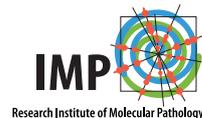


QuEBS 2013

Quantum Effects in Biological Systems Workshop

Institute for Molecular Pathology, Vienna, Austria

June 29th - July 3rd 2013



PROGRAM

Saturday, 29 June 2013

- 15.00-17.00 Registration – Welcome Coffee
- 17.00-18.00 Keynote Lecture by Anton Zeilinger,
Vienna Center for Quantum Science and Technology
Photonic Quantum Entanglement from Small to Large
- 18.00-19.00 Martin Plenio, Ulm University
Noise, coherence and vibrational motion in biology
- 19.00-21.00 Poster Session

Sunday, 30 June 2013

Session 1: Approaching Biology as a Physicist

09.00 – 10.35 Fred Wolf, MPI for Dynamics and Self-Organization
Mathematical Invariants of Brain Architecture Explained Using Symmetries and Fields

Gasper Tkacik, IST Austria
Recent Progress in Understanding the Population Code of the Retina

Bojan Zagrovic, MFPL Vienna
Two Elephants in the Room: On the Role of Cytosolic Microphase Transitions and Conformational Entropy in Biomolecular Interactions

10.35 – 11.00 Coffee break

Session 2: Vibrational Spectroscopy and Phenomena in Biomolecular Systems

11.00 – 13.00 Philipp Kukura, University of Oxford
Probing the Origins of Efficient Photobiology with Vibrational Coherence

Juergen Hauer, Vienna University of Technology
Signatures of Vibronic and Vibrational Coherences in Electronic 2D-Spectra of Molecular Monomers and Aggregates

Tobias Kramer, Humboldt University
Disentangling Vibronic and Electronic Signals in 2D Echo Spectra

Jeffrey Davis, Swinburne University of Technology
Experimental Studies of the Interactions between Electronic and Vibrational Coherences

13.00 – 14.30 Lunch break

14.30 – 16.05 Massimo Olivucci, Bowling Green State University
Insight into the Molecular Mechanism of the Dark Activation of Visual Pigments from Computational Photobiology

Craig Lincoln, Vienna University of Technology
Single- and Double-Quantum Two-Dimensional Electronic Spectroscopy Refine the Energy Level Scheme of β -carotene

Roel Tempelaar, University of Groningen
Probing Vibronically Enhanced Coherences in a Molecular Dimer

16.05 – 16.30 Coffee break

16.30 – 18.25 Joachim Heberle, Freie Universität Berlin
Probing Photon and Electron-Driven Membrane Proteins by Time-Resolved and Surface-Enhanced Infrared Spectroscopy

Fabio Antonio Bovino, Selex-ES S.p.A.
Parametric Optical Interactions in Bacteriorhodopsin Films

Fleming" Efthimios Skoulakis, Biomedical Sciences Research Centre "Alexander
Smelling Molecular Vibrations

18.25 – 20.30 Poster Session

Monday, 1 July 2013

Session 3: Magnetoreception

- 9.00 – 10.30 Hans Briegel, University of Innsbruck
Projective simulation as a model for learning
- Klaus Schulten, University of Illinois
Quantum Biology of a Magnetic Sense: Physical Principle, Chemical Reality, Biological Purpose
- 10.30 – 10.55 Coffee break
- 10.55 – 12.30 Peter Hore, University of Oxford
Chemical Magnetoreception-Quantum Biology of Cryptochromes
- Markus Tiersch, University of Innsbruck
Entanglement Lifetime-Based Magnetic Field Measurements with Chemical Magnetometers
- Jianming Cai, Ulm University
Chemical Compass for Avian Magnetoreception as a Quantum Coherent Device
- 12.30 – 14.00 Lunch break
- 14.00 – 15.30 David Keays, IMP Vienna
Iron-Rich Sensory Neurons in the Pigeon Columbia Livia
- Henrik Mouritsen, University of Oldenburg
Magnetic Compass Orientation in Migratory Birds: Behavioral, Molecular And Neurobiological Evidence
- 15.30 – 15.55 Coffee break

Session 4a: Photosynthesis

- 15.55 – 17.50 Greg Engel, University of Chicago
Engineering Quantum Coherence: Uncovering Design Principles behind Quantum Biology
- Margherita Maiuri, Politecnico di Milano
Explaining the Temperature Dependence of Spirilloxanthin's S* Signal by an Inhomogeneous Ground State Model
- Alan Aspuru-Guzik, Harvard University
Unraveling the secrets of Green Sulfur Bacteria's photosynthetic Apparatus
- 18.15 Departure for the Conference Dinner

Tuesday, 2 July 2013

Session 4b: Photosynthesis

09.00 – 11.00 Jianshu Cao, MIT
Coherent Energy Transfer in Light-Harvesting: Symmetry, Disorder, and Aggregation

Tomas Mancal, Charles University Prague
Excitation Energy Transfer in a Classical Analogue of Photosynthetic Antennae

Jan Roden, University of California, Berkeley
Energy Transfer and Coherence in the PSII Super Complex

Jacob Krich, University of Ottawa
Distinguishing Excitonic from Vibronic Oscillations with Ultrafast Pump-Probe Spectroscopy

11.00 – 11.25 Coffee break

11.25 – 13.00 Birgitta Whaley, University of California, Berkeley
The complex quantum dynamics of electronic energy transfer in Photosynthesis

Dario Polli, Politecnico di Milano
Tracing of Backward Energy Transfer from LH2 to LH1 in Photosynthetic Membranes Grown under High and Low Irradiation

Agata Branczy, University of Toronto
Incoherent Light vs. Ultrafast Pulses

13.00 – 14.30 Lunch break

Session 5a: Emerging Approaches and Techniques

14.30 – 16.25 Susana Huelga, Ulm University
Vibrational structures and long-lasting electronic coherence: from microscopic models to actual experiments

Javier Prior, Universidad Politécnica de Cartagena
Compressed Sampling and Wavelet Transformation: Signal Processing for Quantum Biology

Niek F. van Hulst, ICFO/ICREA
Addressing Quantum Coherence on the Nanoscale

16.25 – 16.50 Coffee break

16.50 – 18.50 Arno Rauschenbeutel, Vienna University of Technology
Interfacing and Investigating Molecules Using Optical Nanofibers

Andre Stefanov, University of Bern
Broadband Energy-Entangled Photons for Light-Matter Interaction and Quantum Information

Lev Mourokh, Queens College of the City University of New York
Bio-Inspired Nanostructures: From Actual Biological Systems Through Physical Models to Semiconductor Counterparts

Francesco Petruccione, University of KwaZulu-Natal
Microscopic Derivation of Open Quantum Walks for Biological Ratchet Models

18.50 Free Evening

Wednesday, 3 July 2013

Session 5b: Emerging Approaches and Techniques

- 09.00 – 10.55 Markus Raschke, University of Colorado
Prospect of Quantum Coherent Interaction and Control with Optical Antennas
- Jörg Wrachtrup, University of Stuttgart
Quantum Probes for Things that Matter in Life
- Jacob Sanders, Harvard University
Compressed Sensing for Molecular Spectroscopy
- 10.55 – 11.20 Coffee break
- 11.20 – 13.15 Yasser Omar, University of Lisbon
Quantum Biomimetics
- Filippo Caruso, University of Florence
Geometry vs. Noise: Towards Biomimetic Efficient Transport Networks
- Markus Arndt, University of Vienna
Quantum Interference Assisted Metrology on Biomaterials
- 13.15 Closing Remarks and Lunch

ABSTRACTS

O02 (IS)

NOISE, COHERENCE AND VIBRATIONAL MOTION IN BIOLOGY

M. Plenio¹

¹ University of Ulm

In this lecture I will discuss the importance of the interplay between environmental degrees of freedom and electronic motion in biological systems. I will expose some fundamental principles and show how diverse effects such as excitation energy transport in photosynthesis, magneto-reception of birds and conjectured mechanisms underlying olfaction fit into this framework. If time allows I will also discuss the need for novel technologies that are required for elucidating some of these questions and some steps towards their development.

O03 (IS)

MATHEMATICAL INVARIANTS OF BRAIN ARCHITECTURE EXPLAINED USING SYMMETRIES AND FIELDS

Fred Wolf¹

*1 Max Planck Institute for Dynamics and Self-Organization, Göttingen, Germany.
Bernstein Center for Computational Neuroscience, University of Göttingen.*

The brains of humans and animals arguably are among the most complex systems in nature. Even the most elementary sensory stimulus activates large ensembles of interacting nerve cells organized in spatially distributed circuits. The information processing capabilities of biological nervous systems result from the collective dynamics of these neuronal circuits. Because the amount of information in a mammalian genome is insufficient to specify circuit wiring in detail, nervous systems are generally assumed to utilize processes of dynamical self-organization to generate functionally useful processing architectures. Over the past decade, techniques for in vivo imaging have matured to a level of accuracy that now enables examining the spatial organization and wiring of neuronal circuits with quantitative precision. Studies of neuronal circuits in the mammalian neocortex indicate a quite volatile process of ongoing circuit turnover even in the adult brain. If neuronal circuits are as dynamic as indicated by these studies, it becomes mandatory to dissect the interactions that stabilize the overall processing architecture asking questions such as: Can the circuit layout be understood as a quasi-stationary state of ongoing circuit turnover? Are there laws of circuit design on a mesoscopic level emerging from the underlying circuit dynamics? Can we identify effective theories that quantitatively explain the biological circuit design and its formation in the young brain?

I will present recent work indicating that for the design of orientation columns - a key feature of visual cortex architecture - all of these questions can be answered affirmatively. Our experimental observations demonstrate that the spatial structure of visual cortical circuits processing form and motion is laid down with surprising precision and statistical invariance across the brains of mammalian species evolved on widely separated phylogenetic paths. A universality class of effective models using a single order parameter field, constructed from elementary symmetries, quantitatively explains all experimentally observed layout rules. Theoretically, we find that the dominance of non-local interactions in this universality class unmasks a massive set of spatially complex ground states that would turn into unobservable repellers if interactions were only local. The spatial organization of these ground states is completely determined by symmetries and is insensitive to model details. Convergence of circuit layout to these ground states predicts a sharp selection of the density of topological defects in the layout of orientation columns that is in excellent agreement with experimental observations. Experimentally we observe a weak breaking of the systems symmetry from $E(2) \times U(1)$ towards $E(2)$. The way the symmetry is broken suggests that orientation detectors in the visual cortex are strategically positioned to optimize the representation of spatially extended scenes.

The modern understanding of spontaneous symmetry breaking and the nonlinear physics of pattern formation have long provided inspiration and qualitative guidance for studies of patterning processes in biology. Our experimental and theoretical results from the visual cortex suggest that they may even provide a predictive quantitative approach to some of the most complex biological pattern formation processes.

Related Publications:

Keil, Kaschube, Schnabel, Kisvarday, Löwel, Coppola, White, and Wolf. *Science* 336 (2012) 413;
Reichl, Heide, Löwel, Crowley, Kaschube, and Wolf. *PLoS Comp Biol*, 8 (2012), e10024 & e10027;
Keil and Wolf. *Neural Systems & Circuits*, 1 (2011) 17;
Kaschube, Schnabel, Löwel, Coppola, White, and Wolf. *Science* 330 (2010) 1113;
Kaschube, Schnabel, Wolf, Löwel. *Proc. Natl. Acad. Sci. USA* 106 (2009) 17205;
Kaschube, Schnabel, Wolf. *New J. of Physics* 10 (2008) 015009.
Wolf. *Phys Rev Lett* 95 (2005) 08701-1.

O04 (IS)

RECENT PROGRESS IN UNDERSTANDING THE POPULATION CODE OF THE RETINA

G. Tkacik¹

1 IST Austria

Retina is one of the best studied sensory circuits, both in terms of functional processing and anatomy. Advances in multi-electrode array technology have enabled us to record simultaneously from a large number of retinal ganglion cells, and thus to explore how populations of neurons collectively represent sensory information. In the talk, I will review our recent attempts to understand this population code and how it deviates from simple "textbook" models. I will put the results in context by asking what would be a theoretically optimal coding strategy, and propose how such predictions can be tested.

O05 (IS)

TWO ELEPHANTS IN THE ROOM: ON THE ROLE OF CYTOSOLIC MICROPHASE TRANSITIONS AND CONFORMATIONAL ENTROPY IN BIOMOLECULAR INTERACTIONS

B. Zagrovic¹

1 MFPL & University of Vienna

A binding event between two biomolecules typically consists of a diffusional search of binding partners for one another, followed by a specific recognition of the compatible binding surfaces and subsequent complex formation. However, it is still largely unclear how binding partners find and recognize each other in the context of the crowded, constantly fluctuating, and interaction-rich cellular environment. Here, we will discuss some of our theoretical and computational work on two major contributors to biomolecular binding interactions, which have only recently come into a wider focus: 1) cytosolic microphase transitions, a potentially general mechanism for binding partner co-localization, and 2) conformational entropy, a key component of binding free energy. In particular, we will present evidence that biomolecular surface hydrophobicity may provide an organizing principle behind dynamic structuring of the cytosol, and discuss the role of correlated motions in biomolecular conformational entropy estimation.

O06 (IS)

PROBING THE ORIGINS OF EFFICIENT PHOTOPHYSIOLOGY WITH VIBRATIONAL COHERENCE

M. Liebel¹, P. Kukura¹

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The speed and specificity of crossing between different electronic states is of critical importance to the efficiency of light induced processes in biology. Both photochemical processes, such as retinal isomerisation, and light harvesting critically depend on rapidly converting photon energy into desired nuclear or electronic motion before dissipative processes become active. I will present recent results where we combined very high time-resolution transient absorption spectroscopy (<15 fs) with electronic population control to conclusively reveal broadband nuclear coherence on excited electronic states in the time-domain. Importantly, we can monitor the evolution of the coherence all the way from the initially populated Franck-Condon region and even across conical intersections. Application to the isomerisation of retinal in bacteriorhodopsin reveals coherent energy transfer from Franck-Condon to reactive nuclear coordinates as the origin of the unique reactivity in the protein. In addition, we reveal for the first time vibrationally coherent internal conversion between electronic states using the example of the electronic dynamics in *b*-carotene. Taken together, our results shed new light on the importance and role of vibrational coherence in photobiological processes.

