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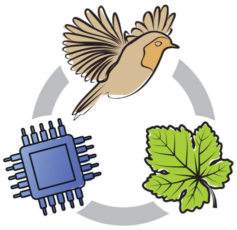
BOOK OF ABSTRACTS



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CRETE fertility CENTRE

ORAL PRESENTATIONS

Darius Abramavičius
Institute of Chemical Physics, Physics Faculty, Vilnius University

Reconstruction of exciton Hamiltonian from 2D electronic spectroscopy

Quantum effects of electronic excitations of pigment molecules in molecular clusters originate from molecular Frenkel exciton Hamiltonian. Its parameters are estimated either from calculations or from fitting spectroscopy experiments. However, the former approach is prone to errors, while the latter approach is often not uniquely defined. We demonstrate of model systems how utilizing additional molecular excitations (e.g. Qx in chlorophylls) and high order excitations can directly reveal the nature of the molecular excitations, their site energies and intermolecular resonant couplings.

Markus Arndt
Faculty of Physics, University of Vienna

Molecules of life in quantum experiments & quantum tools for the life sciences

Quantum Mechanics is often seen as the sciences of small things and restricted to isolated objects. I will review quantum delocalization and matter-wave experiments at the University of Vienna, that we have performed with complex molecules of life, from biodyes and neurotransmitters over vitamins and biomolecular clusters to complex polypeptides. All these experiments are consistent with the expectations of established quantum mechanics but they also show the strong environmental constraints required to observe these phenomena. Coherently manipulating objects even as complex as proteins now requires a set of novel tools, to prepare, slow and coherently manipulate neutral biomolecular beams. I will discuss recent advances in the use of tailored phototags to control their charge state optically and in high vacuum and the use of superconducting quantum detectors to detect them efficiently at low kinetic energy. New interferometer concepts are prepared to serve the next generation of quantum experiments with proteins, which shall also become tools to measure a variety of molecular properties.

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Federico Bertagna
Leverhulme Quantum Biology Doctoral Training Centre, University of Surrey

Investigation of kinetic and magnetic isotopic effects of D20 in neuronal ion channels through a novel electrophysiological technique

The importance of ion transportation in neuronal physiology cannot be overstated. The action potential (AP) generated by the activity of voltage-gated ion channels on neuronal membrane is the principle means of communication in the brain and abnormal function of ion channels has been linked to a growing number of diseases, including but not limited to neurodegenerative diseases, such as Parkinson's and epilepsy and many forms of neoplasia. Yet, the mechanisms underlying ion transportation have not been thoroughly explained and classic models based on coulombic interactions fail to explain the remarkable efficiency and selectivity of voltage-gated ion channels. These transmembrane proteins are indeed only permeable to specific ion species but nonetheless ensuring a transport rate close to the free diffusion limit. To overcome the limitations of classic models, it has been hypothesized that non-trivial quantum effects could play a key role in both selectivity and transport rate through ion channels in nerve membranes. The hypothesis, if true, might help to account for the recent finding that extremely low frequency electromagnetic fields (ELF-EMFs), of the strength and structure of endogenous electromagnetic fields in the brain, influence the pattern of neuron firing. To test this hypothesis, we developed and validated a novel electrophysiological technique allowing a complete pharmacological manipulation of selected patches of membrane, without perturbing membrane dynamics. By replacing the water in the extracellular solution with increasing concentrations of D2O and applying static and oscillating fields to the experimental preparation, we investigated through this new tool the existence of a synergistic action of kinetic isotopic effect, due to the different mass of hydrogen and deuterium, and magnetic isotopic effect, generated by their different spin. We observed a direct correlation between the presence of D2O and both a general decrease of inward and outward current, respectively populated by voltage-gated sodium channels and different types of voltage-gated potassium channels, and a delay in their activation kinetics. This result could be explained by a change in the membrane properties as coordinating with D2O, or a direct effect on ion channel conductance exacerbated through the solvation shell of the ion entering the selectivity filter, as previously suggested by computational studies. Our next experiment will investigate the impact of acute exposure to both static and oscillating magnetic fields, alone or in presence of D2O. In the first case, we do not expect any major effect on the dynamics of voltage-gated sodium and potassium channels since many studies point out a perturbation of Ca2+ homeostasis to be the main effect of electromagnetic radiation. However, if our hypothesis is true, the combination of EMF exposure and D2O replacement will lead to significant effects, that would not be imputable neither to the kinetic isotopic effect alone, nor to the sole exposure to EMFs.

Susannah Bourne-Worster
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Unravelling the mechanism of concentration quenching

Chlorophyll molecules in photosynthetic light-harvesting complexes are surprisingly immune to the rapid fluorescence quenching displayed by solvated chromophores at high concentrations. The effect has consequently not been given much attention in studies of natural light-harvesting [1]. However, its impact cannot be further overlooked in the context of biomimetic antennae, since protection against this unproductive quenching pathway must necessarily be a critical design consideration. We aim to provide concrete theoretical evidence to support of refute the leading hypothesis for the mechanism of concentration quenching: fast internal conversion to the ground state via a low-lying charge transfer state [1,2]. Making use of newly emerging fast methods in quantum chemistry [3], we extract Marcus potential energy surfaces from molecular dynamics simulations of solvated chromophores. These surfaces can be used to calculate the rates of transfer between the ground, excited and hypothesised charge-transfer states, to understand the overall quenching rate for a given chromophore concentration. By comparing these calculated rates to published experimental data [4,5], we aim not only to assess the feasibility of the proposed quenching mechanism, but also to understand the role of the photosynthetic protein environment in preventing it.

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Adam Bradlaugh
School of Biological Sciences, University of Manchester

Essential elements of radical pair magnetosensitivity in Drosophila

Many animals use the Earth's magnetic field (geoMF) for navigation. The favoured mechanism for magnetosensitivity involves a blue-light (BL) activated electron transfer reaction between flavin adenine dinucleotide (FAD) and a chain of tryptophan (Trp) residues within the photoreceptor protein, CRYPTOCHROME (CRY). The spin-state of the resultant radical pair (RP) and hence the concentration of CRY in its active state is influenced by the geoMF. The canonical CRY-centric radical pair mechanism (RPM) does not, however, explain many physiological and behavioural observations. Here, using electrophysiology and behavioural analyses, we assay magnetic field (MF) responses at single neuron and organismal level. We show that the 52 C-terminal (CT) amino acids of CRY, which are missing the FAD binding domain and the Trp chain, are sufficient to facilitate magnetoreception. We also show that increasing intracellular FAD potentiates both BL-induced and MF-dependent effects on the activity mediated by the CT. Additionally, high levels of FAD alone are sufficient to cause BL neuronal sensitivity and, remarkably, potentiation of this response in the co-presence of a MF. These unexpected results reveal the essential components of a primary magnetoreceptor in flies, providing strong evidence that non-canonical (i.e., non-CRY-dependent) RPs can elicit MF responses in cells.

Adam Burgess
Leverhulme Quantum Biology Doctoral Training Centre, University of Surrey

Non-Markovian entanglement dynamics of bio-molecular chromophores

By utilising a spin-boson model, we study the dynamical decoherence of monomeric and dimeric Green-Fluorescent protein (GFP) due to being within a finite-temperature solvent environment. This is undertaken by deploying the Hierarchical Equations of Motion (HEOM) allowing for us to capture non-perturbative and non-Markovian characteristics of the system. We study both the monomeric form of GFPs as well as try to understand the anomalously long decoherence time for coherent energy transfer in the homo-dimeric GFPs. We derive spectral densities using the Fluctuation-Dissipation Theorem and a Debye dielectric model for the solvent environment. Having studied different system architectures, we see some very interesting properties of the evolution. The specific architecture of the GFP appears well suited to preserving the coherences in the homo-dimer system. We also find a dynamical correlation between the coherent energy and the entropy production, even leading to transient reductions in entropy, a distinct feature of the non-Markovian approach. We also find that for a single Debye timescale model the system reduces to a free system Gibbs state appropriate for a weak coupling system. However, by introducing a secondary timescale the system diverges from this Gibbs state and takes the form of pointer states in the excited state basis showing the intermediate coupling strength dynamics.

Demetrios-Domenikos Chryssikos
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Electronic transport through bacteriorhodopsin multilayers

Proteins are often regarded as "nature's conductors" [1], as they enable vital cellular functions that rely on charge transfer, such as respiration and photosynthesis. Recent research has revealed that certain proteins maintain their conductive properties in the "dry" state (with only structural water retained), outside their natural environment [2]. One prominent representative is the proton-pumping purple membrane protein bacteriorhodopsin (bR), known for its thermal stability and photoactivity [3]. Despite its ability to electrostatically self-assemble on solid surfaces [4], the controlled preparation of bR multilayers remains challenging due to the protein's negative surface charge. In this work, we present a new method for the preparation of multilayers of octylthioglucoside-treated bR (OTG-bR) embedded in protein-lipid vesicles, on amino-terminated TiN substrates. The method employs the cationic polymer polydiallyldimethylammonium (PDDA) as an electrostatic linker between the protein layers. As confirmed by atomic force microscopy measurements, we prepared stacked films of OTG-bR, with heights 8.0, 13.6 and 18.3 nm for one, two, and three layers, respectively. Current-voltage measurements were carried out in a vertical configuration using eutectic gallium-indium as the top contact material. Assuming exponential decay of the conductance with the layer thickness, as in non-resonant tunneling charge transport, we extract a small decay coefficient of approximately 0.06 $Å^{-1}$, which is about half the value previously reported in literature [2,5]. In light of this finding, we discuss possible charge transport mechanisms in stacked OTG-bR molecules.

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Extreme parametric sensitivity in model light-induced biological processes

We report extreme parametric sensitivity in simulating the photoisomerization of model rhodopsin, as well as the exciton-exciton annihilation dynamics in bacterial light harvesting pigment-protein complexes. The long-time dynamics as well as the steady-state reaction/fluorescence emission quantum yields are shown to depend erratically on the system parameters, whereas the short-time dynamics remain near unaffected. By analyzing the nonequilibrium steady states of simple quantum models of light-matter interactions that show similar features we connect this phenomenon to resonance-enhanced transport. Possible experimental observables are briefly discussed.

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Localisation determines the optimal noise rate for quantum transport

Environmental noise plays a key role in determining the efficiency of transport in quantum systems. However, transport is also directly affected by disorder and localisation. We present work [1] showing that the optimal dephasing rates for 1D chains consistently depend on their localisation. We explain how localisation and disorder interact with various phenomena that produce noise-assisted quantum transport, and show how the interplay of size-dependent and size-independent effects effects explain our results. Moving beyond phenomenological pure dephasing, we implement a finite temperature Bloch–Redfield model and show the relationship still applies at intermediate and high temperatures.

