Elisabetta Collini
Dipartimento di Scienze Chimiche
Università di Padova
elisabetta.collini@unipd.it

Is quantum-transport really relevant in natural light-harvesting? Does it really represent a mechanism to improve efficiency of sunlight capture? Shall we be able to engineer the Hamiltonian of artificial molecular systems so that quantum mechanics can steer and control the energy migration efficiency and pathway also in man-made devices?

QUANTUM-COHERENT ENERGY TRANSFER: DEFINITIONS, IMPLICATIONS AND EXPERIMENTAL CHARACTERIZATION

One of the most surprising and significant advances in the study of the photosynthetic light-harvesting process is the discovery that the electronic energy transfer might involve long-lived electronic coherences, also at physiologically relevant conditions. This means that the transfer of energy among different chromophores does not follow the expected classical incoherent hopping mechanism, but that quantum-mechanical laws can steer the migration of energy. The implications of such quantum transport regime, although currently under debate, might have a tremendous impact in our way to think about natural and artificial light-harvesting. Central to these discoveries has been the development of new ultrafast spectroscopic techniques, in particular two-dimensional electronic spectroscopy, which is now the primary tool to obtain clear and definitive experimental proof of such effects.

According to standard physics textbooks, quantum mechanics is the theory of the microscopic world. It is a common tool to describe particles, atoms and molecules but it gives way to classical physics on the macroscopic scale of sensible world. Somewhere between molecules and macroscopic world lies a boundary where the strangeness of quantum behaviour ends and the familiarity of classical physics begins. The impression that quantum mechanics is limited to the microworld permeates the general understanding of science. Yet this partitioning of the world is just a convenient way to simplify the description of the different phenomena and it is but a useful approximation of a world that is quantum at all scales. Although quantum effects may be harder to see in the macroworld, the reason has nothing to do with size *per se* but with the way that quantum systems interact with one another. The feature of quantum mechanics that most distinguishes it from classical mechanics is the description of systems as coherent superposition of distinct physical states, as highlighted by the famous Schrödinger cat argument (Fig. 1) [1]. In fact, such superposition states are very fragile in the presence of dissipation, and rapidly collapse to a classical mixture exhibiting no unusual interference features. This is the so called decoherence process. The predictions of quantum mechanics reduce indeed to those of classical mechanics in the macroscopic world, when a system moves to higher energies or–equivalently–larger quantum numbers. Larger objects tend to be more susceptible to decoherence than smaller ones, which justifies why physicists can usually get away with regarding quantum mechanics as a theory of the microworld.
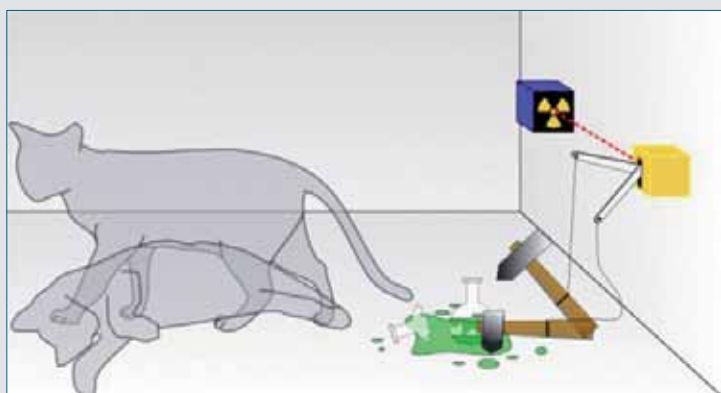
Fig. 1 - Schrödinger's cat experiment. Quantum objects can be in a superposition of two different states or places at the same time until they are observed, at which point they collapse into just one. E. Schrödinger proposed that a cat in a closed, booby-trapped box with a random quantum trigger could be simultaneously dead AND alive. When observed it would just collapse into just one state (dead OR alive)

For this reason very few processes in biological systems require an understanding of quantum theory even though all biochemicals are of quantum origin, in the sense that they are made of atoms bound by quantum-mechanical forces. It is thus legitimate to ask if quantum mechanisms actually play a specific role in the functions of complex biological systems, or if they are unable to maintain a quantum coherent state of sufficient duration to have a significant influence. Going even further, one could also wonder if quantum mechanisms can be suitably engineered in macroscopic artificial systems to steer the performances of man-made devices.

Until the past decade, experimentalists had not confirmed that quantum behaviour persists on a macroscopic scale. Today, however, thanks to recent technological advances, biologists and physicists are starting to demonstrate linkages between various quantum principles like quantum tunnelling, entanglement and coherence in biological processes, illustrating that nature perhaps has exerted some level of quantum control to optimize various processes in living organisms [2]. This possibility is stimulating lot of interest in the chemistry, physics and biology communities because of the tremendous impact that the implications of these mechanisms may have, not only in the way we usually think about natural processes and their evolutionary origin, but also for the future design of advanced artificial devices.

Quantum effects in biology have now been posited in many processes ranging from photosynthetic energy transfer to olfaction, magnetic sensing and even consciousness [3]. The former example is particularly appealing since the possible presence of quantum-coherent mechanisms during the energy migration process in photosynthetic light-harvesting antenna complexes could have significant implications in the efficiency and control of the natural process. Moreover it could suggest new innovative criteria, based on bio-inspiration, for the design of artificial energy-conversion systems.

