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Talks

An open quantum systems approach to entangled Posner molecules

Betony Adams

University of KwaZulu-Natal

The nature of consciousness is a question that has fuelled debate across disciplines from philosophy to physics. In the mid-1990s it was proposed that quantum effects play a role in the mechanism of consciousness. The theory was largely dismissed due to the fact that quantum effects were thought unlikely to occur in biological systems, which are warm and wet and subject to decoherence. However, the research field of quantum biology now suggests otherwise. Quantum effects have been implicated in photosynthesis, a process fundamental to life on earth. They are also possibly at play in other biological processes such as avian migration and olfaction. In 2015 Matthew Fisher outlined a mechanism for quantum computation in the brain in which entangled Posner molecules influence subsequent neural signalling. He also suggested that quantum effects might be at play in the mechanism by which lithium acts as an antidepressant. We propose an open quantum systems approach to a pair of Posner molecules where the dynamics are modelled by a Born-Markov master equation. The aim of this is two-fold. Firstly, to investigate the long decoherence times suggested by Fisher. And secondly, to establish the dynamical effects of replacing the central calcium ion in each Posner molecule with a higher spin lithium ion.

Studies of Natural and Artificial Photosynthesis

Victor Batista

Yale University, Department of Chemistry and Energy Sciences Institute

Mechanistic investigations of the water-splitting reaction are fundamentally informed by structural studies of the oxygen-evolving complex (OEC) of photosystem II (PSII) and biomimetic catalytic complexes. Many physical techniques have provided important insights into the OEC structure and function, including X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) spectroscopy as well as mass spectrometry (MS), electron paramagnetic resonance (EPR) spectroscopy, and Fourier transform infrared spectroscopy applied in conjunction with mutagenesis studies. However, experimental studies have yet to yield consensus as to the nature of the reaction mechanism responsible for oxygen evolution. Computational modeling studies, including density functional (DFT) theory combined with quantum mechanics/molecular mechanics (QM/MM) hybrid methods for explicitly including the influence of the surrounding protein provide powerful modeling tools to explore reaction mechanisms for the fully ligated OEC within PSII and examine whether they are maximally consistent with experimental data. The computational models are useful for rationalizing spectroscopic and crystallographic results and for building a complete structure-based mechanism of water-splitting as described by the intermediate oxidation states of oxomanganese complexes. This talk summarizes our recent advances in studies of water oxidation catalyzed by the OEC of PSII and biomimetic catalysts for artificial photosynthesis.

Structure and efficiency in bacterial photosynthetic light harvesting

Susannah Bourne-Worster

University of Bristol

Descriptions of energy transfer through photosynthetic antenna are influenced by how we choose to model (or neglect) details such as the nature of incident light, coupling to the vibrational environment, or energetic and spatial disorder. Using a Lindblad master equation approach, we aim to draw together recent insights on all these factors in a comprehensive and realistic model that includes detailed descriptions of each step of the transport process. We focus on explicitly modelling the interaction of the antenna with natural, incoherent light and capturing the multiple effects of coupling to vibrational modes with a large range of frequencies. In particular, we include the effect of slow vibrational modes by introducing time-dependent disorder.

Applying this approach to a model antenna system, comprising one each of the LHI and LHII complexes in purple bacteria, we demonstrate that the quantum state of the exciton manifold fluctuates continuously but remains highly mixed at all times. Exciton density moves around the antenna with the aid of the vibrational environment, which drives relaxation towards thermal equilibrium, while also continually changing the identity of the thermal state. The time-averaged state around which the system fluctuates is close to the maximally mixed state within each antenna component.

Additionally, we consider simple artificial systems with randomly arranged chromophores, showing that efficiency depends more strongly on the proximity rather than the specific spatial arrangements of the chromophores. The high efficiency of these systems offers an explanation for the fact that different organisms achieve extraordinarily efficient energy transport with greatly differing structures. It also paves the way for a new approach to designing artificial light-harvesting devices.

On Analog Simulation of the Spin-Boson Model in a Trapped Ion Platform

Joseph Broz

Hartmutt Haeffner Lab @ UC Berkeley

Recently several experiments have been performed to simulate dynamical processes generated by Spin-Boson Hamiltonians as proxied by well-controlled, designer quantum systems such as superconducting circuits, NMR and trapped ions. These experiments have been largely motivated by known quantum effects in biological systems — particularly bath-enhanced energy transport.

Most implementations have focused on the simulation of Haken-Strobl-type Hamiltonians limited to the high temperature/ infinite-size regime of the bosonic degrees of freedom. In contrast, previous experimental work in our lab has uniquely focused on a different regime with a finite-temperature, finite-sized and strongly coupled bosonic bath, i.e. a truly “quantum environment.”

In this talk I will review the previous work performed in our lab with an emphasis on the “toolbox” of techniques used to engineer our simulated Hamiltonian. I will also describe several new techniques that we are currently in the process of implementing and briefly discuss what we believe to be the near-term capabilities of our system (e.g. with respect to system size). Finally, time-permitting, I will mention some of the directions that we have begun to explore for future experiments.

Quantum transport on disordered networks - from single to many particles

Andreas Buchleitner

Albert-Ludwigs-Universitaet Freiburg

Quantum Coherence in Light-harvesting Energy Transfer

Jianshu Cao

MIT

Quantum coherence plays a central role in light-harvesting (LH) systems and is examined in the context of energy transfer, spectroscopy, and light absorption: I. Energy transfer is shown to be optimal in LH systems such as in FMO, which can be explained qualitatively by Forster rate [1]. The balance of energy transfer and light-absorption leads to the optimal composition and distribution, which suggests the structural-function correlation in LH organisms. [2] II. Multi-chromophoric (MC) Forster energy transfer theory accounts for spatial delocalization and the correlation between exciton and its environments (i.e., polaron effect). This correlation is fully counted in two recently-developed methods: stochastic path integrals (SPI) [3] and coherent potential approximation (CPA) [4]. For LH2 B850, the emission and transfer are dominated by the dark state at low temperatures. III. The dynamics excited by incoherent sunlight can exhibit transient beatings and steady-state coherence for parameters relevant to photosynthetic complexes.[5] Further, we analyze the efficiency and energy flux of a LH dimer model and show the optimal performance in the intermediate range of temperature and coupling strength, consistent with our understanding of quantum heat engines.[6]

(1) “Efficient energy transfer in light-harvesting systems: Quantum-classical comparison, flux network, and robustness analysis” Wu, Liu, Ma, Silbey, and Cao, *J. Chem. Phys.* 137, 174111 (2012)

(2) “Adaptation in phycobilisome antennas: Influence on the rod length and structural arrangement”. A. Chenu, N. Karen, Y. Paltiel, R. Nevo, Z. Reich, and J. Cao, *J. Phys. Chem. B* 121, 9196 (2017)

(3) “Forster resonance energy transfer, absorption and emission spectra in multi-chromophoric systems. I-III” Moix, Ma, Cao, *JCP* 142 (9), p094108 (2015)

(4) “Construction of multichromophoric spectra from monomer data: Applications to resonant energy transfer” Chenu and Cao, *Phys. Rev. Lett.* 118, 013001 (2017)

(5) “Can natural sunlight induce coherent exciton dynamics?” Olsina, Dijkstra, Wang, Cao, arXiv:1408.5385 (2014); Yang and Cao (2019, preprint).

(6) “Polaron effects on the performance of light-harvesting systems: A quantum heat engine perspective”. D. Xu, C. Wang, Y. Zhao, and J. Cao, *New J. Phys.* 18, 023003 (2016)

Does light harvesting by Anaerobic Photosynthetic Bacteria show any functionally important ‘Strange Quantum effects’?

Richard Cogdell

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This presentation will give an up to date overview of the structure and function of Photosynthetic Bacterial light harvesting complexes. Then it will be discussed whether there is any real evidence that unexpected, quantum effects actually are important in enhancing the overall efficiency of light harvesting in these complexes. One of the big issues in this area is the following. 2DES studies have found long-lived oscillations (long lived in terms of expected electronic coherence times), but what are these oscillations? It will be useful for this discussion if you are able to read these papers before the conference

Engel, G. S. et al. Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems. *Nature* 446, 782-786 (2007).

Duan, H. G. et al. Nature does not rely on long-lived electronic quantum coherence for photosynthetic energy transfer. *Proc. Natl. Acad. Sci. (USA)* 114, 8493-8498 (2017).

