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Excitation Energy Transfer in Photosynthesis:
The Meaning of Quantum in Biology

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To my wife Anna and my children Kryštof and Klára who constantly remind me what matters the most.

Contents

1. Introduction

In 2007, Nature published an article entitled "Evidence for wavelike energy transfer through quantum coherence in photosynthetic complexes" [1]. The article suggested that the established way of picturing excitation energy transfer in the antennae of some photosynthetic organisms may not hold, and a more refined quantum mechanical picture of this elementary biological process is needed. What could then be called the established picture was the one in which excitations created in a photosynthetic antenna by light proceed in a diffusion like process from state to state in a series of jumps observing certain rate constants. The spectroscopic technique used in the Nature article seemed to reveal that the quantum mechanical state of the antenna is not described only by probabilities of population of its state, but also by their mutual phase relations, the so-called coherences. The state of the antenna, so it seemed, remains coherent (aware of its phase) for much longer than previously appreciated. The paper speculated that the almost unity quantum efficiency of the excitation energy transfer through the system of antennae to the photosynthetic reaction center (the machine converting excitation energy to the chemical energy of separated charges) is due to this long lived coherence.

The author of this habilitation thesis was among the authors of this paper. There was a good reason for satisfaction in seeing the oscillatory signatures in the spectroscopic signal, because the experiment was motivated by a theoretical prediction from another paper he coauthored, Ref. [2]. According to Ref. [2] the Fourier Transformed Two-Dimensional Spectroscopy (FT-2DES), then a very new spectroscopic method in optical region, was able to observe superpositions of electronic states excited in a molecular system by very short laser pulses, and thus measure the lifetime of these superpositions. The experiment [1] was a follow-up on an earlier, proof of the principle experiment on the same system published about two years earlier [3]. The presence of the oscillatory signal roughly fitting the prediction of the Frenkel exciton model (see e.g. [4]) validated the prediction of Ref. [2], although it seemed to suggest that the predicted life-time of the oscillatory signals was significantly exceeded. Some disagreement between the theory and experiment was not very surprising given that the modeling of the photo-induced processes in photosynthetic antennae rested on effective theories parametrized by earlier experiments whose information content seemed to be much smaller than that of the FT-2DES experiment. From a theoretical perspective, the change of the energy transfer description from a diffusion like hopping to a coherent wave-like propagation did not seem to be very radical. Both regimes were contained in the standard density matrix description of excitation energy transfer process, and it was well known that the elements of the density matrix, which describe the coherence of the state, influence the populations of the electronic eigenstates of the system only weakly. None of the speculative proposals of Ref. [1] could be classified as a solid basis for a new research, because the possibilities provided by the standard picture of the energy transfer processes were not at all exhausted. The proposals were offered as speculations whose value had to be thoroughly thought through and validated first.

The questions raised by the paper in the context of the photosynthesis re-

search were not entirely new, nor unexpected. For instance, the only way how coherence could matter for energy transfer was that the usually assumed secular approximation (the decoupling of coherence and population elements of the density matrix) was not valid. The author of this thesis has studied non-secular effects in photosynthetic reaction center already in 2006 [5]. The next logical step of development of the theory at that time was to study the non-secular effects, and to push for a more detailed description of the photosynthetic antennae, including other significant players known to influence ultrafast spectra, the nuclear vibrational modes of the participating molecules [6]. It is important to stress that by 2007, the theoretical tools for describing energy transfer in photosynthesis and the spectroscopic experiments which revealed its details were very well developed, and the quantum theory of these processes was reviewed in at least two well received textbooks [7, 4].

It was therefore a surprise to the theorists of the small photosynthetic community that in about 2008 or 2009, new publications started to appeared, which seemed to build the theory of photosynthetic energy transfer almost from scratch. These publications came with seemingly new concepts, such as "noice or environment assisted energy transfer" (see e.g. the collection of contributions in Ref. [8]), and they often claimed that they come with a radically different description of the energy transfer processes than was usual before. Moreover, a common theme of these publications was that the coherent energy transfer was deemed to represent a typical quantum process, while population hopping process was deemed to be a typical classical process. Quantum features (in the definition above) of photosynthetic energy transfer were portrayed as the main reason for the high efficiency of photosynthesis. The speculative proposals of Ref. [1] were taken as solid facts. The whole topic of quantum effects in biology became a gate for publications in high impart journals. Essentially any experimental observation of oscillatory features in spectra of biologically relevant pigment-protein complex could yield a Nature or Science publication. Theoretical works followed the suit in what could be described as a "quantum hype". Every aspect of the photosynthetic light-harvesting function was recast in a new quantum vocabulary using terms such as quantum coherence, quantum entanglement, quantum speedup etc. ensuring that the continuity of theoretical work in the field was nearly broken.

One can easily demonstrate that the choice of describing something as quantum or classical based solely on whether it is coherent or incoherent is highly questionable. For instance, coherent states of light are the best description of the classical electromagnetic waves quantum mechanics has to offer. Also, statements that the pre-2007 theory of photosynthetic energy transfer was in some sense classical, meaning that it did not rest on quantum mechanics, is in striking contrast to the content of the standard textbooks in the field [7, 4]. Not surprisingly, the 2014 book "Quantum Effects in Biology", Ref. [8], does not contain any significantly new theoretical tools or any new models of photosynthetic systems in comparison to the textbooks from the start of the millennium. It is therefore not surprising that the author of this thesis quickly found himself in opposition to most of the new claims about the nature of photosynthetic energy transfer. Because not all new developments were in all aspects wrong, the author took it as his personal task to absorb all the genuinely new theoretical development in the field into the continuation of the research line set up before the 2007 experiments.

It is the author's firm believe that recent developments confirm that his early judgement of the developments in the field of photosynthesis was right. Around 2012 it was shown that the long lived coherent signatures observed in many photosynthetic systems by FT-2DES are most likely vibrational (not electronic) in nature [9, 10]. Vibrational signatures in FT-2DES are still a hot subject of research to this date, however, in the meantime it was also realized that the main tenets of the theory of photosynthetic energy transfer as understood before 2007 mostly still hold. The high efficiency of photosynthetic energy transfer is not a result of some delicate quantum designs, but rather a consequence of the difference in timescale between excitation loss (in nano-seconds) and the robust thermodynamically rectified (downhill transfer faster than uphill according to canonical detailed balance principle) excitation transfer processes. In fact in order to reproduce the high efficiency of energy transfer in photosynthetic antenna one "only" has to reach the right order of magnitude in the excitation transfer rates. These are fast as a consequence of the close proximity between the pigments, and standard quantum rate theories roughly reproduce their experimental values.

The main text of the thesis has three parts. In Chapter 2 we review the main concepts of the quantum theory of energy transfer in molecular systems with a special attention to photosynthetic antenna in a broader context of physics. This is done with minimum use of equations, with the hope that it can be understood by anybody with the knowledge of the basic concepts of solid states physics (which is far more frequently thought in undergraduate courses than the details of transfer phenomena in molecular systems). Correspondingly, Chapter 2 reads rather as an essay on some aspects of the present state of Quantum Biology and as a statement about what should be its main target in the future.

Chapter 3 on the other hand, deals with a particular problem of the role of system-bath entanglement in the molecular excitation energy transfer. This chapter demonstrates how the program of absorbing valid proposals and ideas from the new quantum biological developments into the pre-2007 research line works. We take the suggestion that quantum entanglement is the signature of quantum effects, we identify where such effects occur, and as a result invalidate the whole idea that coherent effects in photosynthesis constitute non-trivial quantum effects. In turning the leading idea of early quantum biology on its head, we identify the incoherent downhill energy transfer leading to trapping of the excitation in the reaction center to be the only truly quantum effect occurring in the primary excitation energy transfer in photosynthesis.

Twelve selected original papers of the author presented in the Appendix of this thesis demonstrate the main aspects of the author's contribution to the development of the field of Quantum Biology. Chapter 4 describes in brief the content of the selected papers and the context in which they were written.

Quantum Biology is a valid discipline in the border regions of Biology, Chemistry and Physics. In its present form it encompasses several research topics, where quantum effects have been demonstrated or at least proposed as a viable explanation for the experimental facts, such as olfaction, magnetic encompass of birds and photosynthetic primary energy and charge transfer [11]. When defined without prejudice and preconceptions with regards to its content, it is as valid field of research as Quantum Chemistry. For reasons that should perhaps be subject to sociological research, it has a complicated history, often ridded with scientific

inconsistencies. Nevertheless, the basic idea that living matter has something to show us even in the quantum realm is correct. Organisms converting light into energy cannot avoid working on the quantum-classical border. A scientist whose main goal is learning about the inner workings of nature, rather that publishing in high-impact journals at all cost, is offered a full table of interesting problems to feast on even now that the main "quantum hype" is over.