At the base of each energy-conversion device, whether this 'device' is a biological light-harvesting protein or an artificial photovoltaic complex, there is the migration of the excitation energy from the pigments where the solar light is initially absorbed, to the pigments where the conversion reactions take place. This is a typical example of electronic excitation energy transfer process (EET). The efficiency of the final energy-conversion reaction strongly depends on the efficiency of this preliminary energy transfer step, which in natural systems is almost unitary.

Two relevant examples in which EET process plays a crucial role are illustrated in Fig. 2, namely (a) the energy migration along a polymer chain, which is the process underlying the operation of many fluorescent sensors and organic electronic devices and (b) the natural light-harvesting process, first step of the photosynthetic process, in which the initially captured solar energy is funnelled to the reaction centre through energy transfer among different chromophores.

The mechanism of EET in such systems is, in general, well established and well reproduced by the traditional approach that makes use of Förster resonance energy transfer theory [4]. However, in recent years many subtle aspects of the process, not accounted for in the traditional treatments, were found to be relevant - quantum coherence being one of them. Such subtleties have forced researcher to change the conventional way of thinking about EET and led to the introduction of substantial changes to this basic model [4].

Förster theory states that, when two molecules A and B are separated by a distance large compared to their size, their electronic coupling can be represented approximately as a dipole-dipole interaction between electric dipole transition moments (this confers the typical $1/R^6$ distance dependence). Secondly, the energy transfer efficiency depends on the overlap of the emission (fluorescence) spectrum of the donor and the absorption spectrum of the acceptor. This ensures energy conservation. Förster theory holds when the electronic coupling is weak (weak coupling limit), meaning that it is small compared to the coupling to the environment. In this condition, the system explores the nuclear degrees of freedom more effectively than donor-acceptor coupling and, therefore, EET happens after complete vibrational equilibration at the photoexcited state of the donor. In this way any quantum effect between the donor and acceptor excited states
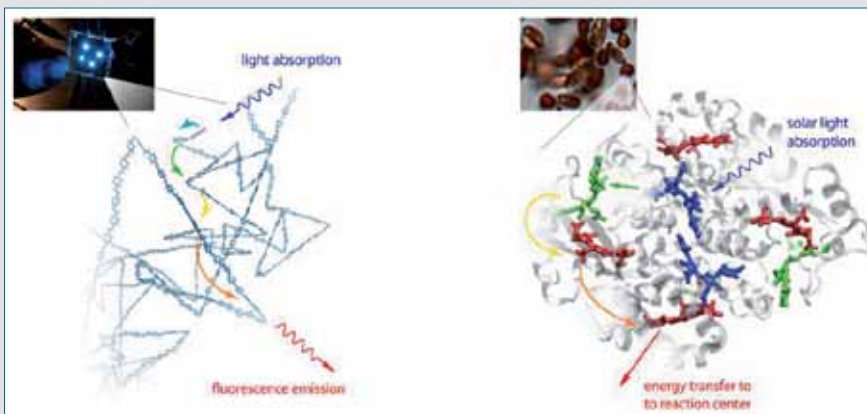

Fig. 2 - Relevant examples of electronic energy transfer (EET); a) energy migration along a polymer chain and (b) biological light-harvesting in an antenna complex of cryptophyte algae
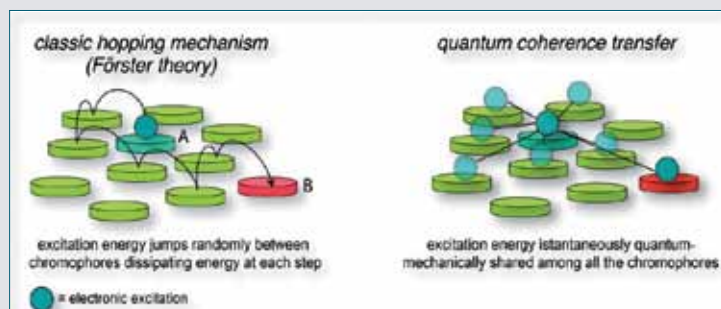
Fig. 3 - Classical and quantum-coherent mechanism of excitation energy transfer (EET). The disks represent the different pigments in a multichromophoric system, like for example an antenna complex. Left panel: classical (Förster) EET; the excitation energy jumps randomly between chromophores dissipating energy at each step. Excitation can be on one chromophore at a time. Right panel: Quantum-coherent EET; the excitation energy is instantaneously quantum-mechanically shared among several chromophores. The system is described as a 'coherent' superposition

is completely quenched by the interaction with the vibrational degrees of freedom. The Förster model yields simple exponential dynamics and provides an excellent qualitative fit of the observed population transfer rates for most systems.

On the other hand, when the electronic coupling becomes stronger compared to the interaction with the environment, the so-called 'strong coupling' limit is reached and EET acquires quantum-coherent character. In the strong coupling limit the donor and acceptor electronic states mix strongly to produce new, delocalized states that are little perturbed by the interaction with the environment. Within these states, known as Frenkel excitons, the energy is shared quantum mechanically among several chromophores. This is the so-called wave-like transfer. The differences in the two mechanisms are pictorially described in Fig. 3.

