Project Title:

Theoretical Modeling of Photosynthesis

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1. Background and purpose

Recently we have studied a model [1] of light-induced proton and electron pump in artificial reaction centers. The model contains a molecular triad, which is inserted between two (either proton or electron) reservoirs. The molecular triad transports protons (mediated by a shuttle) and electrons energetically uphill: from the lower energy reservoir to the higher energy reservoir, using the energy of light. Applying the methods of quantum transport theory, we calculated the ranges of light intensity and potential energy of the electron/proton reservoir that maximize both the light-induced proton/electron current and the energy-transduction efficiency. We also have shown that under resonant tunneling conditions, and strong coupling of molecular triads with leads, the power conversion efficiency increases drastically. Thus, we obtained the optimal-efficiency conditions.

We also have extended our models presented in Ref [1] including additional four light-harvesting pigments (LHP). We consider two different kinds of arrangements of the accessory light-harvesting pigments around the reaction center. The first arrangement allows direct excitation transfer to the reaction center from all the surrounding pigments. The second configuration transmits energy via a cascade mechanism along a chain of light-harvesting chromophores, where only one chromophore is connected to the reaction center. We have shown that the artificial photosynthetic system using the cascade energy transfer absorbs photons in a broader wavelength range and converts their energy into electricity with a higher efficiency than the system based on direct couplings between all the antenna chromophores and the reaction center.

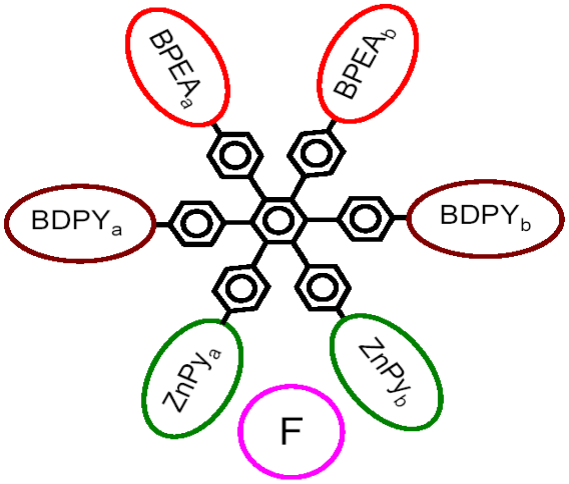

FIG. 1: (Color online) Schematic diagram of the wheel-shaped artificial antenna-reaction center complex reported in ref [4]. We use the short notation, BPF Complex, to denote this photosynthetic device. The antenna-reaction center complex contains six light harvesting pigments: (i) two bis (pheny-lethynyl) anth- racene chromophores, BPEA$_a$ and BPEA$_b$, (ii) two borondipyrromethene chromophores, BDPYa and BDPY$_b$, and (iii) two zinc tetraarylporphyrin chromophores, ZnPy$_a$ and ZnPy$_b$. All the pigments are attached to a rigid hexaphenyl benzene 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.

In our previous studies we examine the steady-state regime of light-to-electricity energy conversion in the molecular triad coupled to the antenna complex. We use steady-state or stationary solutions of the master equations omitting the coherence of density matrix. Because quantum coherent effects do not play any significant role in the process since decoherence time is expected to be in the subpicosecond range even at low temperatures, whereas the time scale for the energy and charge transfer exceeds a few picoseconds. Our master equations are derived when the coupling amplitudes between chromophores and tunneling amplitudes are smaller than the reorganization energies (describing an interaction of the system with the environment. A standard Redfield approach is able to describe quantum oscillations; however, it does not work for strong system-bath couplings.

Recently, we are studying energy transfer and charge separation in a wheel-shaped molecular complex (BPF complex, see Fig. 1) mimicking a natural photosynthetic system. This complex has been synthesized and experimentally investigated in Ref. [3]. 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. The main goal of this study is to explore quantum features of the energy and charge transfer in a wheel-shaped antenna-reaction center complex at femtosecond timescales. To describe quantum effects on a femtosecond time scale, we derive a set of modified Redfield equations taking into account the time evolution of the off diagonal elements of the density matrix. So called Förster theory valid for strong coupling with the environment and Redfield equations are derived at week coupling limit, but our modified- Redfield equations works at both limits.

2. Methods

We described the electron and exciton described with methods of dissipative quantum mechanics. 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. 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 BPF complex we estimate time evolution of the elements of density matrix (160 x 160) by numerical integration.

The simulation part of the above mentioned project has been completed. However, we might need to produce some more simulation results after getting feedbacks from referees and other expert researchers.

3. Result and conclusions

We investigate the quantum dynamics of energy and charge transfer in a wheel-shaped artificial photosynthetic antenna-reaction center complex. This complex consists of six light-harvesting pigments and an electron-acceptor fullerene. To describe quantum effects on a femtosecond time scale, we derive modified Redfield equations taking into account the time evolution of the off diagonal elements of the density matrix. We show that the energy of the initially-excited antenna chromophores is efficiently funneled to the porphyrin-fullerene reaction center, where a charge- separated state is set up in a few picoseconds, with a quantum yield of the order of 95%. In the single-exciton regime, with one antenna chromophore being initially excited, we

observe quantum beatings of energy between two resonant antenna pigments with a decoherence time of ~100 fs. We also analyze the double-exciton regime, when two porphyrin molecules involved in the reaction center are initially excited. In this regime we obtain pronounced quantum oscillations of the charge on the fullerene molecule with a decoherence time of about 20 fs (at liquid nitrogen temperatures). These results show a way to directly detect quantum effects in artificial photosynthetic systems.