SIGNATURES OF VIBRONIC AND VIBRATIONAL COHERENCES IN ELECTRONIC 2D-SPECTRA OF MOLECULAR MONOMERS AND AGGREGATESF. Milota¹, V. Perlík², F. Šanda², T. Mančal², and J. Hauer¹*1 Photonics Institute, Vienna University of Technology, Gusshausstrasse 27, 1040 Vienna, Austria**2 Institute of Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, Prague 121 16, Czech Republic*

From a quantum mechanical perspective, most molecular systems can be reduced to certain simple discrete level structures. Many properties of such multilevel systems do not depend on their exact nature, e. g. vibrational or electronic. While reflecting distinctly different physics, one common feature is the possibility to excite a coherent superposition of energy eigenstates, referred to as a wavepacket. As shown in numerous recent studies on natural light harvesting complexes, [1] two-dimensional electronic spectroscopy (2D-ES) has a unique disposition for the study of such coherences due to its ability to resolve cross peaks. Based on experimental studies on monomers [2] and molecular J-aggregates, [3] we identify and describe vibrational and vibronic modulations in electronic 2D-spectra. We discuss coherences in coupled molecular aggregates involving both electronic and nuclear degrees of freedom. A theoretical model of a vibronic dimer with dissipative dynamics described within Redfield theory successfully reproduces 90° phase shifts found in recent experimental works. We conclude that a general distinguishing criterion based on the experimental data alone cannot be devised.

[1] Schlau-Cohen, G. S.; Ishizaki, A.; Fleming, G. R. *Chem Phys* 2011, 386, 1.

[2] Mančal, T.; Christensson, N.; Lukes, V.; Milota, F.; Bixner, O.; Kauffmann, H. F.; Hauer, J. *J Phys Chem Lett* 2012, 3, 1497.

[3] F. Milota, V. I. Prokhorenko, T. Mančal, H. von Berlepsch, O. Bixner, H. F. Kauffmann, and J. Hauer, *J Phys Chem A*, 10.1021/jp3119605 (2013).

DISENTANGLING VIBRONIC AND ELECTRONIC SIGNALS IN 2D ECHO SPECTRA

T. Kramer^{1,2} and C. Kreisbeck³

1 Department of Physics, Humboldt University, Berlin, Germany

2 Department of Physics, Harvard University, USA

3 Department of Chemistry and Chemical Biology, Harvard University, USA

The prevalence of long-lasting oscillatory signals in the 2d echo-spectroscopy of light-harvesting complexes has led to a search for its physical origin.

We show by an exact computation of 2d spectra within an analytic continuation of GPU-HEOM [1] that in the full 7-site FMO model with the Wendling-type spectral density a rich and time-dependent mutual interplay of oscillatory electronic and vibronic components exists.

This is in contrast to recent works which focus on a reduced FMO Hamiltonians or artificial delta-like spectral densities for an explanation of the measured long-lasting oscillations.

To identify electronic coherence we introduce a versatile windowed-Fourier transform method which tells apart vibrations from electronic coherence in 2d spectra as function of delay time. We find that for the FMO model narrow vibronic modes are not helping efficient transport. Rather efficient transport in the FMO complex relies on the continuous part of the vibronic density [2], which does support long-lasting electronic coherence.

This finding suggests that for designing artificial light-harvesting nanostructures the tailoring of specific vibrational modes is not required.

[1] C. Kreisbeck and T. Kramer, Online 2d spectra tool for analytical continuation of GPU-HEOM at nanohub.org (2013)
<http://nanohub.org/resources/gpuheompop>
DOI:10.4231/D3RB6W248

[2] C. Kreisbeck, T. Kramer, Long-Lived Electronic Coherence in Dissipative Exciton-Dynamics of Light-Harvesting Complexes
Journal of Physical Chemistry Letters, 3, 2828 (2012)

EXPERIMENTAL STUDIES OF THE INTERACTIONS BETWEEN ELECTRONIC AND VIBRATIONAL COHERENCES

GH. Richards¹, CR. Hall¹, JO. Tollerud¹, K. Wilk², PMG. Curmi², JA. Davis¹

1 Centre for Atom Optics and Ultrafast Spectroscopy, Swinburne University of Technology, John St Hawthorn, VIC 3122, Australia

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We utilise a two colour FWM experiment to directly and specifically excite coherent superpositions and probe the subsequent evolution. While temporal resolution is reduced by narrowing the bandwidth, the spectral selectivity allows us to excite and probe different signal pathways in the absence of other contributions. The result is a clearer understanding of how different states and coherent superpositions of states interact with their environment [1]. Further clarity is obtained by controlling the polarization of each excitation beam and the signal, which allows us to determine the relative transition dipole angles involved with each laser interaction.

We have applied these techniques to the phycocyanin 645 (PC645) light harvesting complex from cryptophyte algae and identified the presence of several different vibrational coherences and one potential coherent superposition between excited electronic states [2].

The combination of polarization control and two-colour selective excitation allows us to observe evolution of the signal that would be hidden in 2D spectroscopy techniques regularly used to study this type of system. We see clear interaction between different vibrational modes, including ones that are outside the bandwidth expected to be excited with our pulse configuration. Furthermore, based on a series of experiments at different wavelengths we observe an evolution in the signal spectrum that we speculate is due to evolution of the excited state along its potential energy surface. This type of behaviour has been seen previously [3], and with a simple model based on coupled harmonic oscillators we have qualitatively reproduced this behaviour.

[1] G.H. Richards, K. Wilk, PMG Curmi, HM Quiney, J.A. Davis, *J. Phys. Chem. Lett.* 3, 272-277 (2012).

[2] G.H. Richards, K. Wilk, PMG Curmi, J.A. Davis, *New J. Phys.* (submitted)

O10 (IS)

INSIGHT INTO THE MOLECULAR MECHANISM OF THE DARK ACTI-VATION OF VISUAL PIGMENTS FROM COMPUTATIONAL PHOTOBIOLOGY

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2 Laboratoire Chimie Provence, UMR 6264 - Université de Provence, Campus Saint-Jérôme, Case 521, 13397 Marseille Cedex 20, France.

3 Dipartimento di Chimica, Università di Siena, via De Gasperi 2, I-53100 Siena, Italy.

We show¹ that the observed correlation between the maximum absorption wavelength (λ_{\max}) and the thermal isomerization kinetic constant (k) (the Barlow correlation) as well as the observed blue maximum sensitivity (the Purkinje effect) of rod visual pigments (Rh) can be explained by employing ab initio multiconfigurational quantum chemistry to build QM/MM computer models for a series of Rh mutants. The models reveal the existence of two electronically distinct energy barriers/transition states controlling the thermal isomerization of the retinal chromophore with the lower (TSCT) displaying the same charge transfer character (Φ_{ION}) of the pigment photoexcited state. We show that the existence of TSCT on the pigment ground state potential energy surfaces is the manifestation of the properties of the retinal chromophore wavefunction and, in turn, of the existence of a conical intersection between the ground and excited state of the pigments. Recent work has shown that these same features may be at the basis of the extreme light sensitivity of melanopsin: the non-visual retina pigment responsible for the synchronization of endogenous physiological responses to the dawn/dusk cycle (circadian rhythms).

1. Gozem S., Schapiro, I., Ferré, N. & Olivucci, M. (2012) The Molecular Mechanism of Dark Noise in Rod Photoreceptors. *Science* 337:1225-1

SINGLE- AND DOUBLE-QUANTUM TWO-DIMENSIONAL ELECTRONIC SPECTROSCOPY REFINE THE ENERGY LEVEL SCHEME OF β -CAROTENEF. Milota¹, CN. Lincoln¹, and J. Hauer¹*¹ Photonics Institute, Vienna University of Technology, Gusshausstrasse 27, 1040 Vienna, Austria*

Carotenoids like β -carotene are a family of naturally occurring pigments participating in both light harvesting and photoprotection. All carotenoids share a polyene like structural motif responsible for many of their optical properties. Despite numerous theoretical and experimental studies on carotenoids, their ultrafast dynamics and the underlying electronic energy level scheme are still a matter of controversy. [1] These uncertainties stem from overlapping excited state spectra as derived from pump-probe measurements. It is common practice to disentangle these overlapping excited states by intricate numerical fitting routines. We use two variants of coherent multidimensional spectroscopy [2] on solvated β -carotene, enabling us to vary wave vectors and time orderings of the incident excitation pulses. These degrees of freedom are unattainable in pump-probe techniques. With the aid of a recently developed spectroscopic method, electronic two-dimensional double-quantum spectroscopy (2Q-2D), we provide direct experimental evidence for an excited state above the first allowed state S2 with an excited state absorption (ESA) transition in the visible spectral range. Combining these results with two-dimensional single-quantum spectroscopy (1Q-2D), we obtain a comprehensive picture of the ultrafast dynamics and energy level scheme in β -carotene as well as new interpretations of recent experimental results. [3]

[1] T. Polivka and V. Sundstrom, Chem Phys Lett 477, 1 (2009).

[2] N. Christensson, F. Milota, A. Nemeth, I. Pugliesi, E. Riedle, J. Sperling, T. Pullerits, H. Kauffmann, and J. Hauer, J Phys Chem Lett 1, 3366 (2010).

[3] Oustrumov, E. E.; Mulvaney, R. M.; Cogdell, R. J.; Scholes, G. D.; Science, 340, 52 (2013).

O12

PROBING VIBRONICALLY ENHANCED COHERENCES IN A MOLECULAR DIMER

R. Tempelaar¹, J. Knoester¹, TLC. Jansen¹

1 Theory of Condensed Matter, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

The vivid discussion on the origin of long-lived oscillatory spectra of biological molecular systems has spurred in a new direction since the proposition of vibronic coupling as a mechanism to conserve electronic coherence. However, the problem remains that biological molecules typically are too complicated to unambiguously attribute oscillating spectral features. In this talk, we use a dimer of identical cyanine dyes as a more tractable model system to study the effect of strong vibronic coupling on two-dimensional spectroscopy. Even for an aggregate this simple, most excited state features overlap with ground state vibrational wave packets. However, through computer simulations we demonstrate that a particular spectral region very accurately indicates the coherence between the two strongest radiant vibronic states. According to our findings, these states are vibrationally different but electronically quite similar, hence forming a pair for which coherence is expected to be conserved. Our calculations are compared with experiments on bichanine performed by A. Halpin and coworkers. This comparison highlights to what extent the observed coherence is indeed protected against fluctuations in the environment, and so yields valuable insights on the role of vibronic couplings on coherent processes in biological systems.

O13 (IS)

PROBING PHOTON AND ELECTRON-DRIVEN MEMBRANE PROTEINS BY TIME-RESOLVED AND SURFACE-ENHANCED INFRARED SPECTROSCOPY

J. Heberle¹

1 Freie Universität Berlin, Experimental Molecular Biophysics

Membrane proteins are the target of more than 50% of all drugs and are encoded by about 30% of the human genome. Electrophysiological techniques, like patch-clamp, unravelled many functional aspects of membrane proteins but suffer from structural sensitivity. We have developed Surface Enhanced Infrared Difference Absorption Spectroscopy (SEIDAS) to probe potential-induced structural changes of a protein on the level of a monolayer^{1,2}. A novel concept is introduced to incorporate membrane proteins into solid supported lipid bilayers in an orientated manner via the affinity of the His-tag to the Ni-NTA terminated gold surface³. Functionality was probed by binding assays and electrochemistry.

General applicability of this novel methodological approach is shown by tethering plant photosystems I and II to the gold surface⁴. In conjunction with hydrogenase, the basis is set towards a biomimetic system for H₂-production⁵.

We recorded IR difference spectra of a monolayer of sensory rhodopsin II under voltage-clamp conditions⁶. This approach opens an avenue towards mechanistic studies of voltage-gated ion channels with unprecedented structural and temporal sensitivity.

I will also report on our recent time-resolved step-scan FT-IR spectroscopic experiments on channelrhodopsin-2⁷, the light-driven cation channel from *Chlamydomonas reinhardtii* whose application to neuronal cells founded the vibrant field of optogenetics. Structural changes of the chromophore retinal and the protein backbone were resolved along with internal proton transfer reactions. We were able to show that aspartate 253 accepts the proton released by the Schiff base ($\tau_{1/2} = 10 \mu\text{s}$), the latter being reprotonated by aspartic acid 156 ($\tau_{1/2} = 2 \text{ms}$). Our results merge into a mechanistic proposal that relates the observed proton transfer reactions and the protein conformational changes to the gating of the cation channel.

References:

1. Ataka, K., & Heberle, J. (2003), *J. Am. Chem. Soc.* 125, 4986-4987
2. Ataka, K., Kottke, T., & Heberle, J. (2007), *Angew. Chem. Int. Ed.* 122, 5544 - 5553
3. Ataka, K., Giess, F., Knoll, et al. (2004), *J. Am. Chem. Soc.* 126, 16199-16206
4. Badura, A., Esper, B., Ataka, K., et al. (2006), *Photochem. Photobiol.* 82, 1385-1390
5. Krassen, H., Schwarze, A., Friedrich, B., et al. (2009), *ACS Nano* 3, 4055-4061
6. Jiang, X., Zaitseva, E., Schmidt, M., et al. (2008), *Proc. Natl. Acad. Sci. USA* 105, 12113-12117
7. Lórenz-Fonfría, V.A., Resler, T., Krause, N., et al. (2013), *Proc. Natl. Acad. Sci. USA* 110, E1273-E1281

PARAMETRIC OPTICAL INTERACTIONS IN BACTERIORHODOPSIN FILMS

FA. Bovino¹, C. Gergely², C. Sibilìa³

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2. *Université Montpellier 2, Laboratoire Charles Coulomb UMR 5221, F-34095, Montpellier, France and CNRS, Laboratoire Charles Coulomb UMR 5221, F-34095, Montpellier, France*

3. *Università di Roma "La Sapienza", Dip. di Scienze di Base e Applicate per l'Ingegneria-Sez Fisica (Ex Energetica), Via A. Scarpa 16, 00161 Roma - Italy*

Chiral materials with non linear optical properties can be found also among biological molecules presenting an ordered arrangement and non-inversion-symmetric structure in space, or having a chromophore. The latter group, called chromoproteins, is best represented by bacteriorhodopsin (BR), one of the most studied biomolecules exhibiting NLO properties [1]. We have studied BR in its purple membrane bound form by producing a 15 μm thick oriented film via electrophoretic deposition onto a glass substrate covered by a 60nm thick ITO film. The resulting BR films, composed by ~ 2600 purple membrane layers (of 5nm thickness each) were characterized in terms of homogeneity, optical and electrical properties. In order to study the coherence optical response of BR we performed parametric nonlinear interaction (second harmonic generation (SHG) measurements) in noncollinear configuration. The noncollinear scheme with two input pump beams, offer very high flexibility in the handling and control the SHG signal which becomes selectively addressed by choosing the appropriate polarization state for the fundamental beams [2]. The noncollinear second harmonic generation from the BR film was obtained using the output of a mode-locked femtosecond Ti:Sapphire laser system tuned at $\lambda = 830$ nm (76 MHz repetition rate, 130 fs pulse width, average power of 500 mW) which was split into two beams of about the same intensity. The coherence of the interaction can be handled by an additional input beam in the absorption regime. The presence of the nonlinear magnetization and its contribution to the SHG signal, can be also tuned and modulated by the application of an external static magnetic field of moderate intensity.

