

Workshop on Quantum Effects in Biological Systems – QuEBS 09
Second LQCIL Biennial Meeting

ABSTRACTS OF INVITED AND CONTRIBUTED TALKS



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A quantum walk approach to photosynthesis

Alan Aspuru-Guzik [Harvard University]

Recent ultrafast experiments have shown surprisingly long electronic coherences in photosynthetic complexes and conjugated polymers. For tractable theoretical calculations, the chromophore-protein complex is usually modeled as an open quantum system. We describe a theoretical framework in which coherent energy transport in light-harvesting complexes can be considered as a quantum walk in the presence of environmental effects. We show how in simple models, the environment can assist the energy transport. From a stochastic perspective, the quantum walk is interrupted by jumps generated by the vibrational and optical environments. There is experimental evidence that in some of these complexes, such as the reaction center of purple bacteria, environmental memory effects are important for describing the energy transfer process. I will present a non-Markovian stochastic approach to analyse the energy transfer process in this situation. The quantum trajectory picture can lead to insight into the role of coherence in the energy transfer. I will also describe the prospects for engineering new devices by tuning energy levels and coupling to the bath in a biomimetic approach.

The role of geometry in non-linear quantum transport

Victor Atanasov [SQIG – Instituto de Telecomunicações]

An electron or a quantum of excitation confined within a rod (a protein can be modeled as a rod) feels the bending of the axis of that rod via the induced quantum potential due to R.C.T. da Costa. As a result the quantum motion is coupled with the solutions of the classical equations of motion for this rod. The Kirchhoff model of a rod gives the conformation dynamics which allows for curvature based solitary waves. This means that an electron gets trapped in and travels along with the curvature soliton. We present a microscopic mechanism of the above in which the rod is discretized and represented by a chain local cross-sections, that is molecular bases in the case of a protein. The model is justified since the presence of charge modifies (softens or hardens) the local chain stiffness. It is found that applying the model to the problem of quantum transport, due to the interaction between electrons and the bending (twisting) degrees of freedom, this permits us to formalize and quantify the concept of a conformon that has been hypothesized in biology. Also, we elucidate the role of the helical structure for a generic non-linear quantum mechanism of energy and charge transfer in one-dimensional bio-systems.

Joint work with Yasser Omar [SQIG-IT and ISEG-TULisbon].

Quantum control and entanglement in a chemical compass

Hans Briegel [University of Innsbruck]

The radical pair mechanism is one of the two main hypotheses to explain the navigability of animals in weak magnetic fields, enabling e.g. birds to see the Earth's magnetic field. It also plays an essential role in the field of spin chemistry. Here, we show how quantum control can be used to either enhance or reduce the performance of such a chemical compass, providing a route to further test this hypothesis experimentally. We calculate the dynamics of quantum entanglement in this model, and demonstrate intriguing connections between radical-pair entanglement and the magnetic field sensitivity of the compass. The nature of the nuclear-spin environment plays an essential role for the observed effects.

Joint work with Jianming Cai and Gian G. Guerreschi [University of Innsbruck].

Vibrational coherence transfer in LH-1 and prospects for vibrational control of EET

Jeffery Cina [University of Oregon]

I will review the spectroscopic evidence for non-Markovian effects of molecular vibrations on the time-course of electronic excitation transfer (EET) in the bacterial light-harvesting complex LH-1, along with its theoretical interpretation. With this motivation, I'll describe our simulations of polarized femtosecond pump-probe and wave-packet interferometry measurements on model energy-transfer complexes following the external initiation of coherent intra-chromophore vibrational motion by impulsive stimulated Raman scattering. Signatures of vibrational control of EET will be identified in calculated signals, and the prospects commented on for experimental tests of our predictions.

Proteins are quantum mechanical machines

Leonor Cruzeiro [University of Algarve]

Proteins are the machines of life, they drive essentially all the physical and chemical processes that go on in living cells: they catalyze reactions, pass signals and provide basic structure. Here it is proposed that the first step in protein folding and function is the creation of a quantum vibrational excited state, something I have started to refer to as the

?VES hypothesis. Applications of the VES hypothesis to several biological processes such as energy transfer in proteins, protein misfolding and the acceleration of enzymatic reactions by many orders of magnitude, will be presented.