2. Excitation Energy Transfer in Photosynthesis as a Quantum Biological Problem

2.1 We live in a Quantum World

Over the course of the twentieth century, quantum mechanics has fought its way from a subject of highly abstract and rather obscure academic discussions to an accepted cornerstone of our practical understanding of the world. We are witnessing the rise of quantum technologies [12], we are taught that fundamental micro and macro properties of our universe are intimately related to the existence of some elusive quantum particles, and yes, Life is ultimately enabled by quantum mechanics, too. Strangely enough, unlike the classical physics which ruled our understanding of the world for the past few centuries, the most successful physical theory of the present time, quantum mechanics, describes our universe as a place in which we can hardly feel at home. Our familiar predictable world, instead of being a secure starting point of all our investigations, ultimately ends up on the other end of the logical chain - it becomes a derived concept, a world that, in order to exists, has to emerge from the "true" quantum reality behind it [13]. If we accept such emergence, quantum mechanics applies universally to all the phenomena that we observe. Our experience is that as the classical world emerges, much of the quantum mechanical "strangeness" is erased. We perceive ourselves as living in a world with two classical realms, one containing the wave-like (e.g. electromagnetic) phenomena and one containing the familiar mechanics of particles and solid bodies. Here in the classical world we find the duality, while quantum mechanics provides a single unifying concept for all phenomena. What we usually call quantum phenomena are occurrences of particle properties in instances where classical physics uses wavelike description and vice versa. We will argue in this text, that in the recent debate over quantumness in biology, which has been triggered by the paper of Engel at al. in Nature [1] a decade ago, this trivial fact was overlooked. The whole debate has been concentrating on a wrong target – coherent phenomena in energy transfer – and by doing so, it got seriously off the track, set few decades earlier in the quantum theory of natural light-harvesting phenomena.

2.2 Quasi-particles and emergence of the classical from the quantum

A glimpse of the way how quantum mechanics underlies the existence of our classical world can be found in the well-accepted ideas of the solid-state physics. Many fundamental properties of crystalline matter stem from the properties of its elementary excitations, the quasi-particles like phonons, band electrons and holes, polarons etc. (see any elementary textbook on solid-state physics). The nuclei and electrons, which populate the illustrations of elementary textbooks, enter this

picture only in an indirect, highly collective way. Of course, the properties of matter are determined by the individual characteristics of its constituents, but also, and sometimes overwhelmingly so, by the myriads of interactions between them. The individualities of the building blocks of matter are completely dissolved in the collective, only to give rise to a new set of "individualities", the characteristics of which are very unlike those of the original building blocks. Solid-state physicists therefore find it more natural to leave behind the ordinary space, and they prefer to think in terms of any "space" which gives them the best means to tackle their scientific problems. It is the nature of the studied system itself, which determines what are its "stable" states and particles. Despite the beautiful imagery of spatial arrangements of atoms, it is not the ordinary space in which the physics of the problem feels most at home.

According to the modern decoherence theory, the classical world emerges from its undoubtedly much more complex quantum substrate in a manner similar to the emergence of the quasi-particles from the background of nuclei and electrons. What we know as classical states, the attainable results of an experiment, is selected from the possibly more complex quantum state in the course of interaction between the many constituents of the Universe, including the measuring device and the observer. Counter-intuitively, the strangest of the predictions of quantum mechanics, the non-local entanglement between quantum systems, is directly involved in the selection of the classical, so-called pointer states [13, 14]. Because these states effectively break the invariance of quantum mechanics against representation in different basis, they are often referred to as preferred states, or preferred basis of states. They arise wherever a quantum system interacts with a macroscopic quantum environment. Classicality, almost like the thermodynamics, emerges from interactions between large numbers of physical systems.

2.3   Classical aspects of life – molecules

In studying the machinery of life, we find that disordered, wet and hot environment of the cell does not support conditions for the same kind of elementary excitations like in crystals. Nevertheless, in chemistry and biochemistry, we are also used to the fact that the electrons in a molecule loose entirely their individuality and locality. However, the classicalization seems to start already at the level of nuclei and that of the molecular skeleton represented by their arrangements. The molecule and its functional parts and side-groups are fairly stable concepts. Crystallography and nuclear magnetic resonance gave us powerful high-resolution images of molecular arrangements in the nano-machines of life. A lot of chemical and biochemical science can be illustrated and understood by pointing to spatial arrangements of molecules and their time evolution. It seems to be possible to conceptualize much of the life's function with the powerful and compelling atomic pictures of protein machines, which remind us of the machines of our own length-scale, at least in as much as their rendering to the eye of the observer is not a fundamental problem.

2.4 Quantum aspects of life – delocalized excitons

Yet, over the past 30 to 40 years, through a joint progress in time resolved spectroscopy and theory, it became clear that during the very early processes of photosynthesis, a particular type of collective molecular excitations, the so-called Frenkel excitons, are often found to play the decisive role [4, 7, 15]. We find their signatures in optical experiments on many different photosynthetic antennae, the protein embedded arrangements of photosynthetic pigments like (bacterio)chlorophylls, carotenoids and (bacterio)pheophytins [16]. The collective properties of these excitations are fundamental to efficient excitation energy transfer [17], and the Frenkel excitons are precursors to a more involved and detailed picture of the elementary excitations, that of polarons [18, 19].

Similarly to the solid-state situation, spatial picture of the individual building blocks of the photosynthetic antennae (this time the pigments) is not always the one best capturing the physics of the corresponding optical and energy transfer phenomena. This is despite the fact that there is no better way to specify the problem than to define it starting from the crystal structure of the studied system. However, it is the ratio of inter-pigment interaction strengths on one hand, and the strength of interaction between the pigments and the protein environment on the other hand, which determines whether the ordinary space picture is the valid one, or whether the elementary excitations of the system have a delocalized nature, spanning more than one photosynthetic pigment [20]. Unlike in the crystals, the range of regimes found in photosynthetic antennae stretches all the way from excitations localized on individual pigments to excitations delocalized across a significant portion of the antenna. Both extreme regimes can even be found in a single antenna [21]. This is particularly challenging for a concise description of the optical and energy transfer phenomena in photosynthetic antennae, because elementary excitation in them do not yield to a single theoretical picture.

2.5 Spectroscopy of idealized excitons

An idealized isolated photosynthetic antenna, in absence of any interaction with its protein component, would exhibit delocalized eigenstates. The exciton representation provides an extremely simple picture of the system's dynamics, namely that of non-interacting particles. When such a system is addressed by monochromatic light with varying wavelength, the corresponding absorption spectrum exhibits sharp lines at the frequencies corresponding not directly to the transitions on individual molecules, but rather to energies resulting from energy level repulsion due to intermolecular interactions. Not only the transition energies, but also transition dipole moments of the antenna pigments are redistributed in this way. Unfortunately for excitons, they cannot be easily depicted, as their main characteristics to be pictured are the relations between their quantum phases. However, a powerful classical notion exists, which gets it almost right, namely that of normal modes. In a semi-classical picture, electrons bound to the heavy, positively charged nuclei, are moved by the external electric field of light and create an oscillating dipole. A set of linearly coupled dipoles can be decomposed into a set

of non-interacting modes, the so-called normal modes, through a transformation of coordinates not unlike the transformation we have to apply to the Hamiltonian of the corresponding quantum system of two molecules in order to find its eigenstates. This simple model of a coupled system of two-level pigments can be found formally equivalent to the corresponding quantum model, if we limit the number of excitons excited at a time to maximum one [22]. It explains many features of the photosynthetic antennae, including the absorption frequency change and transition dipole moment redistribution. An idealized excitonic system would yield very clean optical spectra. Provided that we consider finite radiative lifetime of its excited states (without which there would be no finite lineshape width) absorption spectrum would by characterized by peaks at the transitions from the ground state to the eigenstates of the system. The much debated coherent Fourier transformed two-dimensional electronic spectra (FT-2DES) would contain diagonal peaks at the same frequencies. Depending on the interaction between the pigments of the idealized antenna, we would see crosspeaks with amplitudes and even signs dependent on the magnitude of inter-pigment coupling and on the lengths and geometric arrangement of the transition dipoles. The rule of thumb is: no coupling – no crosspeaks. Presence of crosspeaks in a system of two-level molecules indicates inter-pigment coupling.

