

*QuEBS 2010*

Workshop on  
Quantum Effects in Biological Systems

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Organized by  
Robert J. Silbey and Alán Aspuru-Guzik

Abstracts of  
Speaker and Poster Presentations

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Harvard University  
Center for the Environment

Thursday, June 17, 2010

### **Photosynthesis in the near-dark: light harvesting in green chlorophototrophic bacteria**

Donald Bryant, *Pennsylvania State University*

Green bacteria are chlorophototrophs that belong to three kingdoms of the Bacteria: Chlorobi, Chloroflexi, and Acidobacteria. Astonishingly, some members of the Chlorobi have been shown to grow and persist in environments (~110 m below the Black Sea or 2200 m deep in the Pacific Ocean), where the available light (~1-10 nmol photons m<sup>-2</sup> s<sup>-1</sup>) is nearly a million-fold lower than the surface light intensity. To grow photoautotrophically in such light limited environments requires a light-harvesting antenna system that is large, highly efficient, relatively inexpensive to produce energetically, and highly stable. Chlorosomes are unique light-harvesting antennae structures that fulfill all of these requirements. Chlorosomes are membrane-enclosed sacs containing up to 250,000 bacteriochlorophyll (BChl) c, d, or e molecules and small amounts of BChl a, which is associated with the CsmA protein comprising the baseplate of the chlorosome. The paracrystalline baseplate attaches chlorosomes to either the Fenna-Matthews-Olson, BChl a-binding protein (Chlorobi or Acidobacteria) or to a membrane-associated, B806-866/reaction center complex (Chloroflexi), which is similar to the LH I-RC complexes of purple bacteria. Chlorosomes also contain considerable amounts of carotenoids, quinones, wax esters, and glycolipids. Their envelopes are protein-stabilized monolayer membranes, which in the case of the model organism *Chlorobaculum tepidum* contain 10 different proteins belonging to four structure-motif families. Using comparative genomics and bioinformatics and biochemical genetics methods, the pathway for the synthesis of BChl d and c has been determined. This information provides strong support for the Granick hypothesis, which states that biosynthetic pathways evolve as cells evolve new capabilities. Through knowledge and manipulation of the biosynthetic pathway for BChl c biosynthesis, a triple mutant was produced that simplified the pigment content of chlorosomes in *C. tepidum*. By applying cryo-electron microscopy, solid-state, magic-angle-spinning NMR, and modeling methods, the structure of the BChl d molecules in the mutant chlorosomes was determined. The BChl d molecules form syn-anti monomer stacks, which lie roughly perpendicular to the long axis of the chlorosome and which are arranged into rings with a slight helical twist to form surfaces with a spacing of about 2.1 nm. The sheets in turn form concentric, cylindrical nanotubes. By knowing the structure of the BChls in the mutant, it was also possible to discern the major structural features of BChl c molecules in wild-type chlorosomes. Wild-type chlorosomes exhibit a much higher degree of disorder and variability, and the monomer stacks are parallel to the long axis of the chlorosome. The roles of methylation and chiral centers in chlorosome structure and function will be discussed. A comparison of the chlorosomes and FMO proteins of the strict anaerobe, *C. tepidum*, and the strict aerobe, *Chloracidobacterium thermophilum*, will also be discussed.

### **Quantum biology: Light-harvesting and quantum interference in photosynthetic algae**

Gregory Scholes, *University of Toronto*

Coauthor(s): Cathy Wong, Hoda Hossein, and Rayomond Dinshaw

Recent research suggests that electronic energy transfer in complex biological and chemical systems can involve quantum-coherence, even at ambient temperature conditions.<sup>1</sup> Our experiments, using two-dimensional photon echo spectroscopy, have revealed that electronic excitations are coherently coupled in a family of light-harvesting antenna systems isolated from marine cryptophyte algae. We believe the coherence effectively 'wires' together the chromophores in order to promote more rapid energy transfer through the protein when absorbed energy is funneled among these proteins to the reaction centers. The latest results will be reported together with theoretical studies of the length scale over which quantum coherent energy transfer matters in these algae.

## **Absorption and energy transfer of quantum aggregates: Influence of complex exciton-phonon coupling**

Alexander Eisfeld, *Max-Planck-Institute for the Physics of Complex Systems*

A method is presented that efficiently describes the quantum dynamics of an electronic excitation that is coupled to a continuous, highly structured phonon environment. Based on a stochastic approach to non-Markovian open quantum systems, a dynamical framework is developed that allows to handle realistic systems where a fully quantum treatment is desired yet usual approximation schemes fail.

The approach is used to calculate spectra and energy transfer dynamics of molecular aggregates, elucidating the transition from fully coherent to incoherent transfer.

## **Is smell a quantum phenomenon ?**

Luca Turin, *Massachusetts Institute of Technology*

Our sense of smell is extraordinarily good at molecular recognition: we can identify tens of thousands of odorants unerringly over a wide concentration range. The mechanism by which this happens to do so is still hotly debated. One view is that molecular shape governs smell, but this notion has turned out to have very little predictive power. Some years ago I revived a discredited theory of posits instead that the nose is a vibrational spectroscope, and proposed a possible underlying mechanism, inelastic electron tunneling. In my talk I will review the history and salient facts of this problem and describe some recent experiments that go some way towards settling the question.

## **Coherent excitonic transport in FMO: Temperature dependence and the Role of the Protein**

Greg Engel, *University of Chicago*

Life on earth is effectively solar powered, yet how energy moves through photosynthetic complexes prior to the biochemical steps of photosynthesis is still not completely understood. Evidence for a purely quantum mechanical mechanism of energy transfer in photosynthetic complexes was discovered in the Fenna-Matthews-Olson (FMO) complex of *Chlorobium tepidum* in 2007. The quantum beating phenomenon observed in this complex is now much better understood. Further, data indicate that this mechanism is not specific to FMO, but manifests in reaction centers of purple bacteria and antenna complexes of higher plants. Having observed such a mechanism in disparate photosynthetic complexes, we are exploring what the minimal requirements are to support quantum coherence transfer in a biological environment. Emerging details in this story will be presented including the temperature dependence of the process and new data showing new complexities of the system-bath interaction.

## **Towards atomistic-detail exciton dynamics simulations**

Patrick Rebentrost, *Harvard University*

Dynamics for a single exciton in photosynthetic complexes is usually simulated by using master equations with various degrees of approximations. The excitonic Hamiltonian and the environmental spectral density are taken as an input parameters. We provide a step toward a more atomistic treatment based on the fact that the crystal structure of photosynthetic proteins such as the FMO is known. We combine classical molecular dynamics with ab-initio quantum chemistry calculations to obtain the time dependence of site energies and couplings. We obtain the spectral density of the site energy auto-

correlation and cross-correlation functions. The exciton dynamics is evaluated with a time-dependent Hamiltonian and a Redfield master equation approach.

