RICC Usage Report for Fiscal Year 2009

Project Title:

Theoretical Modeling of Photosynthesis

Name : **Pulak Kumar Ghosh**

Affiliation: Digital Materials Team, Single Quantum Dynamics Research Group,
Emergent Materials Department, Advanced Science Institute, Wako Institute

1 . Background and purpose

It would be desirable to find out an efficient mechanism of solar cells in order to convert sunlight energy in a usable form. Over the years considerable attentions has been devoted for this purpose, but the main goal has not been realized due to the very low efficiency of energy conversion. Thus, the conversion of light energy into usable forms of energy with very high efficiency still remains an open challenge to researchers.

An estimate shows that every year, solar energy of order of 3.85 X 10^{24} J hits the surface of the Earth, that amount of energy is four times of the consumption of energy by all humankind (~ 4.1 X 10^{20} J) per year. So, invention of efficient solar cells could provide an unlimited source of clean and renewable energy.

The studies of natural photosynthesis have inspired researchers to perform the photo-induced energy transduction processes in laboratory mimicking the natural photosynthesis mechanisms. The experimental model proposed by Steinberg-Yfrach et al, [2, 3] provides a paradigm for the conversion of light energy to proton potential gradient. The authors in Ref. [2, 3] use a molecular triad as a main light converting element. The triad contains an electron donor (D) and an electron acceptor (A).

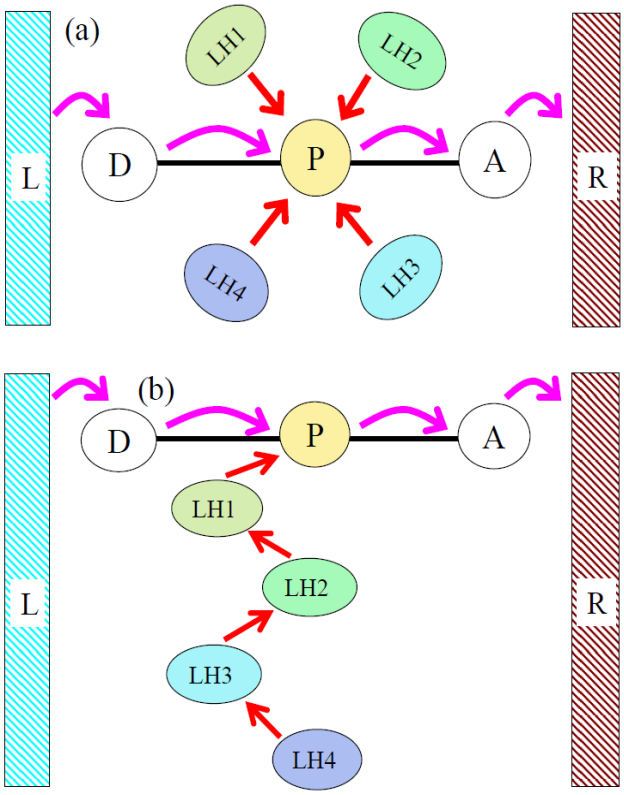

Figure 1: Schematic diagram of an artificial photosystem is comprised of a molecular triad and four accessory light-harvesting complexes. The molecular triad D–P–A is inserted between two electrodes (leads) L and D. We denote energy exchange by red arrow. The curly pink arrows describe the path of electrons transfer L → R via the triad. (a) The photosensitive part of the molecular triad is surrounded by four accessory light-harvesting complexes denoted by LH1, LH2, LH3, and LH4. Here, the surrounding antenna complexes can transfer excitation to the reaction center directly. (b) Present the situation where the antenna complexes are coupled to reaction center via nearest-neighbor coupling.

Both the donor and the acceptor linked to a

photosensitive group (P). The triad molecule (D--P--A) is inserted between two aqueous layers of different PH. Using energy of light the molecular triads translocate protons from the low potential aqueous layer side to the high potential aqueous layer side.

Recently, we have studied a model [3] for light-induced proton pump by molecular triads [1-2] inserted between two proton reservoirs. This study is based on the methods of quantum transport theory [3]. The effect of light intensity, trasmembrane potential and temperature in proton current and energy conversion efficiency have been explored**.** We show that under resonant tunneling condition and strong coupling of molecular triads with proton reservoirs the power conversion efficiency increases drastically. We found out the conditions of maximum efficiency.

In the *present project* we examine a theoretical model for light-induced energy conversion in a molecular triad surround by four additional accessory light-harvesting antenna complexes (shown in Fig.1). The antenna system can absorb energy over a wide range (420-670 nm) of solar spectrum. The main purposes of this study are twofold, *first* how the artificial photosystems are benefited by accessory light-harvesting antenna complexes. *Secondly*, we explore the fundamental issues, how the excitation energy transfer processes leading to generation of photocurrent depends on relative arrangements of the antenna chromophores with respect to reaction center, thermodynamic gradients and reorganization for Föster energy transfer.

2. Method

We characterize the electrons in the electron sites and leads by Fermi operators. We assume each electron state can be occupied by a single electron as the spin degrees of freedom are neglected. The total Hamiltonian of the system is quite complicated. It includes the following terms: (i) Eigen energies of the electrons in the electron sites and leads, and the Coulomb interactions between the electrons in the different sites. (ii) Föster coupling between antenna complexes and the reaction center. (iii) Tunneling coupling between the electrons sites and the leads. (iv) Thermal electron tunneling between electron sites. (v) Coupling of the electron sites with the surrounding environment. (vi) Light-induced electron transfer and (vii) the energy wasting radiative-leakage and as well as quenching processes of the excited states by metallicleads.

Based on the methods of quantum transport theory we have derived master equations (256 coupled equations) for electron state probabilities evolving in time. To analyze the light-induced proton pumping process quantitatively we numerically solved these 256 coupled mater equations.