References

- [1] F.A. Bovino, M.C. Larciprete, C. Sibilìa, G. Varo, C. Gergely, *Optics Express*, 20, 14621 (2012)
- [2] M.C. Larciprete, F. A. Bovino, M. Giardina, A. Belardini, M. Centini, C. Sibilìa, M. Bertolotti, A. Passaseo, V. Tasco, *Optics Letters* 34: 2189 (2009)

O15 (IS)

SMELLING MOLECULAR VIBRATIONS

A. Gaitanidis¹, E. Drimyli¹, K. Maniati¹, L. Turin¹, EMC. Skoulakis¹

1 Biomedical Sciences Research Centre "Alexander Fleming"

We have presented strong evidence that *Drosophila melanogaster* readily distinguish odorants based on their molecular vibrations using a battery of behavioral assays. These results are inconsistent with a shape-only model for smell but support engagement of a molecular vibration-sensing component in olfactory reception. Furthermore, we recently demonstrated that a similar vibrational sensing component is operant in human olfaction. We will report on current efforts using behavioral, electrophysiological and biophysical methods on single olfactory receptor and normal flies to address additional characteristics and properties of the vibration-sensing component. In addition we will report on our experimental efforts to probe the mechanism utilized to sense molecular vibrations by the bipartite (Orco) and single subunit (IR) fly olfactory receptors extrapolating to the single human GPCR receptors.

O17

QUANTUM BIOLOGY OF A MAGNETIC SENSE: PHYSICAL PRINCIPLE, CHEMICAL REALITY, BIOLOGICAL PURPOSE

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The ability of some animals and other biological species to navigate through detection of the Earth magnetic field is widely accepted today.

The reception mechanism is most likely optimal around Earth magnetic field strength, cannot distinguish magnetic North and South, and involves light reception. Lack of a clearly identifiable magnetic compass organ suggests that the magnetic sense is based on a biochemical process integrated with an existing sensory organ, most likely the eye.

Research efforts in magnetoreception are intense, yet little progress has been made in making a solid case for the physical mechanism

underlying magnetoreception. This lecture compares research focussing on magnetoreception with quantum biology research focussing on other sensory (vision) and energy transduction (photosynthetic light harvesting) processes. Such comparison may establish guide posts for resolving the physical mechanism of magnetoreception. The stated comparison suggests that magnetoreception research should strengthen its focus on chemical reality and biological purpose rather than on physical principle. Research on vision and on light harvesting has characterized in great detail the chemical structures as well as biological organization and purpose of the cellular systems involved; this focus provided great guidance for the search into the physical principles underlying the two biological systems.

Magnetoreception researchers seem to be too willing to work without such guidance. The lecture makes the plea that researchers focus on chemical reality and biological purpose as can be found likely, but not definitely, in the activation and deactivation processes of the blue light receptor cryptochrome, the most widely accepted candidate for the biochemical realization of magnetoreception. Questions to be answered through experiment and theory are: What are the elementary reaction steps? How are they linked to activation and deactivation of cryptochrome? Can these steps be magnetic sensitive in principle, given the physical reality of the protein-cofactor system involved? Can a magnetic field dependence be predicted and measured? How is cryptochrome linked to neural sensory processing? Can this link explain magnetoreception?

Answers to some of these questions could enrich the study of physical principles of quantum biology. Theoreticians interested in magnetoreception might have to don a white lab coat for a while! Or at least find suitable experimentalists to work with!

O18 (IS)

CHEMICAL MAGNETORECEPTION-QUANTUM BIOLOGY OF CRYPTOCHROMES

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Migratory birds travel spectacular distances each year, navigating and orienting by a variety of means, most of which are poorly understood. Among them is a remarkable ability to perceive the intensity and direction of the Earth's magnetic field. Biologically credible mechanisms for the sensing of such weak fields (25-65 μT) are scarce and in recent years just two proposals have emerged as frontrunners. One, essentially classical, centres on iron-containing particles. The other relies on the magnetic sensitivity of short-lived radical pairs formed by photoinduced electron transfer. This model began to attract interest following the proposal that the necessary photochemistry could take place in the bird's retina in specialised photoactive proteins called cryptochromes. The coherent dynamics of electron-nuclear spin states of pairs of radicals is conjectured to lead to changes in the yields of reaction products even though the Zeeman interaction with the geomagnetic field is more than six orders of magnitude smaller than kT. In this talk, I will outline some of the experimental evidence for the cryptochrome hypothesis, discuss the interpretation of the reported effects of weak (nanotesla) radiofrequency fields on the magnetic orientation of European robins, compare the magnetic responses of various members of the cryptochrome family of proteins, and comment on the extent to which cryptochromes are fit-for-purpose as magnetoreceptors.

ENTANGLEMENT LIFETIME-BASED MAGNETIC FIELD MEASUREMENTS WITH CHEMICAL MAGNETOMETERS

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Spin effects in photochemical systems are promising candidates for the sensory mechanism of animal magneto-reception.

In biological candidate molecules and artificial chemical model systems that form radical pairs, effects of an external magnetic field have been observed in vitro on the level of the radical pair concentration or the reaction yield, e.g. fluorescence photons. The sensory information is thus obtained from a combination of both the field-dependent spin dynamics and the spin-dependent reaction kinematics.

Based on a known radical pair system, pyrene and N,N-dimethylaniline, we present a scheme for a chemical magnetometer that uses the entanglement lifetime and related quantities of the radical pair spin state for sensing magnetic fields, i.e., without involving the reaction kinematics. We provide an optimal entanglement witness for radical pair systems with isotropic hyperfine interactions, and discuss possible measurement approaches, including the control of the reaction kinematics.

In addition to applications in artificial chemical magnetometers this approach may also provide insight into the functional details of its biological counterparts.

CHEMICAL COMPASS FOR AVIAN MAGNETORECEPTION AS A QUANTUM COHERENT DEVICE

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It is known that more than 50 species use the Earth's magnetic field for orientation and navigation. Intensive studies particularly behavior experiments with birds provide support for a chemical compass based on magnetically sensitive free radical reactions as a source of this sense. However, the fundamental question of whether and how quantum coherence plays an essential role in such a chemical compass model of avian magnetoreception yet remains controversial. Here, we show that the essence of the chemical compass model can be understood in analogy to a quantum interferometer exploiting quantum coherence. Within the framework of quantum metrology, we quantify quantum coherence and demonstrate that it is a resource for chemical magnetoreception. Our results allow us to understand and predict how various factors can affect the performance of a chemical compass from the unique perspective of quantum coherence assisted metrology. This represents a crucial step to affirm avian magnetoreception as an example of quantum biology, which exhibits a direct connection between quantum coherence and biological function.

O21 (IS)

IRON-RICH SENSORY NEURONS IN THE PIGEON COLUMBIA LIVIA

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Two dominant theories attempt to explain how animals detect the Earth's magnetic field: the light dependent hypothesis; and the magnetite dependent hypothesis. The latter holds that magnetic information is transduced into a neuronal impulse employing biogenic magnetite. Recent histological and electrophysiological studies performed by Wu and Dickman (Wu and Dickman, 2011) in pigeons have implicated the lagena macula in magnetite dependent magnetoreception. Here, we investigate this further by employing the Prussian Blue reaction to identify iron-rich cells in the inner ear of pigeons. We report the discovery of a single Prussian Blue positive structure in hair cells that is located directly beneath the stereocilia. Transmission Electron Microscopy coupled with elemental analysis has revealed that this structure is membrane enclosed, is composed of ferritin-like granules, is 200-400 nm in diameter, and is located in the cuticular plate. This new organelle, termed the "Cuticulosome" is not unique to pigeons, and is found in a wide variety of Avian species. We propose that this structure may function either as: (1) an iron store; (2) an intracellular pendulum; or (3) a magnetoreceptor. To our knowledge this is the first report of iron-rich sensory neurons.

O22 (IS)

MAGNETIC COMPASS ORIENTATION IN MIGRATORY BIRDS: BEHAVIOURAL, MOLECULAR AND NEUROBIOLOGICAL EVIDENCE

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Migratory birds can use a magnetic compass to find their way, and, at least in North America, they seem to calibrate this magnetic compass after the sun compass each evening (Cochran et al. 2004); but how do they sense the reference direction provided by the geomagnetic field? Two biophysical mechanisms have become established as the most promising magnetodetection candidates: (1) sensors in the upper beak connecting to the brain through the ophthalmic branch of the trigeminal nerve and/or (2) light-dependent radical-pair processes in the eyes converting the magnetic signal into a visual signal, which is then processed in visual brain areas (for a review, see Mouritsen & Hore 2012). Recently, a third suggestion has been added (Wu & Dickmann 2012).

In the past years, we performed a number of combined experiments involving molecular biology, anatomy, chemical analyses, neurobiology, and behaviour which has brought us to the conclusion that birds do not only have one, but at least two different magnetic senses, and that both of the original hypotheses could be generally correct. We have shown that potentially magnetosensitive molecules called cryptochromes are found in highly active neurons of the retina of night-migratory birds (Mouritsen et al. 2004) and that these cryptochromes possess a number of key biophysical prerequisites that makes them ideally suited as magnetodetectors (Liedvogel et al. 2007a). We have also located a specific forebrain area, named Cluster N, which is the only part of a migratory bird's forebrain being highly active processing sensory information when birds perform magnetic compass orientation (Mouritsen et al. 2005; Liedvogel et al. 2007b; Feenders et al. 2008; Zapka et al. 2010). Input from both eyes (Hein et al. 2010, 2011, Engels et al. 2012) reaches Cluster N via the thalamofugal visual pathway (Heyers et al. 2007). Furthermore, if Cluster N is deactivated, migratory European Robins can no longer use their magnetic compass, whereas their star compass and sun compass abilities are unaffected (Zapka et al. 2009). The lagena and associated pathways remained intact. Bilateral section of the trigeminal nerve had no effect on the birds' ability to use their magnetic compass (Zapka et al. 2009), but does that mean that the putative sensors - they must no longer be iron-mineral-based (Treiber et al. 2012; Mouritsen 2012) - associated with the ophthalmic branch of the trigeminal nerve are not magnetodetectors? No, there is still evidence that the ophthalmic branch of the trigeminal nerve does indeed also transmit magnetic information to the brain (Mora et al. 2004; Heyers et al. 2010). Recently, we have also studied the effects of oscillating magnetic fields of various frequencies on the orientation capabilities of birds and got new hints that the basic mechanism may indeed be quantum rather than classical.

O23 (IS)

ENGINEERING QUANTUM COHERENCE: UNCOVERING DESIGN PRINCIPLES BEHIND QUANTUM BIOLOGY

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University of Chicago

Photosynthetic antenna complexes operate with near perfect quantum efficiency and steer excitonic motion with exquisite precision.

Optimized by evolution, these complexes exploit both incoherent (Förster) energy transfer along with coherent (wavelike) motion of energy. We seek to isolate and copy the microscopic details of this mechanism to enable coherent energy transfer in synthetic systems. We find unusual mixing between bath modes and the electronic states. The implications of this mixing for excitonic transport (under both coherent and incoherent excitation) will be discussed along with new results showing long-lived coherence engineered into a family of novel synthetic small molecules demonstrating the same underlying design principles.

EXPLAINING THE TEMPERATURE DEPENDENCE OF SPIRILLOXANTHIN'S S* SIGNAL BY AN INHOMOGENEOUS GROUND STATE MODEL

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Carotenoids play crucial roles in photosynthetic complexes, acting as light harvesters and photo-protectors. Upon photoexcitation to the first optically allowed S2 state, population transfers from S2 to S1 (the lower-lying dark state) on a sub-200-fs timescale. The electronic structure and energy deactivation pathways of carotenoids are a matter of ongoing debate. The different models proposed deviate in the interpretation of a high-energy shoulder of the S1-ESA band, assigned to a state named S*: either a separate electronic singlet state or a signature from the hot ground state or a different conformer of the S1 state due to the inhomogeneity of the ground state. If the latter case holds, then varying the sample temperature should modulate the S*/S1 ESA-signal ratio.

In this work, we test the inhomogeneous ground state hypothesis by performing a series of pump-probe experiments with sub-20-fs time resolution on spirilloxanthin (N=13 conjugated double bonds) in a PMMA matrix varying the temperature. Following photoexcitation, we observe sub-200-fs internal conversion of S2 state into the lower-lying S1 and S* states, which in turn relax to the ground state on a ps timescale. The photoinduced dynamics were fitted using the target analysis procedure from RT to 77 K, leading to the following scenario, also supported by quantum chemical calculations. Two ground state isomers (S0 and S0*), energetically separated by ΔE , are excited to their respective optically allowed states (S2 and S2*). Consequently, S2 and S2* decay to hot S1 and S*, respectively. Upon cooling down the sample to 77 K, we observe a systematic decrease of the S*/S1 ratio. This result can be explained by assuming two thermally populated ground state isomers. The higher lying one generates the S* state, which can then be "frozen out" by cooling, as the energy difference to the two isomers is close to kBT.

O25 (IS)

UNRAVELING THE SECRETS OF GREEN SULFUR BACTERIA'S PHOTOSYNTHETIC APPARATUS

A. Aspuru-Guzik¹

1 Harvard University

In this talk, I will report our group's recent efforts in understanding the entirety of the light-harvesting component of green-sulfur bacteria's photosynthetic apparatus from a multiscale perspective. We begin with atomistic simulations of the fluctuations of bacteriochlorophylls in the different environments and end up building a model of the chlosome + baseplate + FMO. We carry out the dynamics on systems up to tens of thousands of bacteriochlorophyll molecules and compare our theoretical timescales to the experimental ones. The picture that emerges is that of a robust energy transfer to the reaction center in about 10 PS where delocalization quantum effects play a crucial role in the process. I will compare to the photophysics of J-aggregates and discuss future directions.

COHERENT ENERGY TRANSFER IN LIGHT-HARVESTING: SYMMETRY, DISORDER, AND AGGREGATIONJ. Cao¹*1 Department of Chemistry, MIT*

Quantum coherence plays a central role in natural and artificial light-harvesting complexes and is explored by my group in terms of symmetry, static disorder, and the size and alignment of these complexes.