## **Quasiparticle Coherence and Entanglement in Ultrafast Nonlinear Optical and X-ray Spectroscopy of Photosynthetic Complexes**

Shaul Mukamel, *University of California, Irvine*

Signatures of quasiparticle entanglement in multidimensional nonlinear optical spectroscopy of aggregates are presented. Excitons represent collective optical excitations in which the motions of electrons belonging to different chromophores are correlated. We discuss the utility of the notion of entanglement commonly used in quantum information processing, in the description of these excitations. A distinction is made between some apparent entanglement effects in the linear response that may be removed by a transformation of coordinates and can be handled classically, and genuine entanglement that is fundamentally quantum in nature and shows up in the nonlinear optical response. The harvesting of solar energy and its conversion to chemical energy is essential for all forms of life. The primary photon absorption, transport and charge separation events, that trigger a chain of chemical reactions, take place in membrane-bound photosynthetic complexes. Whether quantum effects, stemming from entanglement of chromophores, persist in the energy transport at room temperature, despite the rapid decoherence effects caused by environment fluctuations, is under current active debate. If confirmed, these may explain the high efficiency of light harvesting and open up numerous applications to quantum computing and information processing. We present simulations of the photosynthetic reaction center of photosystem II that clearly establish oscillatory energy transport at room temperature originating from interference of quantum pathways. These signatures of quantum transport may be observed by two dimensional coherent optical spectroscopy. The manipulation of quantum entanglement of quasiparticles in many-electron systems by attosecond x-ray pulses is demonstrated.

1. "Signatures of Quasiparticle Entanglement in Multidimensional Nonlinear Optical Spectroscopy of Aggregates", S. Mukamel (Submitted, 2010).
2. "Manipulating Quantum Entanglement of Quasiparticles in Many Electron Systems by Attosecond X-ray Pulses", S. Mukamel and H. Wang, *Phys. Rev. A*. (In Press, 2010).
3. "Coherent Multidimensional Optical Probes for Electronic Correlations and Exciton Dynamics; from NMR to X-rays", S. Mukamel, D. Abramavicius, L. Yang, W. Zhuang, I.V. Schweigert and D. Voronine. *Acct.Chem.Res.* *Acct.Chem.Res.* 42, 553-562 (2009).
4. "Coherent Multidimensional Optical Spectroscopy Excitons in Molecular Aggregates; Quasiparticle vs. Supermolecule Perspectives", D. Abramavicius, B. Palmieri, D. Voronine, F. Sanda and S. Mukamel, *Chem. Rev.* 109, 2350-2408 (2009).
5. "Coherent Multidimensional Vibrational Spectroscopy of Biomolecules; Concepts, Simulations and Challenges". W. Zhuang, T. Hayashi and S. Mukamel, *Agnew Chem. Int.Ed.* 48, 3750-3781 (2009).
6. "Quantum Oscillatory Exciton Migration in Photosynthetic Reaction Centers", D. Abramavicius and S. Mukamel, *J. Chem. Phys.* (Submitted 2010).

## **Fluorescence-detected electronic coherence spectroscopy: A powerful tool to study coupled chromophores in biological environments**

Alejandro Perdomo-Ortiz, *Harvard University*

Coauthor(s): Geoffrey A. Lott, Andrew H. Marcus, and Alán Aspuru-Guzik

As a controllable model system for studying closely-coupled light harvesting chromophores, we study nonlinear spectra of magnesium meso tetraphenyl porphyrin (MgTPP) dimers embedded in lipid bilayer

vesicles. Nonlinear optics experiments are valuable techniques for unveiling the dynamics of complex systems. These techniques have been used to study excitonic coherences in photosynthetic systems and in general to study relaxation and dissipation processes in mesoscopic systems. In this talk, we will focus on the fundamental differences between four-wave mixing techniques (FWM) and the fluorescence-detected technique called Phase-Modulation Electronic Coherence Spectroscopy (PM-ECS). Supported by experimental results, we will show how PM-ECS can be used to resolve structural parameters, such as electronic couplings and dipole orientation between chromophores, in molecular environments where FWM experiments might yield poor resolution of the same molecular properties.

## **Quantum Coherence and Decoherence in Equilibrium and Nonequilibrium Environments**

Craig Martens, *University of California, Irvine*

In this talk, we describe recent work on investigating the role of the environment in influencing coherent quantum dynamics. We describe numerical methodology for simulating quantum coherent processes using classical-like molecular dynamics simulation and ensemble averaging, and apply the approach to simulating vibrational dephasing of I2 in cryogenic rare gas matrices and the quantum vibrations of OH stretches of HOD in D2O. We then describe simple analytic and numerical models that highlight novel behavior that can be exhibited by quantum coherent processes in the presence of an environment that is not at thermal equilibrium. We finish with some speculations on the role of nonequilibrium bath effects in quantum biological processes.

## **In search of a consistent quantum description of exciton dynamics in light harvesting complex 2 (LH2)**

Seogjoo (Suggy) Jang, *Queens College, City University of New York*

The light harvesting complex 2 (LH2) is a peripheral antenna complex found in photosynthetic unit of purple bacteria. Numerous spectroscopic and computational studies uncovering essential characteristics of the excitons in LH2 have been conducted. However, a consistent and realistic description of the exciton dynamics in LH2 is still lacking. For example, whether there is elliptic distortion in LH2 as suggested from the single molecule spectroscopy (SMS) has not been clearly resolved. A series of computer simulation results for a plausible set of models are presented, which provide an alternative explanation of the results of SMS. As demonstrated from a recent application of multichromophoric resonance energy transfer, LH2 typifies how nature can exploit multichromophoric quantum coherence to achieve robust energy transfer mechanism immune to disorder and fluctuations. However, whether the rate description is indeed valid has not been carefully examined. A multistate extension of coherent resonance energy is applied to the exciton-bath model of LH2, which is used to assess the validity of rate description and the role of quantum coherence in the overall energy transfer efficiency.

## **Excitation energy transfer dynamics in light-harvesting systems**

Jianlan Wu, *Massachusetts Institute of Technology*

Coauthor(s): Jianshu Cao, and Robert J. Silbey

1) Calculations of model exciton systems and realistic photosynthetic systems suggest that dissipation can help optimize energy transfer efficiency and that spatial-temporal correlations in environmental fluctuations are crucial for quantum coherence in quantum transport processes. [1]

2) An energy transfer system can be mapped to a kinetic network with effective hopping rates as the leading order and with non-local rates as the quantum mechanical corrections. The mapping provides a rigorous partition of quantum transport processes into contributions from thermal hopping and from quantum coherence. [2]

Friday, June 18, 2010

### **Physical origins and models of Energy transfer in photosynthetic light harvesting**

Rienk van Grondelle, *Vrije Universiteit Amsterdam*

Coauthor(s): Vladimir I. Novoderezhkin

In this talk I will perform a quantitative comparison of different energy transfer theories, i.e. modified Redfield, standard and generalized Förster theories, as well as combined Redfield-Förster approach. Physical limitations of these approaches are illustrated and critical values of the key parameters indicating their validity are found. I will discuss the spectra and dynamics in two photosynthetic antenna complexes: phycoerythrin 545 from cryptophyte algae and the trimeric LHCII complex from higher plants. These two examples show how the structural organization determines the directed energy transfer and how equilibration within an antenna subunit and migration between subunits are superimposed.