Long-lived quantum coherence in excited states of carotenoids

Jeffrey Davis [Swinburne University of Technology]

It has recently been suggested that long-lived quantum coherences play an important role in promoting efficient energy transfer in naturally-occurring photosynthetic systems. We show that these peculiarly quantum mechanical effects occur also in the isolated chromophores lycopene and spheroidene. We performed two-colour electronic coherence experiments that provide clear evidence of coherent coupling of excited states, with measured coherence times of up to 1 ps at room temperature. We propose that the observed behaviour is attributable to the formation of vibronically-coupled superpositions of molecular quantum states. A recently-developed non-interferometric scheme for analyzing quantum coherence phenomena is used to assist the identification of the likely mechanism. This work sheds further light on our understanding of the relaxation processes in carotenoids and extends the possible roles of quantum coherence in photosynthetic light harvesting.

Joint work with E. Cannon, L.V. Dao, and P. Hannaford [Swinburne University of Technology and NUGENT University of Melbourne].

Wavelike energy transfer in photosynthesis: Insights from two dimensional electronic spectroscopy

Greg Engel [University of Chicago]

Life on earth is effectively solar powered, yet how energy moves through photosynthetic complexes prior to the biochemical steps of photosynthesis is still not completely understood. Evidence for a purely quantum mechanical mechanism of energy transfer in photosynthetic complexes was discovered in the Fenna-Matthews-Olson (FMO) complex of *Chlorobium tepidum* in 2007. The quantum beating phenomenon observed in this complex is now much better understood. Further, subsequent data indicate that this mechanism is not specific to FMO, but manifests in reaction centers of purple bacteria and

antenna complexes of higher plants. The experiments used to probe these effects and emerging details in this story will be presented along with a preview of upcoming experimental efforts to dissect the details of energy transfer, the basis for the efficiency of the energy transfer process and efforts to isolate signals at room temperature.

The mechanism of enhancement in novel two-photon absorption branched and other macrocyclic materials

Theodore Goodson [U Michigan]

In this presentation I will report a strongly interacting new dendrimer system with an extended spectroscopic unit (coherent domain) beyond the trimer configuration. Strong cooperative enhancement of two-photon absorption cross-section was observed when going from the trimer arrangement to the next generation. Combination of a variety of femtosecond spectroscopy methods such as femtosecond time-resolved fluorescence upconversion, transient absorption, transient grating, three pulse photon echo peak shift experiments complemented with those of steady state spectroscopy allowed us to compare the properties of absorption states with those of fluorescence states, to estimate the reorganization energies, and the extent of inhomogeneous broadening. Our measurements indicated that spectroscopic unit (domain) is different for the trimer system and for the dendrimers of higher generation numbers. This coherent domain extends over the trimer geometry and its size is comparable with the size of the dendrimer G1 comprising nine linear segments. We have also investigated the novel applications of a two-dimensional carbon network structure—its building blocks. The material shows very interesting two-photon absorption properties as well as strongly coupled optical excitations. They have also been suggested as good building blocks for molecular electronics applications. The origin of excitations in multi-chromophore carbon network substructures based on dodecahydrotribenzo [18] annulene was investigated by steady-state and time-resolved spectroscopy, configuration interaction (CIS and CIS(D)) and time-dependent density functional theory (TD-DFT).

Quantum random walks in energy landscapes

Stephan Hoyer [University of California, Berkeley]

Quantum random walks, in continuous time equivalent to a strict tight-binding Hamiltonian, provide one of the simplest models for quantum transport on arbitrary graphs,

as well as a striking example of quantum speedup for use in quantum algorithms. Accordingly, they have recently provided a popular point of departure for studying the influence of features such as disorder, decoherence and trapping expected to be of importance in photosynthetic complexes. Yet these models neglect an essential feature of light harvesting complexes, that sites are tuned to absorb energy across a broad range of frequencies. Thus we study the generalization of quantum random walks with site-dependent energies, in both continuous- and discrete-time. In the presence of strong external energy gradients, coherent models show significantly limited transport even before entering the regime of Anderson localization. In contrast, transport can be efficient and fast when driven by a decoherent environment.

Joint work with Mohan Sarovar and K. Birgitta Whaley [University of California, Berkeley].