More puzzling is the intermediate coupling regime, to which all the photosynthetic light-harvesting complexes and the majority of conventional artificial multichromophoric belong, when electronic coupling and the interaction with the environment have the same magnitude and timescale. In this regime individual chromophores collectively absorb and distribute energy; the electronic coupling is large enough so that the excitation can be coherently shared among chromophores. These excitons provide a means of producing 'new' chromophores from the existing molecular building blocks. These new chromophores take over the roles of donors and acceptors for energy transfer, and can have a profound influence on energy transfer rates compared with a similar system where energy flows through localized states; rather than the excitation hopping incoherently from site to site, the system can coherently control the dynamics of energy migration so that the excitation travels in a wavelike manner, through interference of multiple pathways.

The concept of interference of pathways is peculiar of the quantum-mechanical description of the energy migration. Suppose to want to determine the probability for excitation starting at A and ending up at B, A and B being our donor and acceptor, respectively. Let's call ϕ_A and ϕ_B the wavefunctions of the two states and introduce

an operator $\hat{k}$ corresponding to an observable. For example, $\hat{k}$ could be the dipole operator responsible for optical spectroscopic signals. Suppose to have applied to the system a particular experiment sensitive to the observable $\hat{k}$ which gives result k_A when excitation is on A and k_B when excitation is in B. We then have $\langle\phi_A|\hat{k}|\phi_A\rangle=k_A$ and $\langle\phi_B|\hat{k}|\phi_B\rangle=k_B$. According to classical mechanics, the average result of a large number of measurements on the system would be the weighted sum $|c_A|^2k_A+|c_B|^2k_B$, $|c_i|^2$ being the probability of finding the system in i. However, the individual probabilities do not add in this way for a system in a quantum mechanical superposition state. Instead, the expectation value is $\langle c_A\phi_A + c_B\phi_B|\hat{k}|c_A\phi_A + c_B\phi_B\rangle$ where in addition to $|c_A|^2k_A+|c_B|^2k_B$ there is also another term, $c_A{}^*c_B \langle\phi_A|\hat{k}|\phi_B\rangle + c_B{}^*c_A \langle\phi_B|\hat{k}|\phi_A\rangle$, which accounts for the interference between the so called forward (A to B) and backward (B to A) propagation. The important result of the quantum-mechanical nature of this transport process is that each pathway carries a phase that dictates how competing pathways interfere.

To understand this concept, an analogy can be formulated based on the double slit experiment. When a coherent light source such as a laser beam illuminates a thin plate pierced by two parallel slits, the wave nature of light causes the light waves passing through the two slits to interfere, producing bright and dark bands on a screen (see the example in Fig. 4). This interference process is similar to that which forms the eigenstates representing shared excitation states between two molecules. However, if the frequency of the waves emerging from each slit fluctuates randomly and independently, analogously to the way that system-bath interactions cause the transition energies of the two molecules to fluctuate, the interference pattern
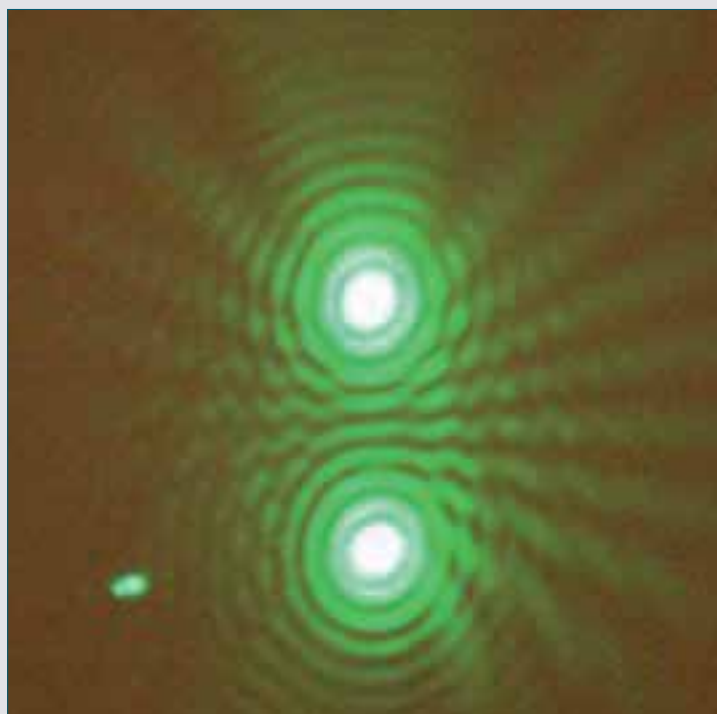

Fig. 4 - Example of interference pattern produced by coherent light

will be less clear and it will completely disappear if the fluctuations are too severe. This is the so called decoherence process: immediately after photoexcitation, the coherence will start dephasing because of small differences within the ensemble: interaction of the system with its surroundings causes random fluctuations, which lead to the loss of memory of the initial electronic transition frequency distribution. The typical time associated with decoherence processes (dephasing time) is particularly critical to determine how relevant is coherence in the dynamics of the overall process: in order to have a significant influence, the quantum coherent state must persist on the same timescale as population terms.

The competition between electronic interaction, which 'builds' superpositions, and decoherence, which destroy them, determines the EET dynamics. In summary, the degree of 'quantumness' of the transport dynamics depends on a delicate balance between electronic properties of the system and its interactions with the environment.