Wang, L. et al. Quantum coherences reveal excited-state dynamics in biophysical systems *Nature Rev. Chem.* 3, 477-490 (2019)

Charge-transfer excitons in light-harvesting complexes

Lorenzo Cupellini
University of Pisa

Creation and transport of excitons are the fundamental physical mechanisms at the basis of light harvesting and photosynthesis. Excitons in light-harvesting complexes are delocalized over several chromophores, and this delocalization shapes the optical and photophysical properties of the complexes. Such collective excitations, however, can couple to optically dark charge-transfer excitations, which has been proven both experimentally [1] and computationally [2] for the LH2 complex of purple bacteria. Dark charge-transfer states can only be measured indirectly, through their effect on bright states. Therefore, their energy and properties are extremely difficult to estimate from experiments alone, and their effect on the photophysics of antenna complexes is still unclear.

In this contribution, I will present an atomistic approach to the characterization of charge-transfer states and their effect in antenna complexes, based on a multiscale strategy [3] which combines an accurate quantum chemical description of the chromophores with a classical description of the environment and its response to the excitation. This strategy unveils the role of charge-transfer states in tuning the optical bands of light-harvesting complexes, and lays the groundwork for a more accurate understanding of their photoinduced dynamics.

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Analytical calculation of the 2D spectrum in a vibrationally coupled homodimer based on the polaron transformation

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Experiments on light-harvesting systems have revealed long-lived coherences in electronic 2D spectra, whose origin is not clear at present [1-2]. It has been suggested that these coherences can be explained by a vibrational coupling of the excitonic states. Sophisticated numerical methods have been applied which confirm this conjecture, yet, they lack of an analytical understanding.

The polaron-transformed Redfield equation has been developed in the recent years, which is an analytical approach to describe the electronic molecular dynamics from weak to strong system-bath coupling on equal footing [3-4]. We apply the polaron transformation to analytically calculate the absorption and the 2D electronic spectrum of a homodimer, at which the excitonic states are coupled to local vibrational modes. We show how the absorption spectra and the 2D spectra are composed of contributions of the vibrational modes, the vibronic eigenstates, and multi-time bath correlation functions.

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- [2] H.-G. Duan, *PNAS* 14, no. 32, 8493 (2017)
- [3] D. Xu and J. Cao, *Front. Phys.* 11, 110308 (2016)
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Relaxation Mechanisms of Chromophores Strongly Coupled to Metals in Plasmonic Realizations of Cavity Quantum Electrodynamics

Daniel Finkelstein-Shapiro
Lund University

Recently realizations of cavity quantum electrodynamics (cQED), which relies on strong light-matter coupling, have been carried out using photosynthetic systems. These have reached Rabi splitting energies of around 150 meV, spurring proposals to engineer charge transfer pathways without underlying structural changes. Cavity-chromophore realizations in the optical region have also suggested new ways to harvest light, as well as changing the ground state reactivity of molecules. They have added a new branch of possibilities for storing solar energy or catalyzing reactions. The synthetic realizations have been accompanied by advanced spectroscopies to characterize this strong light-matter coupling.

Plasmonic-based cQED has opened a version of experiments that are i) no longer limited to dimensions equal or greater than the wavelength of light and ii) easily scalable via wet synthesis methods. Furthermore, plasmons can act very efficiently as antennas and promote chemistry with hot electrons. Plasmonic cQED of light harvesting complexes has also been successfully demonstrated with Au. However, to exploit to the fullest the possibilities offered by this new arrangement, a thorough understanding of the energy levels, their nature and their dynamics is needed.

We investigate the linear and third-order optical response (UV-vis and two-dimensional electronic spectroscopy) of a model system consisting of Ag plasmons covered by J-aggregates, both theoretically and experimentally. We show that the energy levels are not only determined by the electronic coupling but also by the strength of the dissipation. A detailed analysis of the dynamics reveals the relative relevance of the mechanisms from the J-aggregate and from the metal towards the relaxation of the photoexcitation of the hybrid. Our work provides a solid framework to decide to what extent we can modify transitions in more complicated photosynthetic organisms and whether these modifications can be useful for photocatalysis or related applications.

Biologically-inspired quantum-enhanced photocells

Erik Gauger
Heriot-Watt University

TBC

Interplay of multiple environments in open quantum systems

Giulio Giuseppe Giusteri
Department of Mathematics, University of Padua

Open quantum systems can interact with different kinds of external systems. Models of such baths aim at reducing the effective degrees of freedom that need to be followed in detail to understand the dynamics of the system. Two important classes of environments are thermal baths and probability-absorbing ones. For the latter, one can often introduce a non-Hermitian Hamiltonian to take into account decaying states. Moreover, when a system is coupled to more than one bath, a common approach entails an additive superposition of the effects of each bath. The limits of validity of such approximations will be explored and the interplay and competition between disorder or noise and the presence of a probability-absorbing environment will be analyzed in paradigmatic models of light-harvesting complexes.

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Coherent spectroscopy of electron transfer processes

Thorsten Hansen
University of Copenhagen

Coherent multi-dimensional spectroscopy enables direct measurement of the coherences associated with dynamic processes in photochemical systems. Most experiments have reported on energy migration, often in photosynthetic antenna systems. A few recent papers discuss electron transfer. Based on a Keldysh contour formulation of four-wave mixing spectroscopy, recently extended to include molecular vibrations, we discuss theoretically the coherent features of the prototypical electron transfer – Marcus electron transfer. The quantum coherences of electronic processes provide a new window into mechanistic understanding. These prospects will be discussed.

Exciton transport in molecular aggregates imaged by ultrafast microscopy

Libai Huang
Purdue University

Long-range exciton transport is a key challenge in achieving efficient solar energy harvesting in both organic solar cells and photosynthetic systems. However, exciton transport is not well understood in the intermediate regime where many molecular aggregates and photosynthetic antennas belong. Excitons are delocalized over part of the system and the exciton delocalization (coherent) length is defined by the competition between intermolecular coupling strength and disorder and transport has mixed coherent and incoherent characteristics. Within each delocalized segment the excitation energy propagates ballistically. There currently lacks an experimental tool to directly characterize exciton transport in space and in time to elucidate mechanisms. To address this challenge, we develop transient absorption microscopy as a direct tool to visualize exciton diffusion in tubular molecular aggregates with 200 fs time resolution and 50 nm spatial precision. These measurements provided exciton diffusion constants of 3-6 cm²-1 for these aggregates, which were 3-5 times higher than a theoretical lower bound for pure incoherent hopping. Simulation showed that the states crucial for exciton transport are delocalized over < 10 molecules, suggesting that coherent effects play a role despite relatively weak delocalization.

How important is the site-dependence of the coupling of chromophores to the environment in FMO?

David Hutchinson
University of Otago

Recently we have shown that the site-dependent variation of the coupling to the surrounding protein scaffold (environment) of the chromophores in the Fenna-Matthews-Olsen complex is optimised for the efficiency of exciton energy transfer. We further investigate the role of coherence in this optimisation and, particularly, the importance of certain vibronic modes. Implications for synthetic systems for light harvesting will also be discussed.

Insights into Photosynthetic Light Harvesting from 2D Femtosecond Spectroscopy

David Jonas
University of Colorado

In photosynthesis, antenna proteins harvest light and efficiently transfer the electronic excitation energy to reaction center proteins that initiate chemical transformations. The standard Forster framework for understanding electronic energy transfer is based on the adiabatic approximation of slow vibrations and fast electrons. Femtosecond two-dimensional spectra of many antenna proteins exhibit quantum beats with signatures indicative of nonadiabatic vibrational-electronic coupling. The longest lived beats originate from a nonadiabatic enhancement of Raman pathways for excitation of delocalized vibrations on the electronic ground state. These vibrations characterize the initial coupling between excited states and reveal nested funnels in which the adiabatic approximation fails spectacularly over entire vibrational coordinate spaces, driving energy transfer outside the Forster framework. The nonadiabatic dynamics in nested funnels is efficient at low vibrational energies and does not require high vibrational velocities or conical intersections.