Noise-induced Effects in Coupled Quantum Systems

Susana F. Huelga [U Hertfordshire]

The interplay between coherent and incoherent effects in interacting quantum systems often leads to an optimized system's response in the presence of intermediate noise levels. This can be viewed as form of stochastic resonance and quantified using both dynamical and information theoretic figures of merit. Of particular interest is the study of quantum correlations in the steady state. I will discuss the conditions under which interacting spin systems can remain entangled in a noisy environment and the physical mechanisms underlying a non-monotonic dependence of the entanglement on the noise strength for a variety of noise sources. This study may shed light on the issue of assessing the persistence of quantum correlations in complex, noisy quantum systems.

References: M.B. Plenio and S.F. Huelga, Phys. Rev. Lett. 88, 197901 (2002); S.F. Huelga and M.B. Plenio, Phys. Rev. Lett. 98,170601 (2007); C. Di Franco, M. Paternostro, D.I. Tsomokos and S.F. Huelga, Phys. Rev. A 77, 062337 (2008); A. Rivas, N.P. Oxtoby and S.F. Huelga, Eur. Phys. J. B 69, 51 (2009).

Non-trivial Quantum Effects in Radical-Ion-Pair Reactions

Iannis Komninos [FORTH-IESL and University of Crete]

Non-trivial quantum effects in biology have been sought after for a long time. It was recently discovered that a familiar biological system, namely radical-ion pairs and their reactions, exhibits a number of quantum effects until now manifested only in carefully prepared quantum physics experiments with well-isolated atomic systems. Radical-ion pairs are bio-molecules fundamental in the photosynthetic reaction dynamics and are also understood to underlie the chemical compass used by avian species for navigation. It has been shown that magnetic-sensitive radical-ion-pair reactions sustain quantum coherence, exhibit quantum jumps and the quantum Zeno effect and are the first biological system where the full machinery of quantum measurement theory can be fruitfully applied. This opens the way to several vistas in theoretical and experimental quantum biology, from the understanding of the fundamental connections between quantum-dynamic effects and biology, to the design of novel quantum-limited biochemical-reaction magnetometers and last but not least to the exploration of quantum information processing at the biological level. Reference: <http://aps.arxiv.org/abs/0806.0739>

Role of Coherence in Biological Excitation Energy Transfer

Tomas Mancal [Charles University in Prague]

Discussion about the role of coherence in biologically relevant excitation energy transfer in multichromophoric aggregates, which was started by recent advances in non-linear spectroscopy, raises fundamental questions about feasibility of a correct theoretical description of energy transfer within the framework of perturbation theory. The widely used results - Redfield and Foerster equations - and their recent generalizations such as Modified Redfield equations and Multi-chromophoric Foerster equations, all concentrate on the dynamics of the excited state populations, and explicitly or implicitly ignore effects related to the presence of dynamic coherence between different electronic transitions. This limitation is however not fundamental, and in most cases one can derive a corresponding equation of motion that governs a coupled dynamics of both populations and coherences. As it is usually not feasible to go beyond second order perturbation theory in a relevant coupling parameter (the electron-phonon or the resonance couplings) it is important to determine if the experimentally observed long lived coherence and coherence transfer could be reproduced at this level of theory. In this contribution, we compare several second order relaxation theories and indeed identify the full Non-Markovian quantum master equation as a description where the dynamics exhibits both comparatively long living coherences and significant coherence transfer within the range of parameters where second order theory leads to physical results. We demonstrate that second order coherence transfer effects can play a significant role in interpretation of even the simplest spectroscopic measurement - linear absorption. We also address the problems of systems with a weak resonance coupling and formulate equations of motion related to the Foerster

type theory, but including a description of coherence terms. By reviewing several different approaches to the problem, we come to a conclusion that the second order perturbation theory provides sufficient means for the description of the recently reported coherent effects and could be used as a platform for investigation of the influences of external parameters (temperature, degree of correlation between sites, resonance coupling strength etc.) on the details of energy transfer.