### **Towards Understanding the Role of Coherent Dynamics in Natural Light-Harvesting**

Tomas Mancal, *Charles University in Prague*

Coauthor(s): Jan Olsina

Most of the information available about primary processes in natural light-harvesting comes from ultrafast non-linear spectroscopy. Ultrafast spectroscopy subjects photosynthetic antennae to external light influence very dissimilar to the one encountered in vivo. It is therefore reasonable to ask whether results obtained from such experiments bear any relevance to the in vivo situation. In this contribution we study the state of a quantum mechanical system after excitation by external light source of different types. Such state can be written in terms of the first order correlation function of the light, and the reduced evolution superoperator (RES) of the system excited at times separated by certain delay  $\tau$ . We show that such RES is in principle accessible experimentally through ultrafast spectroscopy, and confirm thus the relevance of ultrafast spectroscopic measurements for reconstructing excited state dynamics of molecular antenna weakly pumped by the any type of light. Similar correlation function formalism is then applied to photosynthetic antenna receiving energy from a mesoscopic light harvesting system [1]. In fact the pigment-protein complex FMO, where long living electronic coherence was first observed [2], receives excitation energy from mesoscopic aggregate (chlorosom) of bacterio-chlorophyll molecules [3]. We discuss possible scenarios of coherent excitation of an antenna, such as FMO, by a mesoscopic mediator, such as chlorosom, and present some models of the energy transfer from chlorosom to bacterial reaction center.

### **Quantum non-equilibrium effects in biology driven by motion**

Jianming Cai, *University of Innsbruck*

Coauthor(s): A. Asadian, M. Tiersch, G. G. Guerreschi, S. Popescu, and H. J. Briegel

We investigate the quantum non-equilibrium effects induced by classical motion, and the potential implications in biology.

In the first example, we demonstrate that entanglement can persistently recur in an oscillating two-spin molecule that is coupled to a hot and noisy environment, in which no static entanglement can survive. The system represents a non-equilibrium quantum system which, driven through the oscillatory motion, is prevented from reaching its (separable) thermal equilibrium state. Environmental noise, together with the driven motion, plays a constructive role by periodically resetting the system, even though it will destroy entanglement as usual. As a building block, the present simple mechanism supports the perspective that entanglement can exist also in systems which are exposed to a hot environment and to high levels of decoherence, which we expect e.g. for biological systems.

In the second example, we show that the interplay between classical motion and quantum-coherent evolution of the excitation can enhance the energy transfer along a linear chain. This enhancement is a genuine quantum signature, which has no analogue in the classical incoherent energy transfer. This effect could be exploited in artificially designed systems to optimize transport processes.

### **Self-assembling natural and artificial light-harvesters**

Huub de Groot, *Universiteit Leiden*

Coauthor(s): Swapna Ganapathy, Gert Oostergetel, Michael Reus, Aline Gomez Maqueo Chew, Egbert Boekema, Ute Baumeister, Francesco Buda, Piotr Wawrzyniak, Valerie Huber, Sanchita Sengupta, Frank Wuerthner, Donald Bryant, and Alfred Holzwarth

Solar power remains one of the most promising alternative clean energies. However, low light to energy conversion efficiencies have hampered the technologies under development. We have developed methods to study the structures of materials that form very efficient supramolecular light-harvesting antennas in bacteria and artificial derivatives of these systems. Solid state NMR spectroscopic techniques are combined with quantum mechanical calculations and cryo-EM imaging or X-ray diffraction to image the stacking and supramolecular organization of chlorophylls. These molecules can self-assemble into electronically coupled chromophore stacks, and in Nature they are found in green bacteria, which use chlorosomes, exceptionally efficient chlorophyll assemblies, to harvest the few photons that reach them. Chlorosomes are the largest and most efficient light-harvesting antennae found in nature, and they are constructed from hundreds of thousands of self-assembled bacteriochlorophyll (BChl) c, d or e pigments. Since they form very large and compositionally heterogeneous organelles, they had been the only photosynthetic antenna system for which no detailed structural information was available. In our novel approach, the structure of a member of the chlorosome class was determined and compared with the wild type to resolve how the biological light harvesting function of the chlorosome is established. By constructing a triple mutant, the heterogeneous BChl c pigment composition of chlorosomes of the green sulfur bacteria *Chlorobaculum tepidum* was simplified to nearly homogeneous BChl d. Computational integration of two different bio-imaging techniques, solid-state NMR and cryoEM, revealed a previously undescribed syn-anti stacking mode and showed how ligated BChl c and d self-assemble into coaxial cylinders to form tubular-shaped elements. A close packing of BChls via  $\pi$ - $\pi$ -stacking and helical H-bonding networks present in both the mutant and in the wild type forms the basis for ultrafast, long-distance transmission of excitation energy. The structural framework is robust and can accommodate extensive chemical heterogeneity in the BChl side chains for adaptive optimization of the light-harvesting functionality in low-light environments. In addition, syn-anti BChl stacks form sheets that allow for strong exciton overlap in two dimensions enabling triplet exciton formation for efficient photoprotection. In a next step, we used this knowledge to generate biomimetic systems and study their structure by proton NMR experiments, which provided the resonance assignments of the chlorin rings, allowing for readings of ring currents. Density functional theory calculations revealed that in the biomimetic system the

chlorins self-assemble in anti-parallel  $\pi$ -stacks in planar layers in the solid-state, while X-ray powder diffraction measurements revealed the 3D lattice of the packing. This life-science research could aid in the development of more efficient conductive wires used in solar panels, photovoltaic cells, and in organic electronics.

### **Rhodopsin Photoisomerization: Coherent vs. Incoherent Excitation**

Paul Brumer, *University of Toronto*

Coauthor(s): Kunihiro Hoki

Light induced processes in biological molecules have been studied using coherent light sources, distinct from natural incoherent light sources. The relationship between excitation due to these light sources is examined here through a uniform minimal model of rhodopsin photoisomerization induced by either coherent laser light or low level incoherent light (e.g. ~moonlight). Realistic timescales for both processes are obtained and a simple kinetic scheme involving rates for both coherent and incoherent light excitation is introduced, placing all timescales into a uniform framework. In addition, we remark on the possibility of weak field phase control of photoisomerization dynamics.

### **Quantum Process Tomography of Chromophores via Photon Echo Experiments**

Joel Yuen, *Harvard University*

Vibrational and electronic dynamics of wavepackets in condensed chemical phases are commonly described using the density matrix formalism. However, we are not aware yet of a spectroscopic method which can “image” the density matrix in real time. In the present article, we show that a carefully chosen set of polarization controlled two-color heterodyned experiments can be used to reconstruct the time-evolving density matrix of the one-exciton manifold of a model heterodimer. This possibility in turn allows for the systematic characterization of excited state dynamics via quantum process tomography (QPT). Calculations on the dimer show that QPT can reveal rich information about system-bath interactions, which otherwise appear nontrivially hidden in the polarization monitored in standard four-wave mixing experiments. Extensions of the protocol to study larger systems are also suggested. Our study presents a novel and intriguing framework for analyzing spectroscopic experiments in the language of quantum information processing.