Structure-function relationships of tubular molecular aggregates

Jasper Knoester
University of Groningen

Self-assembled molecular aggregates of dye molecules are interesting from the perspective of optical functionality controlled at the nanometer scale. In this context, tubular aggregates have attracted particular attention over the past decade. Such systems occur naturally, in particular as light-harvesting aggregates in the chlorosomes of green sulphur bacteria [1,2], while a number of synthetic analogues have been created and studied [3-6]. The optical functionality of molecular aggregates is dictated by the energy structure and dynamics of Frenkel excitons, the collective excitations of a number of molecules, which sensitively depend on the details of the molecular packing in the aggregate and the interactions of the molecules with the aggregate's environment. The packing in turn sensitively depends on the subtle interplay between many types of interactions that define the self-assembly, for instance π -stacking, surfactant interactions, and hydrogen bonds. Generally, it is impossible to directly image the details of the packing and little is known about the fluctuations of the packing in space and in time. This leaves many questions concerning the structure-function relationships of molecular aggregates unanswered. In this talk, I will address structure and structural inhomogeneity of tubular molecular aggregates and their impact on the optical functionality of these systems. In the first part, I will report on single-particle excitation fluorescence spectroscopy experiments on individual tubular ZnChl aggregates and their analysis in terms of structural variations [7]. It is shown that the spectra of individual aggregates show surprisingly strong variations, which may be explained in terms of relatively small fluctuations in the packing of the aggregates, where variation both between and within aggregates is observed. In the second part, I will report on the results of multiscale modeling of the structure of C8S3 double-walled molecular aggregates [8]. These aggregates exhibit a complicated optical spectrum with a multitude of excitonic peaks that show strong polarization properties. We show that the details of this spectrum can be explained using a multiscale modeling method in which molecular dynamics simulations of the structure, translation of the molecular dynamics structure into a Frenkel exciton Hamiltonian, and comparison of the optical spectrum calculated from this Hamiltonian with experiment are used to discover the most likely packing. The results obtained are at odds with previous results of molecular modeling. Finally, if time allows, I will address energy transport in (tubular) molecular aggregates [9-11].

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Do Vibrational Modes Assist Energy Transfer? Experimental Evidence in Quantum Dot Dimers

Yuval Kolodny¹, Shira Yochelis¹, Sergei Remennik¹, Carlo Dibenedetto, Marinella Striccoli, Yossi Paltiel¹

¹The Hebrew University of Jerusalem

Signatures of long-lived room temperature quantum coherence in light-harvesting complexes were measured in recent years¹. It has been suggested that the chromophores' environment, the protein, has vibrational modes that allow to bridge over the energy gap between electronic levels and allow stronger pigment-pigment coupling^{2,3}. Since protein-pigment complexes have huge number of degrees of freedom, it is hard to separate variables and compare results to theoretical predictions of noise-assisted coherence. To overcome this challenge, we fabricated a simple and controllable biomimicry system which allows to examine the effect of environment's vibrations on the energetic coupling in a simple donor-acceptor system. We use CdSe quantum dots in two sizes and link them with different organic molecules to form dimers in solution, to study coupling properties. Similar linkers are used, with identical lengths and head groups, that only differ in one atom at the center of their alkyl chain. The additional vibrations that arise from the replacement of one of the carbon atoms correspond to the energy gap between the two nanoparticles that act as donor and acceptor. Explicit differences are seen in spectroscopic measurements, which can shed light on the importance of the vibrations to the coupling, and support the hypothesis that electronic-vibrational coupling drives both the observed coherences and rapid energy transfer.

Are there optical communication channels in the brain?

Sourabh Kumar

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Given that many fundamental questions in neuroscience are still open, it seems pertinent to explore whether the brain might use other physical modalities than the ones that have been discovered so far. In particular it is well established that neurons can emit photons, which prompts the question whether these biophotons could serve as signals between neurons, in addition to the well-known electro-chemical signals. For such communication to be targeted, the photons would need to travel in waveguides. We show, based on detailed theoretical modeling, that myelinated axons could serve as photonic waveguides, taking into account realistic optical imperfections [1]. We propose experiments, both in vivo and in vitro, to test our hypothesis. We discuss the implications of our results, including the question whether photons could mediate long-range quantum entanglement in the brain.

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New horizons in quantum biology: Emergence and coherence in living matter

Philip Kurian

Howard University

The formation of supramolecular complexes, biological polymers, and aqueous topological domains from fundamental constituents and interactions involves a delicate interplay between forces of disorder (chaos) and order (logos) within the living organism. Fundamentally quantum behaviors including electron dispersion and superradiance have risen to the surface of our nano-, meso-, and macroscopic perception within the open systems of biology. Extended van der Waals effects and optically pumped phonon condensation in protein aggregates reveal collective, cooperative, and coherent emergent properties that may be targeted for diagnostic and therapeutic purposes. Perhaps most remarkably, the aqueous environment—matrix of life—challenges purely Brownian descriptions and conspires with living matter in the precise orchestration of nonequilibrium biomolecular processes in the cell.

Novel Quantum and Bio-inspired Designs for Photon Detection

Francois Leonard

Sandia National Laboratories

Photodetection plays a key role in basic science, technology, and biology, with exquisite performance having been achieved down to the single photon level in biological and synthetic systems. Further understanding and improvements in photodetection would open new possibilities across a broad range of scientific disciplines and enable new types of applications. However, it is still unclear what is possible in terms of ultimate performance, and what properties are needed for a photodetector to achieve such performance. In this presentation, I will discuss recent theoretical and experimental work to address this question. On the theoretical front, we present a new general framework to establish the fundamental properties of photodetectors from a fully quantum perspective, and show what basic features are needed to achieve high performance. Novel photodetector designs emerge from these considerations, and we present initial experiments to test these new designs. Interestingly, some of the new photodetector features are similar to those found in biological systems.

System-bath entanglement and thermodynamic behaviour of Frenkel exciton systems

Tomas Mancal

Charles University

We present a systematic re-evaluation of the role of entanglement in excitation energy transfer (EET) in photosynthetic light-harvesting antennae. We discuss examples of entangling and non-entangling interactions between quantum systems. It is demonstrated that non-entangling interactions between electronic degrees of freedom (DOF) and the protein bath render the dynamics of a Frenkel exciton system equivalent to the dynamics of a set of coupled classical harmonic oscillators interacting with a classical bath. Such a system does not exhibit preferential down-hill energy transfer observed in experiments and predicted by quantum theory of energy transfer. Consequently, real photosynthetic systems excited by light exhibit an entangled state of the bath and electronic DOF. Thermodynamic behaviour, such as the downhill energy transfer, is identified as a direct consequence of the system-bath entanglement, which can be demonstrated to last for as long as the system is excited.

Harnessing symmetry to control quantum transport. Applications to biological compounds.

Daniel Manzano

University of Granada

Symmetry is a key concept in Physics. In this poster, we discuss how to harness symmetry to control transport and statistics in open quantum systems. Using tools from open quantum systems and large deviation theory, we show that symmetry-mediated control of transport is enabled by a pair of twin dynamic phase transitions in current statistics, accompanied by a coexistence of different transport channels [1]. Furthermore, we will discuss the importance of symmetries in the study of the conditional probability of non-equilibrium events [2]. We will also discuss how these effects allow the control of energy transport by the use of magnetic fields [3].

Finally, as symmetry is ubiquitous in Nature, we will discuss the importance of this effect in quantum compounds under the effect of an environment.

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Impact of phonon-mediated excitonic interaction on absorption spectra in Photosynthesis

Andrea Mattioni

Ulm University

Typical approximations for the determination of the parameters required to describe excitonic dynamics from optical experiments rely only on the low frequency part of the spectral density of the phonon environment and few vibrations which may have dynamical significance, based on the assumptions that vibrational modes near resonance with excitonic transitions may affect the excitonic dynamics. We show with exact methods (time-dependent density matrix renormalization group and hierarchical equations of motion) that the conventional approach to explain optical experiments neglects environmental contributions leading to a significant renormalization of the excitonic splitting that result in a systematic under (over) estimation of small, $\sim < 400 \text{ cm}^{-1}$ (large, $\sim > 400 \text{ cm}^{-1}$), excitonic couplings in photosynthetic harvesting structures. We propose an accurate solution using the typical techniques based upon the explicit inclusion of zero and one-phonon Hilbert spaces of all the vibrations coupled to the electronic transitions.

Macroscopic coherence as an emergent property in molecular nanotubes.

