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The possibility that biological systems might employ nontrivial quantum effects in their daily behaviour is a surprising and surprisingly well-represented field of research which includes the topic of avian magnetoreception. Experiment suggests that birds make use of a radical pair mechanism to sense the earth’s magnetic field. To investigate a possible model for this behaviour we used the theory of open quantum systems to derive a master equation in the Born-Markov approximation for the simple case of two electrons, each interacting with an environment of N nuclear spins as well as the external magnetic field, then placed in a boson bath and allowed to dissipate. We then solved the master equation numerically to investigate the effects of different hyperfine environments on the dynamics of the radical pair and determine whether our model could verify parameters given in the literature, such as the radical-pair lifetime.
Interference and Molecular Transport—A Dynamical View: Time-Dependent Analysis of Disubstituted Benzenes

ShuGuang Chen, Yu Zhang, SiuKong Koo, Heng Tian, ChiYung Yam, GuanHua Chen, Mark A. Ratner

The University of Hong Kong

The primary issue in molecular electronics is measuring and understanding how electrons travel through a single molecule strung between two electrodes. A key area involves electronic interference that occurs when electrons can follow more than one pathway through the molecular entity. When the phases developed along parallel pathways are inequivalent, interference effects can substantially reduce overall conductance. This fundamentally interesting issue can be understood using classical rules of physical organic chemistry, and the subject has been examined broadly. However, there has been little dynamical study of such interference effects. Here, we use the simplest electronic structure model to examine the coherent time-dependent transport through meta- and para-linked benzene circuits, and the effects of decoherence. We find that the phase-caused coherence/decoherence behavior is established very quickly (femtoseconds), that the localized dephasing at any site reduces the destructive interference of the meta-linked species (raising the conductance), and that thermal effects are essentially ineffectual for removing coherence effects.

Light-harvesting complex arrays as open quantum systems:
Optimal transport exploiting geometric symmetry and system-
bath coupling

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In this contribution we look at the essential quantum effects taking place in light-harvesting pigment-protein complexes. The central focus is on the geometric symmetry possessed by the complexes, optimality of the system-bath coupling, and their biological significance. (i) For the LH2 complexes forming close-pack lattice on the native membrane of purple bacteria, it is found that the 9-fold rotational symmetry of the complexes reduces the geometric frustration originating from the incompatibility of dipolar interaction and hexagonal lattice, while maintaining high packing density of the bacteriochlorophylls. (ii) While the above concerns circular disks packed on 2D plane, we next look at the energy transfer kinetics between parallel linear arrays of chromophores. It is found that the close proximity between the linear aggregates brightens the “dark states” to serve as the main energy transfer channels. Also, due to the energy band structures of J-aggregates, an enhancement of the total energy transfer rate in the intermediate temperature regime is predicted compared to its high temperature classical value. (iii) Finally, we look at the diffusion rate of exciton on a tubular lattice in the axial direction. Depending on the strength of static disorder and environmental noise, the diffusion coefficient is found to be an increasing function of the tube radius, scaling between its 1D and 2D limits. For the gigantic multi-walled tubular antenna chlorosomes in green sulfur bacteria the strong system-bath coupling puts the exciton diffusion in the 2D limits, while in some artificial tubular chromophoric aggregates strong radius dependence of axial diffusion is predicted.


A quantum-information-theoretic approach to the signalling time of cryptochromes in Arabidopsis thaliana

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An important problem in the magnetoreception of birds is the identification of a host molecule for a magnetically sensitive chemical reaction known as the radical-pair mechanism. Current experiments and theory suggest cryptochrome (a class of receptor molecules) as a viable candidate. Cryptochrome functions as a signalling molecule, triggering further chemical reactions that lead to a neural signal when it attains a certain population in a particular state. Here we characterise cryptochrome response times by proposing a simple model to describe its radical-pair reaction. A key element of the reaction is the quantum coherent oscillations between singlet and triplet spin states of the radicals. While this is essential for enabling the magnetic sensing of cryptochrome, coherent state transitions can also increase the speed of certain processes. By using the well-known formalism of Kraus maps from quantum information theory we study the influence of decoherence on how quickly cryptochrome can signal. In particular we describe the radical-pair reaction as a quantum random walk with a variable dephasing parameter for the singlet-triplet oscillations. This allows us to study the state transitions of the radical pair subject to different levels of decoherence. We find that for realistic system parameters (transition rates) obtained from the literature, dephasing induces a change in cryptochrome signalling times of only a few percent. We thus argue that the process is essentially robust to dephasing. This change is seen to occur over only a small window of dephasing noise strengths. Artificial (i.e. “unrealistic”) system parameters are also explored.
Controlling charge and energy transfer in hybrid organic/inorganic nano-structures

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Coherent energy transfer in ambient temperatures was recently observed in light harvesting complexes. According to theoretical models the quantum properties improve the stability and the efficiency of the system. Implementation of quantum elements in man-made logic devices would be an achievement that would radically change the face of communication, information process and sensing. By using insights gained from the natural, biological systems, we aim to harness such quantum phenomena in artificial systems. In our work we demonstrate an approach for creating controlled hybrid organic/inorganic nano-structures. We have used a bottom-up approach for constructing a self-assembled super-molecular nano-structure of CdSe semiconductor quantum dots connected by organic molecules. The quantum levels are controlled by the colloidal quantum dots and the coupling is determined by the organic molecules. These structures enable us to study collective effects – in room temperature – such as electron transfer and excitation energy transfer. Furthermore, the relative simplicity and large flexibility of our systems allows one to compare the results to various existing theoretical models. Time resolved spectroscopy and absorption spectroscopy measurements indicate differences between systems composed of different molecules and core/core-shell quantum dots, and sheds light on how the various factors affect the dynamics on time-scales ranging from femto to nano-seconds and beyond.

