceptor, thus creating a charge-separated state, $ZnPy^+ - F^-$, with a quantum yield of the order of 95%. In the limit of strong interchromophoric coupling, coherent dynamics dominates over incoherent-hopping motion. In the single-exciton regime, when one of the BPEAchromophores is initially excited, quantum beatings between two resonant BPEA chromophores occur with decoherence times of the order of 100 fs. However, here the electron transfer process is dominated by incoherent hopping. For the case where one porphyrin molecule is excited at the beginning, we obtained small quantum oscillations of the fullerene charge characterized by a short decay time scale (~10 fs). More pronounced quantum oscillations of the fullerene charge (with an amplitude ~0.1 electron charge and decoherence time of about 20 fs at $T = 77$ K) are predicted for the double-exciton regime, when both porphyrin molecules are initially excited. We also showed that the contribution of wave-like coherent motion to electron-transfer dynamics could be enhanced by lowering the temperature, strengthening the fullerene-porphyrin bonds, shrinking the energy gap

between the zinc porphyrin and fullerene moieties (e.g., by attaching a charged residue to the fullerene), as well as by decreasing the reorganization energy (by tuning the solvent polarity).

In addition to the above item I used RICC system for simulation of stochastic dynamics in a confined geometry.

Diffusion of small objects in a confined space has been an intriguing issue in physics, chemistry and biology over the last few decades. Nevertheless, a deeper understanding of the underlying mechanisms of diffusion in confined space is required for explaining transport properties of particles in biological cell and in zeolites [4], in controlling transport through artificial micro-and nano-structures [5] and catalytic reactions in porous media [6], or for separation of particles of different masses and sizes [7]. Based on the numerical simulation of Langevin equation we have investigated following issues in FY2011.

(i) **Driven Brownian transport through arrays of symmetric obstacles:** We numerically investigated the transport of a suspended overdamped Brownian particle which is driven through a two-dimensional rectangular array of circular obstacles with finite radius. Two limiting cases have been considered in detail, namely, when the constant drive is parallel to the principal or the diagonal array axes. This corresponds to studying the Brownian transport in periodic channels with reflecting walls of different topologies. The mobility
and diffusivity of the transported particles in such channels are determined as functions of the drive and the array geometric parameters. Prominent transport features, like negative differential mobilities, excess diffusion peaks, and unconventional asymptotic behaviors, have been explained in terms of two distinct lengths, the size of single obstacles (trapping length), and the lattice

constant of the array (local correlation length). Local correlation effects are further analyzed by continuously rotating the drive between the two limiting orientations.

(ii) We are also investigating effects of inertial in confined diffusion. Although we have produced some interesting results, this project is not completed yet. To be specific, we intend to explore here mass dependence of diffusivity and mobility of a Brownian particle in various confined geometries. Mainly, following three categories of channel structures are planed to be considered: *Structure-I*: periodically corrugated channels; *Structure-II*: periodically compartmentalized (septate) channels; and *Structure-III*: periodic channels with structural heterogeneity due presence of non-accessible zones. We have completed investigation of inertial effects in Structure I. To complete the project we have to simulate also other structures too.

4. Future plan
Energy and charge transfer mechanisms natural photosynthetic structures

The multi-step energy-transduction process in natural photo-systems begins with capturing sunlight photons by light-absorbing antenna pigments surrounding a reaction center [8]. 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 time. Recently, two dimensional electronic spectroscopic and theoretical studies reveal that coherences between electronic states play an important role in exciton transfer dynamics [9]. Thus, more precise energy transductions mechanisms have been proposed, but, new questions and controversies have arisen [9]. 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, etc. Keeping in mind all the previous studies in this direction we will charge and energy transfer dynamics in photosysten II (PSII).

The PSII reaction centers a device capable of using energy of light quanta to create a charge separated state; in the next stage energy of the charge separated state is converted into proton motive force. The reaction of PSII contains of four chlorophylls and two pheophytin molecules. The cofactors are arranged with pseudo C_2 symmetry, forming two path of charge and energy transfer. We plan to explore the charge transfer and energy transfer on the special emphasis on short time behavior, where effects of quantum coherence are important. So far, effects of quantum coherence in exciton transfer in natural photosynthetic structures have been addressed by several authors, but in charge transfer dynamics has not been explored yet.

(II) Diffusion mechanisms in confined geometries.

In addition to the above items, I am also interested to study stochastic dynamics in confinement systems. In FY2012 I intend to complete the following task.