Francesco Mattiotti

UCSC, Italy

Nanotubular molecular self-aggregates are characterized by a high degree of symmetry and they are fundamental systems for light-harvesting and energy transport. While coherent effects are thought to be at the basis of their high efficiency, the relationship between structure, coherence and functionality is still an open problem. We analyse natural nanotubes present in Green Sulphur Bacteria. We show that they have the ability to support macroscopic coherent states, i.e. delocalized excitonic states coherently spread over many molecules, even at room temperature. Specifically, assuming a canonical thermal state we find, in natural structures, a large thermal coherence length, of the order of 1000 molecules. By comparing natural structures with other mathematical models, we show that this macroscopic coherence cannot be explained either by the magnitude of the nearest-neighbour coupling between the molecules, which would induce a thermal coherence length of the order of 10 molecules, nor by the presence of long-range interactions between the molecules. Indeed we prove that the existence of macroscopic coherent states is an emergent property of such structures due to the interplay between geometry and cooperativity (superradiance and super-transfer). In order to prove that, we give evidence that the lowest part of the spectrum of natural systems is determined by a cooperatively enhanced coupling (super-transfer) between the eigenstates of modular sub-units of the whole structure. Due to this enhanced coupling strength, the density of states is lowered close to the ground state, thus boosting the thermal coherence length. As a striking consequence of the lower density of states, an energy gap between the excitonic ground state and the first excited state emerges. Such energy gap increases with the length of the nanotube (instead of decreasing as one would expect), up to a critical system size which is close to the length of the natural complexes considered.

Energy conversion efficiency in the cell and non-trivial quantum effects in the work of molecular machines

Aleksei Melkikh

Ural Federal University, Yekaterinburg, Russia

As it known, the energy in the cells is converted with high efficiency. This applies, for example, photosynthesis, as well as the transport of substances through the cell membrane and inside it. However, the reasons for such high efficiency remain unclear. In particular, the papers (Melkikh, 2014, Melkikh, Meijer, 2018) showed that the work of molecular machines leads to a contradiction, since the known interaction potentials between atoms do not allow these machines to be effective. This contradiction is formulated in the form of the “generalized Levinthal’s paradox”. In this paper, we continue the consideration of the work of intracellular molecular machines. In particular, the work of a light-harvesting complexes of photosynthetic organisms, as well as intracellular recognition and sorting of proteins, is considered. Quantum models of these processes are constructed. It is shown that quantum long-range effects can provide high efficiency of molecular machines.

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Physical nanoscale models for biological and bio-inspired structures

Lev Mourokh

Physics Department, Queens College of the City University of New York

Living objects at the nanoscale can be viewed as molecular complexes, whose dynamics is often controlled by the transfer of single charges or single-photon absorption events. In many senses, it is similar to the principles of operation of semiconductor nanostructures and elements of molecular electronics. Correspondingly, well-established methods of condensed matter and statistical physics can be applied. In this talk, I address proton-pumping complexes and proton-driven nanomotor of the thylakoid and mitochondria membranes. These systems convert the energy obtained from the light or food to the proton gradient across the membrane, to the mechanical rotation of the nanomotor, and, finally, to the energy of chemical compounds. We propose simple physical models for these complexes which not only allow the quantitative description but can inspire the implementations in nanoelectronics as well. I also discuss our recent efforts to create a hybrid artificial-natural structure by attaching mitochondrial proton-pumping complexes to functionalized graphene oxide.

Long Distance Electron Transfer in Chiral Bio-Molecules

Vladimiro Mujica

Arizona State University

Electron transfer reactions are fundamental processes in biology. A long-standing issue in this field is to understand why a tunneling mechanism, which implies an exponentially decaying behavior as a function of molecular length, is so pervasive in many bio-molecules. Furthermore, these tunneling processes are very efficient over long distances, sometimes tens of angstroms, something that contradicts experimental evidence about many other chemical reactions where tunneling decays very rapidly.

In this presentation we argue that the process of electron spin polarization that is associated with electron transport in chiral molecules, is essential to understand the survival of long-distance tunneling and the preservation of coherence, which is usually perturbed by electron-phonon interaction. Both phenomena, i.e. long-distance tunneling and the preservation of coherence, are intimately related by the fact that electron spin polarization, associated with spin-orbit interaction in systems with space-inversion and time reversal broken symmetries, cannot be reversed by electron-phonon interaction due to the fact that acoustic and optical phonons do not carry spin angular momentum. We analyze the implications of our theory in light of recent experimental evidence about electron transfer in proteins, DNA, and polypeptides.

Ultrafast spectroscopy and imaging of molecules with x-ray pulses and quantum light

Shaul Mukamel

University of California, Irvine

Ultrafast nonlinear x-ray spectroscopy is made possible by newly developed free electron laser and high harmonic generation sources. The attosecond duration of X-ray pulses and the atomic selectivity of core X-ray excitations offer a unique combination that can monitor elementary molecular events with high spatial and temporal resolution. Applications of these techniques to spectroscopy and imaging of molecules will be presented. X ray sum frequency generation, circular dichroism and time- and frequency-resolved ultrafast diffraction of noisy X-ray pulses will be discussed. Quantum light opens up new avenues for spectroscopy by utilizing parameters of the quantum state of light as control knobs and through the variation of photon statistics by coupling to matter. When a molecule interacts with an external field, the phase information is imprinted in the state of the field in a detectable way. Nonlinear optical signals induced by quantized light fields and entangled photon pairs will be discussed. Combined time and frequency resolution not possible by classical light can be achieved. A novel quantum diffraction-based imaging technique whereby one photon of an entangled pair is diffracted of a sample and detected in coincidence with its twin is presented. Imaging with weak quantum fields is possible, avoiding damage to delicate biological samples.

Robustness of optimal transport in disordered interacting many-body networks

Adrian Ortega

Universidad de Guadalajara

We present an account on transport in disordered interacting many-body efficient networks. After reviewing some results on the efficiency conditions for these types of networks, we will focus on robustness of transport in such networks. Remarkably, our model shows transport efficiency which is always better than the well-known environment assisted transport, despite of the fact that disorder and decoherence are present in the model.

Sun-light pumped lasing with dimers

Nicola Piovella

Università degli Studi di Milano

Molecular aggregates exposed to concentrate Sun light may exhibit population inversion and lasing. We show that a dimer in the single-excitation manifold and under the action of Sun light behaves as a three-levels system exhibiting population inversion. By a simple rate equations model, we describe the conditions for lasing operation of a collection of dimers in an optical cavity. This result may pave the way to a new class of bio-inspired Sun-light pumped lasers. Furthermore, the extension from single dimers to rings of molecules could superradiantly enhance the lasing process.

Local Quantum Uncertainty (subsystem discord-like correlations) as a resource for quantum transport efficiency in chromophore networks of light harvesting systems

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Green sulfur bacteria is a photosynthetic organism whose light-harvesting complex accommodates a pigment-protein complex called Fenna-Matthews-Olson (FMO). The FMO complex functions as a quantum wire that, with exceptional efficiency, transfers excitation energy from the chlorosome antenna to the reaction center. During energy transport, the FMO complex sustains quantum coherence and quantum correlations between the electronic states of spatially separated pigment molecules (chromophores). In the FMO protein a functional role for quantum coherence manifests in an interplay between coherent dynamics of the system and incoherent effects of environment that assists quantum transport efficiency, a phenomenon known as environment-assisted quantum transport (ENAQT). In this work we use the characteristic behaviour of efficiency as a function of the dephasing rate in the ENAQT regime to make an argument of accumulated quantum correlations being a useful resource that support electronic energy transfer through the FMO chromophores network. Specifically, we introduce the Local Quantum Uncertainty (LQU), a subsystem discord-like quantifier of quantum correlations, to calculate non-classical correlations between all subsets of one chromophore with n-chromophores or subsets. The flexibility of LQU metric allows to identify the specific subsystems whose quantum correlations increase simultaneously with transfer efficiency. We find that specific quantum correlations, LQU between chromophore 3 and the rest of the network and LQU between chromophore 3 and chromophore 4, have a strong functional relation with transport efficiency (measured by population transferred to the sink) in the ENAQT regime. These findings represent preliminary evidence that a photosynthetic organism might be taking advantage of specific quantum correlations resource to perform efficient energy transport. Thanks support project UNAM DGAPA PAPIIT IN105717

Quantum Coherence in Photosynthetic Reaction Centers and What to Do with It

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Photosynthesis is the fundamental biological process by which solar energy is converted into fuel in four basic steps: light harvesting, charge separation, water splitting and fuel generation. Photosynthesis therefore holds the key to the efficient use of solar energy by humans using abundant and renewable materials. At the heart of Photosynthesis, the reaction center pigment-protein complexes perform charge separation with near unity quantum efficiency despite their highly disordered energy landscape; they realise the first solar energy conversion step in photosynthesis by transforming sunlight to electrochemical energy. To achieve this amazing feat, the reaction centers exploit The Quantum Design Principles of Photosynthetic Charge Separation [1], complementary and interrelated solutions to ensure rapid forward and irreversible transfer of energy and electrons within a disordered and fluctuating environment. Therefore, these principles provide a guide for the rational design and construction of systems able to transfer energy and electrons with high efficiency and in the right direction. During my talk I will focus on the most sophisticated strategy: the use of quantum coherence in plant and bacterial reaction centers where vibronic [2] and both electronic and vibrational [3] coherence play a role, respectively. In addition, I will present my view on how to implement quantum coherence in bio-inspired systems with the potential to perform efficient energy and electron transfer, with the final goal of achieving the cost-effective conversion of solar energy to fuel.