It is important to note that when an idealized antenna is excited by a short laser pulse of the time resolved optical experiments, its state corresponds to a superposition of the eigenstates (superposition of different delocalized excitons). This superposition evolves coherently in time, and no energy is transferred among different exciton states. Populations of the system eigenstates remain constant. The coherent FT-2DES would demonstrate this coherent dynamics by oscillatory modulations of amplitudes and lineshapes of all the peaks, but without any transfer of amplitude between them. Spectroscopy in general, views the dynamics of the spectroscopically studied system from the perspective of its eigenstates. We can also view the same process equivalently from the basis of states localized on the pigments. From this point of view, energy is coherently passed among the sites and an apparent energy transfer occurs in space. However, the dynamics is reversible and periodic, and the total state of the aggregate has constant energy, so that the most important process for which the antenna is designed, the collection of energy in some predefined state, does not occur. In short, a fully coherent antenna would be a bad design. [1]

It will be important for the subsequent discussion, that when this type of coherent dynamics is described by the density matrix formalism, the populations of the system's eigenstates, represented by diagonal elements of the density matrix, are entirely decoupled from the off-diagonal elements, the so-called coherences. These in turn "measure" the coherence of the system's state, but their presence or absence has no bearing on the energy transfer in the system.

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[1]Here, we use the word "state" in two slightly different meanings. One denotes the physical state describing the system at certain time, the other refers to the energy levels of the system. The former state can be composed of or expressed through the latter.

2.6 Excitons in a protein environment – weak environment

Electronic transitions on the photosynthetic pigments are subject to interaction with the ever-fluctuating environment of their protein surroundings. The fluctuations on individual pigments were found largely independent on the fluctuations of their neighboring pigments [23], and the net effect of the environment is thus that of dephasing any possible phase relations between the individual molecules – normal modes are broken by the constant change of phase produced by interaction with the environment. Nevertheless, if the coupling between the molecular transitions is sufficiently strong, so that we can consider the exciton-protein interaction as a weak parameter, the exciton states not only prevail, but the effective result of the environment's action is the dephasing of any initial superposition of exciton states into the so-called mixed state, an incoherent mixture of states in which only a population probability is assigned to each eigenstate (exciton). No time-dependent coherence exists in such a dephased state. After the dephasing time has passed, the system behaves entirely incoherently, and the populations of exciton states change following a rate equation [4, 7, 15]. This is the content of the weak system-bath coupling theories based on a perturbative treatment of the interaction between the electronic transitions on the pigments and its protein surroundings. The energy transfer rates are directly expressed through a resonance condition between the electronic energy gaps separating different excitonic states on one hand, and the available energy gaps of the environment on the other. The latter is characterized via the so-called spectral density of the bath. Energy transfer is enabled by the resonance between the transitions in the system and those in the bath, a fact expressing directly the conservation of energy in whole composed system. Among the results associated with the weak system-bath coupling limit we find e.g. the canonical detailed balance between exciton states, canonical thermal equilibrium state as a final state of the excited state dynamics, consistent dephasing rates due to the energy relaxation between excitons and pure dephasing dynamics describing correctly absorption lineshapes and accounting for electronic coherence lifetime extension due to exciton delocalization [4, 7, 15].

An integral part of the weak system-bath coupling limit is the so-called secular approximation. With zero system-bath coupling, dynamics of population and coherence elements of the density matrix are exactly decoupled. It turns out that system-bath coupling of any strength introduces rate terms, which couple coherence elements of the density matrix to its population elements and vice-versa. However, when populations of the exciton states change only slowly with respect to the oscillations of the coherence elements, the net effect of feeding the coherence elements of the density matrix to its population elements is zero over one oscillation period. This is the case in the weak system-bath coupling regime. In fact, the more regular is the coherence evolution, i.e. the longer the coherence elements live, the smaller is their net effect on the populations. A similar argument can be used for the feeding of population elements to the coherence elements. The neglect of the terms connecting population and coherence elements of the density matrix is term the secular approximation, and the corresponding neglected terms are known as non-secular terms. While there are spectroscopic effects, which can

theoretically arise from non-secular effects in time-dependent spectra of photo-synthetic antennae [24], in the weak system-bath coupling limit, they are not known to significantly change the populations of the system's eigenstates.

2.7 Excitons in a protein environment – strong environment

The most characteristic feature of the weak system-bath coupling limit is that it preserves the eigenstates of the bare or isolated system as the states in which the reduced density matrix diagonalizes due to the bath induced dephasing and decoherence. In general, however, interaction between the electronic transitions and the protein bath causes the final incoherent state of the system to be different from the canonical density matrix diagonal in the eigenstates of the idealized isolated system (see e.g. [25]). In an extreme case, when the system-protein coupling is much larger than the coupling between molecular transitions, the apparent eigenstates of the molecular system can coincide with the states localized on individual molecules. All phase relationships between the individual molecules that could have been in principle established by the coupling between transitions on different molecules, are effectively prevented by the protein bath caused fluctuations. This limiting case of the ratio between system-bath and inter-pigment interactions is well understood by the so-called Förster resonance energy transfer (FRET) theory [15]. The FRET theory is a simple application of the Fermi Golden rule to a situation in which one molecule (the donor) is excited, while the other (the acceptor) is in its ground state. The Fermi Golden rule expresses the law of energy conservation in the process of energy transfer. All ways how to resonantly pass from the donor to acceptor states are summed up, each obtaining a Fermi rule factor characterized by the square of the inter-pigment coupling energy, which is the small parameters of the theory.

2.8 Advanced spectroscopy of molecular excitons

The methods of advanced time resolved non-linear spectroscopy, especially their multi-dimensional variants, provide a very graphic representation of the different limiting cases of inter-pigment and system-bath (pigment-protein) interactions. They enable spectroscopists to follow the photo-induced dynamics of molecular systems. An isolated system without system-bath interaction can already show cross-peaks between different transition (eigen)frequencies in the FT-2DES (see e.g. [8], chap. 4). The crosspeaks therefore report on correlations between different transitions. These correlations are established by inter-pigment coupling. This property of the FT-2DES spectra stems from its unique three pulse excitation scheme. Three pulses with controlled delays t_1 and t_2 are sent to the sample from different directions $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ and the signal is measured in frequency domain as a function of frequency denoted as ω_3 in a background free direction $\mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$. The method allows spectroscopists to resolve spectrally the excitation axis of the 2D spectrum by varying the delay t_1 between first two

pulses of the sequence and Fourier transforming the result into a function dependent on frequency denoted as ω_1. Energy transfer processes are then followed by the dependence of the 2DES spectrum (a 2D plot in frequencies ω_1 and ω_3) on the delay time t_2 between the second and the third pulses of the sequence. The third pulse stimulates the signal, which is then spectrally resolved after it is mixed with a controlled background, the so-called local oscillator pulse. By this so-called heterodyne detection scheme two things are achieved: first, the signal is detected linearly in analogy to transient absorption signal, were the signal stimulated by the probe pulse is mixed with the probe itself in the so-called homodyne detection scheme. Second, a complex signal can be detected whose phase is set by comparison with an actual transient absorption measurement. This enables us to make a reality check on the FT-2DES measurement – a projection (a collapse) of the FT-2DES spectrum on its detection axis must coincide with the normal transient absorption measurement (up to a different sign convention of the two methods) [26]. In transient absorption experiments we see rises and decays of the absorption, stimulated emission and excited state absorption bands. Unless we pump the system in a narrow spectral window, we cannot say from which excitation wavelength the observed changes originate – we only resolved the detection wavelength. Spectrally narrow pulses mean low time resolution. Increasing the spectral bandwidth leads to a better time resolution, but decreases the spectral resolution in the standard transient absorption experiment. The FT-2DES gets the better from both worlds, as the excitation frequency resolved redistribution of bands can be observed. Good analogy for the gain provided by the additional dimension of 2DES is in viewing a distant mountain range rising from a plateau. From a distant view from the plateau, there is no way to see how the different peaks in the mountain range are connected in the direction perpendicular to the range. These connections are only revealed by a look from the top, which is precisely what FT-2DES technique provides.