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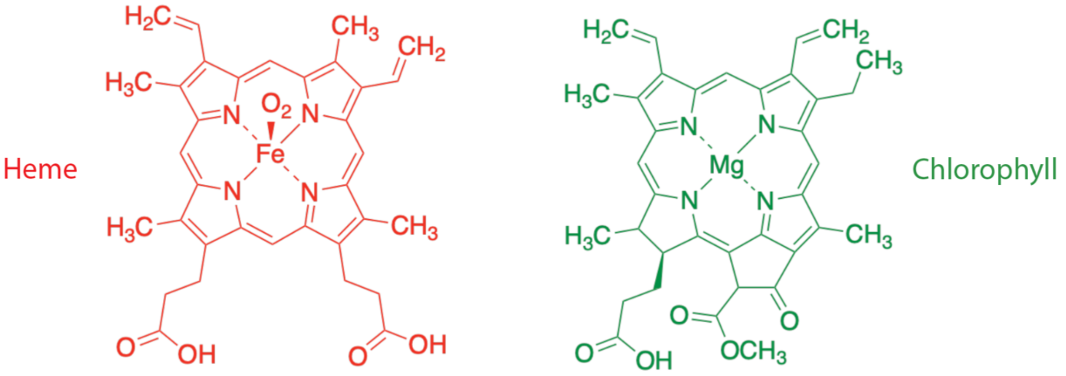
Porphyrin hybrid derivatives, a case study for artificial photosynthesis

Natural processes of photosynthesis have increasingly inspired the fabrication of nanostructured molecular materials with advanced light-harvesting and electron-transfer features. [1-6] In this context, supramolecular chemistry allows diverse and disparate molecular building blocks to be amalgamated into highly ordered architectures through the process of self-assembly. These mimic the key functions of the photosynthetic reaction center; light harvesting, charge separation, charge transport, energy transfer, and catalysis. [7,8] Porphyrinoids, the basic building block of chlorophylls, have emerged as an exceptional class of light harvesters and electron donors in such supramolecular electron donor-acceptor hybrids [9-12]. A variety of significant applications from solar cells, hydrogen production to medical applications have been reported.



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Numerically exact simulations of open quantum systems coupled to arbitrary environments

A thorough understanding of quantum effects in biological charge and excitation transfer systems requires a careful assessment of environment influences. The strong coupling of quantum biological systems to structured environments poses additional challenges as conventional weak-coupling theories can break down. Numerically exact methods, which fully capture all environment influences, have been developed but have so far been available only for special types of environments such as the spin-boson model. Here, we present the novel numerically exact method automated compression of environments (ACE) recently published [1]. The open quantum systems dynamics is expressed in terms of a tensor network, where the influence of the environment is incorporated into a matrix product operator in time, the so-called process tensor. ACE provides a way to calculate this process tensor numerically exactly directly from the microscopic Hamiltonian without requiring any specific derivation for the problem at hand. This made it possible to develop a single computer code that can be used to simulate the dynamics of open quantum systems with environments as diverse as photons, phonons, electrons, and spins. In particular, this includes the treatment of multiple combined environments, which paves the way for numerically exact investigations of phonon effects on biological charge and excitation transfer systems.

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Anomalous viscosity of a racemate: a simple experiment demonstrating chirally induced spin selectivity

It has been known for over a century that racemic solutions of hydrogen-bonded compounds are less viscous than their component enantiomers, but this fact has so far remained unexplained. Here we confirm it using enantiomers of lactic acid, and compare it to molecular dynamics simulations of lactic acid viscosity. The effect is absent in classical MD. We suggest that the anomalous viscosity of racemates may be due to a recently discovered magnetic intermolecular force due to spin-dependent charge reorganization.

Animesh Datta
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Quantum light spectroscopy of complex quantum systems

Quantum light spectroscopy is an emerging field wherein the quantum nature of light is exploited to reveal information about the properties of matter. Although there is evidence that spectroscopy with quantum light may have certain advantages compared to classical spectroscopic methods, this advantage has not been rigorously assessed. We do so by theoretically calculating the precision of estimating parameters of a matter system when probed by a (travelling) pulse of quantum light. Concretely, we consider the estimation of matter system parameters such as dipole moments and dipole-dipole couplings of individual and pairs of dimer systems respectively. To that end, we compare the performances of different quantum states of quantum light, such as single photons and entangled states of light. We also study the experimental attainability of the fundamental quantum limits of spectroscopy. Our theoretical results should guide the design of quantum light spectroscopy experiments.

Yonatan Dubi
Department of Chemistry, Ben-Gurion University of the Negev

On the origin of the chirality-induced spin selectivity – A quantitative theory

When electrons are injected through a chiral molecule, the resulting current may become spin polarized. This effect, known as the chirality-induced spin-selectivity (CISS) effect, has been suggested to emerge due to the interplay between spin–orbit interactions and the chirality within the molecule. However, such explanations require unrealistically large values for the molecular spin–orbit interaction – and provide no quantitative theory to date which can fit available experimental data. We present a theory for the CISS effect based on the interplay between spin–orbit interactions in the electrode, the chirality of the molecule (which induces a solenoid field), and spin-transfer torque at the molecule–electrode interface. Using a mean-field calculation with simple models for the molecular junction, we show that our phenomenological theory can account for all key experimental observations, most importantly the magnitude of the CISS with realistic parameters. We demonstrate that the theory can provide a quantitative fit to various experiments – old and new, small and large molecules, length and temperature dependence etc., and provide a set of predictions which can be readily tested experimentally.

Erik Gauger
School of Engineering & Physical Sciences, Institute of Photonics and Quantum Sciences, Heriot-Watt University

Bio-inspired coherent light-harvesting beyond classical limits

The remarkable molecular structures of photosynthetic complexes can provide inspiration and blueprints for the design of artificial light-harvesting systems. Focusing on such bio-inspired structures, in this presentation I will explore several avenues for going beyond naturally occurring effects in the quest to realise instances of quantum-enhanced light-harvesting. Specifically, I will give an overview of designs which my group has studied in recent years. This includes ring-like light-harvesting antennae, photocells based on strongly-coupled dimers, and optimised molecular wires for efficient long-range energy transport. I will cover the relevance and utility of quantum coherence in those structures, introduce proposals for light-harvesting architectures whose performance scales super-linearly with system size, and provide examples of non-equilibrium effects where the influence of more than one type of environment enhances rather than hinders function.

Angela Gehrckens
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Understanding protein conformational changes that allow avian navigation

Avian navigation is hypothesized to be based on a radical-pair mechanism which allows magnetoreception. Night-migratory birds use the inclination of the Earth's magnet field which triggers the formation of particular radical pair states that are in turn proposed to cause conformational changes. These changes in protein structure can be observed using native as well as hydrogen/deuterium exchange mass spectrometry to interrogate both movements within the proteins and interactions between the proteins and their putative downstream interaction partners. The latter technique is used to probe protein dynamics and interaction surfaces upon exposure to different environmental conditions such as the presence and absence of an externally applied magnetic field as well as different light conditions.

Veljko Janković
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Incoherent light-induced excitation harvesting in molecular energy-conversion systems

There is a remarkable similarity between physical processes at play in (organic) photovoltaic cells and photosynthetic complexes [1,2]. In both types of systems, ultrafast time-resolved studies suggest that quantum coherences may enhance the excitation-harvesting efficiency by favoring non-equilibrated, "hot", and fast pathways involving delocalized states over equilibrated, "cold", and slow pathways involving localized trap states. Here, we present our recent contributions to the on-going debate on the relevance of these findings for excitation harvesting under incoherent light [3-6]. We develop a (numerically) exact description of excitonic dynamics in a molecular aggregate driven by weak-intensity radiation of arbitrary properties [3]. While the interaction with light is included up to the second order, the excitation-environment coupling is treated up to all orders. The resulting exact expression for the reduced density matrix is then recast as the hierarchy of equations of motion (HEOM) that explicitly and consistently includes the photoexcitation step. We then focus on a model photosynthetic dimer and examine its non-equilibrium steady state arising from the interplay between excitation generation, excitation relaxation, dephasing, trapping at the load, and recombination [4]. While the steady-state coherences in the slow-trapping limit are demonstrated to originate from the excitation-environment entanglement, we unveil an interesting relation between the dynamic coherences observed in ultrafast experiments on unloaded aggregates and the steady-state coherences in the fast-trapping limit. We apply a similar formalism to a microscopic effective Hamiltonian of an organic donor/acceptor heterojunction, where we elucidate the energy- and time-resolved dynamics of charge pairs all the way from their photogeneration to their extraction or recombination. The results indicate that charge separation proceeds via the "cold" pathway on which donor excitons first convert to relaxed charge-transfer excitons and then transform to separated charges [5]. We also analyze these results from the perspective of non-equilibrium thermodynamics. We quantify the difference between the equilibrium and non-equilibrium dependence of the charge-pair free energy on the intrapair separation. Our results reveal that this difference is largest when charge separation efficiency is large, which leads us to conclude that charge separation in efficient organic solar cells proceeds via a "cold" but non-equilibrated pathway [6].

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Daniel Kattnig
Department of Physics and Astronomy, University of Exeter

The puzzle of the cryptochrome quantum sensor: Resolving the suppressive effect of inter-radical interactions

Magnetoreception clearly is one of the grand puzzles of (quantum) biology. Despite the phenomenon being ubiquitous among the five kingdoms of life, the sensory mechanism–and even the underlying principle–has remained frustratingly impenetrable for decades. In birds and a few other species, a compass sense has been attributed to a radical pair recombination reaction in the flavo-protein cryptochrome. This proposition has since been supported by ample theoretical insight and is, to some extent, in line with biological observations. The Radical Pair Mechanism (RPM) provides the conceptual framework for cryptochrome magnetoreception. However, open questions remain about its putative quantum nature [1] and whether it can truly deliver the required sensitivity in a noisy biological environment. The majority of theoretical studies so far have used oversimplified models that do not reflect the complexity of the natural systems, for example, neglecting most of the large number of coupled nuclear spins, radical motion, inter-radical coupling, decoherence and spin relaxation. These features can give rise to "imperfections", such as the unavoidable inter-radical coupling of electron-electron dipolar (EED) interaction which suppresses the directional sensitivity of the radical pair reaction in the geomagnetic field [2]. Unlike previously assumed, the mutual compensation of EED and exchange interaction appears to not be able to mitigate this issue in cryptochromes. Here, we show how this RPM-suppression problem can in principle be overcome. First, we focus on systems comprising three radicals instead of a radical pair. Combining principles about the magnetosensitvity of dipolarly coupled three-spin systems, D3M, and the RPM, we demonstrate that a non-reactive bystander radical suitably placed with respect to the primary radical pair provides a solution to the EED-suppression problem [2]. If the third radical furthermore reacts with the primary radical in a spin-sensitive scavenging reaction, the chemical Zeno effect can additionally boost the magnetosensitivity, thereby endowing the sensor with exquisite sensitivity [3]. We discuss methods to potentially enable these models in cryptochrome, with specific focus on the flavin semiquinone/superoxide radical pair, for which fast spin relaxation in the superoxide precludes magnetosensitivity due to the RPM [4]. Radical triad systems comprising an ascorbyl scavenger radical are identified as particularly promising, for cryptochrome magnetoreception and beyond (e.g. hypomagnetic fields on neurogenesis). Second, returning to radical-pair-based models, we demonstrate that the EED limitation may also be overcome by externally driving the spin system through a modulation of the inter-radical distance [5]. We show that this dynamical process markedly enhances geomagnetic field sensitivity in strongly coupled radical pairs via a Landau-Zener-like transition between singlet and triplet states, thereby freeing spin state populations for magnetosensitive dynamics through non-adiabatic transitions. Our finding suggests that a live, i.e. externally driven magnetoreceptor, could be markedly more sensitive than its "dead", i.e. static, counterpart.