Exciton super transfer in biological nano-wires

Ido Eisenberg [1], Shira Yochelis [1], Roy Ben Harosh [2], Hesham Taha [3], Nancy M. Haegel [4], Noam Adir [2], Nir Keren [5], Yossi Paltiel [1]

Presenter: Eyal Cohen


Antenna complexes of photosynthetic cyanobacteria poses superior excitation transfer efficiency at room temperature. In this study we explored how to control and use these properties in order to get an efficient nano to micro scale energy transmission. The energy transfer is examined using Phycocyanin trimers that are modified and dried on several substrates. Results show ordering of the proteins using two different methods. One method is adding salts to the solution which makes them arranged in orthogonal dendrites. Second method is filling micro-trenches by spin-coating. Using this method we achieve bundles of nano-wires of Phycocyanin. We believe that during the drying process the proteins arrange in super-molecular organizations mimicking the native proteins. Optical measurements indicate large distance of ~1μm size excitation transport mechanisms. Time resolved measurements showed that organized structures exhibits shorter exciton life-time than native proteins. Such structures may serve as a nano-meteric energy transmission lines, and may be used to couple light to nano-devices.

Probing Energy Transfer in LHCII Trimers and Aggregates using 2D Electronic Spectroscopy

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Light-harvesting antenna systems in photosynthetic organisms dissipate excess excitation energy of chlorophyll (Chl) under unfavorable light stress conditions through a photoprotective process called nonphotochemical quenching (NPQ). In vitro NPQ is induced by aggregation of the major trimeric light-harvesting complexes denoted as LHCII. In this work the ultrafast dynamics of excitation energy transfer from Chl b to Chl a Qy band in solubilized trimeric and aggregated LHCII are examined using two-dimensional (2D) electronic spectroscopy. Global analysis of the 2D spectra revealed that energy transfer from Chl b to Chl a occurs on hundred femtosecond and few picosecond time scales for both trimeric and aggregated LHCII. It was revealed that on the few picosecond dynamics, energy from Chl b is transferred to an intermediate mid energy state of which the subsequent decay depends on the physical state of LHCII. Monitoring the energy transfer rates and the multistep energy pathway in both trimeric and aggregated LHCII may aid in understanding the photophysical behavior of LHCII complexes in vivo.
Constrained geometric dynamics of the Fenna-Matthews-Olson complex: The role of correlated motion in reducing uncertainty in excitation energy transfer

Alexander S. Fokas, Daniel J. Cole, Alex W. Chin

University of Cambridge, Physics, TCM

The Fenna Mathews Olson (FMO) complex of green sulphur bacteria is an example of a photosynthetic pigment protein complex, in which the electronic properties of the pigments are modified by the protein environment to promote efficient excitonic energy transfer from antenna complexes to the reaction centres. Many of the electronic properties of the FMO complex can be extracted from knowledge of the static crystal structure. However, the recent observation and analysis of long lasting quantum dynamics in the FMO complex point to protein dynamics as a key factor in protecting and generating quantum coherence under laboratory conditions. While fast inter and intra molecular vibrations have been investigated extensively, the slow dynamics which effectively determine the optical inhomogeneous broadening of experimental ensembles has received less attention. Our study employs constrained geometric dynamics to study the flexibility in the protein network by efficiently generating the accessible conformational states from the published crystal structure. Statistical and principle component analysis reveal highly correlated low frequency motions between functionally relevant elements, including strong correlations between pigments that are excitonically coupled. Our analysis reveals a hierarchy of structural interactions which enforce these correlated motions, from the level of monomer monomer interfaces right down to the alpha helices, beta sheets and pigments. In addition to inducing strong spatial correlations across the conformational ensemble, we find that the overall rigidity of the FMO complex is exceptionally high. We suggest that these observations support the idea of highly correlated inhomogeneous disorder of the electronic excited states, which is further supported by the remarkably low variance of the excitonic couplings of the conformational ensemble.
Keeping it simple: Why weak coupling techniques are sufficient for photosynthetic energy-transfer

Amir Fruchtman, Erik Gauger

Oxford University, UK

We examine what theoretical machinery is required for studying the role of environmental noise in the excitation energy transfer (EET) stage of the light-harvesting apparatus of green-sulphur bacteria. This process occurs in the Fenna-Matthews-Olson complex (FMO) which has been extensively studied. Several different models for it appear in recent literature, which differ from each other mainly by the choice for the spectral density function of the environment. Much has been made of the difficulty of modelling EET and the need for advanced techniques, where in fact we find that in many cases weak coupling techniques are sufficient. We check whether the system-environment coupling in different models is weak by comparing explicit high order terms to second order ones, and derive a rigorous definition for when weak coupling treatment is enough, and there is no need for non-perturbative techniques. We examine some well-established models for modelling FMO, and find that some of them, for example the Ishizaki-Fleming model [PNAS 106, 17255 (2009)], are indeed in the weak coupling regime by our definition. We validate our results by comparing exact numerics to a weak-coupling treatment.
Ultrafast Energy Transfer and Quantum Coherences in Biological Light Harvesting Photosystems using Spatial Light Modulator (SLM) based 2D Electronic Spectroscopy