### **Towards a Microscopic Understanding of Light Harvesting in Phycobiliproteins**

Andrew Moran, *University of North Carolina at Chapel Hill*

Transport processes and spectroscopic phenomena in light harvesting proteins are intimately connected to the delocalization of electronic states. Of central importance to electronic structure in these systems is the amount of disorder imposed by thermally driven nuclear motion, which generally competes against intermolecular interactions to localize electronic states (i.e., excitons) to individual pigments. The Franck-Condon progressions of high-frequency intramolecular modes additionally govern the distribution of electrostatic interactions in the basis of pigment sites. This talk investigates the impact of vibronic couplings on the electronic structures and relaxation mechanisms of two cyanobacterial light harvesting proteins, allophycocyanin (APC) and c-phycocyanin (CPC). Both APC and CPC possess three pairs of pigments (i.e., dimers), which undergo electronic relaxation on the sub-picosecond time scale. Electronic relaxation is approximately 10 times faster in APC than in CPC despite the nearly identical structures of their pigment dimers. Femtosecond laser spectroscopies conducted in conjunction with a theoretical

model find that photo-induced electronic relaxation in these closely related proteins is understood on the same footing only in a basis of joint electronic-nuclear states (i.e., vibronic excitons). General implications of the present findings for energy transport in artificial systems (e.g., crystalline organic semiconductors) are discussed.

### **Noise-enhanced classical and quantum capacities in communication bio-networks**

Filippo Caruso, *Ulm University*

Coauthor(s): Susana F. Huelga, and Martin B. Plenio

Recently, the intricate interplay of noise and quantum coherence has been investigated to explain the remarkable efficiency well above 90% for excitation energy transfer in light harvesting complexes during photosynthesis. Here, we analyze this scenario by exploiting the elegant and powerful framework of quantum communication. Indeed, we show the first clear example in which the noise, in terms of dephasing, may enhance the capability of transmitting classical and quantum information, encoded in quantum systems, through biologically inspired communication networks. In particular, we find analytically and numerically the quantum and classical capacities for a large family of quantum channels and show that these information transmission rates can be strongly enhanced introducing dephasing noise in the complex network dynamics. In the case of quantum capacities, the presence of noise may lead to a finite quantum capacity where the noiseless system has vanishing capacity.

### **Ab Initio Descriptions of Electronic State and Electron Transfer in Biological Systems**

Shigenori Tanaka, *Kobe University*

We have developed an ab initio methodology to calculate the electronic states of biomolecules on the basis of fragment molecular orbital (FMO) method. For instance, we have successfully performed large-scale electron-correlated calculations for influenza virus hemagglutinin complexes employing the FMO-MP2 and MP3 methods, providing the world's largest ab initio calculations for biomolecules (more than 36,000 atoms). Since they are completed in several hours on those supercomputers such as the Earth Simulator in Yokohama, we could perform the molecular orbital calculations for many snapshots generated through molecular dynamics simulations in near future. Then, combining the dynamical information about nuclear motion with the electronic one governing the electron tunneling between donor and acceptor, we can evaluate the electron transfer rate constant in an ab initio way even for large biomolecules.

### **Symmetry and asymmetry in quantum transport**

Seth Lloyd, *Massachusetts Institute of Technology*

Recent experimental observations have shown that quantum coherence plays an important role in photosynthetic energy transport. Photosynthetic molecules are large and complex, containing both regular structures, such as rings of chromophores, and apparently irregular structures. This talk proposes a general theory of the role of symmetry and asymmetry in quantum transport in biomolecules. I will show that collective coherent effects, including entanglement, can give rise to substantial enhancements of excitonic lifetimes and energy transport rates.

## **Exciton Transport as a Quantum Engine**

Cesar Rodriguez-Rosario, *Harvard University*

Coauthor(s): Patrick Rebentrost, and Alán Aspuru-Guzik

We study the quantum definition of heat, to include environmental effects beyond thermalization, such as dephasing. We study a simple model for exciton transport and show how it behaves like a quantum engine driven by both dephasing and relaxation. Dephasing can be used as a resource to maximize the efficiency of quantum transport. The proposed theory could be employed to understand recent experiments in which long-lived coherences have been observed in photosynthetic complexes from a thermodynamic perspective.

## **Quantum Coherence and its Interplay with Protein Environments in Photosynthetic Electronic Energy Transfer**

Akihito Ishizaki, *University of California, Berkeley*

Recent experiments suggest that electronic energy transfer in photosynthetic pigment-protein complexes involves long-lived quantum coherence among electronic excitations of pigments. [Engel et al., *Nature*, 446, 782-786 (2007).] The observation has led to the suggestion that quantum coherence might play a significant role in achieving the remarkable efficiency of photosynthetic light harvesting. At the same time, the observation has raised questions regarding the role of the surrounding protein in protecting the quantum coherence. In this presentation, we report our theoretical investigations of photosynthetic electronic energy transfer paying particular attention to the underlying mechanisms of long-lived quantum coherence and its non-Markovian interplay with the protein environment.

When circumstances allow, we would like to discuss our recent work regarding quantum entanglement in photosynthetic systems from the standpoint of condensed phase chemical dynamics.

Saturday, June 19, 2010

## **Surface residues dynamically organize water bridges to enhance electron transfer between proteins**

Barry Sanders, *University of Calgary*

Coauthor(s): Aurélien de la Lande, Nathan S. Babcock, Jan Řezáč, and Dennis R. Salahub

We study the impact of structural and conformational variations on the electronic coupling between the redox proteins methylamine dehydrogenase and amicyanin from *Paracoccus denitrificans*. Based on molecular dynamics simulations to generate configurations, in conjunction with an electron transfer pathway analysis to estimate the electron transfer coupling strength of each configuration, we find that, in the wild type complex, the most frequently occurring molecular configurations afford superior electronic coupling due to the presence of a water molecule hydrogen-bonded between the donor and acceptor sites.

We attribute the persistence of this water bridge to a molecular breakwater comprising hydrophobic residues surrounding the acceptor site; this breakwater supports the function of nearby solvent-organizing residues by limiting the exchange of water molecules between the electron-transfer region and the surrounding bulk. When the breakwater is affected by a mutation, bulk solvent molecules disrupt the water bridge, resulting in reduced electronic coupling that is consistent with recent experimental findings.

Our analysis suggests that, in addition to enabling the association and docking of the proteins, surface residues stabilize and control interprotein solvent dynamics in a concerted way. Our theory of transport between proteins in a complex via a water bridge has implications for studies of coherent quantum transport in redox reactions.

### **Biologically inspired quantum sensors for geomagnetic anomaly detection**

Marco Lanzagorta, *ITT Advanced Engineering & Sciences*

In this paper we present a potential technological application of recent developments in the area of quantum biology. We will describe how avian navigation systems could be synthetically re-engineered to create novel sensor suites to detect geomagnetic anomalies. Exclusively using open literature information we will argue the advantages offered by biologically-inspired nanomagnets for a variety of applications. In particular, we will discuss the highlights in the development of the ITT NOMAD (NanOmagnet-based Magnetic Anomaly Detector) sensor, which may well be the first proposed application of quantum biological phenomena in a non-trivial context.