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Quantum model of allosteric signalling as a non-Markovian effect

A large number of biological `machines' (photosynthetic complexes, proteins, etc.) have been produced by natural selection to perform the electronic or chemical processes necessary for the survival of living organisms. Some of these nano-structures have the ability to coordinate optically induced electronic processes and operate in a regime where the usual assumptions of a structureless, Markovian, bath do not hold. Allosteric control is a known phenomenon where environment-mediated structural `signals' play a major role in the dynamics of proteins, and it has been suggested that similar spatially distant effects could also play a role in light-driven energy and charge transport processes. It has so far been difficult to model non-local spatio-temporal effects because one needs to do beyond simple time-local descriptions of the environment, and instead keep track of how the environment responds to the system over time. We use a numerically exact method relying on a Matrix Product State representation of the quantum state of a system and its environment to keep track of the bath explicitly. Applied to examples motivated by biological systems with an interaction that depends on the spatial structure of a system, this method predicts a non-Markovian dynamics where long-range couplings induce correlations between the system and the environment [1], and reproduces the features of allosteric signals [2]. The environment dynamics can be naturally extracted from our method and shine a light on long time feedback effects that are responsible for the observed non-Markovian recurrences, and show clear signs of the environment having stored information about the early time motion. These results from some of the simplest conceptual examples illustrate the importance of understanding spatio-temporal correlations in nano-scale dissipative systems if one wants to figure out how these biological functions are performed.

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Long-lived coherence in non-Markovian quantum Brownian motion

In open quantum systems, the process which causes quantum systems in contact with environments to rapidly lose quantum information and become effectively classical is known as decoherence. But it is still not understand how, in biology, quantum systems in contact with the cellular environment may retain coherence for times much longer than the expected decoherence time. The dissipative Caldeira-Leggett model provides a natural framework for exploring decoherence in systems which are at physiological temperature, but this model relies on the Markov condition, which implies that the environment has access to modes at infinitely high frequency. We extend the Caldeira-Leggett model using a perturbative Laplace transform method to provide a generalised non-Markovian extension, which allows for information backflow into the system. We provide an exact solution to our novel master equation and analyse it to show that, while the initial rapid decoherence remains unchanged, a new phenomenon called coherence resurgence emerges across times two orders of magnitude longer than the decoherence time. We expect that this coherence resurgence may be responsible for long-lived non-trivial quantum effects in systems which are in contact with environments.

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Faculty of Physics, Vilnius University

Modelling excited states and Raman spectra for carotenoids with complexes

Carotenoids (Cars) excited states and Raman spectra, many properties of which stem from the linear conjugated isoprenoid chain which has intense absorption in the blue-green range, confer colors on fruits, flowers and animals, and are at the basis of complex signaling processes. In photosynthetic organisms, they are implicated in the harvesting of solar photons. The natural carotenoids display a large structural diversity, and more than 1100 molecular species have been now identified. There are more than several photo- physics models of Cars: three-state model, four-state model, and additional four-state model involving excited states which are absent in polyne chain type models. They can be used to interpret the excited state dynamics of Cars with Chlorophylls, containing Qy and Qx states, exhibiting unanticipated complications. Additional states for the red absorption shift are proposed to arise from an Intra-molecular Charge Transfer (ICT) character of the second excited state, generated by the electron-rich keto group [1-3]. Large scale compu-tations provide more detailed information allowing better understanding of carotenoid properties which can be expected in real life biological systems. The chosen Cars were vaucheriaxanthin, fucoxanthin, lutein, beta-carotene and diadinoxanthin. The study was done using a combination of Raman and absorption spectroscopy, and density functional theory modelling, including Car–Parrinello molecular dynamics (CPMD) simulations. The Cars specific bonds were analysed by using enersgetic surface scan methodology by fixing all the other atoms. This methodology allows to identify additional local minima as possible conformers. Using such unstable structures, they were studied by changing local environ- ments such as with water models. The stabilized new structures provide new properties in excited states or Raman activities in various Cars. To find the stability of the investigated structures CPMD simulations are performed. Additional results with fucoxanthin suggest that due to fluctuations and inter-actions with the environment the new conformers can appear what can participate in explaining the ICT states in Cars.

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Alasdair Mackenzie
UK Central Laser Facility

Development of entangled two-photon absorption and fluorescence apparatus: comparison between continuous wave, picosecond and femtosecond light pulses

Fluorescence microscopy has become a staple technique in cell biology, however the high intensities can cause problems from photobleaching to the damage of the cell sample. Entangled two-photon methods have been reported in the literature to give a SNR quantum advantage of 10^10 operating at pW levels. We have developed and implemented an entangled photon (EP) pair source at 810 nm. We describe the set up in detail including system characterisation and common pitfalls. Using coincidence measurements, we compare EP generation using a Type-1 β-barium borate (BBO), from CW 405 nm, 40 ps-80 MHz and 200 fs-80 MHz sources also at 405 nm. EP absorption in standard chemical probes, including rhodamine, fluorescein and ZnTPP were measured. In the pulsed-laser system, entangled two-photon absorption and fluorescence measurements were determined. We compared the relative efficiencies of pulse repetition rate. The practical challenges faced when working with ultra-weak light will be presented.

Tomáš Mančal
Faculty of Mathematics and Physics, Charles University

System-bath entanglement in the photosynthetic excitation energy transfer: Wavefunction interpretation of open quantum system dynamics

The energy transfer dynamics, decoherence, and equilibration of small molecular assemblies, such as the photosynthetic light-harvesting antennae, provide a challenging testbed for open quantum systems theory. More than a decade ago, observation of the decoherence of a photoinduced superposition of electronic states of naturally occurring photosynthetic antennae spurred fierce debates about the role of quantum effects in promoting the highly efficient energy transfer during natural light-harvesting. Interestingly, the disputes were not accompanied by any significant change in the theoretical picture, which remains based on density matrix (statistical operator) formalism and its dynamic equations. Exact methods of propagation of the reduced density matrix (RDM) have been developed to get insight into the dynamics of photosynthetic antennae. However, such methods cannot by themselves solve the main sticking points of the debate because of the inherent unambiguity in the interpretation of the RDM. For instance, RDM does not distinguish between decoherence and dephasing in the system, and it creates difficulties in assigning the state to the environment degrees of freedom. Entanglement between the environment and the system cannot be efficiently discussed. Thus, the RDM formalism allows for a crucial ambiguity in interpreting the observed photoinduced processes. In this contribution, we will look at the relationship between statistics and the density matrix vis-à-vis the past quantum biological proposals. We provide several examples of conceptual questions from quantum biology and beyond, which can be decided (only) from the state vector point of view. We argue that the combined use of the density matrix and state vector representations as computational and conceptual tools, respectively, brings a serious advantage over the use of the density matrix alone. We demonstrate that a wavefunction formalism can always conceptualize the dynamics of open quantum systems. With such a conceptualization, we will prove that the entanglement between the electronic degrees of freedom and the protein environment is crucial for the function of the photosynthetic antennae.

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

Proton-pumping complexes of mitochondrial respiratory chain: Physical principles of operation

A proton gradient across a lipid membrane is a common intermediate form of energy storage in biological systems, which is subsequently converted into a proton current and, finally, into the most stable energy of chemical compounds. Even in a single physical system, the inner mitochondrion membrane, there is a variety of mechanisms pumping protons across the membrane, therefore converting the energy of high-energetic electrons into the proton gradient. With the molecular structures of the proton-pumping Complexes I, II, and IV being resolved in detail, actual physical mechanisms of the energy conversion often remain elusive. In this presentation, I will discuss our old and very recent results in modeling the proton-pumping complexes. In Complex IV, the energy transfer due to the direct electrostatic interaction occurs when the electrons and protons populate the sites in close proximity. In Complex I, where the electron and proton sites are well separated, it is assisted by conformational changes in the protein environment. In Complex III, the energy is transferred by means of the electron-proton interaction on the quinone shuttle. In our quantitative approach, we wrote the Heisenberg equations of motion for the electron and proton operators in the presence of the protein environment. In the high-temperature limit, they can be rewritten as the rate equations for the electron and proton populations with the transfer matrix elements having a Marcus-like form. For Complex I, the rate equations are coupled with the phenomenological Langevin equation describing the dynamics of the conformational changes. For Complex III, the mechanical motion of quinones is also described by the Langevin equations. The obtained equations were solved numerically, and it was shown that the protons can be effectively pumped across the membrane within the proposed models for all the Complexes. Moreover, we demonstrated that for the actual sets of parameters, the proton pumping is the most efficient for physiological temperatures.

Ron Naaman
Department of Chemical and Biological Physics, Weizmann Institute

Chirality and the electron spin in bio-systems

The 'conventional wisdom' about chirality in biomolecules is that it serves as a structural motif to place chemical functionalities in defined positions and orientations that enable biologically relevant functions. While the electron spin is accepted as important in defining structure of atoms and mole-cules, spin based properties, applications, and devices are commonly related to materials that have unpaired electrons (paramagnetic). However, we found that chiral molecules, crystals, and films act as spin filters for photoelectrons transmission, in electron transfer, and in electron transport. The effect, termed Chiral Induced Spin Selectivity (CISS), may explain the role of chirality in living organisms. Its mechanism sheds new light on the electron transfer processes in molecules and specifically in proteins and DNA.

Charlie Nation
Department of Physics & Astronomy, University College London

Quantum optics of single photosynthetic molecules

I will discuss an avenue towards an unambiguous demonstration of quantum coherent effects in photosynthetic exciton transport via measurement of photon correlation functions of emitted light under incoherent illumination. For single molecules this is a significant experimental challenge, and thus an important step is increasing the light emission over a bare molecule via interaction with a cavity. We develop a theoretical model for a multi-level Purcell effect, whereby one may see that a significant increase in light collection is possible with minimal effect on correlation functions of the bare molecule on a simplified system. We see, then, that observation of frequency filtered second order correlation functions of single molecules may provide a route to demonstrating quantum effects in photosynthesis. Numerical analysis is further presented on second order correlation functions of PC645 and FMO complexes, revealing markers of quantum features of transport in such systems.