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We present a novel 2D electronic spectroscopy (2DES) setup using spatial light modulators to investigate dynamics of energy transfer and exciton coherence lifetimes that are crucial in understanding light harvesting processes in biological photosystems such as chlorophylls and bacteriochlorophylls. Using a liquid crystal based spatial light modulator (SLM) in a 4-f pulse shaping configuration, we are able to shape femtosecond laser pulses to generate optical pulse sequences with controlled phases. By applying specific phase cycling schemes on the optical pulse sequence, specific higher order nonlinear optical signals can be obtained in a collinear geometry without any interference from other nonlinear optical processes. We demonstrate our 2DES results using a phase-cycle scheme on the naturally occurring light harvesting photosystems of chlorophylls and bacteriochlorophylls.
Plasmon Coupling Enhanced Two-photon Photoluminescence and Their Applications

Zhenping Guan, Peiyan Yuan, Cuifeng Jiang, and Qing-Hua Xu

SMART biosym

Plasmon coupling between noble metal nanoparticles have been known to display giant local field enhancement, which would result in significantly enhanced excitation efficiency (light harvesting capability) and enhanced optical signals.1 Nonlinear optical responses such as two-photon photoluminescence (2PPL) are particularly sensitive to the local field enhancement due to their quadratic dependence on the incident intensity.2 Our studies showed that aggregation of Au and Ag nanoparticles could result in significantly enhanced 2PPL in solution. An enhancement factor of up to ~50 times was observed for coupled 40 nm Ag nanospheres induced by addition of conjugated polymers.3 We have conducted single particle studies on TPPL of the oligomer of Au nanoparticle. TPPL intensity significantly increases from Au nanosphere monomer to trimer. Up to five orders of magnitude enhancement in 2PPL was obtained for the linear trimer.4 Two-photon excitation has unique advantages in biological applications such as deep tissue penetration of NIR light and the three dimensional excitation. As many chemically and biologically important species can induce aggregation of metal nanoparticles, we have further utilized plasmon coupling enhanced 2PPL to develop various two-photon applications including two-photon sensing of Hg2+, thrombin and DNA as well as two-photon imaging and killing of bacteria.5-7


The effects of temperature on spatio – temporal dynamics of EET in the FMO complex

Garth A Jones and Colm G. Gillis

University of East Anglia

A theoretical methodology is presented in which population dynamics are evolved in the exciton basis. Spatio – temporal movement of excitations are subsequently obtained by projection to the site basis. Fluctuations of system eigenstates are explicitly included through vibrations of the chromophores, which are parameterized by ab initio calculations and state populations are propagated using the quantum Liouville equation (QLE). For QLE simulations, population dynamics show that bacteriochlorophyll a 1 and 2 effectively act as a single unit at 77 K, but as independent chromophores at 300 K. Population beatings for the lower energy exciton states are considerably slower at physiological temperatures thus assisting transfer to the sink. This study supports the view that a coherent mechanism may assist EET at physiological temperatures since the trapping of excitations in intermediate energy sites is prevented. Furthermore, delocalized vibrations (i.e. superpositions of independent oscillators) are found to assist energy transfer at short times.
Coherent dimer dynamics in a dissipative environment maintained by an off-resonant single mode

**Elliott Levi, Dr Brendon Lovett**

University of St Andrews

The role of quantum coherence in efficient energy harvesting has recently been the subject of intense research. In this paper, we explore the extent to which quantum coherence can be induced in a previously incoherent two level system (TLS) by strongly coupling to a single, off-resonant, bosonic mode. The rest of the environment is assumed to comprise a Markovian bath of bosonic modes. The TLS could, for example, represent the position of the exciton in an energy transfer dimer system. The TLS-single mode coupling strength is varied for several different forms of bath spectral density in order to assess whether the coherent dynamics of the TLS are modified. We find a clear renormalisation of the site population oscillation frequency, which also causes an altered interaction with the bath. This new interaction can cause enhanced or reduced coherent behaviour of the TLS depending on the parameters. We will discuss the usefulness and pitfalls of exploiting such a dynamics-altering tool in a quantum device.
Conjugated Polymers as Light Harvesting Complex for Two-Photon Imaging and Photodynamic Therapy