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Indication of quantum mechanical electron transport in substantia nigra tissue from conductive atomic force microscopy tests

Chris Rourk

independent researcher

Electron transport across a 40 micron length of a disordered array of ferritin has been demonstrated in an electronic device. [1] In addition, neuromelanin and ferritin in dopamine neurons of the substantia nigra pars compacta (SNc) have a distribution and density that is similar to disordered arrays of pi-conjugated polymers and quantum dots in photovoltaic devices, which have been experimentally shown to conduct electric energy at room temperature using quantum mechanical electron transport mechanisms. [2] An overview of these devices will be provided, as well as a discussion of how such electron transport could assist with the generation of action potentials in SNc neurons. Results from conductive atomic force microscopy tests that were performed on human SNc tissue at room temperature will then be reviewed. These test results appear to provide evidence of quantum mechanical electron transport from ferritin and neuromelanin at levels that may be sufficient to cause or contribute to generation of action potentials. [3]

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Dissipation-Assisted Matrix Product Factorization

Alejandro D. Somoza

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Charge and energy transfer in biological and synthetic organic materials are strongly influenced by the coupling of electronic states to a highly structured dissipative environment. Non-perturbative simulations of these systems require a substantial computational effort and current methods can only be applied to large systems if environmental structures are severely coarse-grained. Time evolution methods based on tensor networks are fundamentally limited by the times that can be reached due to the buildup of entanglement in time, which quickly increases the size of the tensor representation, i.e., the bond dimension. In this work, we introduce a dissipation-assisted matrix product factorization (DAMPF) method that combines a tensor network representation of the vibronic state within a pseudomode description of the environment where a continuous bosonic environment is mapped into a few harmonic oscillators under Lindblad damping. This framework is particularly suitable for a tensor network representation, since damping suppresses the entanglement growth among oscillators and significantly reduces the bond dimension required to achieve a desired accuracy. We show that dissipation removes the "time-wall" limitation of existing methods, enabling the long-time simulation of large vibronic systems consisting of 10-50 sites coupled to 100-1000 under-damped modes in total and for a wide range of parameter regimes.

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Hidden dynamics in stochastic processes revealed by full counting statistics

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Single-molecule spectroscopy allows nowadays the study of biochemical reactions of individual molecules in real time. Usually, only a small part of the molecule's reaction trajectory can be observed. For example, the detection of a fluorescent product molecule reveals the chemical but not the conformational molecular dynamics. However, the part not directly observable can be revealed in the statistical fluctuations of the measured data. Here, we explain how to use the second- and higher-order statistical cumulants to systematically deduce information about hidden dynamics. We concentrate on the example of a magnetic nanoparticle where electronic dynamics are visible in experiment in contrast to the quantum-mechanical spin dynamics.

Revealing the Ultrafast Excitation Energy Transfer Network in LHCII

Howe-Siang Tan

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Light-harvesting complex II (LHCII), the peripheral antenna of Photosystem II (PSII), is the most abundant antenna complex in the biosphere. Understanding how the light induced excitation travels within the complex and to the PSII reaction centre are therefore of strong interest to scientists. Coherent multidimensional optical spectroscopy has been shown to be an excellent tool to elucidate the various processes of the photosynthetic machineries [1,2]. We have used various tools such 3rd order 2D electronic spectroscopy (2DES) and 5th order 3D electronic spectroscopy (3DES), to study the room temperature excitation energy transfer (EET) dynamics [3,4,5] within the Chl b and Chl a manifolds of solubilized LHCII trimers. We also studied the equilibration dynamics within the Chl a band and reveal uphill and downhill energy transfer dynamics between different Chl a exciton states [6]. Here, we report our recent studies in temperature dependent 2DES to better understand the equilibration dynamics of the Chl a manifold of LHCII. We see clear evidence that at lower temperature, the energy transfer processes are slower, and that the magnitude of uphill EET is decreased [7]. We also performed a phenomenological analysis of 2DES spectra at 77K to map out the excitonic energy transfer network [8]. Our analysis shows that the three lowest energy terminal exciton states are weakly coupled to each other. The excitation energy equilibration between the three termini was found to be independent of the initial excitation conditions, which may be a crucial design for the light-harvesting complexes to ensure the energy flow under different light conditions and avoid excitation trapping. Theoretical simulations at the Hierarchical Equation of Motion (HEOM) level were also performed to analyse the LHCII EET network [9].

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Calculation of coherences in Förster and modified Redfield theories with applications in spectroscopy

Anton Trushechkin

Steklov Mathematical Institute of Russian Academy of Sciences

Förster and modified Redfield theories play one of the central roles in the description of excitation energy transfer in biological light-harvesting complexes. However, in the present state, these theories describe only the dynamics of populations of local electronic excitations or delocalized exciton eigenstates, respectively, i.e., the diagonal elements of the density matrix in the corresponding representation. They do not give prescription for propagating the off-diagonal elements of the density matrix (coherences). This is commonly accepted as a limitation of these theories. In this talk, we present formulas for the dynamics of the coherences in the framework of Förster and modified Redfield theories and, thus, remove this limitation. We adopt a rigorous method based on the projection operator formalism.

We apply the derived formulas for coherences to description of excitation energy transfer in light-harvesting complexes and calculate spectroscopic responses within modified Redfield theory with exciton coherences.

The talk is based on the paper A.S. Trushechkin, Calculation of coherences in Förster and modified Redfield theories of excitation energy transfer, *J. Chem. Phys.* 151(7), 074101 (2019), arXiv: 1902.00554 and some new results.

Models and Mechanisms of Reversible Regulation of Photosynthetic Light Harvesting

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Photosynthesis is one of the most important processes performed by living beings that sustain life on our planet. At low light, it exhibits an unprecedented quantum efficiency: over 90% of the absorbed photons reach reaction center and initiate charge separation. However, at strong sunlight the photosynthetic light-harvesting antenna switches into a photoprotective mode, thus avoiding over-excitation and the concomitant photodamage. On a molecular level, safe dissipation of the excess absorbed light energy occurs via non-photochemical quenching (NPQ)—the feedback mechanism that reversibly activates within seconds or minutes in response to the naturally occurring illumination variations. First experimentally observed as chlorophyll (Chl) fluorescence (FL) quenching in isolated thylakoids, NPQ was later detected in the intact isolated chloroplasts and leaves. However, complex heterogeneous organisation and multiple processes, simultaneously occurring within the thylakoid membrane, have been strongly impeding the directional study of the natural NPQ under in vivo conditions. Instead, artificially produced photosynthetic antenna, like aggregates of purified solubilised major light-harvesting complexes (LHCII) [1] or natural membranes-mimicking liposomes with the embedded LHCII [2], have been widely and deeply surveyed. Nevertheless, it has never been shown directly that FL quenching observed in these artificial systems underlies natural NPQ in thylakoid membranes. Here we present high-resolution time-resolved FL measurements on the dark and light-adapted thylakoid membranes, performed over a broad temperature range. We show that their spectral response perfectly matches that observed in our recent study on the artificial LHCII aggregates [1], thus demonstrating for the first time that the latter in vitro system preserves all the properties of natural photoprotection. The model describing the mechanism of NPQ based on these fluorescence data and on the single molecule spectroscopy measurements of liposomes [2] and mutants of the light-harvesting complexes [3] is formulated and discussed. The regulation ability is mainly attributed to specific interaction between Chl and carotenoid molecules, while the red fluorescence bands visible by lowering temperatures and at specific environmental conditions are due to charge transfer states between Chl molecules.