2.9 Intermediate regime of coupling strength

FT-2DES technique provides a very meaningful and rich source of information even in the cases, which are not as clear-cut as the ones discussed above. In between the two extreme cases: the perfectly delocalized excitons in weak system-bath coupling limit and the completely localized excitons in the strong system-bath coupling limit, lies the intermediate coupling region in which the delocalization is somewhat, but not completely, diminished from what it would theoretically be in an isolated system. The intermediate coupling regime is the theoretical and experimental area where the most progress has been achieved in over past ten years or so. Theoretical methods became widely available, which allowed numerically exact treatment of theoretical models of intermediate interaction regime [27, 28, 29, 30, 31, 32]. Approximate methods based on polaron transformation also gave additional insight into the formation of apparent eigenstates, different from the bare Frenkel exciton prescription and of the excited state quasi-equilibrium which is responsible e.g. for fluorescence signal. The quasi-particle picture, or the apparent eigenstate picture is powerful enough to give interpretation to the FT-2DES measurements even in the intermediate coupling regime. While we do not observe those excitons which would result from the analysis of

the inter-pigment interactions only, we nevertheless see some effective excitons resulting from an effective inter-pigment coupling, perhaps diminished by the action of the bath induced fluctuations.

Plenty of yet unanswered questions arise about the interplay of different time scales involved in the light harvesting processes. The protein evolves on all time scales from the ultrafast homogeneous optical dephasing on the order of tens of femtoseconds, to slow rearrangements occurring in seconds and minutes. On the short timescale end of the spectrum, we can find the bath reorganization effects in response to excitation including those of formation of polarons. This formation can occur as quickly as the dephasing which selects the preferred basis, so that the system decoheres directly into its preferred basis. Or, the formation of the polarons may occur after the decoherence occurs. In the latter case the initial, decoherence-selected preferred states continue evolving to a yet different final set of preferred states. How to observe and disentangle these processes from the currently available experimental methods is not entirely clear, and this direction represents one of the most interesting research directions for the immediate future.

What is clearer, however, is how the very slow motion of the protein expresses itself in the FT-2DES spectra. The changes occurring on the timescale of seconds can be considered static on the timescale of this experiment, and they are perceived as a static inhomogeneity of the system. Unlike in some more standard spectroscopic experiments, in FT-2DES there is a way how to tell the static inhomogeneity apart from the fast, homogeneous dynamics (see e.g. [8] Chap. 4). FT-2DES thus goes at least one step beyond the limitations of all bulk spectroscopies, namely that the experiment is ultimately looking not at one system, but an ensemble of possibly differing system.

The amount of detail and level of time and frequency resolutions which are now available (at least in theory) through the experimental progress over the past decade or so is such, that it allows us to ask detailed questions about the nature of the processes that we observe in biological system. Photosynthesis, as a naturally light induced process, leads the way in science's effort to unravel the microscopic basis of biological systems near the quantum-classical boundary.

2.10   Coherently quantum photosynthesis

Unfortunately, after significant attention has been draw towards coherent phenomena by the 2007 Nature paper of Engel et al. [1], large part of the research community became preoccupied with the discussion of spatial domain energy transfer, and with studying and finding new examples of the time dependent coherent phenomena [33]. Time dependent coherence, observed in the advanced multi-dimensional experiments, corresponds to the beating between the apparent eigenstates of the system. As discussed above, the beating phenomena are in the first approximation entirely decoupled from the dynamics of the eigenstate populations. Moreover, the concept of preferred states in photosynthetic systems, represented, at least approximatively, by Frenkel excitons, was largely ignored in the first years after the 2007 landmark paper. Studying quantum aspects of photosynthesis became synonymous with studying coherent effects in photosynthesis, and photosynthetic systems were viewed as quantum computers. As a consequence, the mental picture of a photosynthetic system was increasingly more

akin to a set of weakly interacting, individually addressable qbits, rather than to a strongly interacting set of sites, whose individualities are to certain extent lost due to the mutual interaction. This research direction achieved such a dominance that popular accounts of photosynthesis disseminate this distorted, and factually wrong, picture of photosynthetic systems among the public [34]. In the new popular accounts, not only the all-important concept of exciton is lost, but also the much more graphical, appealing and simple concept of photosynthetic antenna. All this gives way to quantum strangeness and entanglement, which now seems to be solely responsible for the phase relations between excitations on different pigments [34, 11].

The relevance of coherence in the photosynthetic light-harvesting is debated to this date. The debate is largely complicated by the fact that several phenomena claim the name of coherence. The spectroscopic features, dependence on the studied system parameters, and dependence on the strength of system-bath interaction of these phenomena are very different. What is observed in FT-2DES as oscillatory component of the waiting time t_2 dependence of the spectra stems from the fact that the superposition of the system eigenstates states, initially created by laser pulse, evolves in time, and the coefficients of the superposition change phase with the frequency corresponding to the transition energy between the eigenstates states. The state which is coherent, in this meaning of the word, is profoundly time dependent, and it is not possible to transform this time dependence away by any transformation, although, when represented in the system eigenstates the resulting populations are constant. On the other hand, the fact that some of the system eigenstates are undoubtedly superpositions of the states localized on different molecules is also referred to as quantum coherence in the literature. This type of coherence is related to the notion of eigenstate delocalization. It is important to note that during the time evolution of the system, the coefficients of this superposition do not evolve in time. The notion of coherence presented in this case is a profoundly time-independent one. For historical reasons, and for reasons of their formal similarity (in both cases we deal with a superposition of states), it is difficult to argue that one of these phenomena should not be called coherence. Nevertheless, as with many other homonyms (or rather polysemes) a proper distinction between various usages is possible and easily achievable e.g. by addition of an adjective.

Unfortunately, this is very rarely done in the literature, and often the difference between the two phenomena is completely ignored. Yet, the time dependent quantum coherence is prone to fast dephasing due to interaction of the electronic degrees of freedom with the protein vibrational bath. This type of coherence, once lost (e.g. due to energy transfer process), cannot be reestablished by any standard internal interaction process occurring in the photosynthetic antenna. In contrast, the fact that eigenstates are superpositions of local states is constantly re-established by the presence of resonance interactions between the local states. As described above, it depends on the relative strength of the inter-pigment interaction with respect to the system-bath interaction, to which extent the delocalization, i.e. the superposition of local states, will be established in the system. Delocalization can often be regarded as a time-independent feature of the photosynthetic system. The extent to which states are delocalized does not change over the course of the ultrafast spectroscopic experiment. Initial time

dependent superposition of electronic states created by the laser decays on an ultrafast time-scale to a mixed state composed of delocalized eigenstates. With few exceptions, most of the significant spatial domain energy transfer processes occur on time scales which far exceed the dephasing time of electronic coherence, with the last step between the photosynthetic antennae and the reaction center exceeding tens of picoseconds [16]. Relevant transfer times are, at least, two order of magnitudes slower that the dephasing electronic coherence. If we consider also our previous discussion of secular approximation, it is hard to imagine that the time-dependent coherence plays any role in the energy transfer processes in photosynthetic system beyond the marginal.

2.11 Role of Ultrafast Spectroscopy in Unravelling Sunlight induced Processes

We have mentioned above that the superposition of electronic states observed in FT-2DES is initially created by ultrafast laser pulses. One can obviously ask, how are then the conclusions of these experiments relevant in describing workings of natural photosynthetic systems illuminated by Sun light? The answer can be provided in a surprisingly general way.

The non-linear optical experiments of the class comprising also the FT-2DES are based on the fact that light interacts relatively weakly with the objects such as molecules. The energy absorbed by photosynthetic systems in nature depends linearly on the Sun light intensity (i.e. quadratically on field amplitude). The non-linear signals in 2DES depend on the third power of the field, with excited state populations depending on the second power of the light field amplitude. The light intensity conditions in the two situations are therefore not so dissimilar as one would superficially assume. More importantly, in this regime of perturbation of the matter by light, the changes of the ground state population due to interaction with light can be ignored, and the light contribution to the excited state dynamics can be described by a second order source term [35, 36]. The state of the system driven into excited state by such a source term can be expressed as a convolution of the actual time-dependent profile of the exciting light, and the response of the system to an ultrafast (Dirac delta function) excitation [36]. This in fact puts ultrafast spectroscopy at the position of utmost importance for all the investigation of time induced phenomena. With the information obtained from ultrafast spectroscopy, it is possible to reconstruct dynamics under any (weak, in the above described sense) illumination by light. Nevertheless, the dynamics which occurs in the ultrafast experiments is not the same as the one occurring under other illumination conditions. Observing coherent dynamics in an ultrafast spectroscopic experiment therefore does not mean that the same dynamics occurs under the illumination by Sun. Moreover, based on the fact that natural light harvesting works in the weak light-matter interaction limit, very general arguments can be put forward, which show the time dependent coherent features of the photo-induced dynamics to be irrelevant for the ultimate population of the energy trapping states [37], i.e. of no consequence for the light-harvesting efficiency.