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Two-photon excitation is useful for various non-invasive in vivo applications due to its unique advantages such as 3-dimensional selectivity and deep tissue penetration. However, clinical applications of these techniques are limited by small two-photon absorption cross sections of traditional dyes and photosensitizers. Conjugated polymers have been known to display large extinction coefficients and two-photon absorption cross sections. Our group has demonstrated that conjugated polymers can be utilized to act as two-photon light harvesting materials to enhance two-photon emission of nearby chromophores by up to hundreds of times by two-photon excitation (2PE) energy transfer [a,b,c], which has been utilized for various two-photon applications, in particular two-photon imaging and photodynamic therapy. Here we present conjugated polymer based nanoparticles with enhanced two-photon optical properties and their applications in two-photon imaging and two-photon photodynamic therapy. We have prepared dye doped PFV nanoparticles, in which 2PE fluorescence of red-emitting dyes, MgPc and Nile red, was found to be enhanced by up to 53 times and 220 times. These nanoparticles display excellent biocompatibility and large two-photon brightness in the far-red region. Application of these NPs on two-photon imaging of HepG2 cancer cells gave strong red emission signals with excellent contrast. We have also prepared photosensitizer (TPP) doped PFVCN nanoparticles. These nanoparticles displayed up to 1020-fold enhancement in 2PE fluorescence and ~870-fold enhancement in 2P induced 1O2 generation capability of TPP. Surface functionalized folic acid groups make these nanoparticles highly selective in targeting and killing KB cancer cells over NIH/3T3 normal cells. These nanoparticles could act as novel two-photon nano-photosensitizers with combined advantages of low dark cytotoxicity, targeted 2P-PDT with high selectivity and simultaneous two-photon fluorescence imaging capability, which are required for ideal two-photon photosensitizers.

Vibronic origin of long-lived oscillations in 2D electronic spectroscopy

James Lim, Felipe Caycedo-Soler, Susana F. Huelga, Martin B. Plenio, Javier Prior, David Palecek, Donatas Zigmantas, Craig Lincoln, Jürgen Hauer

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Recent advances in nonlinear optical spectroscopy have led to the discussion of the role of long-lasting coherences in both natural and engineered light-harvesting systems. These observations have sparked an interdisciplinary research effort to unravel the nature and functional relevance of possible quantum effects in these systems. Despite these efforts, the fundamental question of how coherence is sustained for up to several picoseconds at ambient conditions under the decohering effects of their environments has remained open. Here we report for the first time experimental results, obtained by means of polarization controlled two-dimensional electronic spectroscopy for a macroscopically aligned artificial light harvester, called J-aggregates that allow us to decide this question. Theoretical analysis of the data confirms that the recently proposed idea of vibronic coupling explains the observed long-lasting oscillations in J-aggregates. The same analysis rules out, for this system, alternative models such as correlated fluctuations of the environment. The vibronic coupling observed here has the capacity for enhancing transport and can therefore possess functional relevance.
Quantum transport in lattices and networks

D Manzano, Chern Chuang and J Cao

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We analyse both qubits and harmonic oscillators quantum transport in discrete complex systems. Due to the occupation limitation of qubits this transport strongly depends on the system topology. On the other hand, harmonic oscillators transport is similar in almost all topologies. For lineal systems, like D-dimensional lattices, harmonic oscillators transport is ballistic independently of the dimension of the system [1]. In the same case qubits show a strong dependence on the system dimension, being ballistic only for one-dimensional systems. In homogeneous quantum networks harmonic oscillators transport does not depend on the number of sites of the networks, but qubits show a super-ballistic behaviour [2]. In this work [4] we broadly check qubits and harmonics oscillators behaviours by numerical analysis both in lattices and networks, and in the transient and steady state scenarios. Finally, we discuss potential applications of these results to light harvesting in biological and artificial devices, where the differences between this two kind of transport has been already highlighted regarding entanglement features.

A quantum protective mechanism in photosynthesis

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Since the emergence of oxygenic photosynthesis, living systems have developed protective mechanisms against reactive oxygen species. During charge separation in photosynthetic reaction centres, triplet states can react with molecular oxygen generating destructive singlet oxygen. The triplet product yield in bacteria is observed to be reduced by weak magnetic fields [1,2]. Reaction centres from plants' photosystem II share many features with bacterial reaction centres, including a high-spin iron whose function has remained obscure. To explain observations that the magnetic field effect is reduced by the iron [3], we propose that its fast-relaxing spin plays a protective role in photosynthesis by generating an effective magnetic field. We consider a simple model of the system, derive an analytical expression for the effective magnetic field and analyse the resulting triplet yield reduction. The protective mechanism is robust for realistic parameter ranges, constituting a clear example of a quantum effect playing a macroscopic role vital for life. [4]


Molecular basis of the exciton-phonon interactions in the PE545 light-harvesting complex

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Long-lived quantum coherences observed in several photosynthetic pigment-protein complexes at low and at room temperatures have generated a heated debate over the impact that the coupling of electronic excitations to molecular vibrations of the relevant actors (pigments, protein and solvent) has on the light harvesting process [1]. In this work, we use a combined MD and QM/MMPol strategy to investigate the exciton-phonon interactions in the PE545 light-harvesting complex by computing the spectral densities for each pigment and analyzing their consequences in the exciton dynamics [2,3,4]. Insights on the origin of relevant peaks, as well as their differences among individual pigments, are provided by correlating them to normal modes obtained from a quasi-harmonic analysis of the motions sampled by the pigments in the complex. Our results indicate that both the protein and the solvent significantly modulate the intramolecular vibrations of the pigments, especially at low frequencies, thus playing an important role in promoting or suppressing certain exciton-phonon interactions. We also find that these low-frequency features are largely smoothed out when the spectral density is averaged over the complex, something difficult to avoid in experiments that underscores the need to combine theory and experiment to understand the origin of quantum coherence in photosynthetic light-harvesting.