### **Enhanced Intersystem Crossing by Magnetic Nanostructures**

Hohjai Lee, *Harvard University*

Coauthor(s): Nan Yang, and Adam E. Cohen

Biological sensing of the geomagnetic field is important for navigation in birds, fruit flies, and honeybees, though the mechanism is poorly understood. One hypothesis is that the geomagnetic field couples to electron spin dynamics in photogenerated radical pairs, and thereby modulates the outcome of a photochemical reaction. Another hypothesis is that the geomagnetic field generates a torque on biogenic magnetic nanoparticles, leading to a classical “compass” effect. Our group recently proposed that magnetic nanostructures can produce a new magnetic field effect on some photochemical reactions. The large magnetic field gradient around a magnetic nanostructure increases the rate of intersystem crossing in a nearby radical pair, in contrast to the conventional magnetic field effect in which a homogeneous field decreases the rate of intersystem crossing.

We present experimental evidence that photochemical production of a dye formed from benzophenone and diphenylamine is modulated by magnetic nanoparticles or nanomagnetic domains. The radical reaction is initiated by UV absorption. The radical pairs are preserved inside micellar cages, enhancing their susceptibility to the magnetic field. We used optical microscopy to visualize the effect by showing modulated concentration of dye molecules along nanomagnetic patterns. Time-resolved pump-probe experiments show enhanced decay of radical pairs near magnetic nanostructures.

### **Coherent energy transfer in bio-molecules via a vibrationally-induced AC Stark shift**

Vlatko Vedral, *University of Oxford and National University of Singapore*

In my presentation I will begin by discussing the general notion of quantum coherence and its possible roles in biology. I will then present a simple model to show how a narrow band of phonons can induce an AC Stark shift effect in excitonic energies thereby increasing the rate of energy transfer between a donor and an acceptor molecule. This model can also be applied to a more complex situation such as the FMO photosynthetic complex, in which case it leads to a number of readily testable predictions. I discuss some of the more important predictions as well as possible generalisations of the model.

## **Quantum metrology of mixed states and relations to bird navigation models**

Kavan Modi, *Centre for Quantum Technologies*

Coauthor(s): Elisabeth Rieper, Hugo Cable, Mark Williamson, and Vlatko Vedral

In a recent study of correlations in quantum states and their usefulness in quantum metrology we found that for highly mixed states, better precision can be attained with classical states over entangled states. This could have direct implications on bird navigation system, as such systems are measuring phases shift due magnetic fields. Bases on our studies we question whether entanglement is the true resource for such systems, or do classical correlation suffice? If so, how many molecules are needed to classically correlated? And finally, does the metrology scheme have to be quantum?

## **How Do Proteins Regulate The Driving Force Of Excitation Transfer In A Photosynthetic Marine Algae?**

Carles Curutchet, *Universitat de Girona*

Coauthor(s): Jacob Kongsted, Aurora Muñoz-Losa, Gregory D. Scholes, and B. Mennucci

This contribution presents a detailed theoretical study on how proteins regulate the electronic couplings responsible for exciton delocalization and electronic energy transfer (EET) in photosynthetic pigment-protein complexes. Understanding environment effects, which cause line broadening and screen electronic interactions, is fundamentally important because of its central role in the control of EET dynamics. Recent work has furthermore shown that simple models for solvation may not be sufficient to explain effects that go beyond Förster theory, such as coherent contribution to energy transfer.[1][2][3]

Here, we focus on the phycobiliprotein PE545 from the unicellular photosynthetic cryptophyte algae *Rhodomonas CS24*,[3] and apply a novel combined quantum mechanics/molecular mechanics (QM/MM) method[4] that explicitly incorporates environment polarization (protein and solvent) at the atomic level on the calculation of site energies and electronic couplings, thus going beyond the continuum dielectric approximation. In addition, we run molecular dynamics (MD) simulations of the PE545 complex in order to explore the effect of protein structural motions on the predicted properties. Our results unveil strong variations in the effective dielectric properties experienced by the different pigment pairs in the PE545 system. In addition, our results provide insights into the limitations of structure-based methods based on the crystal structure, as opposed to the averaged-structure picture obtained from MD simulations.

## **Why Quantum Coherence in Light Harvesting Complexes?**

K. Birgitta Whaley, *University of California, Berkeley*

Coauthor(s): Mohan Sarovar, and Stephan Hoyer

Experiments have revealed that the initial light harvesting stage in photosynthesis involves surprisingly long-lived electronic coherences, raising questions as to their role and function. We show that while these coherences are accompanied by a significant amount of dynamic long range entanglement, that there is nevertheless only a limited amount of the quantum speedup that is characteristic of quantum information processors. Alternative proposals for the role of quantum coherence in this biological setting include improved efficiency and robustness of electronic energy transfer. We present analysis of a simple model to consider how coherence can enhance unidirectional energy flow and identify a mechanism by which it may indeed lead to increased efficiency for some light harvesting complexes.

## **Manipulating quantum coherence in room temperature liquids to image through scattering media**

Nan Yang, *Harvard University*

Coauthor(s): Adam Cohen

Magnetic fields of ordinary strength can affect the outcome of certain chemical processes in liquids under ambient conditions. This fact is remarkable, considering that the energy of interaction of a typical magnetic field with an electron spin is  $\sim 10^5$  times smaller than thermal energy. Magnetic field effects arise through the interplay of nuclear hyperfine interactions with coherent precession of electron spins in an external field. Together these forces act to alter the symmetry of the spin wavefunction and thereby to determine which reaction pathways are allowed. When the product of a reaction is a fluorescent photon, a magnetic field can modulate the fluorescence intensity. We demonstrate a new imaging mechanism based on the well known magnetic field sensitivity of fluorescence from the electron transfer couple pyrene/dimethylaniline (Py/DMA). Permanent magnets are arranged to create a localized null in field strength. A solution of Py/DMA is placed between the magnets and illuminated uniformly with ultraviolet light. The rate of intersystem crossing is higher, and the fluorescence is lower, at the location of the magnetic null than anywhere else in the solution. By scanning this dark spot around the sample and monitoring the total fluorescence emission, we detect the edges of objects immersed in the fluid. This method of imaging does not require optical image formation, and in principle is not limited by diffraction. Magneto-chemical imaging can image through translucent surfaces or other strongly scattering media.

## **Efficient simulation of strong system-environment interactions**

Alex Chin, *Ulm University*

Coauthor(s): Javier Prior, Susana Huelga, and Martin Plenio

Multi-component quantum systems in strong interaction with their environment are receiving increasing attention due to their importance in a variety of contexts, ranging from solid state quantum information processing to the quantum dynamics of bio-molecular aggregates. Unfortunately, these systems are difficult to simulate as the system-bath interactions cannot be treated perturbatively and standard approaches are invalid or inefficient. Here we combine the time dependent density matrix renormalization group methods with techniques from the theory of orthogonal polynomials to provide an efficient method for simulating open quantum systems, including spin-boson models and their generalisations to multi-component systems.