For many years scientists, although intrigued by the idea of quantum-driven processes, thought that the typical dephasing times associated with our "hot, wet and noisy" world, were too fast to make electronic coherences survive enough to be relevant to the process and their presence was treated mostly as some kind of academic curiosity. Until few years ago, when new technological advances in spectroscopy allowed recording direct experimental proof of long-lived quantum coherent dynamics in natural photosynthetic complexes. These evidences rejuvenated the long-standing discussion regarding relationships between energy transfer efficiency and quantum features. In fact, several works have discussed the possibility that quantum coherent dynamics could boost the efficiency of biological light-harvesting systems and effectively funnel the energy transport. Within this framework, it was proposed that coherence could improve robustness against energetic disorder or dynamical perturbations [5, 6], be used as strategy to overcome energy traps [7] or as a mechanism that may speed up the search for the lowest energy level [8]. Even more bewildering is the possibility that the practical functionality of quantum coherent phenomena may be connected with the ability of natural systems to modulate their function under different environmental conditions. This point was recently raised by the observation that the experimentally detected coherences not only are long-lived in time, but they are also long-range in space since they seem to extend over several molecules across the whole antenna complex, including distant and weakly interacting pigments. This has motivated recent studies to investigate EET from the perspective of quantum entanglement [9, 10]. The concept of entanglement was firstly introduced by Erwin Schrödinger and it has no classical analogues. The theory states that, if two quantum systems are entangled, influencing the properties of one system, instantaneously affects also the properties of the other. The concept of entanglement in light-harvesting complexes thus implies the possibility of an extremely sophisticated and fast communication between different parts of the system, capable to guarantee an effective regulation mechanism. Photosynthetic systems use a range of active mechanisms for regulating excitation transport to reaction centres and ensuring the system is photoprotected. To be able to demonstrate that one of these mechanisms is indeed quantum-coherence, will suggest completely new strategies for the improvement of man-made devices for solar energy conversion, for example a solar panel able to rewire itself based on conditions of sun and cloud during the day using feedback and control loops. The engineering principles to achieve that are well known but the requisite design at the molecular level have not yet been developed [11]. Maybe the answer relays on quantum-transport…

Let's consider a typical artificial organic-based photovoltaic device. It is now well known, for example, the crucial role of the exciton diffusion length (especially with respect to donor/acceptor domains sizes), in order to avoid unwanted charge recombination. Classically, the exciton diffusion is described as a random walk of excitation jumps and the efficiency or distance range (diffusion length) of energy transfer depends on the excited state lifetime compared to the average timescale for a jump. Therefore, keeping fixed the average lifetime and the distances between the chromophores, faster EET 'jump' times guarantee higher efficiencies[a]. Coherence effects could in principle bring EET into a regime where energy jumps are as rapid as possible, thus attaining long-range exciton diffusion.

More insights can be gained by comparing a classic random walk to a quantum walk. For classic diffusion it is known that the mean-squared displacement of the walker (the localized electronic excitation) increases linearly with time. Quantum random walks are considerably more complicated. In the limit of ballistic wave-like diffusion of excitons, for example, an exponential speed-up is possible (see for example the analogy with the quantum Grover algorithm proposed by the pioneering work of Fleming [8]). However, this regime does not apply to multichromophoric biologic or artificial complexes, because of their spatial and energetic disorder. In realistic situations (intermediate coupling regime) it is not yet completely clear whether quantum corrections to classical random walk may speed up EET and if and how much they could improve the device efficiency. Certainly they modify the pathway traversed by the excitation. The main difficulty here is that quantum corrections to the EET dynamics are not intuitive. Of course, the debate about the possible implications and role of quantum coherence in natural process is still open and lot of questions must still be addressed.

The possibility to experimentally detect electronic coherence and quantum transport is intimately linked to the ability to excite the system with ultrashort laser pulses. Using the eigenstate description, a short pulse is indeed needed to prepare a superposition in which different eigenstates are excited in phase. When the pulse is not short enough, it excites many systems with different phases and the cohe-
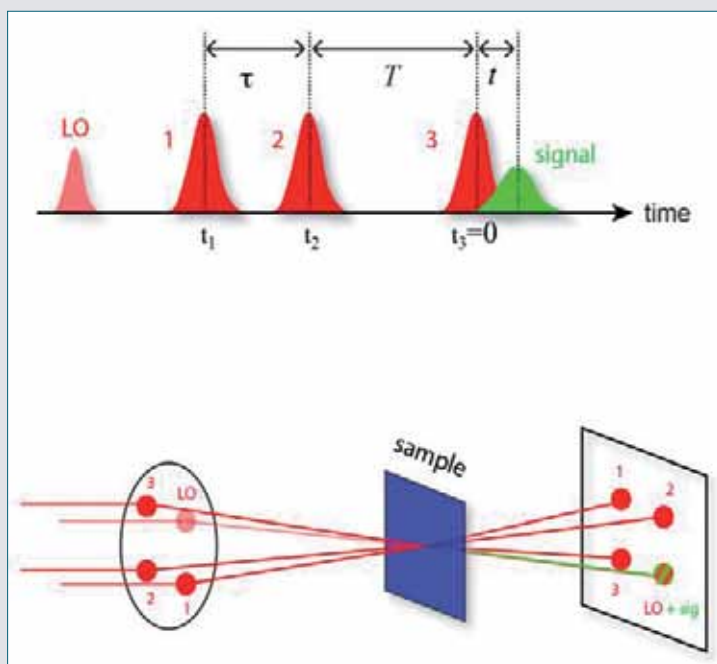
CRITICAL REVIEWS

Fig. 5 - Upper panel: pulse sequence and time delay definition for a two-dimensional photon echo (2DPE) experiment. The time delays between pairs of pulses are conventionally named coherence time (τ), population or waiting time (T) and rephasing time (t), respectively. Lower panel: geometry and phase-matching condition for 2DPE. The three exciting pulses are arranged on three vertices of a square. The signal (green) is emitted along the fourth vertex, where it is mixed with the local oscillator to attain heterodyne detection

rent oscillation disappears upon averaging. In other words, in order to excite a particular superposition and be able to follow its evolution in time, the laser pulse must be sufficiently short compared with the characteristic period of the oscillation. Coherent oscillations may appear in femtosecond spectroscopy as quantum beats when two levels are excited coherently and emit to a common final level: the emission spectrum will oscillate with the two level frequency.