Theory and Simulation of Two-quantum 2D Optical Spectroscopy

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Two-quantum (2Q)-2D optical spectroscopy is a new kind of spectroscopy to measure multiexcitonic coherent states of many chemical and biological systems. Information about electronic correlations or features of the coupling between two dipoles can be revealed using this 2Q-2D spectroscopy. In this study, we conducted the simulations to demonstrate the efficacy of this technique and using optimal phase-cycling scheme to retrieve the desired spectra.

Low energy coherent oscillations in the non-adiabatic excited state of light-harvesting phycocyanin-645 at physiological temperature

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Sustaining the life cycle of our planet, photosynthesis is one of the most important and studied natural phenomena. In the last few years attention has gathered around some pioneering works[1,2] that demonstrate signatures of quantum-coherent effects in biological photosynthetic systems[3-6]. In an attempt to clarify these issues several experimental and theoretical tools have been developed[7]. However, several pivotal open questions remain. The two most crucial are: what is the origin of the oscillations in the non-linear response of these pigment-protein complexes and what is the role, if any, of the vibrations in mediating energy transfer[7-14]. Here we propose a novel approach that permits manipulation of the relative weight of different quantum pathways excited via two-colour narrowband four-wave mixing and allows unambiguous attribution of excited state coherences in photosynthetic systems. We demonstrate the validity of this new approach by addressing the room temperature non-linear response of the antenna complex phycocyanin-645 from cryptophyte algae. Our results indicate how it is possible to disentangle ground-state from excited-state contributions, and clearly points to non-adiabatic mixing occurring in the excited mixed excitonic-vibrational state.

Quantum Langevin formalism is a more general and versatile formalism than the density matrix equation for describing quantum phenomena. It includes quantum noise and dissipation. However, the formalism has been restricted to atomic systems interacting with weak light fields. It is not easy to solve due to the operator nature of quantum variables and the presence of multimode states in the noise operators. We shall explore the possibility to extend the formalism to non-Markovian dissipative environment and try to connect the formalism to the many-body time-correlator transform theory that can describe fluorescence and Raman processes in complex molecules.
Assessing drug-protein binding by simulation of stereoselective energy transfer dynamics: electronic interactions between tryptophan and flurbiprofen

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The fluorescence of proteins is a complex process, often involving several electronic energy transfer (EET) reactions between aromatic amino acids before light emission, typically arising from tryptophan. In protein-ligand complexes, the ligand can also modify the fluorescence properties by participating in these EET processes, as well as by contributing to electron transfer reactions or the formation of exciplexes. The complex interpretation of optical experiments, however, typically precludes a full exploitation of the structural information encapsulated in such experiments and related to the drug-binding events observed. In this study, we simulate how energy transfers involving different flurbiprofen enantiomers modulate the fluorescence properties of model tryptophan-flurbiprofen (TRP-FBP) and flurbiprofen-HSA (human serum albumin) complexes, where stereoselective dynamic quenchings have been recently observed.1 To this aim, we combine classical MD techniques with the a polarizable QM/MM methodology we have recently developed 2 and applied to study the light-harvesting properties of photosynthetic systems.3,4 On the basis of our results, we discuss the potential of structure-based simulations in the study of drug-binding events through fluorescence techniques.


Modeling of the Functional Window in the Avian Compass

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The functional window is a property of the avian compass that enables it to sense magnetic fields selectively, in a somewhat narrow intensity window around that of the geomagnetic field [1-4]. We have investigated the functional window behavior within the radical pair model [5-6] of the avian compass by studying its sensitivity as a function of the geomagnetic (Zeeman) field strength. We report here a biologically-feasible set of hyperfine interaction parameters [7] that yields the two key features of the avian compass as observed from behavioral experiments: the functional window, and the disruption of the compass action by an RF field of a specific frequency [8]. We find that the proposed parameter set continues to give rise to these behaviors even when we deviate from the usual assumption [3-5,9] of equal recombination rates for singlet and triplet radical pair states. Our results enable us to predict a lower limit for the radical pair recombination time, and thereby, the coherence time [9]. Further, we prescribe ways to tune the functional window by adjusting the hyperfine interaction and recombination rate parameters. A similar approach may be used to screen material systems for solid state emulation of the avian compass.

Electron Transfer Rate estimates from first principles: Light induced DNA repair

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UV radiation causes damage of DNA, mostly producing the cyclobutane pyrimidine and (6-4)-pyrimidine-pyrimidone (PP) photodimers. (6-4) photolyase is a DNA repair enzyme that selectively repairs (6-4)PP photodimer, using visible light [1]. This repair process is a complex photocycle comprising of several electron transfer (ET) steps possibly coupled to proton transfer (PT), controlled by the protein [2]. The key repair steps are the forward electron transfer (FET) and the back electron transfer (BET) which involve the FADH− chromophore and the (6-4)PP. Experimentally, the ET rates of these steps have been estimated [2], but the overall repair mechanism remains elusive.