Role of the shape of diffusing particles

The shape of the diffusing particles combined with confined channel geometry greatly impacts the Brownian transport. The shape of both the particles and the confining walls determine the course of interactions between them and hence the boundary conditions. Recently, we have described a new mechanism of stochastic resonance in higher dimensions by adopting extremely sharp geometrical constrictions [10]. Such a manifestation of stochastic resonance requires neither energetic nor entropic barriers. Also recent investigations of transport properties in compartmentalized channels having sharp wall reveal

completely different diffusive behaviors in contrast to corrugated channels with smooth boundary. Again, drastic changes in diffusion dynamics have been observed when shape of the diffusing particle is subjected to changes. A recent study shows that a minimal spatial asymmetry in shape of particles causes absolute negative mobility [11]. Thus, the shape of the confining wall and diffusing particle are important factors in controlling diffusive transport through artificial nanopores artificial ion pumps or in biological channels. In this project, we intend to explore the geometric effects of both boundary walls and the finite-size diffusing particles on transport. Other noise-induced phenomena occurring in confined geometries will also be considered.

To examine effect of particle shape we will consider both the overdamped and the underdamped dynamics in the previously mentioned three categories of channel geometry. For a comparative study the following two categories of particle shapes will be considered: (a) symmetric spherical shape, and (b) asymmetric ellipsoid shape. For asymmetric ellipsoid shaped particle, in addition, to translational motion the rotational degree of freedom has to be considered, as they are coupled by the boundary effects. For numerical simulation of asymmetric shaped particle dynamics in confined system we will exploit the prescription of ref [11].

To address the objectives of confined diffusions we shall use the Langevin description. An exact analytical solution of Langevin equations is typically never possible. We shall numerically solve the Langevin equations using a Milstein algorithm [12] 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.

Currently, I have a "Quick Use" user account and I would like to get extension of computation facilities for next usage term (up to April 2013) in the same user category and the same research topic.

References:

[1] P. K. Ghosh et al., J. Chem. Phys. 131, 035102 (2009); A. Yu. Smirnov et al., J. Phys. Chem. C 113, 21218 (2009); P. K. Ghosh et al, Phys. Rev. E 84, 061138 (2011). [2] G. Kodis et al, J. Am. Chem. Soc. 128, 1818 (2006); Y. Terazono et al, J. Phys. Chem. B 113, 7147 (2009); [3] P. K. Ghosh et al., J. Chem. Phys. 134, 244103 (2011). [4] B. Alberts, A. Johnson, J. Lewis, M. Raff, K. Roberts, P. Walter, Molecular Biology of the Cell, Garland, New York, 2007; J. Kärger, D. M. Ruthven, Diffusion in Zeolites and Other Microporous Solids, Wiley, N. Y, 1992. [5] P. Hänggi et al, Rev. Mod. Phys. 81, 387 (2009); P. S. Burada et al, ChemPhysChem **10**, 45 (2009). [6] M. C. Daniel, D. Astruc, Chem. Rev. **104**, 293 (2004). [7] A. Corma, Chem. Rev. **97**, 2373 (1997). [8] E. Blankenship, *Molecular mechanisms of photosynthesis* (Blackwell Science, Oxford, UK, 2002); V. May and O. Kühn, *Charge and energy transfer dynamics in molecular systems* (Wiley-VCH, Berlin, 2011, third edition). [9] G. S. Engel, *et al.,* Nature **446**, 782 (2007); G. Panitchayangkoon, *et al.,* Proc. Natl. Acad. Sci. USA **107**, 12766 (2010); H. Lee, *et al.,* Science **316**, 1462 (2007); P. Rebentrost, *et al.,* J. Chem. Phys. **131**, 184102 (2009); M. B. Plenio *et al.,,* New J. Phys. **10**, 113019 (2008); A. Ishizaki et al, Proc. Natl Acad. Sci. USA 106, 17255 (2009); A. Ishizaki et al., Phys. Chem. Chem. Phys. 12, 7319 (2010). [10] P. K. Ghosh et al, Phys. Rev. Lett. 104, 020601 (2010). [11] P. Hänggi, et al, Phys. Rev. E 82, 041121 (2010). [12] P. Kloeden et al, Numerical Solutions of Stochastic Differential Equations (Springer, Berlin, 1999).

Fiscal Year 2011 List of Publications Resulting from the Use of RICC

[Publication]

1. *Quantum effects in energy and charge transfer in an artificial photosynthetic complex,* P. K. Ghosh, A. Yu. Smirnov, and F. Nori, J. Chem. Phys. 134, 244103 (2011). (This paper has been selected for the June 2011 issue of JCP: BioChemical Physics.)

2. *Geometric stochastic resonance in a double cavity,* P. K. Ghosh, R. Glavey, F. Marchesoni, S. E. Savel'ev and Franco Nori, Phys. Rev. E 84, 011109 (2011).

3. *Artificial photosynthetic reaction centers coupled to light-harvesting antennas,* P. K. Ghosh, A. Yu. Smirnov, and F. Nori, Phys. Rev. E 84, 061138 (2011)

4. *Driven Brownian transport through arrays of symmetric obstacles*, P. K. Ghosh, P. Hänggi, F. Marchesoni, S. Martens, F. Nori, L. Schimansky-Geier, and G. Schmid, Phys. Rev. E 85, 011101 (2012).

[Proceedings, etc.]

None

[Oral presentation at an international symposium]

None

[Others]

None