2.12   Intramolecular Vibrations

The idea that transient electronic coherence is an important factor in achieving high efficiency of photosynthetic energy transfer was initially motivated by experiment [1]. However, the lack of success in explaining the observed lifetimes by modeling eventually led to doubts about validity of the original assignment of the observed features to electronic degrees of freedom, and to reexamination of the role of nuclear (vibrational) degrees of freedom in the relevant spectroscopic signals [6]. The signatures of superpositions of vibrational and electronic states in FT-2DES are to some extent similar, and their distinguishing requires detailed analysis [38]. The most appealing characteristics of the oscillatory signals induced by nuclear degrees of freedom in FT-2DES is their long life time, which stretches over picoseconds. The only problem seemed to be the relatively low amplitude of these signals, if they were to stem from the known intramolecular modes of pigment molecules occurring in photosynthetic antennae (chlorophylls and bacteriochlorophylls). This problem found two interesting theoretical solutions, both based on the fact that intramolecular vibrational modes are coupled to electronic transitions. Upon resonance between highly allowed purely electronic transitions and the transitions involving e.g. a single vibrational quantum, the latter (usually only weakly allowed transitions) gain oscillator strength, and they may become enhanced. In Ref. [9] we proposed that transitions between eigenstates of a molecular system involving both electronic and vibrational degrees of freedom may exhibit the right life time observed in the experiment of Ref. [1]. A related mechanism by which the weakly coupled intramolecular vibrational modes can contribute with enhanced signal to the FT-2DES signals was proposed in Ref. [10]. In the mechanism of Ref. [9] the relevant signal is produced in form of a stimulated emission and excited state absorption from the electronically excited state, Ref. [10] proposes that the signal originates from the ground state (as the so-called ground state bleach). The two mechanisms are in fact both enabled by the same resonance effect between the purely electronic energy gaps of the participating molecules and the energy gaps involving vibrational quanta [39].

The full extent by which intramolecular vibrational modes influence photosynthetic light harvesting, from excitation energy transfer to charge separation process, is a subject of intensive research. It became clear that in some cases, high frequency, relatively strongly coupled vibrational modes significantly increase energy transfer rates in cases where this transfer competes with fast excitation quenching [40]. The proposals that weakly coupled modes are involved in making the charge separation in the bacterial reaction centers more efficient [41] find perhaps less support in theoretical work, but for the time being have to be considered a viable possibility.

The theoretical investigation of the natural light-harvesting has progressed tremendously in past ten years. The question about the nature of the long lived oscillatory spectroscopic signals, which has been driving the photosynthetic subfield of Quantum Biology for almost a decade, has most likely found its resolution in the synergetic effects of the electronic and vibrational dynamics.

3. Quantum Thermodynamics and System-Bath Entanglement

In Chapter 2 we mentioned that molecular excitonic systems can be mapped on a system of classical oscillators, and their dynamics is therefore fully equivalent to that of a set of classical harmonic oscillators. It can be shown that the classical model of molecular excitons can be also equipped with a physically appealing model of the classical protein bath [42]. Interestingly, equations of motion for this model, derived by perturbation theory with respect to the system-bath coupling and averaged over the degrees of freedom of the protein, are exactly the same as those we know for a fully quantum description of a molecular excitonic system. The only difference is that classical bath correlation function cannot take complex values, and the corresponding bath spectral density (essentially the Fourier transform of the bath correlation function) is symmetric in frequency (if spectral density is denoted $J(\omega)$, then $J(\omega) = J(-\omega)$ for the classical case, but the equality does not hold for the quantum case). This leads directly to the same probabilities of energetically up-hill and down-hill transitions and ultimately to an equilibrium characterized by equal populations of all energy levels regardless of temperature. The main conclusion of Ref. [42] is that the actual exclusively quantum effect in photosynthetic energy transfer is therefore the downhill energy transfer. It is not among coherent, but rather among the incoherent effects, where quantum mechanics plays a decisive role.

In this Chapter we will discuss the question of quantumness/classicality of the excited state dynamics of a photosynthetic antenna from yet another angle. Similar to Refs. [43] and [44] we will start from the quantum mechanical model of the photosynthetic antenna, but we will include also a complete standard model of the protein environment (formally). In Refs. [43] and [44] it was shown that the bare exciton model exhibits dynamics which can be mapped on a classical model, i.e. that its dynamics is classical. In Ref. [42] it was in addition shown that when the protein bath is included in form of a parameter into the Hamiltonian (this is how classical degrees of freedom, such as classical electric field of the laser etc., enter the Hamiltonian), the resulting dynamics exhibits classical behavior, for instance in that that it corresponds to the high temperature limit of the quantum model. Below, we will show that the same classical behavior results from a formulation of the problem which is fully quantum except for the entanglement between the system (electronic degrees of freedom) and the bath (protein degrees of freedom and intramolecular vibrations) which we explicitly forbid.

3.1   Entanglement in Molecular Systems

The existence of quantum entanglement is the most profound deviation from classical picture of the physical world which quantum mechanics has to offer. While the wave-like nature of particles and the particle-like features of waves list among the most important twentieth century insights into the nature of our Universe, none of it questions the consistence of our world view so deeply as the quantum entanglement. After all, light has been believed to be composed of particles

before. Quantum entanglement contradicts our experience much more radically than the duality of particles and waves, as it seems to return the action at a distance into the scientific discourse. Despite the controversy around its existence and experimental confirmation, quantum entanglement was recognized as the feature of quantum mechanics, which actually enables the emergence of our familiar classical world from the more general quantum background through the process of decoherence [14, 13]. The difficulties of experimentation with quantum entanglement might suggest that the effect is hard to come by and that entanglement between two object is somehow inherently fragile. However, quantum mechanics suggests the opposite: Once two systems are put into interaction, it is hard to see why their common state would tend to evolve into a form in which it could be factorized into states of the individual systems. Quantum mechanics rather supports the view that quantum entanglement happens spontaneously whenever quantum systems interact. The difficulty of keeping two quantum systems entangled in laboratory is the difficulty with preventing uncontrolled entanglement with other objects, i.e. the difficulty of keeping the entanglement exclusive. It should therefore not be surprising that on a closer inspection, some rather basic physical phenomena can be shown to be direct consequences of quantum entanglement, without them being usually presented as such.

One process in which entanglement plays a major role and in which it goes essentially unnoticed is the ordinary linear absorption of light. Absorption lineshape is partially due to the effect of finite excited state lifetime (lifetime broadening leading to the so-called natural linewidth), partially due to disorder in ensembles of absorbing molecules or atoms (so-called inhomogeneous broadening causing the ensemble to exhibit a distribution of energy gaps) and partially due to rapid energy gap fluctuations (so-called homogeneous broadening). The last of the three origins of the lineshape is a consequence of processes other than those responsible for the decay of the excited state population, and it can be described by a model involving pure dephasing type of coupling only. Absorption lineshape can be calculated from a response of the molecular system to an excitation by an infinitely short light pulse [45]. The linear response of a two-level molecule can be calculate in density matrix formalism (see e.g. Ref. [45]) with the assumption that the bath degrees of freedom are initially in thermal equilibrium. This standard, so-called spin-boson, model can be solved exactly in the pure dephasing coupling case [46]. It seems at first sight that the thermal equilibrium of the bath precludes the usage of state vector (wave-fucntion) formalism. However, in the case of room temperature (low with respect to energy gap, i.e. $k_B T < \epsilon_e - \epsilon_g$ for optical energy gap of the molecule) the initial state of the molecule is factorizable into the system and bath parts (both in density matrix and wavefunction fosmalisms). Assuming the so-called Condon approximation, in which the transition dipole moment of the molecular system is independent of the environmental coordinates, the linear response function can be calculated from the system evolution from the initial condition

$$|\psi(t_0)\rangle = (c_e|e\rangle + c_g|g\rangle)\,|\Xi_B^{(\mathrm{eq})}(t_0)\rangle, \qquad (3.1)$$

where t_0 is the start of the time evolution, and the state vector $|\Xi_B^{(\mathrm{eq})}\rangle$ describes the bath in equilibrium. We have to first answer the question whether the bath in equilibrium can be described by a state vector at all. To this end we will use the technique developed in Ref. [35].