(1) An intriguing observation of photosynthetic light-harvesting systems is the N-fold symmetry of light-harvesting complex 2 (LH2) of purple bacteria. We have calculated the optimal rotational configuration of N-fold rings on a hexagonal lattice, and established the symmetry principles for the promotion of maximum excitation energy transfer (EET). For certain fold numbers, there exist optimal basis cells with rotational symmetry, extendable to the entire hexagonal lattice for the global optimization of the EET network, such that these basis cells can reduce or remove the frustration of EET rates across the photosynthetic network. [1] Remarkably, one consecutive group of such symmetry numbers consists of the naturally occurring 8-, 9- & 10-fold rings, suggesting the design principle of matching the internal symmetry with the lattice order.

(2) We have studied coherent quantum transport in disordered 1-D and 2-D systems and clearly showed an optimal diffusion constant at an intermediate level of noise. [2] Scaling analysis similar to the mean first passage time analysis [3] indicates the crucial role of localization length. Further detailed studies reveal that optimal diffusion depends critically on dimensionality and range of interactions, and may not be observed in certain systems due to different scaling laws. We are also developing methods to calculate transport in a thermal environment and predict its temperature-dependence.

(3) We have developed a novel numerical method [4] to predict the quantum dynamics of extended systems. Based on the concept of dynamical maps, our method extracts all available information encapsulated in short-time non-Markovian quantum trajectories and compresses it into tensors of reduced size. Efficient propagation of these tensors generates dissipative quantum dynamics of large systems with arbitrary spectral densities, e.g., molecular chains of hundreds of sites with strong quantum dissipation. Further, it can be applied to experimental settings in the same spirit as processing tomography and permits direct reconstruction of dynamical operators, i.e., the Hamiltonian and memory kernel.

[1] Cleary, Chen, Chern, Silbey, and Cao, PNAS 110, p8537 (2013)

[2] Jeremy, Khasin, Cao, New Journal of Physics (submitted)

[3] Wu, Silbey, and Cao, PRL 110, p200402 (2013)

[4] Cerrillo and Cao, PRL (submitted)

O27

EXCITATION ENERGY TRANSFER IN A CLASSICAL ANALOGUE OF PHOTOSYNTHETIC ANTENNAE

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We formulate a classical pure dephasing system-bath interaction model in a full correspondence to the well-studied quantum model of natural light-harvesting antennae. The equations of motion of our classical model not only represent the correct classical analogy to the quantum description of excitonic systems, but they also have exactly the same functional form. We demonstrate derivation

of classical dissipation and relaxation tensor in second order perturbation theory. We find that the only difference between the classical and the quantum descriptions is in the interpretation of the state, and in certain limitations imposed on the parameters of the model by classical physics. The effects of delocalization, transfer pathway interference and the transition from coherent to diffusive transfer can be found already in the classical realm. The only qualitatively new effect occurring in quantum systems is the preference for a downhill energy transfer and the resulting possibility of trapping the energy in the lowest energy state. Contrary to the general opinion we find uniquely quantum effects occurring only in the incoherent mode of energy transfer.

ENERGY TRANSFER AND COHERENCE IN THE PSII SUPER COMPLEXJ. Roden¹, D. Bennett¹, KB. Whaley¹*1 Department of Chemistry, University of California*

Photosystem II super complexes found in plants contain up to 326 pigments bound into an assembly of light harvesting complexes surrounding a reaction center. Recent spectroscopic measurements have shown quantum beating within the major light harvesting constituent subcomplex LHCII, raising the question as to the role of coherence in the function of the entire Photosystem II assembly. In particular, given the relatively small separation between pigments even in different subcomplexes, it may be important to take into account coherences that are formed within and between subcomplexes and to investigate their effect on the overall transfer of energy. We are addressing this question by simulating the energy transfer from the LHCII antenna to the reaction center with a quantum master equation that allows the influence of coherence on the overall energy transfer and the transfer of coherence between subcomplexes to be assessed.

The quantum master equation employed here is based on the non-Markovian quantum state diffusion (NMQSD) approach, which allows the non-Markovian character of the interaction of the electronic excitation with intra-molecular vibrations to be taken into account. The method enables us to handle the relatively large number of interacting pigments that have to be included in any description of the dynamics of multiple subcomplexes and to address the question of the importance of coherences in the longer-range transfer dynamics across the supercomplex. We present preliminary results that give an insight into the dynamics and extent of coherences within and between subcomplexes.

DISTINGUISHING EXCITONIC FROM VIBRONIC OSCILLATIONS WITH ULTRAFAST PUMP-PROBE SPECTROSCOPY

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Ultrafast optical experiments on photosynthetic systems have indicated that coherent delocalization of exciton states significantly contributes to exciton transport, even up to room temperature. Experimental signals due to excitonic delocalization can be similar to those from vibronic oscillations, which are generally not important for exciton transport. We describe a straightforward experiment -- broadband pump-probe -- to distinguish between ultrafast oscillations from excitonic or vibronic-only sources. We show that standard femtosecond laser systems should be able to perform the experiments and give detailed instructions, describing the bandwidth requirements for the optical pulses and how to interpret the resulting data.

O30 (IS)

THE COMPLEX QUANTUM DYNAMICS OF ELECTRONIC ENERGY TRANSFER IN PHOTOSYNTHESIS

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Ultrafast spectroscopies provide powerful tools to probe dynamical phenomena in biological systems, yet the complexity of such systems pose challenges to developing detailed understanding of the microscopic electronic and nuclear motions underlying the spectral signatures. These challenges are particularly severe when quantum dynamical behavior is involved, as in recent two-dimensional photon echo spectroscopy experiments of photosynthetic systems that suggest quantum coherence between electronic excited states may play a role in electronic energy transfer. Analysis of such multi-dimensional spectroscopies generally relies on simulations in which both the dynamics of the photosynthetic system and its interaction with light are described within simplified models, which may result in diverse interpretations. Here I shall address the alternative approach, which is to invert multi-dimensional spectroscopic signals to directly extract the time-evolution of an excited state density matrix of interest (e.g., for a manifold of electronic excited states). I shall then discuss how coherent control of light-matter interactions can provide an additional tool to unraveling the role of quantum coherence in dynamical processes of complex biological systems. Finally, I shall discuss how non-adiabatic effects may affect excitation dynamics of light harvesting complexes following optical excitation.

TRACING OF BACKWARD ENERGY TRANSFER FROM LH2 TO LH1 IN PHOTOSYNTHETIC MEMBRANES GROWN UNDER HIGH AND LOW IRRADIATION

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Purple bacteria are excellent model systems for investigating the basic mechanisms of photosynthetic light harvesting (LH). Their photosynthetic unit is made of peripheral LH2 complexes and central LH1 complexes with the reaction center (RC), where charge separation takes place. The increasing excitonic interaction from LH2 towards LH1 ensures efficient vectorial energy transfer towards the RC. In this work, we trace the real-time evolution of the exciton densities in LH2 and LH1 within integral membranes of purple bacteria following selective photoexcitation. We could extract the rate constants for backward and forward energy transfer between LH1 and LH2 and unambiguously demonstrate for the first time the achievement of an equilibrium between LH2 and LH1 populations. Two key ingredients made possible this observation: (i) a specially designed femtosecond transient absorption spectrometer with 200 fs temporal resolution, combining tunable narrowband (10 meV) pump with broadband white-light probe pulses; (ii) derivative transient absorption spectroscopy, which we introduced to separate the signatures from the various bacterio-chlorophylls which are spectrally overlapped. This analytical method is generally applicable to excitonically coupled systems. We will present results for both *Rhodospseudomonas (Rps.) Palustris* and *Rps. Acidophila* bacteria, grown under high and low illumination conditions. For *Rps. Palustris*, we find that backward energy transfer is strongly reduced in membranes grown under low irradiation conditions, compared to high light grown ones [1]. We conclude that backward energy transfer is managed actively by the bacteria to avoid LH1 exciton deactivation under high irradiation conditions.

[1] L. L uer, V. Moulisov, S. Henry, D. Polli, T. H. P. Brotsudarmo, S. Hoseinkhani, D. Brida, G. Lanzani, G. Cerullo, and R. J. Cogdell, *Proc. Natl. Acad. Sci. USA* 109, 1473 (2012).

INCOHERENT LIGHT VS. ULTRAFAST PULSES

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Two-dimensional electronic spectroscopy (2DES) can reveal spectral and dynamical information hidden in linear spectra. The relevant dynamics of energy transfer in photosynthetic complexes occurs on a femtosecond (fs) time scale and can be resolved using 2DES by mapping interactions and correlations between absorption bands. However, in such experiments, photosynthetic complexes are excited by coherent fs pulses, whereas under natural conditions, they experience almost continuous and almost fully incoherent excitation by sunlight. We report on two approaches toward investigating the interaction of these systems with incoherent light:

We present a theoretical treatment of 2DES, as well as spectra of a model molecular system measured using broadband spectrally incoherent light. This result will motivate the design of experiments that show how dynamics can be initiated by incoherent light.

We also investigate the relationship between incoherent light and fs pulses by constructing a convex decomposition in the multi-mode coherent state (MMCS) basis. We show that for MMCSs that correspond to coherent pulses of light, i.e. with a fixed phase relationship between different frequency components, the decomposition does not satisfy the properties associated with a source of broadband black body radiation. We expect that if we lift the restriction on relative phases, a convex decomposition into MMCSs will be possible. This would be favourable for future calculations due to the elegant properties of the multi-mode displacement operator.

O33

**VIBRATIONAL STRUCTURES AND LONG-LASTING ELECTRONIC COHERENCE:
FROM MICROSCOPIC MODELS TO ACTUAL EXPERIMENTS**

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Recent observations of beating signals in the excitation energy transfer dynamics of a range of photosynthetic complexes have been interpreted as evidence for sustained electronic coherences that are sufficiently long-lived for energy transport and coherence to coexist. The microscopic origin of these long-lived coherences, however, remains to be fully uncovered. Here we present a possible such a mechanism and verify it by numerically exact simulations of system-environment dynamics using a novel methods whose foundations will be explained in the talk. Crucially, the non-trivial spectral structures of the environmental fluctuations and particularly discrete vibrational modes can lead to the spontaneous generation and sustenance of both oscillatory energy transport and electronic coherence. The relation between the proposed model and actual experimental evidence using two dimensional spin echo will be discussed and argued that both vibrational and purely electronic coherence are manifest in those experiments.

COMPRESSED SAMPLING AND WAVELET TRANSFORMATION: SIGNAL PROCESSING FOR QUANTUM BIOLOGY

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In light harvesting systems the role of the different frequencies involved in the dynamics is crucial to understand the presence of quantum effects and to understand which frequencies are supporting the quantum oscillatory behavior. New techniques have been developed to study these complex systems such as 2D Photon echo Spectroscopy. This techniques have introduced an extra degree of resolution and allow to appreciate phenomenon that were impossible to appreciate, for example, in an absorption spectrum. In this techniques the Fourier Transform (FT) has become the standard data analysis tool employed to study the frequencies domain. The problem using the FT is that the information of the temporal domain is lost, and if the process under study is not stationary, the temporal information is relevant to understand the physics behind some processes. Information as if the different frequencies involve in the dynamics are preset at the same or different time is relevant to understand the physics behind those process.

In this sense wavelet transformation plays a very important role because it introduces a temporal resolution study in the frequency. The computation of scientific data require to analyze this light harvesting system can be very time-consuming, even if they are ultimately determined by a small number of parameters. The principle of compressed sampling and wavelet suggests that for typical data we can achieve a considerable decrease in the computation time by avoiding the need to sample the full data set. We demonstrate the usefulness of this approach at the hand of two-dimensional (2-D) spectra in the context of ultrafast nonlinear spectroscopy of biological systems where numerical calculations are highly challenging due to the considerable computational effort involved in obtaining individual data points.

O35 (IS)

ADDRESSING QUANTUM COHERENCE ON THE NANOSCALE

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Efficient photosynthesis occurs in a densely packed network of pigment-protein antenna complexes at ambient temperature. Tracing the role of quantum effects requires both ultrafast coherent spectroscopy and addressing individual complexes within the dense heterogeneous ensemble. Here we combine fs coherent control with single molecule sensitivity and nanoscale confinement of light using optical antennas. We demonstrate ultrafast quantum coherent energy transfer within individual antenna complexes (LH2) of a purple bacterium under physiological conditions. We find that quantum coherences between electronically coupled energy eigen-states persist at least 400 fs, and that distinct, time-varying energy transfer pathways can be identified in each complex. Interestingly the single molecule approach allows to track coherent phase jumps between different pathways, which suggest that long-lived quantum coherence renders energy transfer robust in the presence of disorder. Finally, coupling photosynthetic complexes to resonant optical (plasmonic) antennas we spatially confine the excitation and tune the balance between radiative and non-radiative rates of the complexes, thus controlling quantum efficiency and brightness.

R. Hildner, D. Brinks, J. Nieder, R. Cogdell, N.F. van Hulst, *Science* 340 (june 2013).

O36 (IS)

INTERFACING AND INVESTIGATING MOLECULES USING OPTICAL NANOFIBERS

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Recently, optical nanofibers with diameters smaller than the wavelength of the guided light have attracted considerable interest in the field of quantum optics due to their high potential for efficiently interfacing light and matter. In my talk, I will report on two experiments using such nanofiber-optical interfaces. In the first experiment, we perform ultra-sensitive spectroscopic measurements on 3,4,9,10-perylene-tetracarboxylic dianhydride molecules (PTCDA) deposited on the fiber surface at ambient conditions. We use the guided mode of the nanofiber both for excitation of the molecules and for fluorescence collection and we show that surface coverages as small as 1 ‰ of a compact monolayer still give rise to absorption and fluorescence spectra with a good signal to noise ratio. Building on this experience, we set up an apparatus that allows us to cool the nanofiber to cryogenic temperatures while maintaining its optical properties. Using terrylene molecules embedded in p terphenyl crystals that are deposited onto the nanofiber, we record stable fluorescence excitation spectra of molecular ensembles which exhibit narrow spectral lines ($\approx 5 \text{ cm}^{-1}$ FWHM) in this cryogenic environment. These very encouraging findings show that the realization of nanofiber-based spectroscopy and manipulation of single molecules out of a molecular ensemble is within reach of this technique.

BROADBAND ENERGY-ENTANGLED PHOTONS FOR LIGHT-MATTER INTERACTION AND QUANTUM INFORMATIONA. Stefanov¹, C. Bernhard¹, B. Bessire¹, T. Feuerer¹, S. Lerch¹*1 Institute of Applied Physics, University of Bern, Sidlerstrasse 5, 3012 Bern, Switzerland*

Photonic entanglement is one of the most common methods to generate and study entangled states. Photon pairs can be entangled in different degrees freedom including polarisation, momentum or energy. Theoretical proposals have suggested that energy-entangled photons offer new control parameters for spectroscopy. Varying entanglement parameters permits to access to virtual states whose energy exceed that of the initial-to-final state transition [B. Saleh, et al., PRL, 80(16), 3483 (1998)], while it is expected that excitation of chromophore aggregates with non-classical light reveals the level structure of the double-exciton manifold [F. Schlawin, et al. (2012), PRA, 86(2), 1–10 (2012)].