In addition to the above item I used RICC system for simulation stochastic dynamics in a confined geometry.
We extend our previous work [5] in order examine effects of (i) transverse drive (ii) harmonic mixing of longitudinal and transverse derive and (iii) particle interactions in geometric stochastic resonance.
We have shown how particle suspended in a partitioned cavity can diffuse across a pore opened in the dividing wall, subjected to the combined action of thermal fluctuations and period drives. The particle flow across the pore is time modulated at the drives frequencies with amplitudes that can be optimized by controlling the temperature of the system. This is a geometric effect where the resonance condition depends on the shape of the cavity and on the interactions among the particles it contains. The mechanism of geometric stochastic resonance, however, clearly does not depend on the dimensionality of the cavity (experiments, e.g., on colloidal systems, can more easily be carried out in 3D geometries), but can be affected by other competing effects: (i) Pore structure. For a finite size particle, say, a translocating molecule, the actual crossing time varies with the wall structure inside the pore and in the vicinity of its opening (ii) Micro-fluidic effects. The flow of the electrolytic suspensionuid across the pore generates inhomogeneous velocity and electrical fields which act on drift and the orientation of the driven particles. System specific effects (i) and (ii) can in principle be incorporated in our model by adding appropriate potential terms to the Langevin equation.

4. Future plan

(I) Quantum effects on energy and electron transfer mechanisms in photosynthesis.

Energy transfer in natural and artificial photosynthetic structures has been an intriguing issue in quantum biophysics due to the conspicuous presence of long-lived quantum coherence observed with two-dimensional Fourier transforms electronic spectroscopy [6]. These experimental achievements have motivated researchers to investigate the role of quantum coherence in very efficient energy transmission, which takes place in natural photo-systems

Based on our recently developed methods we plan to study excitation energy transfer processes between two neighboring B850 ring of light harvesting complex II. Most of the previous studies in this direction based on the dynamics of a single exciton and the effects of multiple excitons remain unexplored. We intend to explore mainly following issues: (a) effects of quantum coherence in energy transfer mechanism between two neighboring ring B850. (b) effects of multiple excitons in intra and inter ring energy transfer. For this project we will follow the same methods as described in section 2.

(II) Diffusion mechanisms in confined geometries.

In addition to the above items, I am also interested to study stochastic dynamics in confinement systems. Mainly, I intend to address the following unexplored issues:

A. Effects of inertial dynamics on confined diffusion:

Although almost all the earlier investigations on confined diffusion concern overdamped motion,

the inertia plays an important role, in dictating the nature of motion, in separation of particles of different masses in fluids of low viscosity for example, where it has been shown to affect the direction of flux, and in still several other respects, e.g. see in the review Ref. [7]. In view of this it is worthwhile to investigate diffusion mechanism of underdamped Brownian particles in confined geometries. A first objective in this project is thus to address this specific issue.

B. Role of hydrodynamic interactions on confined diffusion:

In diffusive dynamics of a system of interacting Brownian particles (whose mass and size are larger than the surrounding solvent molecules) the host solvent mediated hydrodynamic interaction comes into play in a significant way [8]. Hydrodynamic effects on the Brownian dynamics in a confined geometry are quite different from the traditional bulk hydrodynamic interaction due to boundary effects [9]. One encounters such typical situations when studying diffusive behavior of colloidal particles in suspensions [10-11], the protein dynamics in plasma membranes [12], and diffusion of large polymer molecules across a pore [8]. A detailed understanding of the underlying diffusive mechanisms of colloidal particles or macro-molecules in confined geometries is required for the description of operation of various bio-inspired nanomechanical devices and for explaining the dynamics of various protein molecules in plasma membranes. Despite the potential demand the problems of the confined diffusion in presence of hydrodynamic interactions remain almost unexplored. *Keeping in mind its applicability we intend to extend the studies of confined diffusion taking into account of hydrodynamic interactions in Brownian dynamics*

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 [13] 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 2012) in the same user category and the same research topic.

References:

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Fiscal Year 2010 List of Publications Resulting from the Use of RICC

[Publication]

1. **P. K. Ghosh**, A. Yu. Smirnov, and F. Nori, *"Artificial photosynthetic reaction centers coupled to light-harvesting antennas"* Submitted for publication, draft available (2011).

2. **P. K. Ghosh**, A. Yu. Smirnov, and F. Nori, *"Quantum effects in energy and charge transfer in an artificial photosynthetic complex"* Submitted for publication, draft available (2011).

3. **P. K. Ghosh**, R. Glavey, F. Marchesoni, S. E. Savel'ev and F. Nori, *"Geometric stochastic resonance in a double cavity"* to be submitted, draft available (2011).

[Proceedings, etc.]

None

[Oral presentation at an international symposium]

None

[Others]

None