Indeed, the first evidence for electronic coherence came through the measure of oscillations in pump-probe anisotropy signals in the late 1990s [12-14]. However, a turning point in the discussion was possible only with the development of bi-dimensional (2D) electronic spectroscopy (2DES), in particular 2D photon echo (2DPE). Thanks to the time and frequency resolution of this technique it is indeed possible to follow directly the evolution of quantum coherences in light-harvesting complexes and differentiate Förster-type EET from quantum-coherent EET [15]. In 2007, 2D spectra recorded for the Fenna-Matthews-Olsen (FMO) complex isolated from photosynthetic green sulphur bacteria showed a striking quantum beating pattern explained by Engel *et al.* to arise from long-lived coherent superpositions of electronic states [8]. Since then many photosynthetic pigment-protein complexes, despite the differences in physiological functions, have been associated with the presence of long-lived electronic coherences both at cryogenic and physiologically relevant conditions: the reaction centre of purple bacteria [16], the light-harvesting complex II of superior plants (LCHII) [17] and phycobiliproteins of cryptophyte algae [18, 19]. Quantum beats, possibly a signature

of electronic coherence, were also detected in 2D spectra of artificial systems such as bi-tubular J-aggregates of carbocyanine dyes [20] and a conjugated polymer [21, 22].

2DES is a four-wave mixing experiment in which three laser fields interact with the sample to induce a polarization. A sequence of three pulses interacts with the sample and causes the stimulation of third-order coherent response (Fig. 5). To understand how the technique works, a comparison to the more familiar pump-probe technique could be useful. In a typical pump-probe experiment, a short pump pulse from a femtosecond laser impulsively excites a fraction of molecules in an ensemble (e.g. a solution) to an electronic excited state. After some time delay T, a weak probe pulse records the changes in the absorption due to the action of the pump. The transmittance of the probe can be increased ('bleaching' or 'stimulated emission') or decreased ('excited state absorption') in different spectral regions. A typical pump-probe spectrum plots differential transmission as a function of probe frequency ω_t. An accessible way to introduce 2DPE spectroscopy is to think about how the pump-probe spectrum can be expanded into a 2D spectrum [23]. The new frequency axis ω_τ can be thought of as the distribution of frequencies excited by the pump pulse. This frequency-frequency correlation reveals information about mechanism as well as kinetics.

The diagonal part of a 2DPE spectrum contains bands located at $\omega_\tau=\omega_t$ that show the positions of absorption features. The intensity of these bands changes as population decays to the ground electronic state, like the signal in pump-probe spectroscopy. The mechanism of the relaxation processes can be elucidated from the off-diagonal ($\omega_\tau\neq\omega_t$) peaks. For example EET from one absorption band at energy ω_A (putting $\hbar$ =1) to another at lower energy ω_B produces a cross-peak at ($\omega_\tau=\omega_A$; $\omega_t=\omega_B$), revealing the kinetics by which the ω_A state relaxes to the ω_B state. If the energy transfer is downhill in energy, then the cross-peak appears in the lower diagonal part of the 2D spectrum when it is plotted so that ω_τ is the abscissa and ω_t is the ordinate [24-28]. The experiment is somewhat more sophisticated than the pump-probe analogy implies; the photon echo method correlates ω_t to ω_τ and therefore, for instance, the mechanism of line broadening can be resolved [29].

In a photon echo experiment, the exciting pulses arrive at times t_1, t_2, and t_3, defined as in Fig. 5. Delay times are usually specified in the notation $\tau=t_2-t_1$ and $T=t_3-t_2$ and the time zero on the general time axis is specified at $t_3=0$. Thus the signal radiates at times $t>0$.

In a typical 2DPE measurement, for fixed values of T, the echo signal is measured while scanning the coherence time τ, by means of a spectrometer and a CCD (charge-coupled device) camera. Thus, the signal evolution over the echo time t is indirectly measured through its Fourier analogue, ω_t.