Broadband energy entangled photons from parametric downconversion are a promising source of light to study those effects. Their wave function can be shaped by techniques similar to the shaping of short laser pulses opening the door to spectroscopy studies. We demonstrate the application of various transfer functions to the entangled photons by simultaneously shaping both phase and amplitude with a pulse shaper based on a spatial light modulator. We show how the two-photon wave function can be characterized by applying interferometric autocorrelation schemes. Additionally we study effects of a dispersive medium on the two photon wave function.

Finally broadband energy-entangled photons possess a very large entanglement content, as shown by computing the entropy of entanglement [T. Wihler, B. Bessire, A. Stefanov, arXiv:1209.2575 (2012)]. This entanglement can be used for quantum information processing in high dimensional spaces. We show results of quantum tomography and Bell inequalities measurement for dimension up to four [C. Bernhard, et al., arXiv:1303.6202 (2013)].

BIO-INSPIRED NANOSTRUCTURES: FROM ACTUAL BIOLOGICAL SYSTEMS THROUGH PHYSICAL MODELS TO SEMICONDUCTOR COUNTERPARTSL. Mourokh¹

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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. We explore this similarity studying artificial analogs of bioobjects.

In this talk, I discuss two systems, cytochrome-c-oxidase (CcO), and F₀-motor. CcO is one of the proton-pumping complexes of the mitochondria membranes. We propose the following mechanism of pumping. The electron- and proton-binding sites are located in close vicinity and have the two energy-levels each. As a result of the dipole-dipole interaction, an electron moves simultaneously to the lower level while the proton is excited to the upper level; thus both particles can proceed to the drain. The semiconductor counterpart of CcO is represented by two double-quantum dots systems formed in two-dimensional electron and hole gas layers, with a hole playing the role of a proton.

The pumped protons move back to the interior of the mitochondrion powering the rotation of the F₀-motor. This motor has about 10 to 15 proton binding sites. When the proton is transferred to the drain, the corresponding site becomes negatively charged and is attracted to a positive charge of the motor's stator. The motor starts to rotate and this site moves to the source to be repopulated. At the same time, the next site proceeds to the drain to be depopulated and, hence, the proton current facilitates the unidirectional rotation of the motor. The semiconductor analog includes a semiconductor, with embedded quantum dots, attached to the carbon nanotube. This system is placed in the uniform electric field and connected to electron reservoirs. When one of the quantum dots is populated by an electron, the negatively charged system would rotate in the presence of the electric field resembling the biological counterpart.

O39

MICROSCOPIC DERIVATION OF OPEN QUANTUM WALKS FOR BIOLOGICAL RATCHET MODELS

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Open quantum walks (OQWs) have been introduced recently as a type of quantum walk exclusively driven by dissipation. OQWs have been shown to have a rich dynamical behaviour with the potential of applications in quantum information processing and quantum biology. Here, starting from a system plus bath model we present the microscopic derivation of an open quantum walk describing the dynamical behaviour of a quantum ratchet. The model is applied to excitation transport in biological systems.

O40 (IS)

PROSPECT OF QUANTUM COHERENT INTERACTION AND CONTROL WITH OPTICAL ANTENNAS

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Combining plasmonic and optical antenna concepts with ultrafast and shaped laser pulses allows for the precise control of an optical excitation on femtosecond time and nanometer length scales. I will discuss concepts describing the induced near-field light-matter interaction in terms of impedance matching to a quantum system. I will extend into questions concerning the competition of radiative and nonradiative decay of the metallic nanostructure against preserving and manipulating the quantum coherence of the coherent excitation. Specific examples from our lab include adiabatic nano-focusing on a tip for nano-spectroscopy, spatio-temporal superfocusing, and optical control at the 10 nm-10 fs level. I will furthermore demonstrate the optical antenna coupled ultrafast free-induction decay in near-field infrared nano-spectroscopy of vibrational resonances and their tip-enhanced decoherence. I will conclude with an outlook for quantum coherent control in the near-field, strong light-matter interaction, and radiative decay engineering.

O41 (IS)

QUANTUM PROBES FOR THINGS THAT MATTER IN LIFE

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Diamond spin probes allow for quantum limited measurements of electric and magnetic fields as well as temperature and pressure under ambient conditions. The method ideally lends itself to achieve unprecedented resolution in e.g. magnetic resonance imaging and sensitive detection of paramagnetic species with relevant cellular function. The talk will describe applications to cellular imaging showing magnetic imaging with subcellular resolution and single protein sensitivity. Quantum control methods rendering the probe selectively sensitive to e.g. temperature or magnetic field will be described and limits are discussed.

COMPRESSED SENSING FOR MOLECULAR SPECTROSCOPY

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Molecular spectroscopy, in particular 2D ultrafast spectroscopy, is one of the key tools for investigating the presence or absence of quantum effects in light-harvesting systems. Developing powerful tools for spectral analysis is therefore essential for evaluating the role of electronic coherences in enhancing the rate of energy transfer in these systems. Compressed sensing is a rapidly-emerging signal processing paradigm that significantly reduces the number of measurements needed to accurately resolve signals. Here we demonstrate how compressed sensing can increase resolution in theoretical modeling of molecular spectra and in post-processing of 2D ultrafast experimental data, such as that used to study light-harvesting systems. As a first illustration, we apply compressed sensing to the computation of one-dimensional vibrational, electronic absorption, and circular dichroism spectra. Compared to the standard discrete Fourier transform approach, the computational cost is reduced by a factor of five. As a second example, we introduce a 2D variant of compressed sensing and apply it to phase-modulated ultrafast spectroscopy experiments. For the model system of atomic rubidium vapor, we obtain an order-of-magnitude improvement in spectral resolution along each dimension, as compared to a conventional discrete Fourier transform, using the same data set. More attractive is that compressed sensing allows for random undersampling of the experimental data, down to less than 5% of the data set, with essentially no loss in spectral resolution. We believe that compressed sensing can become a powerful tool in the quantum biology community for analyzing 2D ultrafast spectroscopy of light-harvesting systems.

O43 (IS)

QUANTUM BIOMIMETICS

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We investigate the conditions to emulate living-systems properties in quantum systems, and in return the potential contribution of quantum effects in the development of biological properties. Work developed in collaboration with Octavi Boada, Enrique Solano, Lucas Lamata, Unai Alvarez and Mikel Sanz.

GEOMETRY VS. NOISE: TOWARDS BIOMIMETIC EFFICIENT TRANSPORT NETWORKSF. Caruso ^{1,2}*1 LENS and Dipartimento di Fisica e Astronomia, Università di Firenze, I-50019 Sesto Fiorentino, Italy**2 QSTAR, Largo Enrico Fermi 2, I-50125 Firenze, Italy*

Transport properties play a crucial role in several fields of science, as biology, chemistry, sociology, information science, and physics. The behavior of many dynamical processes running over complex networks is known to be closely related to the geometry of the underlying topology that can be described by the spectral properties of such graphs, i.e. the spectrum of the so-called adjacency matrices defining these structures. Here, we generalize this connection to the quantum version of such dynamics processes over large complex networks [1]. In particular, we investigate the relation between static measures of geometrical properties of complex graphs (as connectivity, clustering, shortest path length, etc.) and the (dynamical) capability to quickly and robustly transmit energy (or information) from two distant points, remarkably assisted by external noise and quantum features as coherence [2-3], by means of quantum stochastic random walk formalism [4]. Hence, the interplay among geometry, coherence and noise is studied in terms of transport efficiency and relative robustness. These results might pave the way for designing optimal bio-inspired geometries of efficient transport nanostructures that can be used for solar energy and also quantum information and communication technologies.

References

[1] F. Caruso, manuscript in preparation (2013).

[2] F. Caruso, A.W. Chin, A. Datta, S.F. Huelga, and M.B. Plenio, *J. Chem. Phys.* 131, 105106 (2009).[3] F. Caruso, S.F. Huelga, and M.B. Plenio, *Phys. Rev. Lett.* 105, 190501 (2010).[4] J.D. Whitfield, C.A. Rodriguez-Rosario, and A. Aspuru-Guzik, *Phys. Rev. E* 81, 022323 (2010).

O45 (IS)

QUANTUM INTERFERENCE ASSISTED METROLOGY ON BIOMATERIALS

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Throughout the last years we have developed new schemes to probe the quantum wave nature of massive matter [1]. Both the Kapitza-Dirac-Talbot-Lau (KDTLI) interferometer [2] and the Optical-ionization Time-Domain Matter Wave (OTIMA) interferometer [3] allow us now to study the delocalization of complex molecules, clusters and clusters of molecules over mesoscopic times and distances.

These tools permit us to push the frontiers of experimental matter wave physics and they have recently also opened a new avenue to quantum-assisted metrology of molecular properties [4-7].

Here we will discuss in particular the aspect of optical, electronic, collisional or magnetic metrology with regard to biomolecules and ways to image biological nanomatter using quantum methods.

- 1) K. Hornberger, S. Gerlich, P. Haslinger, S. Nimmrichter, and M. Arndt, Rev. Mod. Phys. 84, 157 (2012).
- 2) S. Gerlich, S. Eibenberger, M. Tomandl, S. Nimmrichter, K. Hornberger, P. Fagan, J. Tüxen, M. Mayor, and M. Arndt, Nature Commun 2,263(2011).
- 3) P. Haslinger, N. Dörre, P. Geyer, J. Rodewald, S. Nimmrichter, and M. Arndt, Nature Physics (2013), DOI: 10.1038/NPHYS2542
- 4) S. Gerlich, M. Gring, H. Ulbricht, K. Hornberger, J. Tüxen, M. Mayor, and M. Arndt, Angew. Chem. Int. Ed. 47, 6195 (2008).
- 5) S. Nimmrichter, K. Hornberger, H. Ulbricht, and M. Arndt, Phys. Rev. A 78, 063607 (2008).
- 6) J. Tüxen, S. Gerlich, S. Eibenberger, M. Arndt, and M. Mayor, Chem. Comm. 46, 4145 (2010).
- 7) S. Eibenberger, S. Gerlich, M. Arndt, J. Tüxen, and M. Mayor, New J. Phys. 13, 43033 (2011).
- 8) M. Gring, et al., Phys. Rev. A 81, 031604 (2010).

P01

QUANTUM BIOMIMETICS: SELF-REPRODUCTION BEHAVIOURS IN QUANTUM SYSTEMS

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We propose to emulate biological behaviours in quantum controllable systems as trapped ions or superconducting circuits. We address the issue of reproducing living-system properties, as self replication, self correction, and evolution, in a state of the art controllable quantum system of a few qubits. We aim at defining a quantum concept of life and we also want to explore further whether quantum mechanics plays a significant role in the origin or development of living systems.

P02

AN OPEN QUANTUM SYSTEMS APPROACH TO MAGNETORECEPTION

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The emerging field of Quantum Biology centres on the possibility that living things might employ nontrivial quantum effects in their day to day behaviour. This surprising result has given rise to the investigation of such quantum effects in areas as diverse as photosynthesis and magnetoreception. In the case of magnetoreception, experiment supports the role of a radical pair mechanism in sensing the magnetic field. Following from radical pair theory and using the theory of open quantum systems we have completed the analytical derivation of the master equation in the Born-Markov approximation for the simple case of two electrons, each interacting with an environment of N nuclear spins as well as the external magnetic field, then placed in a boson bath and allowed to dissipate. Solving this master equation will allow us to analyse the dynamics of the radical pair.

P03

SUPPRESSION THE POPULATION OF XANTHOMONAS AXONOPODIS PV. CITRI BY GAMMA RAY AND ITS EFFECT ON QUALITY OF SATSUMA MANDARIN FRUITS

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Citrus canker caused by *Xanthomonas axonopodis* pv. *citri* is one of the most important diseases which should be strictly quarantined in many countries such as Spain, USA, and Brazil. In order to find an alternative methods instead of application of methyl bromide, utility of gamma ray for eradication of citrus canker pathogen *X. axonopodis* pv. *citri* was investigated. By gamma ray level of 50 gray about 50% of the bacterial cells was died. Eradication of the bacterial cells in concentration of 1.0×10^7 cfu/ml was approved after expose of the gamma ray above 300 gray. Even in this level of gamma ray there were no changes in hardness, total soluble solids and acidity of the Satsuma mandarin fruits. Based on these results it was suggested that gamma ray may be useful for eradication of *X. axonopodis* pv. *citri* existing on the surface of Satsuma mandarin fruit.

P04

INTERACTION OF NUCLEOBASES WITH SEMICONDUCTING NANOTUBES AND NANOPARTICLES: DOES THE SOLVENT MATTER?

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Materials and structures at nanoscale have attracted a lot of interest for their potential applications in biosensing, luminescent probes for DNA, drug delivery etc. Gaining fundamental understanding of the interaction of bio-systems with materials is therefore critical in putting all these applications into full play. Despite the fact that most of these interactions appear in aqueous environment, the solvent effect has often been neglected in most of the theoretical studies due to computational complexities.

In this work, we will investigate the role of the solvent effects in determining the accurate interaction energies using first principles method. We will consider the examples of nucleobases interacting with BN nanotubes and chalcogenide nanoparticles for such calculations. The results reveal a significant effect from the aqueous environment, which may largely reduce the interaction strength of the bioconjugated system due to the polarization of the dielectric solvent medium.

P05

BIO-INSPIRED QUANTUM CLONING OF PARTIAL QUANTUM INFORMATION

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The no-cloning theorem forbids copying an unknown state, opening the possibility of cloning partial quantum information beyond the classical realm. Our system consists of a unknown quantum state gathered to a chosen ancillary state, manipulated in order to obtain a coupled two-body state. The resulting state is sequentially gathered to new ancillas and controlled with the same operation, stepwise producing exponentially growing generations of mutually coupled individuals. Therefore, one may naturally wonder which quantum information can be shared through generations under the restriction of the no-cloning theorem. In this work, we focus on the quantum cloning of expectation values of observables. We show how to construct the local operations in such a way that the expectation values and higher-order moments are preserved generation by generation by every individual. Additionally, we also prove that there are state properties which are preserved by each generation as a whole, suggesting a scaling in the problem complexity.