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Environment assisted quantum transport – universality, disorder and interactions

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Environment assisted quantum transport (ENAQT) is the situation in which coupling a quantum system to an external environment results, somewhat counterintuitively, in the enhancement of transport. ENAQT was postulated to play an important role in photosynthetic energy transfer, and was recently demonstrated in artificial quantum systems. We introduce a universal mechanism for ENAQT, based on the observation that the environment tends to uniformize the density of quantum particles along the network [1]. This mechanism explains not only why ENAQT happens, but also under which conditions. I will discuss the role of disorder, and demonstrate that the mechanism is robust against disorder and works even when disorder is extremely strong. On the fly we demonstrate a unique situation where static disorder by itself can assist transport, a unique situation which can now be realized experimentally. Finally, we discuss how interactions and non-linearity affect ENAQT, and may lead to the reverse effect, of environment-hampered quantum transport.

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Environment-Assisted Quantum Photo-Protection in Interacting Multi-Excitons Transfer Complexes

Elinor Zerah

Ben-Gurion university

Transport of excitons through molecular wires is a unique example where the interplay between quantum, environmental and geometrical effects, leads to surprising phenomena such as “environment-assisted quantum transport”, (ENQAT), where, counterintuitively, the environment interrupts quantum transport in a way that enhances the transfer efficiency. Suggested as an active mechanism in photosynthesis, ENAQT has been a focus of intense theoretical study. Most previous studies consider a system occupied by a single exciton, working under the assumption that weak coupling cannot excite more than one exciton. In this work, we show that this is not the case, and even weak excitations can lead to multiple-exciton generation. We then consider the transport of two excitons, which can interact between them. We show that in addition to ENAQT, the system can exhibit environment assisted quantum photo-protection, namely the situation in which increasing the external excitation leads to a reduction in exciton transport. The effect, which we show is due to the interplay between environmental effects, exciton interactions and network geometry, may be related to actual photo-protection observed in living photosynthetic systems.

Collective motion of THz phonons in living matters

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The collective properties in both physical and biological systems are of importance for understanding many peculiar phenomena, e.g., superefficient energy transfer in photosynthesis and giant dipole moments in biomolecules. The studies of these phenomena imply a significant role of quantum coherence. In this regard, Fröhlich suggested a condensation of energy at the lowest mode of polar vibrations once the external energy supply exceeds a threshold. For a full understanding of the Fröhlich condensate one needs to go beyond the mean field level to describe critical behavior as well as quantum fluctuations. In this presentation, we will explain our recent work on the out-of-equilibrium condensate of sub-THz phonons [1]. We developed a quantum statistical theory for such system, revealing its critical behavior. The nonlinearity is shown to be essential for achieving the phonon-number distribution that evolves with energy pump, from quasi-thermal to the super-Poissonian statistics. This yields an analogy to Scully-Lamb theory of the laser [2]. We further show the linewidth narrowing as a spectroscopic feature associated with the phonon condensate. This indicates a long-lived coherence, i.e., cooperative behavior. Finally, we discuss bovine serum albumin and lysozyme [3], as experimentally feasible candidates for observing such out-of-equilibrium condensate through Raman or infrared spectroscopy.

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Posters

Vibrationally assisted quantum optical effects in collective systems

Will Brown

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We investigate two quantum collective effects which can be used to improve the classically predicted performance of light-harvesters. Dark state protection relies upon rapid phonon relaxation after optical excitation to populate a state from which optical recombination is not possible. This effect, which was first predicted in dimers, has been extended to multi-chromophore dark state protection in biologically-inspired ring structures. Our calculations have shown that one can drop the ordered geometry of the ring, and phonon relaxation will still enable random setups of absorbers to hold on to single excitons for a thousand times longer than a single absorber. The fact this ‘darkness’ can be expected both in ordered geometries, as well as random ones, offers validity to the idea that it could be exhibited by biological systems. We have looked at the recently published structure of iron stress induced protein A as a potential candidate for phonon assisted darkness being utilised by real photosynthetic complexes in nature. Instead of suppressing emission, collective effects can also be used to enhance absorption. Guide-slide superabsorption, a proposed effect for artificial light-harvesters, relies on a photonic bandgap environmental control, as well as vibrational relaxation to keep a collection of N optical dipoles in a superabsorbing state, where the optical absorption rate is proportional to N^2 . We use a biologically inspired ring of skewed dipoles as an example guide-slide superabsorbing system, using it to demonstrate the superlinear scaling of power produced per site, which we measure with a quantum heat engine approach. The final system we consider is a lasing dimer. By controlling the relative positions and orientations of two molecular absorbers we investigate if it is possible to achieve population inversion in the system. We then consider scaling up the system size and coupling to field in a cavity.

Predicting and Controlling Entangled Two-Photon Absorption in Diatomic Molecules

Ryan Burdick

University of Michigan

The use of nonclassical states of light to probe organic molecules has received great attention due to the possibility of providing new and detailed information regarding molecular excitations, as well as enhancing nonlinear optical responses through virtual electronic state interactions.[1-4] In order to predict molecular excitations with nonclassical light, we investigated the details of the state-to-state parameters important in calculating the contribution of particular transitions involved in the entangled two-photon absorption process for diatomic molecules.[5] Using quantum chemical calculations of energy levels and transition dipole moments, we estimated in a highly accurate manner the nonmonotonic behavior of the entangled two-photon absorption cross-section. Modeling of this nonmonotonic behavior may allow us to predict and control the nonlinear absorption of a molecule. Using parameters unique to entangled two-photon absorption (in comparison to classical two-photon absorption), we can selectively enhance a molecule’s nonlinear absorption or make the molecule transparent without changing the incident light’s frequency.

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Wigner-Yanase skew information to characterize quantum correlations in subsets of chromophores in light-harvesting complexes

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Green sulfur bacteria is a photosynthetic organism whose light-harvesting complex accommodates a pigment-protein complex called Fenna-Matthews-Olson (FMO). The FMO complex sustains quantum coherence and quantum correlations between the electronic states of spatially separated pigment molecules as energy moves with nearly a 100

We present a method based on the quantum uncertainty associated to local measurements (measured via the Wigner-Yanase skew information) to quantify discord-like quantum correlations between two subsystems where one is a qubit and the other is a qudit.

We implement the method by calculating skew information, concurrence, and coherence between subsystems of pure and mixed states represented by the eigenstates and by the thermal equilibrium state determined by the FMO Hamiltonian. Three partitions of the seven chromophores network define the subsystems: one chromophore with six chromophores, pairs of chromophores, and one chromophore with two chromophores.

Implementation of the present approach allows us to characterize quantum correlations that had not been studied before, identify the most quantum correlated subsets of chromophores, and determine that, in the strongest associations of chromophores, the skew information is a monotonically increasing function of the coherence.

The Wigner-Yanase skew information is more general than entanglement measures and easier to compute than direct definition of quantum discord.

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Investigations on Organic Molecules with Classical and Entangled Photon Spectroscopy

Audrey Eshun

University of Michigan

Quantum entangled photons have been studied over the years because of their potential for novel applications in imaging, microscopy and quantum computing. Furthermore, the use of these nonclassical states of light in spectroscopy has given rise to the opportunity to provide new information about the molecular excitations and transitions within organic molecules.[1-3] In this study, investigations of the optical effects in thienoacene chromophores with different central atoms were carried out.[4] These chromophores provide a basis for the comparison of the linear, two-photon, and entangled two photon properties in organic molecules with varying degree of dipolar or quadrupolar character. Linear absorption and emission as well as time-dependent density functional theory calculations were carried out for the chromophores investigated. Measurements of the classical two-photon absorption (TPA), entangled two-photon absorption (ETPA) as well as entangled two-photon fluorescence were experimentally carried out for the four chromophores. Electronic structure calculations were utilized in order to provide estimates of the classical two photon absorption coefficients. The results of the measured entangled two photon cross-sections were compared with theoretical estimates for the molecules investigated. This work shows that the dipole (transition or permanent) pathway can have an effect on the trends in the entangled photon absorption process in dipolar organic

chromophores. This study helps predict the properties of the entangled two photon effect in chromophores with different dipolar and quadrupolar character.