The time-domain real-valued photon echo signal is thus measured using spectral interferometry as a function of τ, T, and ω_t.[30]. By heterodyne-detecting the photon echo signal, amplitude and phase information can be recovered, enabling the data to be Fourier tran-
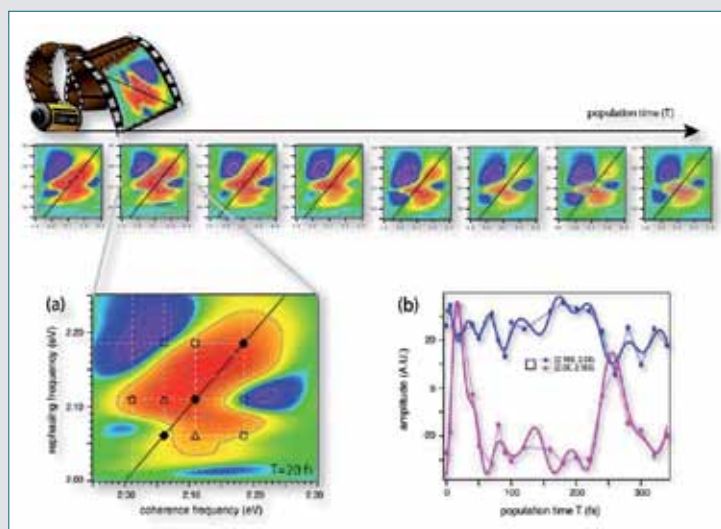
Fig. 6 - 2D photon echo spectra of the antenna complex PC645 recorded at physiological conditions for increasing values of population time *T*. Each map can be thought as a 'snapshot' of the system at time *T*. Putting these maps one after the other, we can obtain a 'movie' to follow in real time the migration of excitation energy between chromophores with time and frequency resolution; a) enlargement of the 2DPE spectrum at *T*=20 fs. The 2DPE spectrum shows the signal intensity on an arcsinh scale (colour scale, arbitrary units) plotted as a function of coherence frequency ω_τ and emission frequency ω_t; b) intensity of the cross-peaks at positions indicated in the 2D map with open squares [(ω_τ, ω_t)=(2.185, 2.06) eV in black and (ω_τ, ω_t)=(2.06, 2.185) eV in red] as a function of time *T*. The dashed lines interpolate the data points (solid circles). The solid line is a fit to a sum of damped sine functions. For further info, see ref. [18, 31]

sformed with respect to τ to give the complex-valued 2DPE spectrum. The final result is a 2D map in which the signal is plotted as a function of the corresponding coherence frequency ω_τ, representing the initial excitation, and the rephasing frequency ω_t, which can be interpreted as the ensuing emission.

One of the advantages of 2DPE in the quest of experimental proofs of quantum coherence is that it can directly reveal electronic couplings and energy transfer pathways by mapping coupled excitonic states onto off-diagonal signals, far from the main diagonal congested region, where the main part of the system dynamics is concentrated. Moreover, the capability of this technique to exploit the phase and coherence information in the time evolution of the optical polarization makes it sensitive to the presence of coherent mechanisms in the energy transfer process, manifested as oscillations of the signal amplitude at diagonal and off-diagonal positions with characteristic frequencies corresponding to energy differences between excitons.

As anticipated before, recent experiments have recorded the presence of coherent oscillations in many structurally and energetically diverse natural light-harvesting complexes, showing that coherence between excitations within a complex is maintained for a surprisingly long time at cryogenic [8, 16, 17] and physiological temperatures [18, 19]. As example, in Fig. 6 the results obtained at room temperature for the light-harvesting protein phycocyanin 645 (PC645) are reported. This protein was isolated from a marine alga, the cryptophyte organism *Chroomonas* CCMP270 [18, 31, 32]. PC645 contains eight light-absorbing bilin molecules covalently bound to a four-subunits protein scaffold [33].

In the 2D spectra of PC645, at least three signals below the diagonal could be clearly distinguished (lower diagonal cross-peaks), as well as three signals at the corresponding positions above the diagonal (upper diagonal cross-peaks). These features correspond to the dynamics of the three chromophores, among the eight bound to the protein, whose exciton states fall in the spectral region 'illuminated' by the laser light used to excite the sample.

Signatures of quantum coherence can be found looking at the amplitude of the signal at cross-peaks positions as a function of *T*. Indeed the plot of the amplitudes of cross-peaks *vs T* (see for example Fig. 6b) showed the presence of periodic oscillations with dominant frequencies corresponding to the energy differences between exciton states of the chromophores.

The relative phases of these beats strongly supported their assignment as due to electronic coherences. Indeed, it can be demonstrated that the coherences giving rise to cross-peaks at symmetric positions with respect to the diagonal are characterized by a phase of oscillation with opposite sign, $e^{-i\phi t}$ and $e^{+i\phi t}$, where ϕ corresponds to the energy gap between the excitons involved in the excited coherent superposition [34].

It must be noticed anyway that the PC645 beating behaviour is complex. This is in general true for any other multichromophoric system, especially at room temperature where line broadening is significant, and overlapping bands partly obscure oscillating features. Moreover, thanks to the improved resolution obtained with more recent apparatus, it was possible to reveal that coherent nuclear motions could induce signals that may be mistaken for electronic coherence [32]. Nuclear coherences have indeed similar energies (and thus beating frequencies) to those of electronic coherences.

In the light of this, many authors are now reviewing 2D data trying to find a final attribution of the recorded beating frequencies in terms of vibrational or electronic coherences. There is now lot of debate about possible experimental protocols capable to unequivocally distinguish between vibrational and electronic coherences [31]. Some author is also questioning the physical meaning of such a distinction, contesting the adiabatic framework, usually invoked in the development of EET models.

In such a framework, originally embraced also by Förster, EET is conventionally considered in an adiabatic framework (the Born-Oppenheimer approximation), where the motions of electrons are separable from those of the nuclei because the electrons are so much lighter and faster. It is now understood that "conical funnels" [35], where electronic potential energy surfaces approach so closely that the adiabatic approximation breaks down, play an important role in photochemistry. For example, it was recently found that femtosecond pulse driven passage through a conical funnel generates coherent vibrational wavepackets on the ground electronic state that exhibit many signatures of coherence between the excited electronic states connected by the funnel [36]. Since the coherences observed in the 2D experiments on antennas seem in many cases to have both electronic and vibrational

properties, it comes natural to suggest the similar non-adiabatic dynamics could also drive EET.