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Department of Electrical Engineering, Indian Institute of Technology Bombay

Spin-selectivity based Enantioselective Electronic Nose Sensor

Chirality or 'handedness' makes a chiral molecule distinguishable from its mirror image. The left-handed and right-handed versions of a chiral molecule are referred to as enantiomers. They form the building block of life in the form of proteins, amino acids, and DNA. Now, it is difficult to distinguish enantiomers artificially. However, nature seems to have ways to isolate them, and critical biochemical processes are known to be enantioselective [1]. The response of the human nose is influenced by the chirality of the molecule [2], as enantiomers usually have a different smell. The different smell of enantiomers is one of the limitations of Inelastic Electron Tunneling Spectroscopy (IETS) based Vibrational Theory of Olfaction [3]. Chiral molecules have been traditionally probed using circularly polarized light. A recent phenomenon called chirality-induced spin selectivity (CISS) explains that charge polarization in chiral molecules is accompanied by spin polarization. CISS is a relativistic effect that implies that the electron traversing through a chiral molecule can move freely in one direction over the other depending upon the spin orientation of the electron [4]. The Rashba type spin-orbit coupling arising due to the lack of structure inversion symmetry stabilizes one type of spin orientation over the other. The stabilization energy is dependent on the amount of spin-orbit coupling. There is experimental evidence that spin polarization should be considered while calculating the strength of the interaction energies between chiral molecules. The spin polarization imposes a symmetry constraint on this interaction between two chiral molecules. These interactions, being short-ranged, are accompanied by electron exchange and charge penetration and are stabilized depending upon the spin of the interacting electrons [5]. To understand spin polarization in chiral systems, we performed Symmetry Adapted Perturbation Theory (SAPT) calculations [6]. We restricted ourselves to enantiomers with different odors to facilitate an enantioselective electronic nose sensor. SAPT is a method that is used to calculate the non-covalent intermolecular interaction energies between the molecules in terms of their various components, i.e., electrostatic, induction, dispersion, and exchange. The imposition of spin symmetry on the charge polarization causes the difference in the interaction energy. The SAPT calculation forms the physical explanation of which part of the interaction energy can give rise to enantioselectivity in the system. We observed in our results that the interaction energy for the case in which the two molecules have opposite handedness (RS) is more repulsive than when the two molecules have the same handedness (SS). This result is similar to the results reported in the literature [7]. In our most straightforward demonstration of an enantioselective e-nose sensor, we assume that the receptor is chiral because the protein that makes receptors are chiral in nature. In a sensor based on IETS [8], the vibrational mode of a foreign molecule opens an additional inelastic channel which manifests itself as a peak in the second derivative plot of the current characteristics. The inelastic channel is the result of a second-order effect of electron-phonon (e-ph) coupling. But a sensor based purely on IETS cannot differentiate between enantiomers because their vibrational spectrum is similar. The e-ph coupling is an important parameter in IETS that measures the change in force provided by the phonon mode for electrons to move from one site to another. The inclusion of short-range repulsions due to the exchange and overlap of electrons modifies the e-ph coupling. The e-ph coupling becomes large for molecular systems of same handedness and small for opposite handedness. Due to this difference in the e-ph coupling, the IETS signal generated is different for both the configurations, thus creating an enantio-selection in the sensor.

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Isotope substitution effects on the magnetic compass properties of cryptochrome-based radical pairs

The biophysical mechanism of the magnetic compass sense of migratory songbirds is thought to reply on the photochemical reactions of flavin-containing radical pairs in cryptochrome proteins located in the birds' eyes. A consequence of this hypothesis is that the effect of the Earth's magnetic field on the reaction product yields should be sensitive to isotopic substitutions that modify the hyperfine interactions in the radicals. In this report, we use spin dynamics simulations to explore the effects of 1H → 2H, 12C → 13C and 14N → 15N isotopic substitutions on the functioning of cryptochrome 4a as a magnetic direction sensor. Two main conclusions emerge. (1) Perdeuteration of the flavin chromophore appears to be the best way to boost the anisotropy of the magnetic field effect and to change its symmetry. (2) 13C substitution of three of the 12 flavin carbons, in particular C4, C4a, and C8α, seems to be the best way to attenuate the anisotropy. Once spectroscopic techniques are available for measuring magnetic field effects on oriented protein samples, these predictions should give insight into the factors that control the magnetic sensitivity.

Ali Pedram
Department of Physics, Koç University

Using quantum states of light to probe the retinal network

The minimum number of photons necessary for activating the sense of vision has been a topic of research for over a century. The ability of rod cells to sense a few photons has implications for understanding the fundamental capabilities of the human visual and nervous system and creating new vision technologies based on photonics. We investigate the fundamental metrological capabilities of different quantum states of light to probe the retina, which is modeled using a simple neural network. Stimulating the rod cells by Fock, coherent and thermal states of light, and calculating the Cramer-Rao lower bound (CRLB) and Fisher information matrix for the signal produced by the ganglion cells in various conditions, we determine the volume of minimum error ellipsoid. Comparing the resulting ellipsoid volumes, we determine the metrological performance of different states of light for probing the retinal network. The results indicate that the thermal state yields the largest error ellipsoid volume and hence the worst metrological performance, and the Fock state yields the best performance for all parameters. This advantage persists even if another layer is added to the network or optical losses are considered in the calculations.

Martin Plenio
Institute of Theoretical Physics, Ulm University

Electrons, excitons and phonons in quantum biology

This lecture aims to cover two aspects. First, we explore momentum conservation in models of chiral induced spin selectivity as a fundamental design principles that underlie this still incompletely understood phenomenon. To this end we consider the non-equilibrium dynamics of electron transmission from a straight waveguide to a helix with spin-orbit coupling. Transmission is found to be spin-selective and can lead to large spin polarizations of the itinerant electrons for finite width interface regions and we identify momentum conservation as crucial ingredient and confirm that this mechanism is robust against static disorder. In a second part I will establishing a quantitative connection between spectroscopic data and underlying microscopic models of PPC dynamics with two numerically exact simulation methods that demonstrate that vibronic coupling across the entire vibrational spectrum, including high-frequency modes, needs to be accounted for to ensure quantitatively correct description of optical spectra significantly modifying electronic parameters estimated from spectroscopic data. These quantitative changes can have significant effects on our interpretation of the nature of long-lived oscillatory dynamics in photosynthetic complexes.

Onur Pusuluk
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Proton delocalization in hydrogen bonds and its implications in enzyme catalysis and DNA replication

One of the principal contributions of quantum mechanics to chemistry has been the description of chemical bonding as a quantum superposition phenomenon. This allows us to explain how particle delocalization stabilizes the bonded atoms and molecules by a certain amount of energy [1, 2]. However, particle delocalization through a chemical bond does not only decrease the energy but also creates correlations such as entanglement and discord [3, 4]. In this talk, we will discuss the role of proton delocalization in biological catalysis within the frameworks of quantum information theory and thermodynamics. We will consider the quantum correlations generated through two hydrogen bonds between a nucleotide and a prototypical enzyme. We will show that classical changes induced in the binding site of the enzyme can transfer these correlations to the nucleotide, which in turn ends in a transition state corresponding to a quantum superposition of different tautomeric forms [5]. Open quantum system dynamics can then naturally drive the reaction in the forward direction from the major tautomeric form to the minor tautomeric form without needing any additional catalytic activity. We will find that in this scenario the enzyme lowers the activation energy so much that there is no energy barrier left in the tautomerization, even if the quantum correlations quickly decay. Finally, we will question the relationship of this putative model with the base-pairing mechanism in DNA replication [6].

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Institute of Electronic Structure & Laser, FORTH

Applications of cavity-based polarimetry

We describe how recent improvement in signal-reversing cavity-ringdown polarimetry [1,2] can achieve optical-rotation sensitivities of order μdeg, and we give examples of applications including measuring chiral optical rotation from single drops, from thin films with effective thickness of about one monolayer, and from chiral emissions from a tree [3]. Single proteins can be detected with whispering gallery mode microresonators [4,5], and we discuss the possibility that the two methods can be combined, to measure the chirality of a single protein molecule.

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Electronic charge transport measurements through Photosystem 1 layers on titanium nitride

The photosensitive protein Photosystem 1 (PS 1) is considered one of the most efficient light- harvesting molecular complexes that exist in nature [1]. As a building block of the photosynthesis scheme, PS 1 upon excitation transfers an electron from a primary donor (P700 center) to a primary acceptor (4Fe-4S cluster) at the picosecond time scale [2] with very high efficiency. This remarkable efficiency of electron transfer property has attracted attention due to its potential applications in biologically inspired solar cells. Previously, electron transport studies via PS 1 molecules have been carried out using self-assembled monolayers (SAMs) formed on metallic contacts (highly doped Silicon or, in the majority of cases, Gold), using various soft top contact schemes with high reproducibility [2- 4]. In the present study, we introduce titanium nitride (TiN) as an alternative promising contact material to investigate the electronic transport properties of photosynthetic proteins. TiN is a hard, conductive ceramic that is well-established in CMOS technology, chemically inert, and biocompatible. Here, we were able to immobilize PS 1 layers on TiN substrates, using SAMs of amino-terminated phosphonic acids as linkers to the oxygen plasma-activated TiN surface. Atomic force microscopy (AFM) images confirm the formation of a PS 1 monolayer of thickness ~6 nm, with about 40% coverage. Electrical measurements using eutectic gallium-indium soft top contacts show asymmetric IV characteristics, which may be assigned to a possible PS 1 orientation preference on the functionalized surface, as has been similarly reported for PS 1 layers on Au before [2, 4]. Possible charge transport mechanisms will be discussed.

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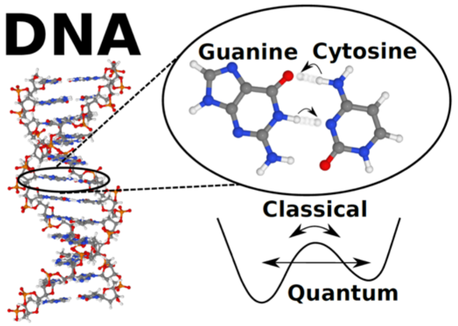
Quantum and classical effects in DNA point mutations: Watson-Crick tautomerism in AT and GC base pairs



Proton transfer along the hydrogen bonds of DNA can lead to short-lived but biologically relevant tautomeric bases [1, 2] that can lead to point mutations and cancer. The energy landscape of the transfer reaction from the canonical (standard) A-T and G-C base pairs to tautomeric (non-standard) A*-T* and G*-C* Watson-Crick DNA base pairs is modelled with density functional theory and machine-learning nudge-elastic band methods. We calculate the energy barriers and tunnelling rates of hydrogen transfer between and within each base monomer (A, T, G and C). We show that the role of A-T tautomerisation is statistically unlikely due to the presence of a small reverse reaction barrier. On the contrary, the thermal populations of G*-C* could be significant and propagate through the replisome. A substantial energy barrier hinders the direct intramolecular proton transfer; however, our calculations indicate that tautomeric bases in their monomeric form have remarkably long lifetimes. In addition, we show that the quantum motion of the protons should be treated within an open quantum systems approach [3], where the system is evolved while coupled to a thermal bath of quantum oscillators representing its surrounding noisy cellular environment of water molecules [4]. The combination of first-principles molecular modelling and open quantum treatment of the proton transfer process allows us to accurately calculate the rate of proton tunnelling in a decoherent and dissipative environment, which plays an important role in DNA replication [5].

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Photodegradation of rhodamine moieties by bio-analogous controllable porphyrin – nanocarbon agglomerates with resonant non-linear quenching properties

Biological light-harvesting systems display variable self-quenching properties, although in-vivo optical measurements have inherent difficulties. Using acid functionalised multi-walled carbon nanotubes (o-MWCNT) and aminophenyl tetraporphyrins, a novel synthetic pigment-scaffold was created that does not follow the trend of traditional concentration fluorescence quenching and isolates energy transfer mechanisms. Our steady-state and time-resolved data suggest an optimal concentration that offers a luminescence enhancement compared to the expected standard Stern-Volmer quenching relationship. The quenching is further modified by controlling the pigment-distance via agglomerate size to near the upper limit for Dexter transfer of 10Å as confirmed by dynamic light scattering measurements and chromophore – chromophore nearest neighbour calculations. Additionally, solvent effects are investigated by varying solvent dielectric environment. Increasing solvent dielectric results in a movement of the optimal concentration for resonant luminescent response. Additionally, the fast electron transfer characteristics of the chromophore-nanocarbon system are utilized to efficiently photodegrade toxic Rhodamine compounds in freshwater environments. Our results highlight a potential synthetic complex with facile synthesis to investigate resonant electron transfer processes that do not follow traditional luminescence quenching relationships and their potential uses in photodegradation environments.