## **Optimization of energy transfer processes in photosynthetic systems**

Jianshu Cao, *Massachusetts Institute of Technology*

Coauthor(s): Jianlan Wu, and Robert J. Silbey

With the facilitation of surrounding protein environments, excitation energy transfer (EET) in photosynthetic systems can be highly efficient and robust. This talk compares different descriptions of dissipative exciton dynamics, discusses the generic mechanism of optimal energy transfer, and explores its implications for light-harvesting systems. (i) In comparison with numerical solutions of the spin-boson model, the exact second-order solution provides a reliable description of exciton dynamics over a broad range of parameter space, whereas further approximations, including time-local, Markovian, and secular assumptions, lead to large deviations or even unphysical predictions. (ii) The generic mechanism of optimal efficiency allows us to examine the interplay of quantum coherence, dynamics noise, and static

disorder in a unified conceptual framework. (iii) The topological symmetry and network structures in photosynthetic systems reveal useful insights for the optimal design of artificial energy transfer systems.

## **Renormalization approach to scalable environment-assisted multichromophoric excitation energy transfer**

Andrew Ringsmuth, *University of Queensland*

Coauthor(s): T. M. Stace, and G. J. Milburn

A recent surge of interest in the theory of environment-assisted quantum transport of photoexcitations has focused mainly on isolated photosynthetic light harvesting complexes (LHC) such as LH1 of purple bacteria (eg. [1]), and also on monomeric LHC subunits such as that of the trimeric Fenna-Matthews-Olson (FMO) complex of green sulfur bacteria (eg. [2-5]). In vivo, LHCs cooperate in aggregates in which the transition couplings between chromophores in neighbouring LHCs are typically less than intracomplex couplings but nonetheless allow for efficient intercomplex energy transfer. Such aggregates are often coupled to multiple chemical reaction centres (RC), to which energy is transported over distances which can be large compared with the average nearest-neighbour interchromophoric separation [6, 7]. In general, one may consider an LHC-binding photosynthetic membrane as a structure of nested clusters; chromophores cluster within LHCs, which cluster within aggregates, and so on. In natural photosynthetic membranes there exists a high degree of structural variability across the spectrum of spatial scales, between species, and under different environmental conditions. Nonetheless, there is evidence that in some such membranes, exciton trapping time can be transfer-to-trap-limited, and that intracomplex and intercomplex transfer can proceed on comparable timescales, with the latter possibly being faster in some cases [8]. Accordingly, an accurate description of long-range multichromophoric energy transfer through LHC-RC aggregates, including an account of any nontrivial coherence effects within and/or between complexes, is essential to a complete understanding of photosynthetic light harvesting efficiency.

Previous theoretical studies [6, 8-10] have assumed a fixed crossover from coherent (tunneling) to incoherent (hopping) dynamics at some level of the clustering hierarchy; usually at the level of inter-LHC transfer. We have relaxed this assumption to investigate the tunneling-hopping crossover at different levels of the clustering hierarchy within a simple chromophoric network. To do so, we have formulated an iterable renormalization procedure by which clusters of sites are coarse-grained into single effective sites subject to renormalized on-site, transition coupling and system-bath coupling energies. For simplicity in demonstrating the renormalization procedure for the first time, we work in the weak system-bath coupling limit and our treatment is Markovian. Two main benefits are provided by our approach: (1) The theoretical sophistication required to accurately describe energy transfer at a given hierarchy level can be quantitatively assessed so that, where a hopping model will suffice, the computational demands associated with modelling coherent transfer in large networks can be avoided; (2) In principle, network structures which under certain conditions support coherent transfer on spatial scales large compared with the average interchromophoric separation can be predicted. Preliminary results indicate that, surprisingly, a tunneling-hopping crossover appears at some scale only in the presence of on-site static disorder.

## **The importance of continuous variable entanglement in biological systems**

Elisabeth Rieper, *Centre for Quantum Technology*

Coauthor(s): Janet Anders, and Vlatko Vedral

We consider a chain of harmonic oscillators with dipole-dipole interaction between nearest neighbors resulting in a van der Waals type bonding. The binding energies between entangled and classically correlated states are compared. We apply our model to DNA. By comparing our model with numerical simulations we conclude that entanglement seems crucial for explaining the stability of the DNA double helix.

Sunday, June 20, 2010

### **Modelling light-driven proton pumps in artificial photosynthetic reaction centers**

Anatoly Smirnov, *RIKEN Japan*

Coauthor(s): P.K. Ghosh, L.G. Mouroukh, and F. Nori

(a) We study a model of a light-induced proton pump in artificial reaction centers. The model contains a molecular triad with four electron states (i.e., one donor state, two photosensitive group states, and one acceptor state) as well as a molecular shuttle having one electron and one proton-binding sites. The shuttle diffuses between the sides of the membrane and translocates protons energetically uphill: from the negative side to the positive side of the membrane, harnessing for this purpose the energy of the electron-charge separation produced by light. Using the methods of quantum transport theory we calculate the range of light intensity and transmembrane potentials that maximize both the light-induced proton current and the energy transduction G16efficiency. We also study the effect of temperature on proton pumping. The light-induced proton pump in our model gives a quantum yield of proton translocation of about 55%. Thus, our results explain previous experiments on these artificial photosynthetic reaction centers.

(b) We theoretically examine the light-to-electricity energy conversion in a molecular triad coupled to conducting leads. This coupling allows us to drive a current through the system. We derive the equations of motion for the electron density operators and determine the dependence of the current, quantum yield, and thermodynamic efficiency on temperature, the electrochemical potentials of the leads, as well as on the light intensity and frequency of the external electromagnetic field. For the molecular triad consisting of ferrocene, porphyrin, and fullerene molecules, we find that, in the case of relatively strong coupling to the leads, the power-conversion efficiency can exceed 40% and the quantum yield can be more than 90%, instead of the 25% quantum yield observed in experiments. Thus, this system is highly attractive for solar cell applications. The large predicted increase in the efficiency of this system is due to the stronger coupling to the contacts, which allows the triad to move more electrons through it, absorbing more photons per unit time, and doing more work.

### **A possible mechanisms for quantum coherence assisted ion transport in ion channels**

Alipasha Vaziri, *Howard Hughes Medical Institute*

Coauthor(s): Martin Plenio

Recently it was demonstrated that long-lived quantum coherence exists during excitation energy transport in photosynthesis. It is a valid question up to which length, time and mass scales quantum coherence may extend, how to one may detect this coherence and what if any role it plays for the dynamics of the system. Ion-channels are involved in many physiological processes. In the nervous system their coordinated opening and closing generates action potentials that form the basis for intra-neural communication which are essential for information representation and processing.

We have recently suggested that the selectivity filter of ion channels may exhibit quantum coherence which might be relevant for the process of ion selectivity and conduction. I will discuss some of our current experimental efforts in this direction and show that quantum resonances could provide an alternative approach to ultrafast 2D spectroscopy to probe these quantum coherences. The emergence of resonances in the conduction of ion channels that are modulated periodically by time dependent external electric fields can serve as signatures of quantum coherence in such a system. Assessments of experimental feasibility and specific paths towards the experimental realization of such experiments are presented.