The simulation part of the above mentioned project has been completed. Now we are preparing manuscript to publish our results.

3. Result and conclusions.

We numerically calculate pumping current, efficiency and quantum yield as function of leads potential, light intensity, wavelength of light, temperatures and other system parameters such as coupling to leads, Föster energy transfer rates, thermal tunneling rates, reorganization energy etc.

We have shown that under strong Föster couplings, the amplitude of the photocurrent is increased by almost four times due to presence of antenna system. This is due to the fact that incorporation of many accessory light-harvesting complexes into a single unit (reaction center) facilitates energy transduction processes by using electron transfer chains with a maximum efficiency. We obtain quantum yield of the light-induced energy transduction process about 90 % at the wavelength where the antenna complexes absorb light.

We consider two different kinds of arrangements of the accessory light-harvesting pigments around the reaction center. First, arrangement allows direct excitation transfer to reaction center from the accessory pigments and the second one corresponds to

the energy transfer via a funneling mechanism by nearest-neighbor excitation transfer. We have shown that antenna complexes to reaction center energy transfer processes via a funneling mechanism are more efficient than direct excitation transfer to reaction centers. Thus we explore the fundamental issues of light-to-electricity energy conversion in an artificial photosystem with antenna complexes.

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

A Brownian particle moving across a porous membrane subject to an oscillating force exhibits stochastic resonance with properties which strongly depend on the geometry of the confining cavities on the two sides of the membrane. Such a manifestation of stochastic resonance requires neither energetic nor entropic barriers, and can thus be regarded as a purely geometric effect. The magnitude of this effect is sensitive to the geometry of both the cavities and the pores, thus leading to distinctive optimal synchronization conditions.

4. Future plan

(I) Solar energy conversion in artificial reaction centers.

The main goal of the proposed research for the coming year is to design an efficient artificial photo-system mimicking natural photosynthetic structures.

Keeping in mind recent research results of organic solar cells, here I address the following issue.

Recently, Johansson *et. al.* [4], have examined a model for electron transfer through a moving island (a nanomechanical oscillator) which can accommodate one or two excess electrons. This study shows that transport through mobile island enhances conductance. Motivated by this work, we plan to study a model for light-electricity power conversion, with only one group instead of molecular triads (with three groups). We will use fullerene (C_{60}), inserted between two conducting leads. Fullerene absorbs light of energy about 1.7 eV. This absorbed energy will be converted into electricity if there is a mechanical motion of C_{60} between two conducting leads. In presence of an electric field, charging and discharging mechanism of C_{60} will provide its mechanical motion. We explore this model to provide an insight into the simplest organic solar cell.

We will approach this problem using methods of quantum transport theory. For quantitative calculation of the current and efficiency we need to solve 16 coupled master equations by numerical integration. We have used very small time step (0.01) for numerical integration to minimized numerical error. As a result to reach at stationary limit one needs around 50,000,000 iteration steps for numerical integration over the whole time series. Moreover, our model contains ~20 parameters. I wish to run this job with different parameters to calculate observables (proton current, quantum yield, thermodynamic efficiency) as a function of parameters.

(II) Diffusion mechanisms in confined geometries.

In addition to the above item, I also plan to simulate stochastic dynamics in confinement systems. Recently, we have described a novel physical situation [5], where a Brownian particle is confined to two boxes separated by a small bottleneck. The Brownian particle is driven additionally by an oscillating force and transitions between the two boxes are investigated. The first harmonics of the averaged motion of the Brownian particle exhibits the phenomenon of stochastic resonance (SR). Such a manifestation of stochastic resonance is regarded as a purely geometric effect. Again, SR occurs if the amplitudes of the oscillating field are larger a critical one and for low frequencies (lower a critical one). Under these conditions the amplitude of the first harmonics depends non-monotonously on the noise intensity of the Brownian particle. Based on these recent observations, I address the following issues as the goals of the coming year.

(a) In our recent studies [5], we have shown that all the geometric effects on the dynamics of driven Brownian particle can not be explained by a dependence on entropy. But, the volume which is accessible to the Brownian particle can be understood as entropy. Therefore we expect strong correlations between both, geometric and entropic SR. We intend to explore this issue by studying stochastic dynamics of a Brownian particle in various types of confined geometries.

(ii) Mobility of a Brownian particle in 2D Channels of finite cross section is a hot topic in the technology of microporous media. As the diffusion orthogonal to the channel axis depends on the channel geometry. Here, we intend to explore the geometric effects on mobility of a Brownian particle in 2D channels.

To explore the above mentioned issues we need to numerically solve the Langevin equations describing stochastic dynamics of Brownian particles in a confined system. We will solve the Langevin equations using standard the Heun's algorithm. 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 2011) in the same user category and the same research topic.

References:

[1] G. Steinberg-Yfrach et al, Nature **385**, 239-241 (1997).

[2] G. Steinberg-Yfrach et al, Nature **392**, 479-482 (1998).

[3] P. K. Ghosh et al., J. Chem. Phys. 131, 035102 (2009).

[4] J. R. Johansson et al., Phys. Rev. B 77, 035428 (2009).

[5] P. K. Ghosh et al.,Phys. Rev. Lett. **104**, 020601 (2010).

Fiscal Year 2009 List of Publications Resulting from the Use of RICC

[Publication]

1. Geometric Stochastic Resonance;

P. K. Ghosh, F. Marchesoni, S. E. Savel'ev, and F. Nori, Phys. Rev. Lett. **104**, 020601 (2010).

2. Artificial photosynthetic reaction centers with accessory antenna systems;

P. K. Ghosh, A. Yu. Smirnov, and F. Nori, 2010 (manuscript under preparation).