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A differential lithium isotope effect on in vitro calcium phosphate formation at biologically relevant conditions

Calcium phosphate mineralization is important in several biological contexts including the formation of bone and in mitochondrial pathways, where amorphous calcium phosphate granules act as biological stores of calcium and phosphate ions. In the context of quantum biology, symmetric calcium phosphate nanoparticles, known as Posner molecules, have also been hypothesized to reside in brain mitochondria and act as a biological qubit via the phosphorus spin states of the molecule. Within the framework of this "Quantum Brain theory", the two isotopes of lithium, lithium-6 (~8% abundance) and lithium-7 (~92% abundance), have been hypothesized to incorporate into Posner molecules and differentially affect the lifetimes of the phosphorus spin states, and thus the chemical bonding of these Posner molecules. These two lithium isotopes have almost identical physical and chemical properties, with a measured mass diffusion difference of only 0.6%, but differ in their nuclear spin. Remarkably, however, these two isotopes have been found to have differential impacts on a wide range of biological systems, from animal behavior to organelle function. Here, we present results that show a measurable differential lithium isotope effect on the in vitro formation of amorphous calcium phosphate in aqueous solutions that are mildly supersaturated with respect to calcium phosphate. Dynamic light scattering measurements during amorphous calcium phosphate growth in the absence and presence of lithium salts at biologically relevant pH reveal that while the size of amorphous calcium phosphate particles that form is insensitive to which lithium isotope is present, their concentration is enriched in the presence of lithium-6. Ongoing experiments are aimed at understanding the potential mechanism(s) for this effect, and whether they may be linked to the different nuclear spin states of the two isotopes and their interaction with the phosphorus spin states in Posner molecules. Given the biological importance of calcium and phosphate regulation, as hypothesized by the Quantum Brain theory as well as in several other biological processes, these results could have wide implications for the interpretation of the milieu of differential lithium isotope effects that have been seen in biological systems.

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Coherence and population dynamics in molecular aggregates and photosynthetic pigment-proteins

High-frequency intramolecular vibrations might be essential by determining dynamic phenomena of electronic excitations manifested in nonlinear electronic spectroscopy via spectral lineshape formation, transition dipole moment borrowing, vibrational and mixed coherences. All these implications together with vibronic enhancement of energy and charge transfer can be explained in terms of vibronic molecular exciton theory. Here we will theoretically demonstrate that vibrations may assist the excitonic energy transfer and charge separation, hence contributing to energy transport and energy conversion efficiency. Three theoretical approaches usually used for characterization of the excitation dynamics and charge separation, namely Refield, Förster and Marcus model descriptions, regarding this question will be considered. It will be shown that two out of the three mechanisms require explicit resonances of excitonic splittings and the nuclear vibration frequencies. However, the third one related to the electron transfer is in principle off-resonant. It will be also demonstrated that the coherences of mixed electronic-vibrational (vibronic) nature may enhance the rate of the charge separation in PSII reaction center and by determining the excitation energy transfer in light-harvesting antenna complexes. The situations when the separtion of the electronic and vibrational origins of coherences is possible will be discussed.

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Pseudo-dynamical matrix based olfactory classification of molecules using convolutional neural networks

Olfaction is the process of chemoreception in biological systems. Even after being the primarily important sense for understanding the surroundings, olfaction is still an enigma. There are two competing theories about the signal transduction mechanism in olfactory systems. One states that the shape of the odorant molecule gets sensed [1], and the other states that olfactory receptors act like a spectroscope and sense the vibrational frequencies of the odorant molecule [2,3]. In our earlier attempts [4], we have tried to understand the connection between the structure, shape, and vibrational spectrum of a molecule, and chemical graph theory proved to be an excellent technique. Graphs are an efficient way to understand molecules, with atoms acting as nodes and bonds as edges. With the help of the graphical representation of molecules [5], it has become possible to employ deep machine learning techniques to predict various biochemical activities of molecules. In our present study, we are trying to understand the structural properties of molecules and their relationship to the perception of the smell using deep learning techniques. The methodology not only attempts to unify the two competing theories but also paves the path for vibration-based generic odor sensors. The proposed method utilizes a novel representation of molecular structure in terms of a simplified Dynamical Matrix [6], referred to here as Pseudo-Dynamical Matrix (PDM). Dynamical matrix (DM) is a detailed matrix of force constants whose eigenvalues are the vibrational frequencies of the molecule. DM is constructed considering all the connections (next-neighbor, next to next neighbor, etc.). However, in PDM, only the nearest-neighbor approximation is considered while calculating the bond stiffness. This simplification ignores the effect of the molecule's secondary structure. Also, the force constants used in PDM construction only include stretching modes. This exercise attempts to incorporate physical insight into the brute force machine learning process. The utilization of Graph Neural Networks (GNN) for generating molecular feature embeddings has shown great success in the task of odor prediction [7]. The molecular node feature matrix is a matrix containing each node's physical and chemical properties, which is given as the input to the GNN model. These node features get recursively updated by aggregation with neighbor node features, ignoring the edge-level features [8]. This GNN model outperformed other simpler deep learning based pipelines like Convolutional (CNN) and Dense (DNN) Neural Networks. In our method, we trained a parallel-CNN-based model for the task of binary classification among different odor categories. The molecular feature embeddings are extracted from two parallel convolutional layers, taking in the node feature matrix and the PDM as inputs, which are then fused. We trained and tested our models on the olfaction dataset from GoodScents company [9], comprising 4209 molecules, each with multiple perceptual labels. For comparison, we also trained a GNN model for feature extraction. The CNN-based pipeline achieved comparable classification accuracy as the GNN model across multiple classes in our dataset. This comparison shows the promise of using PDM as a molecular representation for quantitative structure-property relation tasks. Going forward, we are developing a bond strength scaled 3D graph convolutional neural network [10]. The model will utilize the 3D structure of the molecule coupled with bond strength values from the PDM for molecular interpretation and feature extraction. We will attempt to include information about distances and bond angles between different atoms and functional groups to enhance feature extraction further.

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Quantum computer simulations of the radical pair mechanism

The Radical Pair Mechanism (RPM) is the cornerstone mechanism of spin chemistry, that is involved in such phenomena as artificial and natural photosynthesis, and avian magnetoreception. Due to the quantum effects at play in the radical pair (RP) reactions, the RPM is an important quantum biological system where quantum information science approaches can be applied [1]. Recently, first programmable, gate-based quantum computers became available to the broad research community. Finding new practical applications, including those in the fields of chemistry and biology, is extremely important for the quantum computation field. The RPM, as an inherently quantum phenomenon, appears to be an ideal system to be simulated on a quantum device. In this work, we simulate several simple model RPM systems on an IBM Q quantum computer, as well as on the IBM's Qiskit Aer quantum simulator. As the quantum devices available today are still small and noisy, we have chosen the simplest RPM phenomenon for which experimental data is available: quantum beats in radiation-generated RP's in alkane solutions. Quantum beats are oscillations in the singlet RP recombination product yield that reflect the time evolution of the RP spin state. In such systems, one only has to take Zeeman interaction and isotropic hyperfine couplings (hfc's) into account. If one of the radicals is deuterated, hydrogen hfc's present in that radical can also be neglected. The systems we have simulated include diphenyl sulfide-$d_{10}^{+\cdot}$/*para*-terphenyl-d_{14} (PTP)$^{-\cdot}$ radical pair (no significant hfc's); 2,2,6,6-tetramethylpiperidine (TMP)$^{+\cdot}$/PTP$^{\cdot}$ radical pair (two different hfc's); (TMP)$_2^{+\cdot}$/PTP$^{-\cdot}$ radical pair (single nitrogen hfc); 9,10-octaline$^{+\cdot}$/PTP$^{-\cdot}$ radical pair (eight equivalent proton hfc's); and 2,4-dimethylbutane$^{+\cdot}$/PTP$^{-\cdot}$ radical pair (two groups of equivalent proton hfc's). We were able to achieve good agreement with both theory and experiment for all those systems. More complex systems where no analytical solution is available can be addressed in the future with more powerful quantum computers. The RPM is an open quantum system which poses an additional challenge for quantum simulation. To implement the T_1 and T_2-decoherence, we have devised a novel approach that leverages the inherent qubit noise and makes it possible to simulate the T_1 and T_2 relaxation in spin systems with no additional computational overhead. The results are in good agreement with both theory and the simulation based on the Kraus representation of quantum channels.

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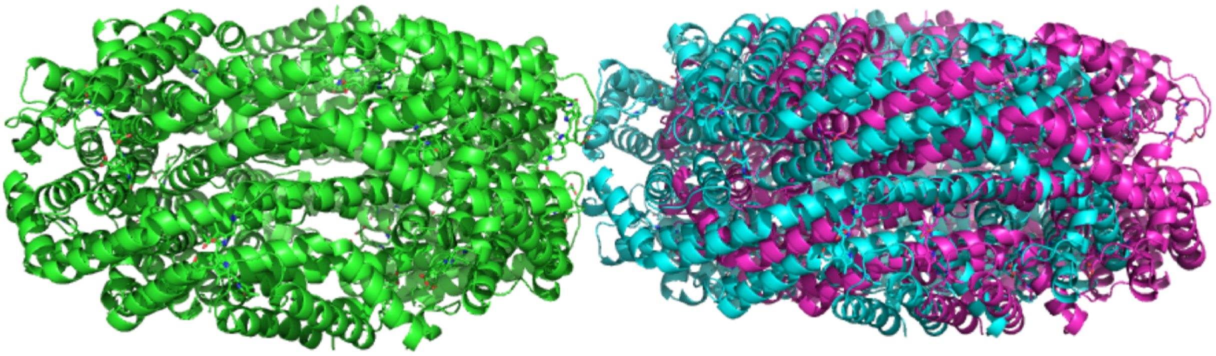
Modelling quantum energy transport in cyanobacteria

Phycobilisomes (PBS) are the remarkably versatile light-harvesting antennae of cyanobacteria and red algae. Structurally, these antennae are rods assembled from stacks of hexamers, each individually composed of a varying number of chromophores. It is across bundles of these rods that sunlight-driven excitations travel, moving from chromophore to chromophore, towards their destination - the reaction centre. The spatial arrangement of chromophores at the bottom of this structural hierarchy is at the nanoscale where energy transfer dynamics obeys the laws of quantum mechanics. This observation is corroborated by recent work which has shown that the arrangement of hexamers plays a decisive role in energy transport across the full PBS complex. Motivated by this, we combine structural data of antennae in Synechococcus elongatus with the theory of open quantum systems to provide a realistic description of quantum energy transport within cyanobacteria. Importantly, we include the surrounding optical and vibrational environments in our description of system dynamics. Through this approach we find a subtle architecture that demonstrates a robust mechanism is at play, channeling excitations and thereby expediting transport across the interface of antennae rods.



A pair of hexamer structures, S. elongatus, which constitute phycobilisome antennae.