### **Coherent Excitation Energy Transfer (EET) Along the P-loop of KcsA Ion Channel Models: Feasibility and Possible Effects on Filter Gating**

Vahid Salari, *University of Salzburg*

Coauthor(s): Johann Summhammer, and Gustav Bernroeder

The selectivity filter (SF) of ion channel proteins is responsible for the selective and fast conduction of ions across the membrane of excitable cells. Other and generally larger parts of the molecule such as the pore-domain gate control the access of ions to the channel protein. After the determination of an atomic resolution structure of the bacterial KcsA channel by Mac Kinnon and co-authors [1], the question was raised whether the selectivity filter can also adopt non-conducting states, acting as a ‘filter-gate’ and how these states could become synchronized with the mechanical opening and closing of the pore-domain gate facilitating conduction. In particular, it was found that ‘selectivity’ can be attributed to the specific Coulomb-coordination geometry between the ion and the surrounding dipolar carbonyl ligands lining the so-called P-loop domain of the filter region [2,3]. The forces of the ion-coordinated filter complex that facilitate preferential binding sites (e.g. the ‘up’ 1,3 and ‘down’ 2,4 location of 2 ions in the filter) originate from and propagate along the P-loop region of the filter. Free energy MD simulations have further indicated, that the potential mean force (PMF) landscape of the filter-complex can couple to the amide plane orientation of a peptide linkage between Val76-Gly77 of the loop and render the filter non-conductive for about 0.1 ms, essentially establishing a filter-gate [3].

In this paper we address the question whether and how the observed picosecond amide oscillations can be derived from coherent interchain energy transfer along one monomer of the P-loop TGVT peptide backbone. We test the hypothesis whether the pico-second binding force changes underlying the ion-oxygen coordination in the filter can couple via coherent vibrational energy transfer and dipole-dipole interactions to excite the Val76-Gly77 peptide linkage in the model KcsA-P-loop monomer chain. Employing an N-body system Hamiltonian we model the excitations along the four peptide repeats in dependence of 1, 2 and 3 ion occupancy states next to the loop and estimate the resulting sink population at the carbonyl location of Val76. We provide estimates about the amount of thermal fluctuations and include N-site dissipation rates according to previous models [4,5]. A comparison to purely classical energy transfer indicates that delocalized quantum interferences effecting the loop backbone chain can possibly contribute to the observed association of ion-filter coordination states and single site carbonyl orientation, explaining why a single ion occupancy in the filter domain can have a permissive or unpermissive effect on filter gating.

### **Robustness and optimality of energy transfer in light-harvesting complexes**

Masoud Mohseni, *Massachusetts Institute of Technology*

Coauthor(s): A. Shabani, S. Lloyd, and H. Rabitz

Recent advances in 2D electronic spectroscopy have provided direct evidence for existence of quantum dynamical coherence in photosynthetic energy transfer at physiological temperature. These experimental observations lead to two main questions: why quantum coherence could even exist in such warm and noisy environments and what is the role of quantum effects and their interplay with environmental interactions in the performance and robustness of these biological complexes. In this talk, we explore these issues by using a non-perturbative and non-Markovian master equations approach in high-temperature limit for Ohmic and Drude-Lorentz spectral densities. In particular, we study the effects of spatial and temporal environmental correlations and symmetries on the energy transport. For Fenna-Matthews-Olson protein of green sulfur bacteria we find that the natural parameters to lay within the optimal regimes of energy transfer efficiency.

### **Quanta of local conformational change: conformons in alpha-helical proteins**

Yasser Omar, *SQIG-IT & ISEG-Technical University of Lisbon*

We propose the conformon as a quantum of local conformational change for energy transfer in alpha-helical proteins. The underlying mechanism of interaction between the quantum of excitation and the conformational degrees of freedom is nonlinear and leads to solitary wave packets of conformational energy. The phenomenon is specific to alpha-helices and not to beta-sheets in proteins due to the three strands of hydrogen bonds constituting the alpha-helical backbone.

Pump-probe experiments revealed that low-frequency nonlinear modes are essential for functionally important conformational transitions in proteins containing alpha-helices (Xie A, van der Meer L and Austin R H, *Phys. Rev. Lett.* 88, 018102, 2002). The characteristic lifetime of these states is 15 ps (although for the vision-relevant bacteriorhodopsin it can go over 500 ps). The same experiments also revealed that amino acids and predominantly beta-sheet proteins do not have such long-lived states. The proposed quanta of conformation already make the qualitative distinction between sections of the secondary structure of proteins due to the full use of the geometry of the hydrogen bonds' network in alpha-helices. Quantitatively, we estimate the relevant physical constants, but their experimental determination remains an open problem. Other nonlinear mechanisms of energy transport in alpha-helical proteins fail to exhibit such a long lifetime. Thus the conformons proposed here might have the answer for the mechanism of direct coherent flow of conformational energy for a variety of vital biological processes ranging from electron transfer to enzyme action.

## Poster Presentations

### **Anti-Zeno Effect for Quantum Transport in Disordered Systems**

Keisuke Fujii, *Dept. of Nuclear Engineering Kyoto University*

Coauthor(s): Katsuji Yamamoto

We demonstrate that repeated measurements in disordered systems can induce quantum anti-Zeno effect under certain condition to enhance quantum transport. The enhancement of energy transfer is really exhibited with a simple model under repeated measurements. The optimal measurement interval for the anti-Zeno effect and the maximal efficiency of energy transfer are specified in terms of the relevant physical parameters. Since the environment acts as frequent measurements on the system, the decoherence-induced energy transfer, which has been discussed recently for photosynthetic complexes, may be interpreted in terms of the anti-Zeno effect. We further find an interesting phenomenon,

where local decoherence or repeated measurements may even promote entanglement generation between the non-local sites.

### **Strong-pulse effects in optical 2D spectra of FMO complex**

Maxim Gelin, *University of Technology Munich*

Coauthor(s): A. Yu. Smirnov, F. Nori, and W. Domcke

In recent years, the femtosecond three-pulse photon-echo (3PPE) technique has been developed into a powerful spectroscopic tool, enabling us to learn about dissipation, dephasing, and solvation mechanisms in various molecular systems. Normally, information about the material system under study is believed to be encoded into the 3PPE third order polarization. However, recent 3PPE experiments performed by the Fleming group (on nanotubes) and by the Wright group have demonstrated that interesting new effects and valuable information on material systems can be obtained by using relatively strong pulses. The standard perturbative approach which is based on the third order nonlinear polarization is inadequate for the description and interpretation of such experiments. A nonperturbative theory is necessary.

Inspired by the progress in strong-field 3PPE spectroscopy, we have developed an approach for computing 2D optical spectra beyond the weak-pulse limit. The approach is based on the generalized Redfield equation and numerically exact nonperturbative evaluation of the nonlinear polarization in the 3PPE phase-matching direction. We apply the approach to the simulation of strong-pulse effects in 2D optical spectra of a subunit of Fenna-Matthews-Olson (FMO) complex. We investigate how the strong-pulse excitation affects relaxation and redistribution of energy among different bacteriochlorophylla molecules. We demonstrate how the contributions from the higher lying excitonic states (which are unattainable by weak pulses) modify the 2D spectra. We also study the sensitivity of these new strong-field-induced features in the 2D FMO spectra to the parametrization of the excitonic Hamiltonian and strength of the bath-induced dissipation.