Waiting for future developments, the state-of-the-art protocol currently employed to discriminate electronic coherences from vibrational beats requires the analysis and comparison of the beating behaviour at different positions of the 2D maps in the rephasing and non-rephasing portion of the signal. As commented before, the first step is to look for anti-correlated oscillations at symmetric corresponding upper and lower diagonal cross-peaks. Moreover differently from nuclear coherence, the electronic beat frequencies should be strongly correlated to the location in the 2D spectrum.

On the other hand, vibrational modes are characterized by similar Frank-Condon overlap for various nuclear configurations. Therefore, vibrational coherences should show beating with the same frequencies across the entire 2D spectrum [32]. When possible, the comparison of 2D spectra of native complexes with their partially deuterated analogous is useful [37] as well as to perform measurements at different temperatures [38].

The emerging picture is that the distinction between vibrational and electronic coherence is not so neat as it was initially thought [8, 18, 22]. Moreover, the possible presence of nuclear vibrations in close resonance with excitonic energy gaps contributing to the overall oscillating pattern is now arousing increasing interest. Such modes are indeed believed to be responsible for the activation of the energy transport and for the long-time oscillations experimentally detected. A possible important implication of this close energy match is that vibrational modes can activate resonances that promote directed and effective energy transfer. For example, it was shown that coherent interactions between excitonic states and quasi-resonant fast vibrations could generate long-lived room-temperature excitonic coherences and enhance population transfer [39].

From these preliminary studies it is clear that a better understanding of the interactions between the electronic states and the vibrational modes of the chromophores and of the surrounding medium is required. This represents now the frontier of the field, both theoretically and experimentally. From the experimental side, it is important to develop more direct measurements of the influence of localised vibrations in channelling and/or enhancing excitation energy transfer as well as identify conclusive signatures of the importance of their quantum behaviour in conditions of biological relevance. To this aim many groups around the world are now trying to develop new experimental techniques.

As example, an alternative approach, recently proposed, consists in the use of relatively narrow-band pulses, centred at suitable wavelengths able to excite specific coherence pathways and exclude population pathways from contributing to the signal [40]. Another suggested solution is to implement the use of circularly polarized light in a 2DES scheme with the idea of exploiting the sensitivity of the circularly polarized based techniques, like circular dichroism, to the nuclear distortions accompanying the excitation transport [41].

Moreover, the recently acquired technical capability to merge ultrafast spectroscopy and single-molecule detection, made possible the development of single-molecule techniques particularly promising for the study of coherent dynamics in single complexes, bringing us closer to understanding the physiological significance of quantum coherence in light-harvesting [42-44].

Concluding remarks

Quantum effects in biology have been posited in many processes ranging from photosynthetic energy transfer, described here, to olfaction, magnetic sensing and even consciousness. Although at the atomic level all the biological materials can be considered 'quantum', the extent to which quantum mechanics may really affect the mechanism, dynamics and efficiency of biological processes in physiologically relevant conditions has been seen for many years mostly as a negligible curiosity.

Two main landmarks have started changing this opinion. First, the recent development of quantum information theory, revealing that quantum mechanics could, in some situation, do things better than an equivalent classical theory (for example speeding up a computation process). Thus, in the same way, it has been suggested that, for example, quantum transport of energy could be more efficient than classical transport. Second, the possibility to directly detect signatures of the dynamical evolution of such quantum coherences through recently developed spectroscopic techniques, allowing, in principle, the experimental verification of the role of quantum effects in biological processes.

To date, conclusive evidences of that are still lacking, and the presence, the role and even the experimental method of detection of such quantum effects are under scrutiny and debate. It is not clear at present what opportunities may be presented, but it will fruitful to pursue this idea, for example developing new experiments capable of giving new answers. Many approaches are being followed to this aim, ranging from the employment of narrow-band pulses [40], circularly polarized light [41] and single molecule techniques [44].

In any case, it is important to highlight that even if proven non-relevant in natural processes, the characterization of the role of quantum effects may result anyway valuable if the underlying principle can be applied regardless of whether biology exploits it. The possibility of practically exploit electronic coherence and quantum transport to enhance the performances of artificial devices represents itself an achievement of considerable value, despite that mimics or not the natural process.

Born in 1979, Elisabetta Collini obtained her BSc and PhD degrees in Chemistry at the University of Padova (Italy) where she is presently Research Associate and PI of the ERC Starting Grant QUENTRHEL. Her main research interests are focused on the study and characterization of nonlinear properties and excited state dynamics of multichromophoric systems with particular attention to energy transfer processes. Her research activity was recently awarded with national and international awards ("G. Borgia" prize in Chemistry from the Accademia Nazionale dei Lincei; "Donne Talento ed Innovazione" prize from the M. Bellisario Foundation; "P. Levi" prize in Chemistry from the Italian Chemistry Society; European Young Chemist Award 2012, gold medal).

References

[1] E. Schrödinger, English translation: John D. Trimmer, Proc. of the American Philosophical Society, 124, 323-38 (1980), 1935, **23**, 807.

[2] G.D. Scholes, *J. Phys. Chem. Lett.*, 2010, **1**, 2.