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Delocalization length in the context of biological exciton transfer processes

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Exciton delocalization in natural light harvesting structures is a well-known phenomenon, recognised as an important factor in photosynthetic excitation energy transfer efficiency. Standard attempts to define delocalization length within the dynamic environment of a protein, and over biological timescales, results in a single real number or an integer range of pigments. We argue that such a notion of delocalization is not particularly informative or characteristic of the potentially complicated connection network of pigments represented by a photosynthetic antenna. Add to this there seems to be some mixing of concepts under the term delocalization due to the ultra-fast methods of measuring it. We aim to disentangle the delocalization relating to transitions between molecules as a result of resonance coupling, from the coherent state caused by laser excitation in spectroscopic experiments. This is done by respecting the uncertainty of delocalization in time, which we show by analysing the structure of the coherent state excited by ultrashort laser pulse. We demonstrate, on a system exhibiting static disorder only, how a generalised notion of delocalization can be introduced. With this is we can give a better representation of the states, including specific pigment contributions to the delocalized states as this can be crucial to the overall function of the system. We revisit past pump-probe measurements of LH1 and LH2 as well as new 2DES spectra to reexamine the concept of delocalization and try to come to grips with what it means in biological excitation energy transfer processes.

A Step Towards a Comprehensive Steady-State Picture of Photosynthetic Solar Energy Conversion

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The interpretation of oscillating experimental signals observed in ultrafast nonlinear spectroscopies [1] has been motivating vigorous interest in quantum effects in photoinduced biological processes. However, electronic dynamics triggered by natural light, which is stationary and incoherent, is generally substantially different from the one observed in pulsed laser experiments. It has been suggested that the physically correct picture of photosynthetic excitation energy transfer (EET) should be in terms of a steady state [2], which is formed when the photosynthetic antenna is continuously photoexcited and continuously delivers the excitation energy to the reaction center, in which charge separation takes place.

We study EET triggered by a low-intensity photoexcitation of an initially unexcited molecular aggregate, whose molecules interact with their unstructured local environments and which is coupled to the reaction center. We treat the aggregate–environment coupling in a numerically exact manner and extend previous theoretical treatments [3,4] by formulating the hierarchy of equations of motion (HEOM) which explicitly takes into account the photoexcitation process. We investigate the properties of the steady state arising when the aggregate is subjected to a continuous-wave excitation, while photoinduced electronic excitations can either recombine or undergo charge separation from the reaction center. The developed theoretical formalism enables us to approach questions ranging from the influence of the short-time dynamics (which is accessible in pulsed laser experiments) on the steady state to the relevance of steady-state coherences for the EET process.

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Matrix-product-state-based calculations of exciton-phonon dynamics for light-harvesting complexes

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Excitonic systems with one to a few dozen sites are an important and commonly studied topic in various contexts, such as quantum optics, molecular spectroscopy or the dynamics of light-harvesting complexes. However, in reality the dynamics are often strongly influenced by their coupling to the environment or internal vibrational modes. Computing such systems with non-negligible and non-perturbative interactions is a challenging problem, and oftentimes simplifications such as the Markov assumption are made to assist in such calculations. In our approach, we investigate the dynamics of excitonic oligomers with such interactions without neglecting the internal dynamics of the bath using a symmetry-adapted state-of-the-art matrix-product-state (MPS) code [1]. By employing this approach together with the analytic transformation of the bath Hamiltonian into discrete sites (TEDOPA) proposed by Martin Plenio et al. [2], we may also model non-Markovian dynamics of exciton systems with strong bath coupling. The insights gained from these analyses help us better understand the phonon-assisted transport effects in photosynthetic complexes such as the purple-photosynthetic-bacterial light-harvesting complex LH2, which exhibits a remarkably efficient energy transfer and notable symmetric structure [3].

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Pathway Analysis of Protein Electron-Transfer Reactions by Using Ab Initio Electronic Structure Calculations

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We have developed a novel computational scheme [1] to analyze electron transfer (ET) reactions in protein. Our scheme combines the fragment molecular orbital (FMO) method with an electron tunneling current analysis, which enables an efficient first-principles analysis of ET pathways in huge biomolecules. This poster presents our recent results [2] and discusses the roles of the protein environments in mediating long-distance electron tunneling and quantum interference effects among multiple ET pathways. We also discuss its applicability to a non-Condon theory [3] for analyzing the inelastic electron tunneling mechanism in protein, such as a hypothesis of the vibrational theory of olfaction. We acknowledge support from JST, PRESTO Grant Number JPMJPR17G4.

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Analyzing the Eigenvalue Spectra of Simplified Light-Harvesting Model Systems

Ron Koshita
Tulane University

In photosynthetic bacteria, natural light-harvesting antenna complexes of chlorosomes contain networks of chromophores, photoactive chlorophyll molecules that can absorb sunlight with high efficiency and transfer excitations throughout the given system. Superradiance is the key ability of these molecules to absorb and emit excitations at rates much faster than in comparison to the single molecular rate. Each individual chromophore can be modeled as a two-level system with an excitation energy and a varying dipole moment due to coupling with an electromagnetic field. The energy dynamics and efficiency of the given overall system changes depending on its geometry; for the case of the green sulfur bacteria known as *Chlorobium tepidum*, highly-symmetrical cylindrical structures created from stacked rings are present. Using the modified non-Hermitian effective Radiative Hamiltonian for an open quantum system and the classical Dipole-Dipole Approximation, we analyze the energy spectra of the bchQRU triple mutant (MT) type of *Chlorobium tepidum* in the single-ring, single-chain, double-chain, and multiple-ring systems with simplified parameters to gain insight into the natural cylindrical complex.

Anomalous conical emission with Bessel beams

Áulide Martínez Tapia
Universidad Autónoma Metropolitana, Unidad Iztapalapa

We have observed anomalous conical emission from the first resonant transition of calcium ($\lambda_{Ca} = 422.67$ nm) using two types of laser beams: on one hand, a regular Gaussian beam, and on the other hand, a non-diffracting zeroth-order Bessel beam produced by an axicon lens. Both laser beams were generated with a dye laser inside a homemade Littman-Metcalf setup pumped by the third harmonic of a Nd:YAG laser (355 nm). The conical emission featured different half-angles for the same wavelength as a function of the profile of the excitation beam (Gaussian or Bessel). The results of our experiments support conical emission models based upon four-wave mixing, and we believe this is due to the fact that we have modified the phase-matching condition with the new wave vector of the Bessel beams.

Sun-light pumped lasing with molecular aggregates

Francesco Mattiotti
University of Notre Dame

Molecular aggregates exposed to concentrated Sun light may exhibit population inversion and lasing. We demonstrate that a dimer in the single excitation manifold and under the action of Sun light behaves as a three-level system exhibiting population inversion. By a simple rate equations model, we describe the conditions for lasing operation of a collection of dimers in an optical cavity. This result may pave the way to a new class of bio-inspired Sun-light pumped lasers. Furthermore, the extension from dimers to larger aggregates of molecules could superradiantly enhance the lasing process.

Susceptibility of the quantum fisher information as a measure of the non-stationary multipartite entanglement in the linear response regime in the radical pair mechanism of the avian compass model

José Luis Meza Cabañas

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The leading hypothesis to explain how migratory birds can detect the direction of the Earth's magnetic field is the Radical-Pair(RP) mechanism, which is by now a well established theoretically and experimentally mechanism [1]. A radical pair is bipartite system of atoms or molecules that has an odd number of electrons were the key terms involved are the Zeeman effect, the hyperfine interaction and the Singlet-Triplet interconversion; consequently are magnetically sensitive. In this work, we focus on the interaction between nuclear and electron spin of the radical pair under the influence of constant and weak time-dependent magnetic field and obtain the non-stationary non classical multipartite correlation present in the system. In this work, we calculate the susceptibility of the quantum fisher information (QFI) in the linear response regime [2] and show that it can be a good measure of the non-classical correlations induced by the oscillatory field which available between the multipartite system composed of the nuclear spins and the molecule spins of the RP. We derive expressions of the QFI susceptibilities as a function the frequency and direction of the constant external magnetic field. We evaluate the regions of frequency and angular magnetic field where the system can have maximum multipartite entanglement between nuclear spins and RP spins.

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A Unified Master Equation for Strong and Weak System-Bath Couplings with Time-Scale Interpolation

Sue Ann Oh Oh
Charles University

We derive a general non-perturbative master equation for the reduced density matrix (RDM) of a molecular excitonic system embedded in its environment. In our method, we can continuously vary assumptions about the excited state delocalization, allowing us to interpolate between the strong and weak system-bath coupling limits. By devising a suitable parametric ansatz for the state of the bath, we can reproduce the well-known Redfield and Förster equations (i.e. the approximate equations of motion (EOM) in the weak and strong system-bath coupling limits), as two extremes of the same parameter. Because the theory treats the whole RDM, we also gain access to the EOM of its coherence elements, including non-secular terms. We obtain consistent EOM of the coherence elements in the special cases of the Förster equations and the so-called Modified Redfield equations. Finally, we test the validity of our equations in the intermediate system-bath coupling regime by comparison with exact propagation methods.