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The replisome environment and DNA point mutations: multiscale simulations of G-C tautomerism and PcrA Helicase

Proton transfer between the DNA bases can lead to non-standard, potentially mutagenic tautomeric forms [1,2]. If the tautomers successfully pass through the replication machinery, they are thought to adopt a Watson-Crick-like shape and mismatch with the wrong base, thus evading proof-reading and potentially leading to replication error [3]. There is heated debate over the true biological impact of the tautomeric forms. Previously it was proposed that if the tautomeric lifetime is much shorter than the helicase cleavage time, no tautomeric population would successfully pass the enzyme [4]. In our work, we have determined that the proton transfer energy landscape drastically changes during the first two Angstrom cleavage of the base. Density functional theory (DFT) calculations indicate a sequential mechanism where the forward reaction barrier increases linearly concerning the cleavage distance, suggesting increased stability of the tautomer. In addition, molecular dynamics simulations indicate that cleavage time is much quicker than previously thought, with our models describing both aqueous DNA, and DNA in complex with the bacterial replisome enzyme PcrA Helicase. Our results indicate that a static picture of the proton transfer oversimplifies the biological event. We observe that the nucleobase pairs undergo a wide range of fluctuations, contrary to the idealised manner which is modelled by quantum chemical calculations to date. To further elucidate the complicated environment in which tautomers may be formed, and the dynamics in which they must survive, we employ multiscale quantum mechanics / molecular mechanics (QM/MM) calculations which marry the accuracy of DFT with the large-scale dynamics of MD. The tautomerisation reaction is mapped using Umbrella Sampling to obtain a potential of mean force for DNA in complex with PcrA Helicase. We also observe the dynamic environment at the duplex DNA–Helicase interface caused by the stepping motor action described in [5], and comment on the implications for Löwdin's hypothesis for single point mutations.

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Harnessing vibronic coherences to study vibronic mixing in chlorophylls and photosynthetic complexes

Electronic-vibrational (vibronic) coupling has been suggested to play an important role in photosynthetic processes, such as energy transfer and charge separation. Even though this coupling in molecules has been suggested nine decades ago, it has proven to be a highly elusive phenomenon to investigate. It can, however be revealed by studying coherence signals. To this end we employed polarization-controlled 2D electronic spectroscopy together with advanced analysis [1] that allows to extract full information about coherences, including their nature, which in turn directly reports on vibronic mixing. I will present a couple of studies of vibronic mixing in molecular systems. In one we investigated chlorophyll a molecule in solution, where we found a clear evidence of vibronic mixing of the two lowest electronic states, Qx and Qy, which has been already identified in chlorophyll c molecule as well [2]. Importantly, we distinguish multiple modes that are involved in vibronic mixing. Since this type of coupling seems to be general, vibronic mixing is anticipated in all chlorophyll-type molecules, as have been previously suggested in a theoretical study [3]. We also revisited coherence dynamics in the light-harvesting complex FMO from green sulfur bacteria at 77 K [4]. We detected and sorted out a wide range of coherence signals. At early times purely electronic coherences were observed, which dephased on the ~100 fs time scale. All long-lived coherences, on the other hand, had clearly vibrational origin. Importantly, we observed that specific vibrational coherences both on ground and excited electronic states are excited via vibronically-coupled excitonic transitions. In principle vibronic mixing allows for subtly adjusting molecular quantum states to match resonances important for energy and electron transfer functions. Presence of the ubiquitous vibronic mixing rises an intriguing question, if it is an unavoidable consequence of the properties of the porphyrin-type molecules, or an optimization mechanism, which nature employs to finely tune primary processes of photosynthetic.

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POSTER PRESENTATIONS

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Entanglement and nuclear spin dynamics in pure and doped Posner molecules

The potential role of quantum spin in biological systems is by now well documented in research that focuses on magnetoreception and reactive oxygen species. The radical pair mechanism, in which a superposition of spin states can give rise to magnetic field dependent chemical products, has been proposed as the means by which birds sense the weak geomagnetic field. The radical pair mechanism consists of paired electrons but a recent hypothesis has suggested that paired nuclear spins might also have measurable effects in biological systems. This hypothesis outlines how phosphorus nuclear spins might be prepared in an entangled state, how this entanglement is protected by assembly into Posner molecules and how this entanglement might modulate calcium ion production and concomitant neural activation. It has been suggested, however, that entanglement in radical pairs is not strictly necessary for the avian compass to function. We investigate the importance of quantum effects such as coherence and entanglement in Posner molecules and how these effects are directly dependent on specific parameters such as spin-spin coupling strengths and Posner molecule symmetry. We also investigate how lithium isotope substituted Posner molecules effect coherence and entanglement and whether this is a viable explanation for lithium's mechanism of action in bipolar disease. Finally, we illustrate how entanglement might possibly be preserved through exploitation of the biological environment.

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Quantum vision studies: pupillometry and biometrics

We here present recent work on the synthesis of quantum optics with the physiology of human vision. This synthesis dates back to the work of Hecht et al [1], who first demonstrated the retina's photodetectors' ability to detect single photons. A nuisance of their experiment was the fact that each of the three authors, who were the actual subjects of the measurement, had different optical losses along the light's path from the cornea to the retina. In [2] we flipped the coin around and took advantage of those losses to introduce a new biometric authentication scheme, based on our perception of weak light. To experimentally realize this scheme, a laser light source with the laser beam profile modulated in discrete pixels is required. Such light source was developed in [3] and was first used to study the pupil light reflex with spatially selective stimulus of the retina. Such measurements have the potential to unravel new information about brain function and disease, as reviewed in [4]. Finally, in [5] we demonstrate a quantum advantage in our biometric authentication scheme when using quantum light sources, in particular single photons. This work further advances the new field of quantum vision.

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Fluorescence quenching and energy transfer between fluorescent proteins

Förster's Resonance Energy Transfer (FRET) using fluorescent protein (FPs) has become a powerful tool to study protein-protein interactions and their incoherent energy transfer dynamics. It is assumed that FRET requires fluorophores in close-proximity (< 10 nm), involving a donor-acceptor pair with weak Coulombic dipole-dipole coupling. The energy transfer between the FP fluorophores has typically been considered as incoherent because close fluorophore proximity is limited by the FP scaffold structure (i.e., β-barrel structure). In addition, the general conundrum of quantum coherence occurring in warm, wet living biological environments remains difficult to observe due to the nature of decoherence and dephasing in such systems. Nonetheless, evidence suggests that non-radiative excitation energy transfer can be facilitated by coherent energy transfer between FPs. Coherent energy transfer requires stronger dipole-dipole coupling to bring to terms excitonic coupling, allowing for the energy transferred between the interacting states to be near instantaneous. It is not well understood as to what properties, surrounding the FPs, may impact the energy transfer between the fluorophores. To understand the potential quantum nature of the energy transfer dynamics in FPs it is warranted to become aware of their interactions with their environment as well as with themselves. It is well known that the fluorescence intensity for any given substance will decrease after a quenching process occurs. However, it is unclear whether quenching FPs will influence the energy transfer dynamics. We speculate that the feature of coherent energy transfer between FPs is attributed to the relative rate of energy transfer and the rate of the excited-state vibrational dephasing. Here, time-resolved fluorescence anisotropy is used to study the energy transfer dynamics between FPs in conjunction with introducing different concentrations of the external quenchers that induce modulating the interplay between the FP system and their surrounding environment. In this study, we attempt to establish the impact on the energy transfer dynamics between fluorophores by introducing varying concentrations of external quenchers to the FPs environment. We examine the photophysical properties and spectral changes of the FPs, after adding external quenchers to both the FP monomeric and dimeric structures to further characterise the energy transfer dynamics. Furthermore, we explore whether the addition of external quenchers will contribute to inducing additional dephasing factors between the system and the environment by analysing the time-resolved anisotropy measurements of the system after excitation.

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Eliminating radiative losses in long-range exciton transport

We demonstrate that it is possible to effectively eliminate radiative losses during excitonic energy transport in systems with an intrinsic energy gradient. By considering chain-like systems of repeating 'unit' cells which can each consist of multiple sites, we show that tuning a single system parameter (the intra-unit-cell coupling) leads to efficient and highly robust transport over relatively long distances. This remarkable transport performance is shown to originate from a partitioning of the system's eigenstates into energetically-separated bright and dark subspaces, allowing long range transport to proceed efficiently through a 'dark chain' of eigenstates. Finally, we discuss the effects of intrinsic dipole moments, which are of particular relevance to molecular architectures, and demonstrate that appropriately-aligned dipoles can lead to additional protection against other (non-radiative) loss processes. Our dimensionless open quantum systems model is designed to be broadly applicable to a range of experimental platforms.

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ROS-mediated magnetic field effects of the radical pair mechanism in cells expressing Drosophila melanogaster cryptochrome

Magnetic field effects (MFE) have been asserted to have a role in biology. However, the interaction mechanism by which even low magnetic fields (MF), such as the geomagnetic field (50 μT), could significant effect biochemical reactions have remained opaque. One way by which biochemical processes could in principle acquire sensitivity to the geomagnetic field is via the radical pair mechanism (RPM), as exemplified the cryptochrome hypothesis of magnetoreception [1]. Cryptochrome, the putative magnetoreceptor molecule, and its flavin cofactor are thought to generate spin-correlated, charge-separated radical pairs. Due to radio-frequency resonance, a lack of hyperfine couplings, and some evidence of the magnetically-sensitive step occurring during reoxidation in avian CRY, an oxygen radical may be a potential candidate partner for RPM in CRY. As radicals and other molecules with non-zero electronic spins such as reactive oxygen species (ROS) are prevalent across biology, ROS generation and modulation in response to magnetic fields may be an important [2] and understudied element of the whole picture of biological magnetic-sensitivity. Investigating the role of blue light and magnetic fields on growth parameters and ROS production may elucidate, in part, the story of MFEs and the role of CRY in a pseudo-in vivo approach. Using an overexpression model of Drosophila CRY (DmCRY) in E. coli, we investigate maximum growth rate, and associated toxicity, as an phenomenological indicator for possible ROS-induced cellular responses, on application of narrow bandwidth light and a homogenous magnetic field. We further probe ROS-based fluorescence and autofluorescence in this model. We hope this will contribute to our understanding around the age-old fear of environmental MF impacts on health metrics and disease risk.

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Exploring the role of quantum tunnelling in DNA mutations using neutron crystallography

Cancer genome sequencing reveals that ⅔ of the mutations in human cancers are due to spontaneous mutagenesis. High fidelity polymerases replicate the DNA at a very high accuracy and do not incorporate base pairs that do not conform to stereochemical complementarity between the polymerase and the base pairs. However, rare tautomeric forms of base pairs, which have been proposed to be formed through quantum tunnelling of protons, can mimic the canonical Watson-Crick forms with cognate pairing. This change can allow these forms to evade DNA repair mechanisms long enough to become incorporated into the new DNA strand, resulting in spontaneous point mutations. Although many theoretical studies have demonstrated the feasibility of the proton transfer reactions, it has been very challenging to experimentally detect the rare tautomeric forms as they are relatively short lived. Also, the positions of protons involved in the hydrogen bonding between the bases are not resolved with X-ray crystallographic approaches. As well as their potential role in mutations that can cause cancer and genetic diseases, tautomeric bases may also be of value in pharmacology for design of oligomeric sequences that can block DNA duplex and RNA biochemistry by enhancing the structural and functional diversity of RNA enzymes. To investigate the presence/likelihood of the rare tautomers in DNA, we propose to utilise the technique of neutron scattering to map the position of protons involved in hydrogen bonding between DNA bases in DNA crystals.