P06

DISSIPATIVE APPROACH TO QUANTUM NEURAL NETWORKS

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Classic models of neural networks find a wide range of application in the field of physics, computational science and especially neural biology as they show properties like associative memory and pattern completion. In recent years, the possibilities of quantum effects leading to computational advantages have been explored. Research into these so called Quantum Neural Networks has been mainly based on quantum computation algorithms. In order to reproduce the nonlinear dynamics of biological neural networks we suggest to introduce dissipative elements into QNN models.

P07

QUANTUM DYNAMICS AND ELECTRONIC SPECTROSCOPY WITHIN THE FRAMEWORK OF WAVELETS

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This paper serves as a first-time report on formulating important aspects of electronic spectroscopy and quantum dynamics in condensed harmonic systems using the framework of wavelets, and a stepping stone to our future work on developing anharmonic wavelets. The Morlet wavelet is taken to be the mother wavelet for the initial state of the system of interest. This work reports daughter wavelets that may be used to study spectroscopy and dynamics of harmonic systems. These wavelets are shown to arise naturally upon optical electronic transition of the system of interest. Natural birth of basis (daughter) wavelets emerging on exciting an electronic two-level system coupled, both linearly and quadratically, to harmonic phonons is discussed. It is shown that this takes place through using the unitary dilation and translation operators, which happen to be part of the time evolution operator of the final electronic state. The corresponding optical autocorrelation function and linear absorption spectra are calculated to test the applicability and correctness of the herein results. The link between basis wavelets and the Liouville space generating function is established. An anharmonic mother wavelet is also proposed in the case of anharmonic electron–phonon coupling. A brief description of deriving anharmonic wavelets and the corresponding anharmonic Liouville space generating function is explored. In conclusion, a mother wavelet (be it harmonic or anharmonic) which accounts for Duschinsky mixing is suggested.

ENVIRONMENTAL EFFECTS ON THE EXCITON DYNAMICS IN THE FMO LIGHT-HARVESTING COMPLEX

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In light-harvesting systems, antenna complexes absorb the sun light and transfer the excitation energy to the photosynthetic reaction center for further processing. Experimental observations of long-lived quantum coherences in the Fenna-Matthews-Olson (FMO) light-harvesting complex at different temperatures has led to considerable effort trying to explain this phenomenon. Based on a QM/MM method [1,2], we performed simulations of the FMO complex in a glycerol-water mixture at 300 K as well as 77 K, matching the conditions of earlier 2D spectroscopic experiments by Engel et al. In this method, in order to calculate vertical excitation energies of the individual bacteriochlorophylls, the quantum calculations are performed along a molecular dynamics trajectory. The calculations yielded spectral densities of each individual pigment of FMO, in water and glycerol-water solvents at 300 K and 77 K [3]. This allows us to compare simulations using different environments with the experimental results.

[1] C. Olbrich, Th. la Cour Jansen, J. Liebers, M. Aghtar, J. Strümpfer, K. Schulten, J. Knoester, and U. Kleinekathöfer, From Atomistic Modeling to Excitation Transfer and Two-Dimensional Spectra of the FMO Light-Harvesting Complex, *J. Phys. Chem. B* 115, 8609–8621 (2011).

[2] C. Olbrich, J. Strümpfer, K. Schulten, and U. Kleinekathöfer, Theory and Simulation of the Environmental Effects on FMO Electronic Transitions, *J. Phys. Chem. Lett.* 2, 1771–1776 (2011).

[3] M. Aghtar, J. Strümpfer, C. Olbrich, K. Schulten, and U. Kleinekathöfer, The FMO Complex in a Glycerol-Water Mixture (submitted).

ELECTRONIC, VIBRONIC AND MIXED COHERENCES OBSERVED IN 2D SPECTROSCOPY OF MOLECULAR SYSTEMS

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The role of coherent excitation dynamics and migration within molecular complexes and its influence on the efficiency of energy and charge transfer is intensively discussed during the last few years. The robustness of quantum coherences is proven by the long-persisting spectral oscillations observed by femtosecond nonlinear spectroscopic techniques for many different photosynthetic systems. Such a quantum-like behavior is evident even for extremely large and disordered systems in ambient conditions.

It was recently shown that actually molecular vibrations may be responsible for intensive long-lived coherence oscillations. As the common ground state model is widely accepted, one would expect the observed quantum beatings to reflect the vibrational ground state wavepacket motion. Such coherences, as well as the excited state vibronic coherences, would be less sensitive to disorder than the purely electronic coherences.

In this contribution, the vibronic molecular aggregate is theoretically considered. In the model, coupling of electronic transitions to a single mode of intramolecular vibrations is implemented by considering the electrostatic interaction between the electronic states of molecule constituents and the set of discrete vibrational states. Time-resolved 2D spectra are analyzed while simulating different environment conditions. The oscillatory behavior dependence on the system-bath coupling strength and energetic disorder lets us clearly discriminate between electronic and vibronic coherence oscillations. Also, the electronic coherences are more likely to be suppressed due to energetic system disorder. The conclusions on requirements for the electronic, vibronic or mixed coherences to be observed simultaneously in 2D spectra of molecular aggregates are rigorously supported by the experimental results of photosynthetic bacterial reaction center.

P10

IS ENERGY TRANSFER IN NATURAL PHOTOSYNTHETIC SYSTEMS A SUPERRADIANT PHENOMENON?

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Evidence of quantum coherent effects has been recently found in photosynthetic light-harvesting systems (G.S. Engel et al., Nature 446, 782 (2007)), and in other biological systems, even at room temperature. These findings raise many questions: how Nature can preserve quantum coherence in macromolecules in a wet and hot environment?

What is the functional purpose of quantum coherence in natural systems? All these questions are of paramount importance for building scalable quantum devices able to work at room temperature and their study is at the center of the newly born field of quantum biology. In this talk we consider the interplay of different coherent effects, localization and superradiance, in determining energy transfer in natural photosynthetic systems. We will show our results on one of the most studied photosynthetic complexes, the Fenna-Matthews-Olson complex, and new results of our group on the LHI-RC complex.

Our results suggest that Nature employs quantum coherence to maximize energy transfer efficiency through superradiance.

REFERENCES:

G.L. Celardo, F. Borgonovi, V.I. Tsifrinovich,
M. Merkli and G.P. Berman,
The Journal of Physical Chemistry C, 116, 22105 (2012).

ENHANCEMENT OF VIBRONIC AND GROUND-STATE VIBRATIONAL COHERENCES IN 2D SPECTRA OF PHOTOSYNTHETIC COMPLEXESA. Chenu^{1,2}, N. Christensson¹, G. Scholes² and T. Mančal¹*1 Faculty of Mathematics and Physics, Charles University in Prague, Ke Karlovu 5, 121 16 Prague 2, Czech Republic**2 Department of Chemistry, University of Toronto, 80 Saint George Street, Toronto, Ontario, M5S 3H6 Canada*

A growing set of evidence shows that the long-lived oscillations observed in various 2D spectra of photosynthetic systems can originate from electronic, vibrational or a mixture of both coherences, and distinguishing the different contributions is not trivial [1]. We present a selection of recent experimental results exhibiting long-lived coherences and propose a theoretical model showing that coherences of vibronic origin with ps lifetime can be enhanced in coupled systems, such that they become of significant amplitude in experiments using non-linear spectroscopy.

We use a vibronic model to investigate the recently proposed mechanism of enhancement of coherent oscillations due to mixing of electronic and nuclear DOF [2,3]. We study a dimer system to elucidate the role of resonance coupling, site energies, vibrational frequency and energy disorder in the enhancement of vibronic and ground-state vibrational coherences, and to identify regimes with significant enhancement. For a heterodimer representing coupled BChls of the FMO complex, the initial amplitude of the vibronic (vibrational) coherences are enhanced by up to 15 (5) times compared to the vibrational coherences in the isolated monomer. This maximum enhancement occurs when there is a resonance between the electronic energy gap and the frequency of the vibrational mode.

The excitonic mixing of electronic and vibrational DOF leads to additional dephasing relative to the ground-state vibrational coherences. Long-lived vibronic coherences are found to be generated only when the frequency of the mode is in the vicinity of the electronic resonance. Although the vibronic coherences exhibit a larger initial amplitude compared to the ground-state vibrational coherences, due to the dephasing of the former, both type of coherences have a similar magnitude at longer population time.

1. Turner et al. PCCP, 14, 4857 (2012).
2. Christensson et al. JPCB, 116, 7449 (2012).
3. Tiwari et al. PNAS, 110, 1203 (2013).

P12

ADIABATIC AND NON-ADIABATIC EFFECTS IN ELECTRONIC ENERGY TRANSFER THROUGH LIGHT HARVESTING ARRAYS

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Two-dimensional photon echo spectroscopy experiments of photosynthetic systems have suggested that quantum coherence between electronic excited states may play a significant role in electronic energy transfer. We present a theoretical approach to characterize the adiabatic and non-adiabatic effects of vibrations on the energy transfer dynamics, and illustrate this explicitly for a model system consisting of an excitonic dimer strongly coupled to two vibrational modes. We analyze the implications of these effects for quantum process tomography, finding that under two-pulse excitation the local adiabatic effects produce correlations between electronic and vibrational states that imply the corresponding dynamics are governed by a non-completely positive map.

A SPECTROSCOPIC WITNESS FOR ELECTRONIC COHERENCEJ. Goodknight¹, J. Yuen-Zhou¹, and A. Aspuru-Guzik¹*1 Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, USA*

In many photosynthetic complexes, it appears as if the excited electronic states of nearby chlorophylls stay in a coherent excited state for far longer than would be expected given their surrounding environments. Commonly-used methods for inferring this electronic coherence suffer, however, from ambiguity. The usual inference method--oscillations in off-diagonal peaks of 2D electronic spectra--can also occur as a result of the component molecules' vibrational structure (vibrational coherences) and thus do not provide a definitive answer to whether the excited states stay coupled[1]. We have proposed an unambiguous tool to determine this: an experimental witness for electronic coherence[2]. By doing pump-probe spectroscopy at a series of different pulse widths, we can extrapolate to the impulsive (broad-band) limit. In this limit, pump-probe signal oscillations due to vibrational coherence disappear and all that remains are oscillations due to electronic coherence.

References:

- 1) Joel Yuen-Zhou and Alán Aspuru-Guzik. Quantum Process Tomography of Excitonic Dimers from Two-dimensional Electronic Spectroscopy. I. General Theory and Application to Homodimers. *The Journal of Chemical Physics* 134, no. 13 (April 7, 2011): 134505.
- 2) Joel Yuen-Zhou, Jacob J. Krich, and Alán Aspuru-Guzik. A Witness for Coherent Electronic vs Vibronic-Only Oscillations in Ultrafast Spectroscopy. *Journal of Chemical Physics* 136, no. 23 (June 2012): 234501.

**A SIMPLE APPROACH TO DISSIPATIVE ENERGY TRANSPORT IN NON-
PERTURBATIVE REGIMES**J. Iles-Smith¹, A. Nazir¹*1 Blackett Laboratory, Department of Physics, Imperial College London, SW7 2AZ, UK*

The role of quantum mechanics in energy transport has attracted much interest in recent years. In particular, the mechanisms responsible for the highly efficient and robust energy transport observed in photosynthetic complexes remains an open question. One possible explanation for this is the interplay between quantum coherence and dissipation, making understanding such systems of both practical and foundational importance. However, complex system-environment interactions make modelling and understanding the behaviour of these systems a daunting task. By taking a master equation approach we can acquire a set of simple and often intuitive equations describing the system dynamics. Unfortunately, however, many of these techniques struggle to accurately describe system behaviour in highly non-Markovian regimes.

In this poster we present a mapping between the spin-boson model to the so-called reaction coordinate model, in which a two level system is coupled to a single harmonic mode, which is in turn coupled to a dissipative bath. By deriving a second order master equation for the mode-bath coupling and treating the system-mode coupling non-perturbatively, we can account quantitatively for non-Markovian behaviour in strong coupling and high temperature regimes.

P15

TWO-DIMENSIONAL SPECTROSCOPY AS A TOOL TO STUDY QUANTUM PHENOMENA IN BIOLOGY

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With the observation of oscillations in the two-dimensional electronic spectrum of FMO this technique has become popular for studying quantum phenomena in chemistry and biology. The interpretation of two-dimensional spectra is, however, far from trivial. The oscillations observed in FMO have both been attributed to coherent electronic transport, vibrational motion and a mixture of those. Here we will discuss the principles of two-dimensional spectroscopy and the power of this method in the study of quantum phenomena using illustrative examples. We will consider a simple dimer, amide I vibrations of proteins, a J-aggregate, and the FMO complex. We will focus the discussion on energy transfer in those systems and how it is reflected in the two-dimensional spectra. The utilization of polarization directions and the difference between rephasing and non-rephasing spectra will be included.

**VIBRATION ASSISTED RESONANCE FOR ENERGY TRANSPORT IN PIGMENT-
PROTEIN COMPLEXES**EK. Irish¹, R. Gómez-Bombarelli¹, BW. Lovett¹*1 School of Engineering and Physical Sciences, Heriot Watt University, Edinburgh, EH14
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The surprising demonstration of long-lived quantum coherence in photosynthetic pigment-protein complexes has provoked substantial interest across several disciplines. From a physicist's point of view, one problem with quantum coherent energy transport in biological systems is the presence of disorder in the electronic excitation energies of different pigment molecules. Energy differences between sites dramatically reduce the efficiency of population transfer across a network undergoing pure quantum coherent dynamics. This difficulty can be overcome, at least to some extent, by the addition of environmental noise. However, the proliferation of increasingly sophisticated numerical techniques for treating the environment has yet to settle the debate over the origin and functional role of the observed quantum coherence.

Recently it has begun to be appreciated that discrete intra- and/or intermolecular vibrational modes identified in fluorescence experiments may play a role in improving energy transport across pigment-protein complexes. We present a microscopic mechanism by which intramolecular vibrational modes create resonant energy transfer pathways, enhancing the efficiency of both coherent and dephasing-assisted transfer. The principles of this vibration-assisted resonance are illustrated in a simple model based on one energy-transfer branch of the well-characterised Fenna-Matthews-Olson complex. Despite its simplicity, this model captures the interplay between strong electronic coupling that produces delocalised exciton states and resonance-enhanced weak coupling to local vibrational modes. We show that intramolecular vibrations can enhance energy transport efficiency, without invoking correlated fluctuations or delocalised phonon modes.