To estimate the ET rates from first principles, we have set up a multiscale computational apparatus based on a combination of QM, hybrid QM/MM and MD methodologies. With this approach, we have computed the energies of the FADH−-(6-4) PP (Donor-Acceptor) complex in different electronic states, formally describing the ET reactions of interest. We evaluate the effects of the protonation state of key residues, the effects of the protein, solvent and DNA counterions. By employing the semi classical Marcus formalism, we predict the FET and BET rates and compare them against the experimental observations. We establish that coupling of ET and PT reactions accelerates FET and significantly slows down BET in the (6-4) photolyase active site.


Coherent quantum transport in extended, disordered systems

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The large-scale energy transport processes occurring in many of the highly efficient natural light harvesting systems can be characterized as an excitonic transport process in an extended, disordered system that is coupled to an environment. We have recently studied this fundamental transport process in both simplified Haken-Strobl environments[1] and more realistic quantum baths[2,3]. At short times, non-diffusive behavior is observed that can be characterized by the free-particle dynamics in the Anderson localized system. Over longer time scales, the environmental noise is sufficient to overcome the disorder-induced Anderson localization and allow for transport to occur which is always seen to be diffusive. Analytical scaling relations for the diffusion coefficient are obtained in both the band-like and hopping transport regimes, and a highly accurate polaron transformed master equation allows us to bridge these two limits.[1,3] The scaling behavior implies the existence of a maximum in the diffusion constant as functions of both the temperature and system-phonon coupling strength which is confirmed numerically. The mobility based on our polaron calculation agrees well with experimentally measured mobility in organic semiconductors.[3] Current efforts are directed towards understanding quantum transport in lattices with long-range interactions, two-dimensional dipolar systems, and nanotubes.

Functional relevance of extended delocalization in purple bacteria

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Light absorption in photosynthetic complexes occurs predominantly at light-harvesting (LH) antenna complexes, composed of many pigments, followed by excitation energy transfer (EET) between antenna complexes and the reaction centre (RC), containing far fewer pigments. Photon absorption is completed on timescales (~10 fs) much shorter than both the coherence time (~100 fs) and EET (~1-10 ps), which means quantum mechanical delocalization across extended domains must be accounted for in an accurate description of the absorption process, regardless of the nature of transport (1-2). We develop a theory to characterize delocalization over extended domains in photosynthetic membranes of purple bacteria—well beyond the current paradigm which conjectures delocalization within single LH complexes or RCs—and show that the excitonic coupling among different units effects experimentally measurable redistributions of absorption intensity. We find theoretically that coupling between LH complexes leads to a polarized optical response which depends on the geometry of the array, the measurement of which would allow the experimental determination of the inter-complex Förster rate, and show theoretically and experimentally that delocalization across LH complexes and RC leads to an 80 % increase in direct optical absorption of the RC (3-4).

(3) Caycedo-Soler, F. and Schroeder, C. et. al. (submitted)
(4) Schroeder, C. and Caycedo-Soler, F. et. al. (submitted)
Universal definition of non-Markovianity and its implications for quantum biological calculations

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A universal definition of Markovianity for the dynamics of open quantum and classical systems is proposed. The key to distinguish Markov and non-Markov processes is the comparison between measured correlation functions and those constructed from the results of quantum process tomography. The suggested definition is based on the fact that the knowledge of both the initial state of the system and the solution of the quantum master equation for the density matrix is not enough to fully characterise the system. Using examples of the spontaneous emission and pure dephasing it is shown explicitly that the proposed definition is essential for an adequate description of the typical observables. It is demonstrated that existing non-Markovianity measures based on the analysis of the properties of dynamical maps lead to inconclusive results. The implications for calculations of the emission spectra, 2D-spectra and higher order correlation functions will be discussed as well.

Refining Frenkel Exciton Model for Carotenoid-Carotenoid Interactions

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Carotenoids are some of the most abundant building blocks of photosynthetic antennae. While realistic model of exciton interaction between Chlorophylls can be constructed using dipole-dipole approximation, the size and shape of carotenoids prevents the usage of this simple method for carotenoid-carotenoid interactions in their usual mutual distances. Inspired by a classical model of excitonic interaction [1] we propose an classical method for calculation of resonance interaction between optically allowed states of pi-conjugated electronic systems. We compare the results of our classical method with quantum chemical calculations and find excellent quantitative results for the coupling between astaxanthins after parametrization involving only rescaling of the total transition dipole moment. The classical method is remarkably easy to implement, and it provides performance advantage over even the simplest quantum chemistry. Applying our calculations to the absorption spectra of astaxanthin aggregates we find the necessity to go beyond the usual Frenkel exciton model limited to the interaction between singly excited states. A careful derivation of the interaction elements in a multi-chromophoric aggregate reveals important contributions of the multiply excited states already at the level of absorption spectra. We study the magnitude of these effects for carotenoid aggregates and their dependence on the aggregate structure.