### **Sharpening Occam's Razor with Quantum Mechanics**

Mile Gu, *National University of Singapore*

Much of science involves the construction of mathematical models that make predictions about the future, based on relevant information collected from the past. In the spirit of Occam's razor, simpler is often better; should two predictive models equally simulate the future, the one that requires less information from the past is preferred. For a large class of stochastic processes we show that by encoding possible pasts into non-orthogonal quantum states, we can construct predictive models that require less information about the past than any possible classical approach. This indicates that to construct a device of minimal entropy that perfectly replicates the behavior of such systems, quantum dynamics is a necessity. These results imply that certain biological phenomena could be significantly simpler than classically possible, should quantum effects be involved.

### **Why Quantum Coherence in Light Harvesting Complexes?**

Stephan Hoyer, *University of California, Berkeley*

Coauthor(s): Mohan Sarovar, and K. Birgitta Whaley

Experiments have revealed that the initial light harvesting stage in photosynthesis involves surprisingly long-lived electronic coherences, raising questions as to their role and function. Here we evaluate two hypotheses for how coherence might lead to enhanced energy transfer efficiency. We show that while coherence in these systems is long-lived, the quantum speedup characteristic of quantum algorithms is not, suggesting these complexes do not use a "quantum search." Alternatively, we analyze a simple model for how coherence could enhance unidirectional energy flow. In this case, our results support a mechanism by which coherence could indeed lead to increased efficiency for some systems.

### **Efficiency of excitonic energy transfer and trapping in photosynthetic systems**

Tobias Kramer, *Harvard University*, Christoph Kreisbeck, *Fakultät für Physik, University of Regensburg*, and Mirta Rodriguez, *CSIC*

We calculate the temperature-dependent efficiency of the energy-transfer through a 7-site excitonic system populated from an initial ground state and radiatively decaying into the reaction center. The radiative excitation and de-excitation is modeled via a second photonic bath besides the vibronic one. We analyze the spectra obtained by different time-propagation for the density matrix (Markov, non-Markov, Ishizaki-Fleming (HEOM)), which demonstrates the need to use non-perturbative propagation techniques.

### **Quantum models of energy transfer from electrons to protons in electron-driven proton pumps**

Lev Mourokh, *Queens College of CUNY*

Coauthor(s): Anatoly Yu. Smirnov, and Franco Nori

We discuss quantum-mechanical models of energy transfer from electrons to protons in various electron-driven proton pumps. These pumps, located in the inner membrane of the mitochondria in the living cells, carry protons against the electrochemical potential creating and maintaining the proton gradient, which is used thereafter for the adenosin triphosphate synthesis. We describe this system using approaches from condensed matter physics, starting from the effective Hamiltonian written in terms of electron and proton creation/annihilation operators. This Hamiltonian includes the energies of several electron/proton sites, their couplings to corresponding reservoirs, interaction with the environment, as well as electron-electron, proton-proton, and electron-proton (on-site and inter-site) Coulomb couplings, with the electron-proton Förster term being of special interest. During the resonant Förster process, an electron moves from a higher-energy state to a lower-energy one; whereas a proton jumps from a lower-energy state to the higher-energy one. The same mechanism is responsible for the fluorescence resonant energy transfer (FRET) in biological systems, as well as for exciton transfer in condensed matter. It should be noted, however, that in these processes the electron-hole system is involved, instead of the electron-proton pairs in our system. Using this Hamiltonian, we derive and solve numerically the master equation for the density matrix, which allows us to obtain the electron and proton currents through the structure. Studying voltage and temperature dependences of these currents, we determine the range of parameters where the pumping of protons is possible, and show that it is the Förster process which is responsible for the energy transduction from the electron to proton subsystems.

### **Robustness and optimality of energy transfer in a photosynthetic complex at physiological temperature**

Alireza Shabani, *Princeton*

Coauthor(s): M. Mohseni, S. Lloyd, and H. Rabitz

Photosynthetic complexes have evolved to function efficiently in absorption and transfer of light energy to photochemical reaction centers, all in unprotected conditions. It remains a challenge to understand how this dynamical fault-tolerance property is achieved. In this work we study the robustness and optimality of energy transfer efficiency in Fenna-Matthews-Olson protein of green sulfur bacteria in presence of ambient and structural disorders. To this end, we use a non-Markovian and non-perturbative dynamical equation that captures the essential features of a realistic condition in high-temperature for both Ohmic and Drude-Lorentz spectral densities. In particular, we study excitonic energy transfer in different regimes of the complex Hamiltonian parameters and environmental couplings. For FMO complex, we find that the natural parameters lay within the both optimal and robust regimes of energy transfer efficiency.

### **On the quantum criticality in the ground and the thermal states of XX model**

Wonmin Son, *CQT, National Univ. of Singapore*

We compare the critical behavior of the ground state and the thermal state of the XX model. The full energy spectrum and the eigenstates are analyzed to reconstruct the ground state and the thermally excited state. With the solutions, we discuss about several physical properties of the states, including purity, which are related to quantum phase transition, in various limits, at zero temperature as well as at a thermal equilibrium.

### **Broadened Linear Spectra from Time-Dependent Density Functional Theory**

David Tempel, *Harvard University*

We will present an approach for describing environmentally broadened spectra using Time-Dependent Density Functional Theory (TDDFT). The method is based on an extension of TDDFT to open quantum systems, evolving according to a general master equation. We will present some calculations of linear spectra for molecules interacting with Markovian environments.

### **Quantum Stochastic Walks for Transport Dynamics**

James Whitfield, *Harvard University*

We axiomatically derive the general framework of quantum stochastic walks to model classical and quantum transport when environmental effects are important. The quantum stochastic walk is more general than both the classical random walk and the quantum walks since both are subsumed by quantum stochastic processes. We believe this is the correct way to view transport dynamics in photosynthetic complexes.

### **Entanglement and Non-Classical Correlations in Light-Harvesting Complexes**

Dmitry Uskov, *Physics Department, Tulane University*

The main direction of research in the quantum biological program is to identify and quantify the role of “quantumness” in basic biological processes, exploiting appropriate tools of quantum information theory. Using the tight-binding Hamiltonian and the Lindblad form of master equations, we calculate the time evolution of the density matrix of an exciton in the Fenna-Matthews-Olson (FMO) protein complex during the energy transfer from an antenna to a reaction center at cryogenic  $T=77^{\circ}\text{K}$  and physiological

T=300°K temperatures. The quantum information toolbox is then applied to analyze the resulting density matrix. We compute quantum discord functional to identify the amount of non-classical quantum correlations and compare the result with relative entropy of entanglement. We observe an interesting phenomenon that the value of discord is typically one order of magnitude larger than the value of relative entropy of entanglement, indicating that non-classical correlations may be more robust against phase decoherence than the quantum entanglement.

**Electron spin relaxation in B-form DNA probed by muon labeling method: Classical and quantum interpretations**

Momo Yaguchi, *International Christian University*

Coauthor(s): Kazuo Kitahara

In order to explain the experiment of Torikai et al. on the muon spin relaxation on DNA in both A-form and B-form conformations, we applied the methods of classical perturbation theory and random frequency modulation. Perturbing the electron spin and angular momentum by the circular pitch and assuming the angular frequency is totally random, we obtained the first order of electron spin as a form of an exponential function, which shows relaxation. We examine the validity of spin-orbit coupling in the helical space of B-form DNA from the view point of quantum mechanics in a curved space.