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EXCITATION ENERGY TRANSFER EFFICIENCY: EQUIVALENCE OF TRANSIENT AND STATIONARY SETTING AND THE ABSENCE OF NON-MARKOVIAN EFFECTS

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We analyze efficiency of excitation energy transfer in photosynthetic complexes in transient and stationary setting. In the transient setting the absorption process is modeled as an individual event resulting in a subsequent relaxation dynamics. In the stationary setting the absorption is a continuous stationary process, leading to the nonequilibrium steady state. We show that, as far as the efficiency is concerned, both settings can be considered to be the same, as they result in almost identical efficiency. We also show that non-Markovianity has no effect on the resulting efficiency, i.e., corresponding Markovian dynamics results in identical efficiency. Even more, if one maps dynamics to appropriate classical rate equations, the same efficiency as in quantum case is obtained.

Reference: arXiv 1303.2046 (accepted for publication in JCP)

QUANTUM COHERENCE IN PHOTOSYNTHESIS - A RACE BETWEEN WAVE LIKE MOTION AND PROTEIN VIBRATIONSC. Kreisbeck¹, T. Kramer^{2,3}*1 Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA**2 Institute for Physics, Humboldt Universität zu Berlin, 12489 Berlin, Germany**3 Department of Physics, Harvard University, Cambridge, MA 02138, USA*

Recent advances in two-dimensional (2d) electronic spectroscopy (ES) reveal remarkable energy transport properties in light-harvesting complexes (LHCs). In particular, oscillatory components in 2d echo-spectra are considered as evidence for quantum wave like motion. This relevance of wave like motion is surprising and inspires to design artificial excitonic devices, which take full advantage from robust quantum coherence. In order to guide experimentalists in the fabrication process it is of fundamental importance to unambiguously characterize and probe the intended transport properties of the designed functional unit.

The most outstanding question is how to read the detected wiggles in the 2d-echo spectra. There is a discrepancy between the experimental interpretation as wave-like motion and recent theoretically proposed models that interpret the wiggles in terms of vibronic coherence induced by underdamped vibrational modes. We show that the energy transfer is most dominantly affected by electronic coherence, while the influence of vibronic coherence is two orders of magnitude smaller. However, the situation is different in the experimental 2d echo-spectra. Here, the ground state vibrations lead to an enhanced contribution of vibronic coherence, while electronic coherence is underestimated due to destructive interference of stimulated emission and excited state absorption. Additional analysis like the proposed witness for electronic coherence (J. Yuen-Zhou et al., J. Chem. Phys., 136, 234501 (2012)) may be used to filter the contribution of the ground state vibrations.

References:

[1] C. Kreisbeck and T. Kramer, Online 2d spectra tool for analytical continuation of GPU-HEOM at nanohub.org (2013), <http://nanohub.org/resources/gpuheompop>, DOI:10.4231/D3RB6W248

[2] C. Kreisbeck, T. Kramer, Long-Lived Electronic Coherence in Dissipative Exciton-Dynamics of Light-Harvesting Complexes, Journal of Physical Chemistry Letters, 3, 2828 (2012)

HIGHLY EFFICIENT NOISE-ASSISTED ENERGY TRANSPORT IN CLASSICAL OSCILLATOR SYSTEMS

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Photosynthesis is a biological process that involves the highly efficient transport of energy captured from the sun to a reaction center, where conversion into useful biochemical energy takes place. Even though one can always use a quantum perspective to describe any physical process, since everything follows the laws of Quantum Mechanics, is the use of quantum theory imperative

to explain this high efficiency? Making use of the quantum-classical correspondence of electronic energy transfer recently introduced by Eisfeld and Briggs [Phys. Rev. E 85, 046118 (2012)], we show that the highly efficient noise-assisted energy transport described by Rebentrost et al. [New J. Phys. 11, 033003 (2009)], and Plenio and Huelga [New J. Phys. 10, 113019 (2008)], as the result of the interplay between the quantum coherent evolution of the photosynthetic system and noise introduced by its surrounding environment, it can be found as well in purely classical systems. The wider scope of applicability of the enhancement of energy transfer assisted by noise might open new ways for developing new technologies aimed at enhancing the efficiency of a myriad of energy transfer systems, from information channels in micro-electronic circuits to long-distance high-voltage electrical lines.

A QUANTUM CONTROL MECHANISM FOR PHOTOSYNTHETIC ELECTRON TRANSFER

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Photosynthetic reaction centers convert excitation energy into the free energy of charge-separated states extremely efficiently. Purple bacterial reaction centres were the first to be biochemically isolated and characterised, and while they are arguably the best understood, aspects of the relation between the structure and function of these reaction centres have yet to be fully understood. For the reaction centre of the purple bacterium *Rhodobacter sphaeroides*, such aspects include the contrast between the twofold structural symmetry and the evidence for asymmetry in the path of the electron transfer, as well as the rates of recombination of the charge-separated states being significantly slower than those of the forward electron transfer.

We propose a simple model for electron transfer in an open quantum system, and investigate the extent to which environmental spins provide a control mechanism for the kinetics of the electron transfer process. This model of electron transfer is applied to the reaction centre of the purple bacterium *Rhodobacter sphaeroides*, and aspects of the structure-function relation are discussed in the context of the model.

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QUANTUM DYNAMICS OF NON-ADIABATIC VIBRONIC STATES IN REACTION CENTRE ENERGY TRANSFER

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The recent observation of long-lasting (picosecond) quantum beating signals in the ultrafast spectroscopy of a range of photosynthetic pigment-protein complexes has led to tremendous, multidisciplinary interest in the role that coherence and quantum effects might play in the often high internal efficiency of light-to-charge conversion found in these biological systems. Amongst other ideas, strong non-adiabatic coupling mediated by sharp and resonant vibrational modes has been shown to effectively increase the electronic coherence time of energy-carrying excitons, and also to induce novel energy transfer that transiently violates detailed-balance. This work explores the character of the vibronic states that emerge during these dynamics and sets out in detail how these lead to the phenomenology above, as well as the effective optical responses of these systems. Using these insights, we suggest a functional role for non-adiabatic dynamics and demonstrate how they can be used to rationalise recent experimental data on bacterial reaction centres.

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ENERGY TRANSFER PROPERTIES AND ABSORPTION SPECTRA OF THE FMO COMPLEX: FROM EXACT PIMC CALCULATIONS TO TCL MASTER EQUATIONS

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We investigate the excitonic energy transfer (EET) in the Fenna-Matthews-Olsen complex and obtain the linear absorption spectrum (at 300 K) by a phenomenological time-convolutionless (TCL) master equation which is validated by utilizing Path Integral Monte Carlo (PIMC) simulations. By applying Marcus' theory for choosing the proper Lindblad operators for the long-time incoherent hopping process and using local non-Markovian dephasing rates, our model shows very good agreement with the PIMC results for EET. It also correctly reproduces the linear absorption spectrum that is found in experiment, without using any fitting parameters.

NONLINEAR OPTICAL RESPONSE IN MOLECULAR DIMERS WITH SIGNATURES OF VIBRONIC DYNAMICS

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In recent studies interaction between electronic and vibrational degrees of freedom has been proposed as a plausible explanation of long lived oscillatory modulation observed in two-dimensional coherent spectra of light-harvesting complexes [1] and its important role in energy transfer dynamics [2] has been suggested. Realistic computer simulations are costly for large photosynthetic aggregates. We study a simple toy model: vibronic dimer where some pronounced vibrational modes are explicitly included into eigenstates analysis. These vibronic (exciton-vibrational) eigenstates are linearly coupled to harmonic bath, resulting dephasing and population relaxation is treated by Redfield relaxation theory. We will present theoretical analysis and numerical simulation of absorption and 2D spectra of the vibronic dimer and demonstrate that this simple model well reproduces key features observed in spectra of photosynthetic antennae such as long live oscillatory modulations, phase shift in amplitude oscillation of diagonal and cross peak and fast transfer rate.

[1] Christensson, N., Kauffman, H. F., Pullerits, T., Mančal, T. Origin of long lived coherences in light-harvesting complexes. *J. Phys. Chem. B.* 116, 7449 (2012)

[2] Kolli, A., O'Reilly, E. J., Scholes, G. D., Olaya-Castro, A. The fundamental role of quantized vibrations in coherent light harvesting by cryptophyte algae. *J. Chem. Phys.* 137, 174109 (2012)

PHOTOSYNTHESIS EXPLOITS QUANTUM COHERENCE FOR EFFICIENT SOLAR ENERGY CONVERSION

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Photosynthesis has found an ultrafast and highly efficient way of converting the energy of the sun into electrochemical energy: the Photosystem II Reaction Center (PSII RC) converts the energy into a charge separated state [1] with almost 100% efficiency. That separation of charges creates an electrochemical gradient across the photosynthetic membrane which ultimately powers the photosynthetic organism. The understanding of the molecular mechanisms leading to charge separation will provide a template for the design of efficient artificial solar energy conversion systems.

In this work we have applied two-dimensional electronic spectroscopy on the fully functional PSII RC from higher plants at cryogenic and room temperature as well as standard Redfield modelling in order to investigate the presence and the role of quantum coherence in determining the high speed and efficiency of the charge separation process.

On the one hand, the experimental results show clear long-lived quantum beats in the 2D spectral traces at both temperatures. The set of frequencies contained in the beats (retrieved by Fourier transform) corresponds to intramolecular Chl a vibrational modes and, interestingly, these frequencies match the difference in energy levels between the electronic states in the system. The 2D frequency maps (frequency amplitude distribution in the 2D spectra) strongly indicate that we observe vibronic coherence between the electronic states in the system, i.e. the long-lived electronic coherences are sustained by non-equilibrium vibrational modes [2]. On the other hand, the calculated 2D spectra by standard Redfield modelling using our current "disordered exciton-charge-transfer" model [3] are in excellent agreement with the experimental 2D spectra. This model also shows that the presence of electronic coherence between excitons and between excitons and charge-transfer states enhances the speed and efficiency of energy and electron transfer, respectively.

In conclusion, the combination of experimental and theoretical evidence strongly indicates that the PSII RC performs charge separation via a quantum coherent mechanism and, therefore, it operates as a quantum designed light trap. We propose that this design principle should be applied to the construction of artificial devices in order to reach photoconversion efficiencies close to 100%.

[1] a) E. Romero, B. A. Diner, P. J. Nixon, W. J. Coleman, J. P. Dekker, R. van Grondelle, *Biophys. J.* 2012, 103, 185-194; b) E. Romero, I. H. M. van Stokkum, V. I. Novoderezhkin, J. P. Dekker, R. van Grondelle, *Biochemistry* 2010, 49, 4300-4307.

[2] a) A. Kolli, E. J. O'Reilly, G. D. Scholes, A. Olaya-Castro, *J. Chem. Phys.* 2012, 137, 174109; b) A. W. Chin, J. Prior, R. Rosenbach, F. Caycedo-Soler, S. F. Huelga, M. B. Plenio, *Nat. Phys.* 2013, 9, 113-118.

[3] a) V. I. Novoderezhkin, J. P. Dekker, R. van Grondelle, *Biophys. J.* 2007, 93, 1293-1311; b) V. I. Novoderezhkin, E. Romero, J. P. Dekker, R. van Grondelle, *ChemPhysChem* 2011, 12, 681-688.

FINITE TEMPERATURE SIMULATIONS OF EXCITON DYNAMICS IN BIOLOGICAL STRUCTURES

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The Time Evolving Density Matrix with Orthogonal Polynomial Algorithm (TEDOPA) is a numerically exact technique to simulate open quantum systems interacting with arbitrarily structured environments.

The algorithm has been developed in order to analyse excitonically coupled systems in structures of biological relevance at physiological temperatures, though there is a wide range of applications in solid state physics as well. These technical developments are illustrated, based upon its successful application to reproduce the experimental observation of long-lived coherences in the Fenna-Matthews-Olson complex. Further applications regarding similar harvesting pigment protein structures are also considered.

INFLUENCE OF DIFFERENT SPECTRAL DENSITIES ON ENERGY TRANSFER IN THE FMO COMPLEX

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Recently, many models have been put forward for computing the spectral density of the Fenna-Matthews-Olsen (FMO) complex, combining molecular dynamics approaches with quantum chemistry methods. In this poster we study what influence the different existing prescriptions for the spectral density have on the excitation energy transfer and on spectroscopic observables such as the absorption spectrum. In particular, this is done for the spectral density in the harmonic approximation by Valleau et. al [1] and for the spectral density introduced by Olbrich et. al. [2]. The dynamics is described by our recently introduced phenomenological time-convolutionless (TCL) master equation [3]. This model combines both coherent transport and incoherent transfer processes induced by the non-Markovian interactions with the protein environment.

References:

- [1] J. Chem. Phys. 137, 224103 (2012)
- [2] J. Phys. Chem. Lett. 2011, 1771-1776
- [3] Submitted to J. Phys. Chem. B (arxiv: physics.chem-ph/1301.0839)

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EXCITONIC DELOCALIZATION IN CHROMATOPHORE VESICLES OF RB. RUBRUM

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The very symmetrical macromolecular arrangement of purple bacteria *Rb. rubrum* provides a favorable scenario for coherent dynamics and its experimental verification with standard linear spectroscopic techniques. Based on available structural and spectroscopic characterization of the light harvesting complex 1 (LH1) in these organisms, we provide theoretical evidence for the yet-unexplored possibility of witnessing excitonic delocalization within single and among neighboring LH1 structures.

COHERENT CHARGE SEPARATION IN AN ORGANIC DEVICESL Smith¹, AW Chin¹*1 Theory of Condensed Matter, Cavendish Laboratory, Cambridge, UK*

In recent years quantum-biological research into photosynthesis has focused on two questions: is the process of exciton transport towards the reaction centre quantum coherent, and can coherence play a role in increasing photosynthetic efficiency? Since coherences are expected to decay rapidly in organic systems, a relevant coherent process timescale must lie within the coherence lifetime.

Similar questions have emerged in the organic photovoltaics community. Here solar cells are formed from composites of electron accepting and electron donating organic semiconductors. Excitons generated by light absorption are separated at interfaces between these two species. This process has traditionally been understood in terms of semi-classical incoherent hopping dynamics, however such dynamics cannot account for the near-unity quantum efficiencies of the best devices. These typically contain fullerene molecules as acceptor species.

The electron and hole formed during exciton dissociation must overcome their mutual Coulomb attraction, which is typically an order of magnitude greater than $k_B T$. Hopping dynamics would self-trap, generating bound charge pairs at the interface. In this work we develop a simple tight-binding model of the heterojunction interface. We demonstrate that coherent dynamics is able to efficiently separate electron and hole, overcoming their mutual attraction. We find that the timescale of coherent charge separation is on the order of 100 fs, short enough to lie within realistic estimates of the coherence lifetime of an organic system.