Quantum stochastic limit and coherent energy transfer in photosynthetic complexes

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Stochastic limit of quantum theory [1] puts together the scattering (long times) and perturbation (small parameter) theories by studying the long-term cumulative effects of weak actions. It works as a magnifying glass of all phenomena pertaining to the scales of magnitudes we are interested in and as a filter of those pertaining to all the remaining scales. This is a kind of approximating theory from which the individual approximations can be obtained by standard procedures. In particular, it allows to derive an improved generalized Forster theory and all known types of quantum master equations in a mathematically rigorous and general way. In this talk we give some applications of quantum stochastic limit to excitation energy transfer in photosynthetic light-harvesting complexes and discuss further perspectives. In particular, we derive new master equations starting from a system interacting with two reservoirs (one reservoir models vibrational modes of the protein, another one models the sink) and compare the results with conclusions of [2] on a role of noise in the excitation energy transfer in light-harvesting complexes. General properties of quantum dynamics in bounded nanoscopic domains are also discussed [3].


Quantum processes and nuclear transmutation of stable and reactor isotopes in growing biological systems

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In the work the process of stimulation and effective control of nuclear reactions with participation of stable (e.g., Mn55+d=Fe57) and radioactive (including utilization of reactor Cs137 isotope: Cs137+p=Ba138) isotopes in microbiological cultures has been studied [1-3]. The process is connected with transmutation of different isotopes during growth and metabolism of microbiological cultures. The most speeded transmutation takes place in microbiological MCT compound. The MCT is the special granules that include: concentrated biomass of metabolically active microorganisms, sources of carbon and energy, phosphorus, nitrogen, etc., and gluing substances. The quantum mechanism of isotopes nuclear transmutation in growing biological system is connected with formation of coherent correlated states of interacting nuclei in nonstationary potential wells in biomolecules [4,5]. We have observed speeded up nuclear transmutation of Cs137 isotope in all experiments with MCT and with the presence of different additional salts during more 100 days. In control experiment (flask with active water) the law of decay was "usual" and the life-time was about 30 years. The most speeded up decay of Cs137 isotope with 310 days (accelerated by 35 times) was observed at the presence of Ca salt.


CAN NATURAL SUNLIGHT INDUCE COHERENT EXCITON DYNAMICS?
Coherent exciton dynamics have been extensively investigated in the light-harvesting systems and recently measured by two-dimensional electronic spectroscopy, revealing the long-lived coherence. This directly leads to the heated debate regarding the importance of the photon coherence in sunlight to the coherence of the excitonic energy transfer. It is believed that decoherence in photosynthetic systems mainly arises from two sources: 1) incoherent light induced persistent pump; 2) exciton-phonon interaction induced entanglement. Although there have been many studies to model incoherent light excitation and influence of phonon baths, the exact quantum descriptions of the light and phonons are still not available. Here, we propose a V-shape three-level model, which constitutes the prototype for the light-induced coherent transfer process [1], and solve the model both numerically and analytically. The exciton dynamics of the closed system pumped incoherently can be described analytically using the white-noise model. The light-induced exciton dynamics can sustain coherent beatings for hundreds of femtoseconds. The system-bath coupling results in dephasing at the short time scale and the exciton-phonon entanglement for the long time evolution. Moreover, the coherent-to-incoherent transition of the quantum coherence is clearly revealed by enhancing the exciton-phonon coupling strength, which can be qualitatively described using the Redfield scheme.[2] By including the trapping effect for excitons, the generalized non-equilibrium steady state is established, which bridges the photon-induced and phonon-induced limits. Our results demonstrate that the incoherent nature of sunlight excitation indeed includes transient coherence in the exciton dynamics, but this transient dynamics may not play a dominant role in the efficiency of energy transfer, considering picoseconds time-scale of the exciton trapping process in typical light-harvesting systems.

Recent ultrafast optical experiments show that excitons in large biological light-harvesting complexes are coupled to molecular vibration modes. These high-frequency vibrations will not only affect the optical response, but also drive the exciton transport. Here, a model dimer system is employed to show that the frequency of the under-damped vibration has a strong effect on the exciton dynamics such that quantum coherent oscillations in the system can be present even in the case of strong noise [1]. Two mechanisms are identified to enhance the transport efficiency: critical damping due to the tunable effective strength of the coupling to the bath and resonance coupling when a vibrational frequency coincides with an energy gap in the system. The interplay of these two mechanisms determines parameters responsible for the most efficient transport, and these optimal control parameters are comparable to those in realistic light-harvesting complexes. Interestingly, the lifetime of oscillations in the coherence at resonance is suppressed in comparison to the case of an off-resonant vibration.

A Continued Fraction Resummation Form of Bath Relaxation: High-Order Corrections to Fermi’s Golden Rule Rate

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In the two-site system, the quantum kinetic expansion (QKE) approach introduce high-order corrections of the bath relaxation to Fermi’s golden rule (FGR) rate and the noninteracting blip approximation (NIBA) in the second order. Following a time separation approximation, a continued fraction form is proposed to systematically resum high-order QKE rate kernels, which can recover the Pade approximation in the lowest order. For both unbiased and biased systems, the continued fraction resummation can predict the exact time-integrated effective rate and the detailed time evolution of the system population. The exact quantum equilibrium population is also recovered, with the improvement from the classical Boltzmann distribution in the second order prediction to the quantum canonical distribution. The high-order corrections allow us to evaluate the Forster rate beyond the weak excitonic coupling limit for energy transfer systems and to incorporate solvent-diffusion effects beyond the Marcus-Zusman formulation for electron transfer systems.