3.2 State Vector Description of a Thermodynamic Bath

We assume that initially a molecular system S is embedded in a large bath B, which is in a weak contact with some other large macroscopic system (reservoir) denoted as R. We assume that the system $B + S$ is put into a state of canonical equilibrium at temperature T by the contact with R. As long as the system $S+B+R$ is closed, it can be described by a state vector. The temperature and the level structure of the system S are such that populations of all states of S except of the ground-state are negligible in equilibrium. We assume that the system $S + B + R$ is described by a single state vector $|\Xi(t)\rangle$, in which the ground-state $|s_0\rangle$ of the state S is approximately factorized from the rest of the state vector, i.e. $|\Xi(t)\rangle \approx |\Xi_{R+B}(t)\rangle|s_0\rangle$, due to the sufficiently low temperature. Now we remove the system R from the contact with B, and the system $S + B$ will, from now on, be insulated from the rest of the universe. Nevertheless, B is still a macroscopic bath surrounding the system S. The state of the system B should correspond to the canonical equilibrium described by the standard canonical statistical operator. Using the state $|\Xi_{B+R}(t)\rangle$, which is a non-factorizable state vector of the two, now non-interacting, systems B and R, we can easily express the expected canonical statistical operator. First, we decompose $|\Xi_{B+R}(t)\rangle$ into eigenstates $|B_n\rangle$ of the Hamiltonian H_B $(H_B|B_n\rangle = \epsilon_n|B_n\rangle)$ of the bath as

$$|\Xi_{B+R}(t)\rangle = \sum_n |c_n|e^{-i\epsilon_n t}|B_n\rangle|R_n(t)\rangle, \tag{3.2}$$

where

$$|R_n(t)\rangle = \frac{1}{c_n}\langle B_n|\Xi_{B+R}(t)\rangle, \tag{3.3}$$

and $c_n = |\langle B_n|\Xi_{B+R}(t)\rangle|$. As the systems B and R are non-interacting, the absolute values of the coefficients c_n do not change. The statistical operator of the system $B + R$ reads as

$$W_{B+R}(t) = |\Xi_{B+R}(t)\rangle\langle\Xi_{B+R}(t)|, \tag{3.4}$$

from which we obtain the statistical operator of the system B by tracing over the degrees of freedom (DOF) of the system R

$$W_B(t) = \mathrm{tr}_R \left\{|\Xi_{B+R}(t)\rangle\langle\Xi_{B+R}(t)|\right\}$$

$$= \sum_{nm} c_n c_m^* |B_n\rangle\langle B_m|\langle R_m(t)|R_n(t)\rangle. \tag{3.5}$$

The stationarity of the bath state is achieved when the states $|R_n(t)\rangle$ are all mutually orthogonal to each other so that

$$\langle R_n(t)|R_m(t)\rangle = \delta_{nm}, \tag{3.6}$$

and the stationary reduced state vector $W_B(t)$ reads as

$$W_B(t) = \sum_n |c_n|^2 |B_n\rangle\langle B_n|. \tag{3.7}$$

Mutual deviation of the states $|R_n(t)\rangle$ related to different states $|B_n\rangle$ of the subsystem to an extent that $\langle R_n(t)|R_m(t)\rangle \to 0$ for $n \neq m$ is one of the basic tenets of the decoherence theory, and it can be demonstrated on many examples [13, 47].

In addition, canonical equilibrium requires the relation

$$|c_n|^2 = \frac{e^{-\frac{\epsilon_n}{k_B T}}}{\sum_n e^{-\frac{\epsilon_n}{k_B T}}}. \tag{3.8}$$

As a consequence, the state $|\Xi_{B+R}(t)\rangle$, expressed e.g. in form of Eq. (3.2), can describe the bath B in equilibrium.

3.3 Evolution of a Subsystem Interacting with Non-Entangling Bath

When we now excite the system S into an excited state, and this state is coupled to other states via some system-bath coupling terms (like in the case of Frenkel excitons), the bath will evolve out of strict equilibrium following the Scrödinger equation

$$\frac{\partial}{\partial t}|\Xi(t)\rangle = -\frac{i}{\hbar}\left(H_S + H_B + H_R + H_{S-B}\right)|\Xi(t)\rangle. \tag{3.9}$$

We assume no direct interaction between R and S, and at the time the system S is excited, we also assume no interaction between B and R. The initial condition for Eq. (3.9) is

$$|\Xi(t = t_0)\rangle = |\psi_s(t = t_0)\rangle|\Xi_{B+R}(t = t_0)\rangle, \tag{3.10}$$

where $|\psi_s(t = 0)\rangle = \sum_k a_k|s_k\rangle$ is the initial state of the system S produced by ultrashort excitation (we need the response of the system to ultrafast pulse as discussed in Chapter 2, sec. 2.11). In general, the state $|\Xi(t)\rangle$ for $t > t_0$ will not be factorizable into the system and bath components. However, we could speculate about what happens if the interaction between the system and the bath were such that the two components not entangle.

Non-entangling interactions in quantum mechanics are also possible, and they are characteristic for systems that behave similar to classical systems. To name an example, we can consider a single molecular system in an interaction of with coherent laser light with high number of photons. The state of the light corresponding to the molecule left in the ground state and the molecule excited into its excited state by such a light state can be made arbitrarily small (by increasing the intensity of light). In discussing absorption, we demonstrated that the protein bath likely entangles with the exciton system. We can see that depending on a situation, the same system - a set of harmonic oscillators, bosons, representing either protein bath or light - can interact in both entangling and non-entangling fashion. We can now answer the question, what would happen, if the protein did not entangle with the electronic degrees of freedom of the photosynthetic antenna.

If the factorization similar to Eq. (3.10) remained valid for the rest of the evolution of the state $|\Xi(t)\rangle$, we could easily write the equation of motion for the

system S alone by multiplying Eq. (3.9) from the left by the state $\langle \Xi_{B+R}(t)|$. In order to simplify the discussion, we first rewrite Eq. (3.9) into interaction picture with respect to H_B and H_R, so that it reads as

$$\frac{\partial}{\partial t}|\Xi^{(I)}(t)\rangle = -\frac{i}{\hbar}\left(H_S + U_B^\dagger(t)H_{S-B}U_B(t)\right)|\Xi^{(I)}(t)\rangle. \tag{3.11}$$

This equation needs to be multiplied by $\langle\Xi_{B+R}^{(I)}(t)| = \langle\Xi_{B+R}(t)|U_B(t)U_R(t)$ to turn it into equation of motion for the vector $|\psi_s(t)\rangle$ alone. We obtain

$$\frac{\partial}{\partial t}|\psi_s(t)\rangle + \langle\Xi_{B+R}^{(I)}(t)|\frac{\partial}{\partial t}|\Xi_{B+R}^{(I)}(t)\rangle|\psi_s(t)\rangle =$$

$$= -\frac{i}{\hbar}\left(H_S + \langle\Xi_{B+R}(t)|H_{S-B}|\Xi_{B+R}(t)\rangle\right)|\psi_s(t)\rangle. \tag{3.12}$$

In the Eq. (3.12), the expectation value of the system–bath coupling operator does not contain interaction picture anymore. Because the state $|\Xi_{B+R}^{(I)}(t)\rangle$ is normalized, the second term on the left-hand-side of Eq. (3.12) is purely imaginary

$$\langle\Xi_{B+R}^{(I)}(t)|\frac{\partial}{\partial t}|\Xi_{B+R}^{(I)}(t)\rangle = i\kappa(t), \tag{3.13}$$

and it only adds a global phase to the state vector. We could remove it by switching into an interaction picture $|\tilde{\psi}_s(t)\rangle = e^{i\int_{t_0}^t d\tau\kappa(\tau)}|\psi_s(t)\rangle$, but we will simply remove it by hand here, because all physics remains the same. We will also denote $H_{B+R}(t) = \langle\Xi_{B+R}(t)|H_{S-B}|\Xi_{B+R}(t)\rangle$. The equation of motion for the system S alone reads now

$$\frac{\partial}{\partial t}|\psi_s(t)\rangle = -\frac{i}{\hbar}\left(H_S + H_{S-B}(t)\right)|\psi_s(t)\rangle. \tag{3.14}$$

This is an ordinary Schrödinger equation in which the interaction with the bath appears only parametrically, exactly as classical contributions normally do. We can see that from the perspective of equations of motion, the classicality of the external influence is characterized by the lack of entanglement between the system and the external degrees of freedom.