Susceptibility of the quantum fisher information as a measure of the non-stationary multipartite entanglement in the linear response regime in the radical pair mechanism of the avian compass model

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The leading hypothesis to explain how migratory birds can detect the direction of the Earth's magnetic field is the Radical-Pair(RP) mechanism, which is by now a well established theoretically and experimentally mechanism [1]. A radical pair is bipartite system of atoms or molecules that has an odd number of electrons were the key terms involved are the Zeeman effect, the hyperfine interaction and the Singlet-Triplet interconversion; consequently are magnetically sensitive. In this work, we focus on the interaction between nuclear and electron spin of the radical pair under the influence of constant and weak time-dependent magnetic field and obtain the non-stationary non classical multipartite correlation present in the system. In this work, we calculate the susceptibility of the quantum fisher information (QFI) in the linear response regime [2] and show that it can be a good measure of the non-classical correlations induced by the oscillatory field which available between the multipartite system composed of the nuclear spins and the molecule spins of the RP. We derive expressions of the QFI susceptibilities as a function the frequency and direction of the constant external magnetic field. We evaluate the regions of frequency and angular magnetic field where the system can have maximum multipartite entanglement between nuclear spins and RP spins.

[1] A Model for Photoreceptor-Based Magnetoreception in Birds. Thorsten Ritz, Salih Adem, and Klaus Schulten. Biophysical Journal, Volume 78 , February 2000 ,707–718.

[2] Nonequilibrium Statistical Physics, Linear Irreversible Processes, Noelle Pottier, Oxford University Press, 2014, First Edition

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Non-normality and open quantum systems

Dominik Bartłomiej Orłowski

University of Copenhagen

We study non-normality of open quantum systems. In particular we turn our interest to Lindblad and Redfield superoperators and plot their pseudo spectra. We then try to predict system dynamics at transient times.

Enhancing quantum phase transitions in the critical point of Extended TC-Dicke model via Stark effect

Ahmed Salah

Atomic Energy Authority

A system of N two-level atoms, Tavis-Cummings Dicke (TC-Dicke) model, interacting with a one-mode electromagnetic radiation field in the presence of the Stark shifts is studied, which is expected to predict new phenomena that are not explored in the original TC-Dicke model. We obtained the potential energy surface of the system using a trial state the direct product of coherent states in each subspace. In the frame of mean-field approaches, the variational energy is evaluated as the expectation value of the Hamiltonian for this state. The order of the quantum phase transitions is determined explicitly and numerically. We estimate the ground-state energy and the macroscopic excitations in the superradiant phase. Moreover, we investigated the critical properties of the TC-Dicke model in the classical spin limit and coherent state. We observed that in the thermodynamic limit, the energy surface takes a simple form a direct description of the phase transition. Moreover, it is found that when the microwave amplitude changes the new phase transition occurs with the Stark shift. The analytical solutions and numerical results, which appear in this paper are agreement with our paper which published recently in Int. J. Mod. Phys. B when we studied the same model using a different coherent state.

Drugs Vectorization and Encapsulation using Boron Nitride Nanotubes

Jonatan Isai Sánchez Sánchez
Benemérita Universidad Autónoma de Puebla

Boron Nitride Nanotubes (BNNT) have excellent properties that make them viable for various applications, one of them in biomedicine. In this work two types from nanotubes are analyzed, the so-called “armchair” and the “zigzag” (names that provide their geometric conformations) using different DFT (Density Functional Theory) functions, calculating in particular two of their physicochemical properties important for their notorious medical application, the Dipolar Moment and their Solvation Energy. It is found that it is important to find out how these properties are related to each other and in reference to the geometry. Once a good model of the nanotube that will be viable for study is obtained, the quantum chemistry semi-empirical method PM7 is used in Gaussian 16 to study the encapsulation of the anti-cancer drug Carboplatin in the gas phase and with water as a solvent of the medium (using the PCM approach). In both phases an optimization of geometry is obtained, that is, the variables are relaxed in all directions looking for a minimum of energy. Finally, drug vectorization methods in blood are proposed through these BNNT using aluminum and magnetite as functions addendums.

Non-Markovian evolution: exact and approximate

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We consider an exactly solvable model for the multi-level system interacting with several reservoirs at low temperatures. We compare the population decay rates and decoherence rates predicted by exact solution and several approximate master equations: a second-order non-Markovian master equation (Born approximation master equation), both Markovian and non-Markovian Redfield master equations. We analytically analyze the cases where this approximate equation gives exact results and which of them gives the result closest to the exact one for different regions in the space of parameters of the model. We also study numerically how they are actually close. So we examine the accuracy of the widely used Markovian and non-Markovian approximate master equations. They are usually used for modeling the energy transfer in light harvesting complexes. Our results could be directly applied to the cases of high frequency vibrational peaks in the reservoirs spectral density (which is the case for several models of exciton transfer in cryptophyte algae) and for low temperature reservoirs (which is the case for some experimental setups with Fenna-Matthews-Olson complexes). The research was supported by Russian Science Foundation (project No. «17-71-20154»).

Theoretical and experimental study of Tryptophan in water

Diana Milena Uriza Prias
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Diana Milena Uriza Prias¹, Juan Francisco Rivas Silva¹ and Antonio Méndez Blas¹ ¹Instituto de Física LRT, BUAP Tryptophan (TRP) is an amino acid that is found in many fundamental proteins and has important and useful luminescent properties in different fields of science, such as medicine, biology, chemistry and physics. The fluorescence of TRP has been highly studied, in a general goal, due to the sensitivity of TRP to its local environment in both polar and non-polar media. In this work we focus on studying experimentally solutions prepared with TRP and water in different concentrations. We found a strong dependence of its excitation as emission spectra on the degree of the concentration of the compound in the solutions. To obtain general and qualitative explanations of these results, theoretical calculations are made at the semi-empirical level and of DFT (quantum chemistry methods) in built systems that allow modeling the behavior of these solutions. Some complementary theoretical and experimental results were found too.

Interplay between structure and macroscopic coherence in nanotubular molecular aggregates

Alessia Valzelli

Università cattolica del Sacro Cuore Brescia

In this work we compare macroscopic coherent effects that occur in the Antenna systems of the Green Sulphur bacteria and in some artificial models, like C8S3. Coherent effects, such as super-radiance and super-transfer, make natural and artificial aggregates very efficient in the absorption and transport of the incoming solar radiation. The systems that we study are molecular nanotubes containing special molecules arranged in tubular aggregates with more concentric rolls and curved lamellae. They are characterized by a high degree of symmetry that is related to their coherence and functionality. In this work we look for those structures with super-radiant states (SRSs) in the lowest part of the energy spectrum and we want to show their ability to support macroscopic coherent states even at room temperature, assuming a canonical thermal state. After that, we compare the robustness to static disorder of natural and artificial light-harvesters.

The study of proteins by non-linear absorption of quantum light

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During the last two decades entangled photons (EP) have been theoretically proposed for novel applications in spectroscopy, as well, experiments have been performed to probe the potential of quantum light to study non-linear phenomena in molecules.¹ Particularly, EP have been tested as the excitation source for two-photon absorption (TPA) of organic molecules.²⁻⁴ In entangled TPA (ETPA), EP pairs (highly correlated in time and frequency) are absorbed simultaneously by a chromophore. Due to entanglement, the absorption photon rate depends linearly on the input photon flux, conversely, for classical TPA this dependence is quadratic.⁵ Here, we present an advance towards the application of ETPA in biological systems. Flavins -endogenous probes in many cellular systems- were tested in a real bio-environment at extremely low intensity of the excitation light. Free and protein embedded flavins were studied in aqueous solutions. In the search of new photon sources to study biomolecules, this is the first time that quantum light is used to study a naturally occurring class of proteins.⁶ The ETPA response of flavins were found to be relative better compared with classical two-photon absorption. Interestingly, we found that the ETPA signal enhances when flavins are protein embedded compared to free flavins. The EP response of these proteins and considering the existence of proteins with a good fluorescence quantum yield, clears the path to new spectroscopic and imaging applications in which proteins itself act as reporters of particular biochemical process on cells.

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