1. Z. H. Gong, Z. F. Tang, X. I. Ou-yang, J. L. Wu* and J. S. Cao, to be submitted.
Polaron effects on the efficiency of a quantum heat engine

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A three-level system working as a heat engine was studied in the case of weak coupling heat bath [H. E. D. Scovil and E. O. Schulz-DuBois, PRL 2, 262 (1959), E. Boukobza and D. J. Tannor, PRL 98, 240601 (2007), etc.]. A simple expression of the efficiency, bounded by the Carnot efficiency, was given in the case when both the hot and cold baths are weakly coupled with the heat engine. In this work, we explore the thermodynamics of the three-level system, which can also serve as a model of energy transfer through a strong coupling environment in bio system. An excitation is transferred through the upper two excited states, which are coupled to a strong phonon bath before trapped in the ground state. The phonon bath here plays the role of the cold bath. The efficiency of this three-level system is explored by steady state analysis via polaron-transformed Redfield equation (PTRE), which covers a wide range of the system-phonon bath coupling strength. The PTRE approach is consistent with the Redfield equation and Föster rate equation in the weak and strong coupling limits, respectively. Due to the competition between the excitation hoping and the noisy environment, an optimal value of energy flux appears in the intermediate coupling region where the efficiency is not very low. It is found that when the populations of the upper two excited states are inversed, the efficiency of the current model is beyond result η0 given by Scovil and Schulz-DuBois. As the system-bath coupling increases, the steady state coherence disappears and the efficiency approaches to the limit value η0.

Dazhi Xu, Chen Wang, Yang Zhao, Jianshu Cao, in preparation.
Development of Fifth-order Two-quantum Two-dimensional Electronic Spectroscopy

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Multi-dimensional optical spectroscopy has been of fundamental interests in the study of molecule structure and dynamics for the past few decades. Among those, third-order two-dimensional nonlinear electronic spectroscopy (2DES) has been widely developed and become a powerful tool to reveal the hidden coupling and high lying excited states. Based on a pulse-shaper assisted 2DES using a pump-probe geometry, here we propose a fifth-order two-quantum two-dimensional electronic spectroscopy (2Q2DES). Experiments were carefully conducted on chlorophyll a (Chl a) molecules solubilized in ethanol due to the interest of study on its role played in energy conversion in light-harvesting complexes (LHC). 1 by 4 phase-cycling scheme was performed to retrieve the desired 2Q2D signal for a three-level system. Additionally, in order to verify the validity of the obtained 2Q2D spectrum, a pump intensity dependence study as well as a concentration relationship study was completed.
Noble metal nanoparticles are known to display localized surface plasmon resonance (LSPR). When two particles are placed in close vicinity, their LSPR modes interact and a hot spot is formed in the gap, where local field can increase by orders of magnitude. This property could be utilised to enhance light harvesting capability of nearby chromophores to result in significantly enhanced optical response such as fluorescence. In this work, we present a self-assembly method to couple gold nanorods by using DNA origami as the template. This method provided precise control over the dimer spacing and orientation, both of which were critical for fluorescence enhancement. Single molecule fluorescence measurements were conducted on enhanced fluorescence of chromophores flowing through the gold nanorod dimer. A maximum fluorescence enhancement of 500-fold was achieved from a high quantum yield dye ATTO-655. A series of dimer with different spacing were measured. It was found that as the spacing increased, the enhancement effect gradually dropped and approached that from a monomer.
Improved Dyson series expansion for steady-state quantum transport beyond the weak coupling limit - divergences and resolution

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Steady-state quantum transport for nonlinear systems is an important problem encompassing the fields of biology, chemistry and physics. Traditionally quantum master equation (QME) is a suitable tool to study nonlinear systems but it is limited to the weak system-bath coupling regime. In this work we address the nonlinear quantum transport problem beyond weak-coupling limit via the calculation of higher order contributions. We show that simply using a truncated Dyson series leads to divergences in higher order terms in the steady-state limit. In order to resolve the divergences we propose a unique choice of initial-condition for the reduced density matrix, which removes the divergences at each order. We show that this unique initial-condition leads to steady-state solution in long, but finite time, and this state will no longer depend on the initial preparation. Using this approach we evaluate the electronic and heat currents up to fourth order in system-bath coupling for the solvable quantum dot model and harmonic oscillator model. Our results show agreement with the exact approaches via non-equilibrium Green’s functions at each order. Lastly, to demonstrate the advantage of our approach we deal with nonlinear spin-boson model to evaluate current up to fourth order and find signatures of cotunnelling process.

Short-time to long-time dynamics: A transfer matrix approach

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The dynamical maps method (also termed the transfer tensor method, TTM) introduced by Cao et. al., which is originally applied to open quantum model systems, looks for the dynamical maps between the density matrices at different times based on a black-box analysis. In this work, a similar approach is applied to the reduced single-electron density matrices (RSDMs) of a device coupled to two leads. We look for the dynamical maps between the RSDMs based on a black-box analysis of the initial evolution of the system. The dynamical maps can then be used to propagate the system to arbitrarily long time. The results are compared to those obtained from direct quantum calculation of the NEGF–HEOM method.