3.4 Dynamics of Frenkel Excitons

We will now assume that the system S represents a Frenkel exciton system

$$H_S = \sum_k \varepsilon_k |k\rangle\langle k| + \sum_{kl} J_{kl}|k\rangle\langle l|. \tag{3.15}$$

Here, the states $|k\rangle$ represent collective singly excited states of an aggregate of two-level molecules

$$|k\rangle = |e_k\rangle\prod_{l\neq k}|g_l\rangle, \tag{3.16}$$

with $|e_k\rangle$ the excited state of the kth molecule and $|g_k\rangle$ the ground state of the kth molecule. We set the ground state energies to zero, and ε_k thus represents the transition energy of the kth molecule of the aggregate. The Hamiltonian, Eq.

(3.15), represents the standard model of the electronic part of the photosynthetic antenna [4].

The Frenkel exciton system will be coupled through pure dephasing interaction to the bath B of a macroscopic number of harmonic oscillators. The usual form of the bath Hamiltonian is

$$H_B = \sum_k H_{B_k} = \sum_{k\xi_k} \frac{\hbar\omega_{\xi_k}}{2} \left(\hat{p}_{\xi_k}^2 + \hat{q}_{\xi_k}^2 \right), \tag{3.17}$$

and the system–bath interaction operator read as

$$H_{S-B} = -\hbar \sum_{k\xi_k} \omega_{\xi_k} d_{\xi_k} \hat{q}_{\xi_k} |k\rangle\langle k|. \tag{3.18}$$

Here, the bath B is composed of components B_k associated with individual molecules of the aggregate, $\hat{q}_{\xi_k}$ is the coordinate operator of the oscillator ξ_k on the kth molecule, ω_{ξ_k} is its frequency and d_{ξ_k} represents a shift the potential energy surface of the given vibrational mode when the kth molecule is in the excited state $|e_k\rangle$. The system-bath interaction on each molecule is in general different as the potential shifts d_{ξ_k} of the ξth oscillator coupled to the kth molecule can be different. The so-called reorganization energy of the bath is already absorbed into the excitonic energy ε_k.

When the system and the bath do not entangle, the system-bath interaction Hamiltonian enters the equation of motion, Eq. (3.14), only through its expectation values with respect to the bath

$$H_{S-B}(t) = -\hbar \sum_{k\xi_k} \omega_{\xi_k} d_{\xi_k} q_{\xi_k}(t) |k\rangle\langle k|, \tag{3.19}$$

where

$$q_{\xi_k}(t) = \langle \Xi_{B+R}(t) | \hat{q}_{\xi_k} | \Xi_{B+R}(t)\rangle. \tag{3.20}$$

The quantity $H_{S-B}(t)$ is an operator on the Hilbert space of the system S only, and it can be written as

$$H_{S-B}(t) = \sum_k \delta\omega_k(t) |k\rangle\langle k|, \tag{3.21}$$

with $\delta\omega_k(t) = -\hbar \sum_{k\xi} \omega_{\xi_k} d_{\xi_k} q_{\xi_k}(t)$. The quantity $\delta\omega_k(t)$ can be directly interpreted as a time dependent fluctuation of the transition frequency. This terms exactly corresponds to the classical model of the bath induced fluctuations [42].

The Frenkel exciton system alone, i.e. without interaction with a quantum bath, can be mapped on a system classical linear oscillators [22, 43, 44]. For the same system, now coupled by pure dephasing type of interaction (i.e. modulating frequencies of the oscillators of the system S) to a classical bath of harmonic oscillators, it was shown that transfer of oscillation/excitation energy fulfills infinite temperature detailed balance, and not the canonical detailed balance condition with temperature T. The effects of energy trapping in the lowest energy state (represented by lowest frequency mode in classical system) do not exist in classical oscillator systems with pure dephasing type of coupling to a bath [42]. Due to the equivalence between classical oscillator systems and the single-particle Frenkel exciton systems, one can conclude that *without system–bath entanglement a quantum system of Frenkel excitons coupled to a quantum bath of harmonic oscillator*

would not relax to canonical equilibrium. System–bath entanglement is thus directly responsible for the observed thermodynamic behavior of Frenkel excitons, that is for the main function of the photosynthetic light-harvesting antennae.

4. Author's Selected Contributions to Quantum Biology

The author of this habilitation thesis has contributed by several papers to the inception of the field of Quantum Biology in its present form, as well as to the heated discussions over the definition and meaning of its content, which followed it. Except for the papers initiating the field (Paper I and III) and those related to it but published before the field became widely popular (Paper II), most of the selected works reflect the rather critical view of the past roughly ten years of the development in the field of Quantum Biology held by the author of this thesis. Especially Papers IV, V, VI and IX give significant support to the view that the proposals, which got the field started, namely, that the coherent spectroscopic features measured for the FMO protein are a signature of non-trivial quantum mechanical nature of the photosynthetic systems, and that this quantum mechanical nature is the reason for high efficiency of photosynthesis, do not stand against the theoretical scrutiny.

The papers discussed in this chapter were selected to represent the authors participation in the conceptual development of the field of Quantum Biology. They are presented in chronological order in the appendix. Only papers which bring new concepts or emphasis to the field were selected, leaving out those that deal with details of particular photosynthetic systems or those developing new theoretical and experimental tools for studying quantum biological problems.

4.1 Inception of Quantum Biology in its Current Form

Paper I (Ref. [2]), which is a second paper in a series with Ref. [5], identifies certain oscillatory characteristics of the Fourier transformer 2D electronic (FT-2DES) spectra as signatures of electronic coherence. This is the paper which motivated the measurements of the FT-2DES spectra of FMO which then lead to Ref. [1].

Paper II (Ref. [48]) provides an explanation for temperature-dependent absorption band shifts in a bacterial reaction center in terms of non-secular effect. The non-secular dynamics of optical coherence elements of the related density matrix is reflected in the absorption spectra as a bath induced renormalization of the electronic transition energy. This problem was studied completely independently from the emerging problem of long lived electronic coherences, but it eludes to the interpretation of apparently time-dependent phenomena (optical coherence transfer) in terms of electronic state basis renormalization.

Paper III (Ref. [1]) is a cornerstone of the particular notion of quantum biology which is criticized in this thesis. Based on an analysis of experimentally observed beating of the amplitude of the electronic 2D spectrum of FMO at certain prominent excitation and emission frequencies, and based on their com-

parison with predictions of the standard exciton model (predicted frequencies of the beats, and predicted lifetime of the features), it was concluded that the beats are of electronic origin and that the lifetime of these features is unexpectedly long. It was speculated that the beats are signatures of electronic coherence (as predicted in Paper I), and that electronic coherence plays a fundamental role in achieving the near unity quantum yield of the initial excitation energy transfer in photosynthesis. The latter speculation became a prime motivation for the surge of interest in the applicatiton of quantum mechanics in biology and for the inception of the field of Quantum Biology [8].

4.2 Vibrational Explanation of the Key Experiments

In Paper IV (Ref. [6]), signatures of the distinctly vibrational dynamics were studied by the same experimental method (the FT-2DES) as the FMO complex, for the first time. The response theory formalism for explanation of the vibrational features was verified, and the way was paved for a later vibrational explanation of the dynamics observed in Paper III.

Paper VI (Ref. [9]) represented a turning point in the debate about the origin of the long lived coherence in the FMO complex. In Paper VI, it was suggested that the features that were assigned to electronic superpositions of states can result from the mixing of electronic transitions on pigment molecules (which provided transition dipole moment) and the intramolecular vibrational transitions residing on the same pigment molecules (these vibrational transitions provide long decoherence times). The mixed vibrational-electronic (vibronic) transitions are enhanced with respect to purely vibrational contributions which were deemed too weak to influence measured spectra. Together with Ref. [10] this paper helped to promote an alternative explanation of the experiment of Paper III.

Paper VII (Ref. [39]) extends the work of Paper VI and provides an unified treatment of the effects described in Paper VI and Ref. [10]. In short, while Paper VI suggests that the long lived oscillatory signals originate from the mixed electronic-vibrational states in the excited state manifold of the excitonic aggregate, Ref. [10] places these signals into the ground state of the aggregate. In Paper VII we show that both contributions coexist and they are enabled by the same mixing mechanism. We discuss in detail resonance conditions between the vibrational and electronic energy gaps which enable enhancement of the otherwise weak vibrational contributions.