Joint work with Jan Olsina, Vytautas Balevicius, and Leonas Valkunas [Charles University and Vilnius University]

Studies of EET in biological macromolecular complexes using 2D electronic spectroscopy

Andrew Marcus [University of Oregon]

When a macromolecular complex is labeled with two or more closely spaced fluorescent chromophores, the resulting resonant dipole-dipole coupling is sensitive to the local macromolecular conformation. I will discuss some of our recent experiments that monitor the low signal fluorescence fluctuations of a collection of fluorescent protein complexes (DsRed), which are free to diffuse in solution [1, 2]. These phase-selective measurements of incoherent electronic energy transfer (EET) among chromophore sites within the complex allow us to map out competing kinetic pathways of the protein's switching optical conformations. I will also discuss our ongoing studies of coherence energy transfer in membrane bound porphyrin containing systems. In these latter experiments, we apply a recently developed fluorescence-detected phase-modulation 2D femtosecond technique [3, 4] to study exciton coherences supported by porphyrin aggregates ordered in a lipid membrane.

References: [1] Lott, G. A., E. N. Senning, M. C. Fink, A. H. Marcus (2009). "I. Conformational dynamics of biological macromolecules by polarization-modulated Fourier imaging correlation spectroscopy." *J. Phys. Chem. B* in press. <http://pubs.acs.org/articlesonrequest/AOR-z3nmCIyGbhtIb6R3Nhix>; [2] Senning, E. N., G. A. Lott, M. C. Fink, A. H. Marcus (2009) "II. Kinetic pathways of switching optical conformations in DsRed by 2D Fourier imaging correlation spectroscopy." *J. Phys. Chem. B* in press. <http://pubs.acs.org/articlesonrequest/AOR-chxY7CmKsDiQAjJyX5Ry>; [3] Tekavec, P. F., T. R. Dyke, A. H. Marcus (2006). "Wave packet interferometry and quantum state reconstruction by acousto-optic phase modulation." *J. Chem. Phys.* 125: 194303. [4] Tekavec, P. F., G. A. Lott, A. H. Marcus (2007). "Fluorescence-detected two-dimensional electronic coherence spectroscopy by acousto-optic phase modulation." *J. Chem. Phys.* 127: 214307.

Quantum dimension of photosynthesis revealed by angular resolved coherent imaging

Ian Mercer [University College Dublin]

Coherent electronic motion may play a role in the remarkable efficiency of energy transfer in photosynthesis. Coherent optical four wave mixing has been used widely to obtain information on the timescales of energy transfer in complex molecular systems. However, the interpretation of such measurements is difficult in particular where chromophores are strongly coupled, such as in photosynthetic systems, and new methods are required for an improved feedback to simulation. We present a novel non-linear optical method, Angle-Resolved Coherent (ARC) imaging, that separates out coherent quantum electronic couplings from energy transfers in to orthogonal dimensions, in an instantaneous two-dimensional mapping¹. The power of the new method is demonstrated with the light harvesting complex II (LH2) of purple bacteria at ambient temperature. We show that the position of a feature can map uniquely to each of the four laser beam interaction energies that produce the signal. We reveal an coherent quantum electronic beating with a time-ordered matter-selection of transition energies at ambient temperature. Relaxation of this coherence is observed to be accompanied by a reduction in the quantum beat frequency.

Dynamical role of quantum coherence and environment in chromophoric energy transfer

Masoud Mohseni [Massachusetts Institute of Technology]

Recently long-lived quantum coherence has been observed experimentally via ultrafast nonlinear spectroscopy in photosynthetic energy transfer and multichromophoric aggregates. However, the interplay between coherence and environmental effects within quantum dynamics of these systems has not been fully explored. Here, we introduce two complementary theoretical approaches, based on a Green's function method and energy transfer susceptibilities, to partition directed quantum walks in such systems. We quantify the role of fundamental physical processes involved in energy transport. In particular, we examine the contributions of coherent excitonic Hamiltonian and phonon-induced decoherence to the overall energy transfer efficiency. These techniques allow for dissecting the energy transfer process into spatial pathways. Moreover, we study the effect of spatial correlations in the phonon bath and slow protein scaffold movements on the efficiency. We

investigate the Fenna-Matthews-Olson protein complex, in which we find a contribution of coherent dynamics of about 10% in the presence of uncorrelated phonons and about 30% in the presence of realistically correlated phonon bath. References: M. Mohseni, P. Rebentrost, S. Lloyd, and A. Aspuru-Guzik, J. Chem. Phys. 129, 174106 (2008); P. Rebentrost, M Mohseni, and A. Aspuru-Guzik, J. Phys. Chem. B, in press (2009).