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Quantum tunnelling in galactose oxidase

Proton transfers in enzymes can occur via quantum tunnelling through free energy barriers and may be observed through pressure or temperature dependent kinetic isotope effects (KIE). The object of this work is to find a tunnelling estimation for Galactose Oxidase and its contribution towards the reaction at the active site, A model system is studied using Gaussian 9 and 16, mainly using DFT B3LYP or PBEPBE functionals with a 6-31g +(d,p) basis set, running optimization calculations on the reactant and product states before attempting to find the transition state. The transition state is found using Gaussian 9 and 16 running QST2 on the reactant and product states or by a Berny transition state guess. To perform the tunnelling approximation, a Wentzel–Kramers–Brillouin (WKB) approximation is used through a Python code to perform an estimate of the contribution of hydrogen tunnelling based on the energies provided by the reactant, product and transition state. This can then be compared to the classical reaction rate to judge the contribution towards catalysis via tunnelling.

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Strategies to simulate dephasing-assisted quantum transport with digital quantum computers

Simulating charge and energy transfer in extended molecular networks requires an effective model to include the environment because it significantly affects the quantum dynamics [1]. A prototypical effect known as environment-assisted quantum transport (ENAQT) consists in the enhancement of the transfer efficiency by the interaction with an environment [2]. A simple description of this phenomenon is obtained by a quantum master equation describing a quantum walk over the molecular network in the presence of inter-site decoherence. We consider the problem of simulating the dynamics underlying ENAQT in a digital quantum computer [3]. Two different quantum algorithms are introduced, the first one based on stochastic Hamiltonians [4] and the second one based on a collision scheme [5]. We test both algorithms by simulating ENAQT in a small molecular network on a quantum computer emulator and provide a comparative analysis of the two approaches. Both algorithms can be implemented in a memory efficient encoding with the number of required qubits scaling logarithmically with the size of the simulated system while the number of gates increases quadratically. We discuss the algorithmic quantum trajectories generated by the two simulation strategies showing that they realize distinct unravellings of the site-dephasing master equation [6]. In our approach, the non-unitary dynamics of the open system is obtained through effective representations of the environment, paving the way to digital quantum simulations of quantum transport influenced by structured environments.

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Can the human eye detect multipartite entangled state?

In a recent article [1], an entanglement witness was developed to discover whether or not the human eye can detect bipartite photonic entanglement. For this purpose, an interferometry setup was proposed, where the low photon numbers are amplified using coherent state generators before the detection by the human eye. We ask and explore if the coherence generation can increase the quantum noise and hinder the generalization of the setup to higher-order entanglement detection. We find that the quantum noise can be significant to get conclusive results for higher-order entanglement, but the situation can be remedied by using an amplitude squeezing operation instead of coherence generation before detecting the photons by the eye. We also consider quadrature squeezing relative to the amplitude squeezing before the detection and find the latter is more successful [2]. We generalize the setup in the experiment [1] to explore if the human eye can detect multipartite entanglement. For that aim, we specifically consider the case of W state detection. Amplitude squeezing becomes more critical when we consider a larger number of photons to recognize the W state by the human eye successfully. The generalized interferometer allows for measuring W-state entanglement witness [3]. To simulate the associated psychophysical experimental scenario based upon the generalized interferometer and W-state entanglement witness, we use a machine learning model of human subjects to be interrogated as photodetectors. Our simulations and their analysis conclude that psychophysical experiments can be used to probe W-state entanglement.

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Effect of oxidation on quantum coherent exciton transport in FMO

Demonstrations of quantum coherence in photosynthetic molecules have been marked with controversy due to conflicting experimental results on the coherence time of FMO during exciton trsansport [1,2]. We analyze a possible source of this deviation in coherence lifetimes, noting that the natural environment of FMO is anaerobic, and its functional structure is highly sensitive to oxidation. Here we discuss a model of how the effects of oxidation can degrade the coherent transfer properties of FMO and consider its effects to the coherence time as a result by analyzing the basis-independent coherence.

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The repair and thermodynamic properties of UV-induced DNA pyrimidine lesions

This computational research will focus on the repair and thermodynamic properties of UV-induced DNA pyrimidine lesions. A study of the thermodynamic and gas state properties of the cytosine-cytosine cyclobutane pyrimidine dimers (C=C CPDs) and the thymine-thymine (T=T CPDs) dimers was carried out using DFT and TD-DFT. QM/MM and MM was used to model DNA chains containing the T=T and C=C CPDs. This enzyme photolyase is found in a wide variety of organisms and can work to break these lesions (therefore repairing the DNA) before they cause mutation. Photolyase can be described as taking two forms: one which targets the (6,4) T-T lesion and one which targets the T=T CPD[1]. The (6,4) T-T photolyase will donate a proton and electron exchange to the lesion[2], while the T=T photolyase has electron donation only[1]. Marcus theory and NEB along with QM/MM will calculate these proton and electron transfer pathways.

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Modeling molecular aggregates using Dirac-Frenkel variational method

The linear absorption and fluorescence spectra of H and J molecular aggregates is analyzed, where both the electronic and vibrational molecular degrees of freedom are considered. It is made up of a collection of molecules (sites) coupled via an electrostatic dipole-dipole interaction. Inter- and Intra-molecular vibrational modes are modeled as harmonic oscillators with frequency shift in an excited electronic state. Molecular aggregate excitation dynamics and spectra can be computed using the wavefunction based time-dependent Dirac-Frenkel variational principle with multi-Davydov D2 (mD2) Ansatz, which ought to be complex enough to represent all the necessary electron-vibrational (vibronic) quantum states of the aggregate. mD2 wavefuction is built as a superposition of D2 wavefunctions (multiple). Each D2 multiple corresponds to an excitonic state associated with an aggregate vibrational state, represented using coherent states. By considering numerous multiples, complexity and, in principle, accuracy of the mD2 Ansatz can be increased. By inspecting and comparing absorption spectra of both the ring and chain aggregates over a range of electrostatic nearest neighbor coupling and temperature values, we find mD2 Ansatz with multiplicity $M > 1$, is required to obtain accurate aggregate absorption spectrum. For H aggregates, multiplicity is required to obtain positive spectra lineshape and accurate peak intensities, while for J aggregates, multiples mostly redshifts absorption spectrum, keeping the overall lineshape qualitatively the same. Further, we looked at the impact of vibrational mode frequency shift upon electronic excitation on absorption and fluorescence spectra, and found it necessary to include at least couple of multiples, even in monomer spectrum, when frequency shift is applied. For larger aggregates, multiplicity is also necessary even without frequency shift.

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Homo-FRET and relative dipole orientation fluorescent protein tandem dimers using time resolved fluorescence anisotropy and Monte Carlo simulations

Förster Resonance Energy Transfer (FRET) is a non-radiative energy transfer mechanism mediated by Columbic dipole-dipole interactions by which excitation energy is transferred from an excited state donor fluorophore to a ground state acceptor fluorophore. Recent evidence indicates that exciton coupling between fluorescent proteins (FPs) is achievable under physiological conditions when FPs dimerise, suggesting that FPs have evolved a mechanism to prolong quantum coherence under physiological conditions. Upon excitation FRET-type interactions between FPs occur at close proximity for which donor and acceptor fluorophores have common atomic transitions with a permissive relative transition dipole orientation. When calculating FRET efficiency, it is typically assumed that the dipole orientations of the donor and the acceptor randomise quickly as the relative dipole orientation factor (kappa squared, k2) becomes 2/3. However, this assumption should be revisited to take into account dimerisation. To study this, we use time-resolved fluorescence anisotropy (TRFA) to study the energy transfer dynamics between FPs in a tandem dimer (TD) linked by a 33 amino acid flexible linker. For a control experiment, we test mEGFP and other monomeric versions of FP as reference and estimate the relative dipole orientation factor between fluorophores in the FP homodimers using a combination of TRFA measurements and Monte Carlo simulations.

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Long-range coherent tunneling induced by fractional vibronic resonances

Coherent coupling between electrons or excitons and molecular vibrational degrees of freedom can have a profound impact on the dynamics of various nanoscale phenomena including light harvesting and charge transport. Using a method of calculating quantum dynamics that was tailored from the ground up towards rapid, parallelized execution on graphics processing units (GPU), we investigate the dynamics of such coherently coupled vibronic systems, uncovering unexpected resonance behavior that enables long-range tunneling over multiple chromophores [1]. These results are clearly demonstrated in both a strong electron–phonon coupling regime and a regime corresponding to the recently proposed tunable array of Cy3 dyes [2]. Experimental applications of these phenomena may also include molecular junctions or organic photovoltaics, with potential expansions towards cavity QED.

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Memory assisted model for photoisomerization

In this work we propose a sophisticated microscopic model of an electron-phonon system to describe the photoisomerization process. The model consists of a 3-level system coupled to discrete modes undergoing a Lindbladian evolution. However, looking for the reduced system dynamics, relevant quantities of the electronic system under a non-Markovian dissipative dynamics can be obtained. Detailed numerical studies of the dissipative dynamics and population transfer are presented. We aim to gain a microscopic understanding of which properties of the model determine the efficiency of the photoreaction process and what conditions i.e memory effects lead to a high quantum yield.

Nicola Lorenzoni
Institute of Theoretical Physics, Ulm University

Electronic and vibronic dissociation of strongly bound electron-hole pairs in photovoltaics

In organic photovoltaics, strongly coupled electron-hole pairs are efficiently dissociated, despite the strong Coulomb potential when compared to the thermal energy and the electronic coupling between its constituents. An accurate description of these phenomena requires efficient non-perturbative numerical methods, capable of encoding the non-perturbative nature of the coupling with the vibrational environment (vibronic coupling). In here, we apply DAMPF, our recently developed non-perturbative method for simulating the dynamics of Open Quantum Systems, in order to fully address the processes behind charge dissociation. In particular, we show the key role played by high-frequency, long-living vibrational excitation, whose accurate description cannot be reach via a Markovian description.

Anna Munro
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The C-terminus of Drosophila cryptochrome plays a critical role in the neuronal signalling of magnetosensitivity

Despite many years of investigation, the biological basis of Magnetoreception is yet to be fully elucidated. The most popular hypothesis is founded in the electron chemistry of the FAD binding flavoprotein Cryptochrome (CRY), where light exposure triggers the formation of radicals via electron transfer. Previous work highlights the importance of the C-terminal (CT) of Drosophila CRY (DmCry) in mediating MF effects, as deletion of this region renders DmCry insensitive to a MF, despite the presence of the Trp residues which form the canonical radical pair mechanism. We have previously demonstrated through both behavioural and electrophysiological assays, that ectopic expression of the terminal 52 amino acids of the DmCry-CT is sufficient to render Drosophila neurons sensitive to a MF, despite the lack of FAD binding pocket, as well as the Trp residues believed to be essential. Building on this, we further demonstrate the importance of the CT in magnetosensitivity by making a number of mutations to key residues and testing these transgenics in our well established assays. A number of protein interaction sites are present in the DmCRY-CT, and here we show that point mutations in these domains impairs the signalling of MF effects of both full length DmCRY and just the 52 aa CT fragment, without effecting their blue light sensitivity. Thus, suggesting that the CT may in fact act as a signal amplifier of effects on upstream radicals, priming downstream signalling partners in a magnetoreceptive pathway, perhaps by providing a nucleation point for other key players in a so-called "magnetoreceptor signalplex". Additionally, we eliminate the possibility that the remaining Trp residue in the CT (aa: 536) alone is an essential radical partner by substituting the residue for a phenylalanine and demonstrating a persistent MF sensitivity, albeit weakened, likely through perturbation of signalling caused by structural changes. Thus, here we suggest that the ability of DmCRY-CT to mediate MF sensitivity may lie in it's role as a signal amplifier/nucleation point for downstream partners of the magnetoreceptive pathway: perhaps acting to localise key partners to important cellular compartments such as the plasma membrane.