[3] J.T. Trevors, L. Masson, *Curr. Issues Mol. Bio.*, 2011, **13**, 43.

[4] A. Olaya-Castro, G.D. Scholes, *Int. Rev. Phys. Chem.*, 2011, **30**, 49.

[5] M. Mohseni *et al., J. Chem. Phys.*, 2008, 129.

[6] M.B. Plenio, S.F. Huelga, *New J. Phys.*, 2008, 10.

[7] A. Ishizaki, G.R. Fleming, *Proc. Natl. Acad. Sci. USA*, 2009, **106**, 17255.

[8] G.S. Engel *et al., Nature*, 2007, **446**, 782.

[9] F. Fassioli, A. Olaya-Castro, *New J. Phys.*, 2010, **12**, 085006.

[10] G.D. Scholes, *Nature Phys.*, 2010, **6**, 402.

[11] G.D. Scholes *et al., Energy Environ. Sci.*, 2012, **5**, 9374.

[12] M.D. Edington *et al., J. Phys. Chem.*, 1995, **99**, 15699.

[13] S. Savikhin *et al., Chem. Phys.*, 1997, **223**, 303.

[14] D.C. Arnett *et al., J. Phys. Chem. B*, 1999, **103**, 2014.

[15] J.D. Hybl *et al., J. Chem. Phys.*, 2001, **115**, 6606.

[16] H. Lee *et al., Science*, 2007, **316**, 1462.

[17] T.R. Calhoun *et al., J. Phys. Chem. B*, 2009, **113**, 16291.

[18] E. Collini *et al., Nature*, 2010, **463**, 644.

[19] C.Y. Wong *et al., Nature Chem.*, 2012, **4**, 396.

[20] F. Milota *et al., Acc. Chem. Res.*, 2009, **42**, 1364.

[21] E. Collini, G.D. Scholes, *J. Phys. Chem. A*, 2009, **113**, 4223.

[22] E. Collini, G.D. Scholes, *Science*, 2009, **323**, 369.

[23] P. Hamm *et al., J. Phys. Chem. B*, 1998, **102**, 6123.

[24] T. Brixner *et al., Nature*, 2005, **434**, 625.

[25] Y.C. Cheng *et al., Chem. Phys.*, 2007, **341**, 285.

[26] Y.C. Cheng, G.R. Fleming, *Annu. Rev. Phys. Chem.*, 2009, **60**, 241.

[27] M.H. Cho *et al., J. Phys. Chem. B*, 2005, **109**, 10542.

[28] D. Zigmantas *et al., Proc. Natl. Acad. Sci. USA*, 2006, **103**, 12672.

[29] D.M. Jonas, *Annu. Rev. Phys. Chem.*, 2003, **54**, 425.

[30] C. Dorrer *et al., J. Opt. Soc. Am. B*, 2000, **17**, 1795.

[31] D.B. Turner *et al., Phys. Chem. Chem. Phys.*, 2012, **14**, 4857.

[32] D.B. Turner *et al., J. Phys. Chem. Lett.*, 2011, **2**, 1904.

[33] T. Mirkovic *et al., Photochem. Photobiol. Sci.*, 2007, **6**, 964.

[34] S. Mukamel, Principles of Nonlinear Optics and Spectroscopy, Oxford University Press, New York, 1995.

[35] M. Klessinger, J. Michl, Excited States and Photochemistry of Organic Molecules, VCH, New York, 1995.

[36] D.A. Farrow *et al., J. Chem. Phys.*, 2008, **128**, 144510.

[37] J.R. Caram, G.S. Engel, *Faraday Discuss.*, 2011, **153**, 93.

[38] D. Hayes *et al., Faraday Discuss.*, 2011, **150**, 459.

[39] A. Kolli *et al., arXiv:1203.5056 [physics.bio-ph]*, 2012.

[40] G.H. Richards *et al., J. Phys. Chem. Lett.*, 2012, **3**, 272.

[41] E. Collini, www.chimica.unipd.it/quentrhel, 2012.

[42] J.M. Dawlaty *et al., Phil. Trans. R. Soc. A*, 2012, **370**, 3672.

[43] M. Aeschlimann *et al., Science*, 2011, **333**, 1723.

[44] R. Hildner *et al., Phys. Chem. Chem. Phys.*, 2011, **13**, 1888.

CRITICAL REVIEWS

RIASSUNTO

Trasferimento di energia quantistico-coerente: definizione, implicazioni e caratterizzazione sperimentale

Una delle scoperte più sorprendenti e significative nello studio della fotosintesi è la scoperta che il trasferimento di energia elettronica durante il light-harvesting potrebbe coinvolgere la presenza di coerenze elettroniche di lunga durata, anche in condizioni fisiologicamente rilevanti. Ciò significa che il trasferimento di energia tra cromofori non segue le leggi della fisica classica (trasporto incoerente), ma che la migrazione di energia avviene secondo le leggi della meccanica quantistica (trasporto quantistico). Le implicazioni di un possibile regime di trasporto quantistico, anche se attualmente ancora in discussione, potrebbero avere un enorme impatto nel nostro modo di interpretare non solo il processo naturale di light-harvesting, ma anche i suoi possibili sviluppi tecnologici. Di fondamentale importanza per queste scoperte è stato lo sviluppo di nuove tecniche spettroscopiche ultraveloci, in particolare la spettroscopia elettronica bidimensionale, che ora rappresenta il principale strumento di indagine per lo studio di tali effetti.