Joint work with Patrick Rebentrost, Seth Lloyd, and Alan Aspuru-Guzik [Harvard University and MIT]

Coherent energy transfer and trapping in quantum aggregates

Oliver Mülken [University of Freiburg]

Recent findings suggest that processes such as the electronic energy transfer through the photosynthetic antenna display quantum features, aspects known from the dynamics of charge carriers along polymer backbones. Hence, in modeling energy transfer one has to leave the classical, master-equation-type formalism and advance towards an increasingly quantum-mechanical picture, while still retaining a local description of the complex network of molecules involved in the transport, say through a tight-binding approach. Interestingly, the continuous time random walk (CTRW) picture, widely employed in describing transport in random environments, can be mathematically reformulated to yield a quantum-mechanical Hamiltonian of tight-binding type; the procedure uses the mathematical analogies between time-evolution operators in statistical and in quantum mechanics: The result are continuous- time quantum walks (CTQWs). However, beyond these formal analogies, CTRWs and CTQWs display vastly different physical properties. In particular, here we focus on trapping processes on a ring and show, both analytically and numerically, that distinct configurations of traps (ranging from periodical to random) yield strongly different behaviors for the quantum mean survival probability, while classically (under ordered conditions) we always find an exponential decay at long times.

Correlation-dependent coherent to incoherent transitions in phonon-assisted energy transfer dynamics

Ahsan Nazir [University College London and Griffith University]

Excitonic energy transfer is fundamental to the dynamical properties of a wide variety of multi-site systems, ranging from those in the solid-state (e.g. quantum dots) to photosynthetic complexes. In its simplest (Foerster-Dexter) form, energy transfer is considered to be incoherent and results from weak inter-site (donor-acceptor) transition-dipole interactions, treated perturbatively using Fermi's Golden rule [1]. However, recent experimental progress in demonstrating quantum coherent energy transfer in a variety of systems [2] has highlighted the importance of theories which describe the dynamics of energy transfer beyond the weak inter-site coupling regime [3]. Furthermore, such systems are still embedded in a larger host matrix and are therefore susceptible to couplings to their external environment. The resulting interplay between coherent and incoherent processes can fundamentally alter the nature of the energy transfer processes, destroying quantum coherent effects as well as significantly modifying the transfer rate. A particularly important issue, both in view of interpreting experiments and identifying potential regimes for optimal energy transfer, is to determine the criteria for transfer to be coherent. How these criteria change with variations in parameters such as donor-acceptor separation, system-bath coupling strengths, or temperature, is also key. In this presentation, I shall outline an analytical theory of excitation energy transfer dynamics that goes beyond the weak system-bath coupling regime. Considering a pair of two-level systems, I shall derive and solve a time-local master equation that accounts for multi-phonon effects in the bath-assisted energy transfer process. I shall further show it to be capable of interpolating between the weak (single-phonon) and strong (multi-phonon) system-bath coupling regimes, while still capturing the full coherent dynamics due to the donor-acceptor interaction. As one of the main results, I identify a transition from coherent to incoherent transfer dynamics with increasing temperature, and show that the resulting crossover temperature has a pronounced dependence on the degree of spatial correlation between bath-induced fluctuations experienced at the donor and acceptor sites. For strongly correlated fluctuations, this leads to the possibility of coherent dynamics surviving into a high temperature regime.

References: [1] Th. Foerster, Discuss. Faraday Soc. 27, 7 (1959); D. L. Dexter, J. Chem. Phys. 21, 836 (1953) [2] H. Lee, Y.-C. Cheng, and G. R. Fleming, Science 316, 1462 (2007); G. S. Engel et al., Nature 446, 782 (2007); E. Collini and G. D. Scholes, Science 323, 369 (2009) [3] See, for example, Y.-C. Cheng and G. R. Fleming, Annu. Rev. Phys. Chem. 60, 241 (2009) for a recent review.