Manisha Patel
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Probing a differential lithium isotope effect on amorphous calcium phosphate formation in simulated body fluids

Calcium phosphate plays an important and multi-faceted role in biological systems, ranging from mitochondrial signaling pathways to key biomineralization processes such as bone growth. Moreover, symmetric calcium phosphate nanoparticles known as Posner molecules have been theorized to serve as a putative 'neural qubit' via protected phosphorus nuclear spin states in a biological environment. Thus, understanding calcium phosphate nucleation and aggregation is key to elucidating the theory for Posner-mediated quantum activity in the brain. Here, we demonstrate using a combination of in vitro experimental methods that the prenucleation and aggregation behavior of amorphous calcium phosphate is differentially influenced by two isotopes of lithium, 6Li and 7Li, which have nearly identical chemical behaviors in solution, but have been shown to differentially impact a number of biological systems. This phenomenon suggests a quantum mechanical effect on calcium phosphate nucleation and aggregation, which may help to explain lithium isotope effects seen in vivo in various contexts. Specifically, our experiments suggest a direct correlation between lithium isotope effects observed in vitro and those observed in the dynamics of calcium signaling between isolated mitochondria ex vivo. Furthermore, we situate this differential isotope effect within the context of calcium phosphate phase behavior, which helps to isolate pathways in which quantum mechanics may be at play. This work has the potential to advance our understanding of a wider range of nonclassical isotope effects in biology.

Jessica Ramsay
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Mobile radicals enable magnetoreception in cryptochrome

A popular hypothesis ascribes magnetoreception to a magnetosensitive recombination reaction of a pair of radicals in the protein cryptochrome. Many theoretical studies of this model have ignored inter-radical interactions, particularly the electron-electron dipolar coupling (EED), which have a detrimental effect on the magnetosensitivity [1, 2]. Here we set out to elucidate if internal motion of the radical pair sensor can overcome this issue. Our model considers the effects of the diffusive motion of one radical partner along a one-dimensional reaction coordinate. Such dynamics could in principle be realized as (1) actual diffusion of a radical through a protein channel, or (2) via bound radical pairs subjected to protein structural arrangements and fluctuations. Our results conclude that the motion of a radical pair is able to alleviate the suppressive effect of the EED interactions and, for particular conditions, can enhance the magnetic field sensitivity. Interestingly, marked magnetosensitivity was only present when the reaction coordinate was oriented within the isoalloxazine-plane of the flavin co-factor. Two main/potential contributors to enhanced magnetosensitivity were considered: (1) an attractive interaction potential and (2) gating at the far end of the reaction coordinate, both of which reduce the competing escape of the radical into the bulk. For a short diffusion domain of 1 nm, the enhancement appeared to be weakly dependent on the diffusion coefficient and the interaction strength of the attractive potential. Whereas at 2 nm, a strong dependence on the interaction potential gave rise to large magnetosensitivity. Overall, we show that a diffusive motion of a radical preserves the sensitivity even in the presence of EED. We suggest that the effect could be enhanced in cryptochrome by a gating mechanism, as implicated by recent molecular dynamics studies [3], and electrostatic interactions within the flavin binding pocket.

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Applying Shannon's noisy channel coding theorem to magnetoreception

The process of magnetoreception by migratory songbirds can be mathematically understood as a communication channel that takes the bird's heading direction as input and the singlet yield at a receptor cell as output, with the conditional probability distribution of the output on the input controlled by the radical pair mechanism. This channel (or its variants) is known to be highly noisy, and does not transmit information reliably on its own (Hiscock 2019). Assuming that the bird's brain is complicated enough to be capable of constituting a typical set decoder, I argue that by carefully choosing input values (corresponding to selecting specific receptor cells across the bird's eye's retina), a very low error probability can be achieved despite of the high level of noise provided that the rate of communication is not necessarily required to be close to the channel capacity (as the bird gets memory). The idea is motivated by Shannon's noisy channel coding theorem. It gives an explanation for why the birds can still accurately sense the earth magnetic field even when the number of photons available is extremely few (night migratory songbirds such as European robins migrate at night under low light condition).

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Non-equilibrium variational polaron theory

Models of excitons interacting strongly with vibrational modes are important in understanding a variety of physical processes in organic molecules, such as decoherence and excitonic energy transfer. Moreover, strong vibrational coupling induces unique non-additive effects when the exciton is coupled to additional non-commuting environments. For example, when molecules simultaneously interact with an electromagnetic field, it has recently been shown that the vibrational coupling can break detailed balance and create a population inversion in two-level emitters [1]. Polaron theory has been successful in treating strong vibrational coupling in open quantum systems. In this, a unitary transformation is used to diagonalize Hamiltonians that describe a system interacting with a vibrational bath. The transformation incorporates the bosonic bath modes into the definition of the exciton, describing a quasi-particle known as a polaron. However, in situations involving laser-driven molecules, multiple molecules coupled together or molecules interacting with additional non-commuting baths, the polaron transformation no longer exactly diagonalizes the Hamiltonian. In these cases, polaron theory fails when the laser-driving, intermolecular couplings, or interactions with the additional baths, are strong. A variational form of polaron theory can be used to extend the validity within these regimes. This entails optimizing the unitary transformation such that the contributions of the non-diagonalizable terms to the free energy are minimized. Variational polaron theory can accurately treat models of laser-driven molecules and multiple molecules coupled together, so long as these interact with a single environment. However, when the molecules couple to multiple environments, variational polaron theory cannot be used because the free energy is not defined out of equilibrium. In this poster, I derive an extension of variational polaron theory to non-equilibrium problems and apply it to the model of a laser-driven molecule interacting with multiple vibrational baths. This technique will extend the validity of polaron theory into non-equilibrium problems, enabling analysis of non-additive effects, photosynthetic energy transfer and decoherence, through the intuitive lens of polaron theory.

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Elucidating quantum coherence in the complex system of the avian compass

Quantum coherence has been suggested as a resource that nature may utilise in the spin dynamics of the hypothesised radical-pair mechanism of the avian compass. Whilst theoretical studies have provided insight [1,2], they often assume a small number of coupled nuclei in the radical-pair and thus lack sufficient complexity of the biological system. Here, we investigate realistically large radical-pair models with up to 21 nuclear spins, inspired by the magnetic field sensitive protein cryptochrome [3]. By varying relative radical orientations, we reveal correlations of several coherence measures [4] with compass sensitivity. Whilst electronic coherence is found to be an ineffective predictor of compass sensitivity, in some cases producing a strong anti-correlation, a robust correlation is established with a measure of the global coherence of electron and nuclear spins [5]. The results demonstrate the importance of realistic models, and appropriate choice of coherence measure, in elucidating the quantum nature of the avian compass [6].

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Quantum resource theory models for photoisomerization

Quantum resource theory formulations of thermodynamics offer a versatile tool for the study of fundamental limitations to the efficiency of physical processes, independently of the microscopic details governing their dynamics. Here we consider a model for photoisomerization inspired by the resource theory of athermality, and we make use of the theory of divisibility classes for quantum channels to prove that memory effects can increase the efficiency of photoisomerization to levels that are not achievable under a purely thermal Markovian (i.e. memoryless) evolution. This provides rigorous evidence that memory effects can provide a resource in biological quantum dynamics, and, more generally, quantum thermodynamics at the nanoscale.

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Exploring the role of quantum tunnelling in DNA mutations using neutron crystallography

Cancer genome sequencing reveals that ⅔ of the mutations in human cancers are due to spontaneous mutagenesis. High fidelity polymerases replicate the DNA at a very high accuracy and do not incorporate base pairs that do not conform to stereochemical complementarity between the polymerase and the base pairs. However, rare tautomeric forms of base pairs, which have been proposed to be formed through quantum tunnelling of protons, can mimic the canonical Watson-Crick forms with cognate pairing. This change can allow these forms to evade DNA repair mechanisms long enough to become incorporated into the new DNA strand, resulting in spontaneous point mutations. Although many theoretical studies have demonstrated the feasibility of the proton transfer reactions, it has been very challenging to experimentally detect the rare tautomeric forms as they are relatively short lived. Also, the positions of protons involved in the hydrogen bonding between the bases are not resolved with X-ray crystallographic approaches. As well as their potential role in mutations that can cause cancer and genetic diseases, tautomeric bases may also be of value in pharmacology for design of oligomeric sequences that can block DNA duplex and RNA biochemistry by enhancing the structural and functional diversity of RNA enzymes. To investigate the presence/likelihood of the rare tautomers in DNA, we propose to utilise the technique of neutron scattering to map the position of protons involved in hydrogen bonding between DNA bases in DNA crystals.

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Single ion free energy calculation in ASIC1: The importance of the HG loop

Acid Sensing Ion Channels (ASICs) are one of the most studied channels of the Epithelial Sodium Channel/Degenerin (ENaC/DEG) superfamily. They are responsible for excitatory responses following acidification of the extracellular medium and are involved in several important physiological roles. The ASIC1 subunit can form a functional homotrimeric channel and its structure is currently the most characterised of the whole ENaC/DEG family. Here we computed the free energy profiles for single ion permeation in two different structures of ASIC1 using both Na+ and Cl- as permeating ions. The first structure is the open structure of the channel from the PDB entry 4NTW, and the second structure is the closed structure with the re-entrant loop which contains the highly conserved 'HG' motif form PDB entry 6VTK. Both structures show cation selective free energy profiles, however the profiles of the permeating Na+ differ significantly between the two structures. Indeed, whereas there is only a small energetically favorable (-0.5 kcal mol-1) location for Na+ in the open channel (4NTW) near the end of the pore, we observed a clear ion binding site (-7.8 kcal mol-1) located in between the 'GAS' belt and the 'HG' loop for the channel containing the re-entrant loop (6VTK). Knowing that the 'GAS' motif was determined as the selectivity filter, our results support previous observations while addressing the importance of the 'HG' motif for the interactions between the pore and the permeating cations.

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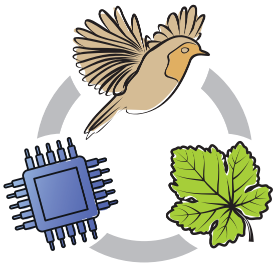
Chiral-Induced Spin Selectivity and Momentum Conservation

Experiments have demonstrated that unpolarized photoelectrons can become highly spin-polarized due to interaction with helical molecules. We present a simple and natural model that exhibits this so-called chiral-induced spin selectivity (CISS) effect and whose underlying mechanism can be understood using intuitive physical concepts: Electron transmission from a straight waveguide to a helix with spin-orbit coupling is found to be spin-selective due to momentum conservation conditions that arise from extended interfaces. We therefore identify interface structure and conservation of momentum as crucial ingredients for chiral-induced spin selectivity, and we confirm that this mechanism is robust against static disorder. Our results demonstrate that an achiral system can show spin-selective effects when coupled to helical systems.



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