We propose that the high efficiency of fullerene based devices is most probably explained by a reduced vibronic coupling, which increases the coherence lifetime. Our work provides a clear theoretical example of an organic light-harvesting system whose efficiency can be dramatically improved by quantum coherence, and suggests that evolution may have optimised photosynthetic processes by increasing coherence lifetimes.

CHARGE TRANSFER IN PHOTOSYNTHETIC REACTION CENTRES AND THE ROLE OF COUPLING TO UNDERDAMPED VIBRATIONAL MODES

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Ultra-fast electron transfer in the photosynthetic reaction centre is strongly influenced by coupling to vibrational degrees of freedom. These vibrational modes may arise from inter-molecular origin or from collective environmental motions and can provide a reaction coordinate along which the electron transfer occurs. We consider the primary charge separation step in the special pair of a purple bacteria and investigate how the transfer dynamics depends on diagonal or off-diagonal coupling between electronic and vibrational degrees of freedom.

WAVELET ANALYSIS AND ITS APPLICATION TO ULTRAFAST SPECTROSCOPY

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Traditionally, the data coming from an experiment have been analyzed either in the temporal or the frequency domain. Typically, in ultrafast spectroscopy the analysis are done in the frequency domain, which provide much information about the system under study and can help to understand the processes involved in it. But it will be interesting to make a time-frequency analysis of the data and have information of how the frequencies change over time.

A time-frequency analysis can be done using the Wavelet transform. The Wavelet transform refers to several transformations and signal processing techniques that have in common that they use a zero mean and short-time oscillating function called wavelet, to decompose a signal into different scales. By means of the Continuous Wavelet transform, which is the integral transformation of the data using wavelet functions, it is possible to know which frequencies are present in a give time and how important they are.

The processes that appear in Quantum Biology are very complex and it is necessary to have all the possible information that experiments can provide to be able to understand them and make accurate theoretical models. Combining a wavelet analysis of experimental data with more traditionally techniques, like the one or two-dimensional Fourier transform, it is possible to obtain much more knowledge than with traditional data analysis techniques.

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NON-MARKOVIAN QUANTUM MAPS FOR SIMULATING TRANSPORT ALONG MOLECULAR CHAINS

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Recent progress in studying energy transfer in light-harvesting systems has stimulated our interest in quantum transport in molecular wires, conjugate polymers, thin films, nanotubes, and other nanostructures. To explore this problem, we have developed a novel numerical method to predict the quantum dynamics of extended systems.

Based on the concept of a dynamical map, our method extracts all available information encapsulated in short-time non-Markovian quantum trajectories and compresses it into propagation tensors of reduced size. It can be applied to experimental settings in the same spirit as quantum process tomography and permits direct reconstruction of dynamical operators such as the Hamiltonian, the Markovian decay of the bath, the memory kernel or the underlying environmental correlation functions.

Alternatively, a bottom-up perspective can be adopted in which the compact propagation tensor is constructed for a given system-bath Hamiltonian. Efficient multiplication of these tensors can generate dissipative quantum dynamics of very large systems with arbitrary spectral densities. As an illustrative example, diffusion and thermal properties of molecular chains of one hundred or more sites with strong environmental effects are explored and analysed using this method.

VIBRONIC AND VIBRATIONAL COHERENCES IN TWO-DIMENSIONAL ELECTRONIC SPECTRA OF ARTIFICIAL LIGHT HARVESTERSF. Milota¹, A. Galestian Pour¹, J. Hauer¹*1 Photonics Institute, Vienna University of Technology, Gusshausstrasse 27, 1040 Vienna, Austria*

J-aggregates of cyanine dyes result from closely packed molecules forming mesoscopic tubes of nanometer-diameter and micrometer-length [1]. They are chemically versatile and self-assemble into various extended supramolecular architectures, in aqueous solution. Among these are cylindrical structures, sharing local dye packing features with naturally occurring chlorosomes [2]. Their efficient energy transfer pathways make them suitable candidates for artificial light harvesting systems. This great capability calls for an in-depth spectroscopic study of the underlying energy deactivation network and coherence dynamics. We apply two-dimensional electronic spectroscopy (2D-ES) with sub-10 fs laser pulses in combination with two-dimensional-decay associated spectra analysis to explain the population flow within different aggregates. Based on the analysis of Fourier-transform amplitude maps, we distinguish between vibrational or vibronic coherence dynamics as the origin of pronounced oscillations in our two-dimensional electronic spectra.

[1] Milota, F.; Prokhorenko, V. I.; Mancal, T.; von Berlepsch, H.; Bixner, O.; Kauffmann, H. F.; and J. Hauer, *J Phys Chem A*, 10.1021/jp3119605 (2013).

[2] Ganapathy, S.; Oostergetel, G. T.; Wawrzyniak, P. K.; Reus, M.; Chew, A. G. M.; Buda, F.; Boekema, E. J.; Bryant, D. A.; Holzwarth, A. R.; de Groot, H. J. M.; *P Natl Acad Sci USA* 2009, 106, 8525-8530.

A COMPARISON OF THEORETICAL MODELS FOR QUANTUM TUNNELLING OF H-BOND PROTONS

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The temporal evolution and decoherence of a quantum state in an asymmetric double well potential is investigated using a time-dependent density matrix in both position (pointer state) and energy eigenstate bases. The Liouville-von Neumann master equation for open quantum systems is solved for a proton in such a well, in order to model a hydrogen bond, such as those found in A-T base pairs in DNA.

Dissipation is modelled by coupling the double well potential to a heat bath, representing the external environment. This is done with the addition of a “Lindblad” term in the energy eigenstate basis (defined in terms of transition probabilities between states), and by directly manipulating the off-diagonal, non-physical elements of the density matrix in the pointer state basis to simulate measurement. The two methods are investigated and compared in terms of their effect on tunnelling times and decoherence of the quantum state. The latter method, whilst computationally more expensive, could prove useful due to its greater flexibility.

Using typical parameters in a test system, a large anti-Zeno effect is seen and tunnelling can occur much faster than decoherence (mainly due to energy being transferred to the system from the environment, allowing the proton to jump the barrier), on picosecond timescales, suggesting that tunnelling could play a part in some biological events. As expected, the effect of the environment on tunnelling rates is highly dependent on temperature (for the Lindblad term) and also on the frequency of the interaction and preciseness of the measurements (for pointer state measurements).

QUANTUM DYNAMICS IN CAROTENOID PHOTOCHEMISTRY

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Carotenoids have a rich photochemistry of paramount importance for photosynthesis, yet a detailed understanding of their excited states eludes us. Quantum coherences as measured by two-dimensional electronic spectroscopy will help us choose between the proposed level schemes in the literature.

We present simulated 2D spectra of coherent dynamics in carotenoids and discuss the possibility of measuring these.

The simulated 2D electronic spectra have been calculated using a non-equilibrium Green's functions method developed by the authors. The electronic part of the theory was presented in [Thorsten Hansen, Tõnu Pullerits Nonlinear Response Theory on the Keldysh Contour J.Phys.B: At.Mol.Opt., 45, 154014 (2012).] Vibrational theory has been developed. The contributing Liouville space pathways are expanded to second order in the level coupling to describe population transfer in the excited state manifold of Carotenoids.

CONTRIBUTION OF QUANTUM TUNNELLING EVENTS IN CHEMICAL RATESS. Jevtic¹, J. Anders²

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Chemical reactions are thought to happen when a particle crosses an energetic barrier and into an energetically favourable state. Traditionally one thinks of the particle classically in the sense that it may only cross this barrier if it acquires enough thermal energy from the environment to hop over the barrier. However, there has been evidence to suggest that, for certain chemical reactions that include proton transfer, the transferring particle may tunnel through the barrier [1]. This is surprising because these reactions take place in a biological environment, where one would not expect to observe quantum effects. We compare, for a various energetic potentials, the classical transition state theory (TST) rate with the rate that fully includes quantum effects. Traditional TST is used to estimate the rate that results from classical hopping: it assumes that an initially equilibrated system is suddenly exposed to a non-equilibrium situation which then results in dynamics as the famous TST reaction rate. Our quantum model traces the same assumptions and extends TST by accounting not only for hopping over the barrier but also the tunnelling through the barrier. In our talk we will discuss the temperature dependence of both rate contributions, predict the qualitative behaviour of the kinetic isotope effect (KIEs) for this particular model and hypothesise what these results imply for reactions catalysed by enzymes.

[1] Temperature-Dependent Isotope Effects in Soybean Lipoxygenase-1: Correlating Hydrogen Tunneling with Protein Dynamics, M. J. Knapp, K. Rickert and J. P. Klinman, *J. Am. Chem. Soc.* 2002, 124, 3865-3874

A RIGOROUS TREATMENT FOR COHERENT DELOCALISATION OF EXCITONS IN QUANTUM NETWORKS.

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We investigate the role of quantum coherence in excitation transport across molecular networks. Our goal is to understand the impact of constructive multi-path interference on the transport dynamics. Necessary condition for multi-path interference is the coherent delocalisation of the excitation over multiple network sites.

For the identification of this coherent delocalisation we introduce a notion of coherence length for discrete systems and present techniques to characterize it for mixed states. More specifically, we construct a hierarchy of criteria which provide a sufficient condition for coherent delocalisation of an excitation over a given number of sites.

With this hierarchy we investigate coherence properties in networks of different geometries under both coherent and incoherent driving, and substantiate the essential role of quantum coherence for fast transport.

POPULATION ASSISTED IMPULSIVE RAMAN SPECTROSCOPY OF ULTRAFAST CHEMICAL REACTION DYNAMICS IN THE TIME-DOMAIN

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The 13-cis to all-trans photoisomerization of the retinal chromophore in bacteriorhodopsin (bR) is a prototypical ultrafast isomerization process. Within the protein, the reaction is faster, more efficient and more specific than in solution.

We present population assisted impulsive Raman spectroscopy (PAIRS), that combines high temporal resolution (<20 fs) over an extremely broad probing bandwidth (500-900 nm) combined with specific electronic population control. This allows us to conclusively assign and extract reactive vibrational coherences of excited electronic states and follow the energy flow from Frank-Condon active into reactive coordinates such as hydrogen-wagging and backbone torsion. By taking a comparative approach between bR and an unreactive retinal-protonated Schiff base derivative (QY = 0, lifetime = 3 ps) we are able to demonstrate that the unique reactivity and specificity of bR is a result of the efficient channeling of excitation energy into reactive coordinates. PAIRS allows us to sample full excited state potential energy surfaces and thus rationalize the evolutionary optimization of photochemical processes found in nature.

MODELING TWO-DIMENSIONAL SPECTRA OF COMPLEX MOLECULAR SYSTEMS

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Two-dimensional spectroscopy is a powerful tool in studying vibrational and electronic dynamics in complex molecular systems down to a femtosecond timescale. The spectra provide direct information of the size of the couplings between energy levels, which provides structural information. By varying the time between the pump and the probe pulse one can study excited state dynamics and for instance follow the different energy pathways in light harvesting systems. In order to interpret the spectra, however, theoretical models and simulations are needed. Unfortunately a full quantum mechanical description of biological systems is often not feasible due to the many degrees of freedom. We present two novel mixed quantum-classical methods for simulating two-dimensional spectra that allow a general treatment of the interaction between the molecular system and its environment. In particular we include the previously neglected change in potential energy that solvent molecules (treated classically) feel when transitions occur in the quantum subsystem, using a mean field theory and a surface hopping method respectively. We consider two-level electronic systems to study the influence of this feedback and compare to the exact result. We show that the feedback leads to the expected Stokes shift of the energy levels in the quantum subsystem, which subsequently leads to changes in the population transfer between quantum sites and, therefore, is crucial to include.

SELF ORGANIZED QUANTUM CRITICALITY IN EVOLUTIONARY BIOMOLECULESG. Vattay¹, S. Kauffman², D. Salahub³, AM. Nassim³, I. Csabai¹*1 Department of Physics of Complex Systems, Eötvös University, Budapest, Hungary**2 Vermont Complex Systems Center, University of Vermont, Burlington VT, USA**3 Department of Chemistry, University of Calgary, Calgary, Canada*

Statistics of energy levels provides key insight into the dynamics of quantum systems. Strongly ergodic quantum dynamics and delocalized quantum states are associated with level distribution determined by random matrix theory (Bohigas-Giannoni-Schmit 1984). In non-ergodic, strongly localized quantum systems energy levels form a random sequence characterized by a Poisson point process (Berry-Tabor 1977). Very exceptional “critical quantum chaotic” systems at the border of localization-delocalization/ergodic-non-ergodic transition show a unique critical level statistics (Shklovskii, et al. 1993). Also, as we showed before (GV and SK 2011), coherence decay is exponentially fast in quantum ergodic systems while it is just algebraic in localized systems.

In this talk we argue that critical quantum dynamics is beneficial for chemical evolvability. Molecules with critical electronic energy structure can stay quantum coherent for a long time and can participate in charge transport. These molecules can participate in more chemical bond forming reactions and can benefit from quantum parallelism in trying out new conformal possibilities. While molecules with localized electronic states cannot rearrange their charge distribution structure and molecules with extended states lose coherence too quickly to harness quantum optimization.

We investigated the quantum level statistics of the electronic states of about 5000 organic compounds found in public databases. Since critical level statistics requires a fine-tuning of system parameters to bring the system to the edge of the spectral transition, one would not a priori expect to find a large fraction of critical molecules. Quite unexpectedly, about 55% of classifiable compounds have critical level statistics, 40% Poisson statistics and of 5% random matrix statistics. All common compounds known for their biological importance (lipids, carbohydrates, amino acids, hormones, vitamins ...) seem to belong to the critical class.

Quantum Effects in Biological Systems Workshop 2014

Organizer: Jianshu Cao (MIT)

website: <http://web.mit.edu/jianshucaogroup/quebs2014.html>

Following the success of the previous workshops, the next and sixth workshop, QuEBS-2014 will take place in Singapore. The 2014 workshop will cover the most recent developments in this interdisciplinary field and foster exchange of ideas among scientists from different backgrounds and continents. This will be the first QuEBS workshop in Asia, and, by choosing Singapore, we hope to engage the fast-growing scientific community in the area.

The scientific program of the workshop will feature a variety of topics including:

- (i) Intriguing effects of quantum coherence in photosynthesis and other complex biological processes.
- (ii) Novel developments in optical spectroscopy, single molecule technology, quantum dissipation, coherent transport, quantum information, and computational methods.
- (iii) Emerging examples to demonstrate how the insights learnt from biological systems can guide the optimal design of artificial systems with potential applications to solar cells and chemical sensors.

In the tradition of the previous workshops, we will schedule a mix of invited and contributed talks to highlight the recent contributions and arrange a number of poster presentations to encourage the participation of young or new scientists.