Energy transfer efficiency and correlated dephasing in photosynthetic systems

Alexandra Olaya-Castro [University College London]

Recent experimental works have highlighted that quantum coherent dynamics plays a role in electronic energy transfer at room temperature when dephasing perturbations are correlated [1,2,3]. In this talk I would like to present our research on energy transfer efficiency in large multichromophoric systems under the assumption that dephasing rates at different sites are spatially correlated in contrast to the usual theoretical treatment where sites interact with independent environments. The model system considered here is a photosynthetic core consisting of a highly symmetric light-harvesting antenna connected to a reaction centre, as observed in purple bacteria. We show that in the presence of correlated bath-induced fluctuations, the transfer efficiency at room temperature could distinguish quantum phase relationships present in the initial exciton state. For the same system-bath coupling strength, such distinguishability is not necessarily possible when only local dephasing is assumed. Our results indicate that an optimal exciton delocalization length may then be necessary to guarantee high quantum efficiency in such closely packed photosynthetic complexes [4]. Finally, I will discuss possible relationships between transfer efficiency and the way quantum correlations are shared among different parts of the system.

References: [1] G. S. Engel et al, “Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems”, *Nature (London)* 446, 782 (2007); [2] H. Lee, Y-C. Cheng and G. R. Fleming, “Coherence Dynamics in Photosynthesis: Protein Protection of Excitonic Coherence”, *Science*, 316, 1462 (2007); [3] E. Collini and G. D. Scholes, “Coherent Intrachain Energy Migration in a Conjugated Polymer at Room Temperature”, *Science* 323, 369 (2009); [4] F. Fassioli, A. Nazir, and A.Olaya-Castro, “Photosynthetic systems could use correlated fluctuations to exploit initial state delocalization” (to be submitted).

Principles of noisy quantum dynamics in networks

Martin B. Plenio [Imperial College]

Quantum dynamics is often subjected to uncontrollable interactions with the environment. These are generally assumed to have a detrimental effect but this is not always the case. In this talk I will discuss the dynamics of dissipative and noisy quantum networks and will show how noise, both dephasing type and dissipative noise may actually improve the transport performance of the network. I will use the example of the FMO complex to elucidate the principles that govern the dynamics of such networks and use them to explain specific features of this dynamics.

References: M.B. Plenio & S.F. Huelga, *New J. Phys.* 10, 113019 (2008); F. Caruso, A.W. Chin, A. Datta, S.F. Huelga & M.B. Plenio, [quant-ph/0901.4454](https://arxiv.org/abs/quant-ph/0901.4454); F. Caruso, A.W. Chin, A. Datta, S.F. Huelga & M.B. Plenio, in preparation.

Detecting and characterizing entanglement in photosynthetic light harvesting complexes

Mohan Sarovar [University of California at Berkeley]

Light harvesting in photosynthetic antenna proteins: Quantum energy funnels at room temperature

Gregory Scholes [University of Toronto]

After photoexcitation, energy absorbed by a molecule can be transferred efficiently over a distance of up to several tens of Ångstrom to another molecule by the process of resonance (electronic) energy transfer. Examples of where energy transfer is observed include natural and artificial antennae for the capture and energy conversion of light in photosynthesis, amplification of fluorescence-based sensors, and optimization of organic light-emitting diodes. Förster theory has proven to be very successful at estimating the rate of energy transfer in many donor-acceptor systems, but it has also been of interest to discover when this theory does not work. By identifying these cases researchers have been able to obtain, sometimes surprising, insights into excited state dynamics in complex systems. In this talk I will describe new experiments, 2D electronic spectroscopy, that reveal mechanisms of dynamics in addition to rates. I will report data for some photosynthetic complexes and will explain what is meant by electronic coherence, show how we see evidence for it, and discuss why it is so surprising that we see it playing a role in energy transfer dynamics.

Electronic Energy Transfer in Molecular Aggregates: Theoretical Approaches from Förster, Redfield and beyond

Robert Silbey [Massachusetts Institute of Technology]

In this talk, we will discuss various approaches to electronic energy transfer, including the Förster, Redfield, Haken-Strobl, Lindblad, Stochastic Liouville and Generalized Master equation equations, with emphasis on their successes and failures. Issues that will be discussed include classical vs. quantum noise; how to choose the zeroth order Hamiltonian; and the interplay between dephasing, coherence and trapping.