Vibrational explanation of the long lived coherent oscillations observed in Paper III is now widely accepted. It is also now often claimed that intramolecular vibrational modes play decisive role in making energy transfer in photosynthesis efficient. This is often done based solely on the fact that vibrational signatures are almost ubiquitous. In Paper X (Ref. [40]) we study one particular case of ultrafast energy transfer in photosynthesis, namely the carotenoid-to-bacteriochlorophyll energy transfer. Excited states of a carotenoid molecule are very short lived (sometimes with lifetime on the order of 100 fs) and yet they achieve a very high yield of transfer to neighboring bacteriochorophyll despite the fact that

the transfer occurs across a relatively high energy gap. Because the energy is conserved in the transfer process, the excess energy must be efficiently removed to enable the transfer. It turns out that this role of an intermediate energy storage is played by the ground state nuclear modes of the carotenoid. The utrafast energy transfer rate can only be explained by the involvement of this nuclear mode.

4.3 Excitation Dynamics under Different Excitation Conditions

One of the often overlooked questions in Quantum Biology is the one of the relevance of the laboratory experiments for the processes occuring in vivo in Nature. Paper V (Ref. [35]) has addressed this issue in detail. It formulates the quantum theory of the process of excitation of a molecular system by weak light to connect the experimental conditions of spectroscopics method using ultrashort laser pulses to the biological conditions, were excitation is induced by incoherent Sun light. In fact, the literature which promoted the importance of findings of Paper III for natural photosynthesis was up to that point full of various speculations about the nature of Sun-light [49]. In Paper V, a fully quantum mechanical treatment of light-matter interaction within wavefunction formalism was presented, with very interesting results. First of all, it turns out that the information needed to reconstruct the dynamics of a system weakly driven by incoherent right is precisely the one than can only be obtained in the ultrafast experiment. The ultrafast spectroscopic experiments measure the "response function" of the system, which can be used to calculate the dynamics under any type of excitation. While the dynamics under the Sun-light excitation and the laboratory pulsed laser excitation are very different, they share the same universal "response function".

The point made in Paper V was further extended in Paper IX (Ref. [36]). There we studied the excited state dynamics and especially the extent to which this dynamics is coherent for a model photosynthetic antenna under various excitation conditions. We find that even systems that lack any dephasing mechanics show very little coherence when they are excited by a source of energy which does not have a pulsed character. In particular we studied the case that the famous FMO protein is excited by its neighboring photosynthetic antenna, the so-called Chlorosom (this case corresponds to the actual biological situation) to find no evidence for involvement of coherence.

One of the important results of the debate about the importance of coherence in light-induced photosynthetic processes is the renewed appreciation of the significance of the slow time-scale processes in photosynthetic antennae. The slow processes may significantly influence the microscopic conditions under which photosynthetic light-harvesting proceeds, e.g. by rearranging the antennae. Spontaneous fluctuations of the structure of photosynthetic systems may have similar effect. In Paper XI (Ref. [50]), we studied ultrafast energy relaxation rates in the bacterial LH2 antenna by means of single molecule spectroscopy. It was possible to measure how the rates, which correspond to roughly 100 fs energy transfer times, change on the time scale of seconds to minutes. Surprisingly, the rates seem to change only on this very slow time scale, because we can see the full expected range of their variation in an experiment which averages over roughly

one second of time evolution. It seems that the protein dynamics, covering at least 12 orders of magnitude of the timescale, proceeds without much influence on the energy transfer rates, and they are only modulated on the macroscopic time scale of seconds.

Paper XII (Ref. [51]) discusses and simulates the fluorescence detected version of the FT-2DES spectroscopy. As the dynamic coherence was decisively shown in recent years to be of little importance for the function of the photosynthetic antennae, the focus of the research has shifted back to the really significant factors, such as exciton delocalization. Fluorescence detected FT-2DES has been claimed to reveal the "true" amount of delocalization in photosynthetic antennae, in contrast to the standard FT-2DES, in which some aspects of delocalization supposedly remain hidden. The fluorescence detected variant of the method exhibited much larger spectroscopic cross-peaks - the signs of large delocalization - than the standard method. We have shown that the cross-peaks in the fluorescence detected method originate from the process of exciton annihilation, and we verified that after one subtracts the annihilation contribution, the relation between the exciton delocalization and the crosspeaks in the fluorescence detected FT-2DES is very similar to the one which exhibits the standard FT-2DES method. The accepted notions of delocalization and its experimental measures are therefore not in any eminent need of revision.

4.4 Classicality of Photosynthetic Energy Transfer

Quantum Biology was conceived as a field studying the importance of quantum effects in biological processes. As described in Chapter 2, the operational definition of quantum effects was based on the identification of quantum effects with coherent effects. There are ample examples that this cannot work as a general principle, however, no attempt at identifying the classical model representative of the photosynthetic antennae was made before the initial claims of quantum effects in photosynthetic energy transfer. Classicality of the coherent dynamics of the Frenkel excitons can be, however, rigorously demonstrated [43, 44]. Paper VIII (Ref. [42]) studies such a classical model of photosynthesis, which is built from physical considerations, rather than by formal similarities between classical and quantum equations. The paper shows that the only significant difference between the classical and quantum model of photosynthetic antenna is the lack of down-hill energy transfer in the classical antenna. The only effect, which is quantum in a sense that it appears exclusively in the quantum model, is the tendency towards canonical equilibrium distribution of energy between the electronically excited eigenstates of the molecular system. The distribution of energy between the corresponding classical eigenmodes of the classical antenna corresponds to the infinite temperature limit of the quantum model. Energy transfer to the energetically low lying reaction center (the energetic funnel formed in the light-harvesting antenna), the central process of photosynthetic light-harvesting, would not be possible without quantum mechanics. Also, counter-intuitively, the degrees of freedom that are required to exhibit quantum properties for the funneling to be functional are those of the protein bath.

5. Conclusion

The field of research commonly referred to as Quantum Biology is an exciting interdisciplinary area connecting rather distinct and distant research subjects such as the theory of olfaction, bird navigation and photosynthetic primary energy transfer. The common theme among these areas of research is the application of quantum mechanics to problems related to biology.

In this habilitation thesis, we have described some aspects of both the history and the recent state of the photosynthetic sub-branch of Quantum Biology, together with the particular contribution of the author of this thesis to the development of the field. We have pointed out that while the term Quantum Biology appeared only after 2007 in wake of the experimental progress in spectroscopy, the core aspects of the theory of photosynthetic energy transfer and those of the theory the related spectroscopic topics did not change significantly over the past decades. Quantum theory has been an integral part of this field for many decades, and no "quantum revolution" has occurred in or after 2007. The original proposal that the long lived coherent oscillations observed in the Fenna-Matthews-Olson photosynthetic pigment-protein complex are signatures of non-trivial quantum effects, and that these non-trivial quantum effects are the reason for high efficiency of photosynthesis, has been invalidated on several fronts. First of all, it is very likely that the original assignment of the coherence to electronic degrees of freedom was wrong, and that these effects arise from intramolecular nuclear motion. Second, the idea that the same coherent dynamics as observed in laboratory occur also under the natural illumination of photosynthetic organisms has been disproved theoretically - a general quantum mechanical formulation of the problem does not allow for any ultrafast dynamics induced by slowly varying sources of light. Finally, coherent dynamics of photosynthetic antennae has been show to be equivalent to certain classical dynamics, and no non-trivial quantum effects can be therefore expected from it. It was the privilege of the author of this thesis to participate in all three of these achievements.

Despite the bleak fate of the original ideas behind the term "Quantum Biology", significant progress in understanding of the details of photosynthetic energy transfer has been achieved over the past decade. The influx of researchers into to the field and an exchange of ideas with other fields of physics has stimulated development of new theoretical tools. The heated discussions about the meaning of quantum theory in the context of photosynthesis have deepened our understanding of this fundamental biological process. Ultimately, more exciting new problems and new research avenues were opened than closed in recent years without unnecessary claims of non-trivial quantum effects. Apparently even "trivial" quantum mechanics is rich enough to support life.

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Original Papers

5.1 Paper I

Authors:	A. V. Pisliakov, T. Mančal, and G. R. Fleming
	Two-dimensional optical photon echo spectroscopy. II.
Title:	Signatures of coherent electronic motion and
	exciton population transfer in dimer 2D spectra.
Journal citation:	J. Chem. Phys. 124 (2006) 234505
DOI:	10.1063/1.2200705

5.2 Paper II

Authors:	T. Mančal, L. Valkunas, and G. R. Fleming
Title:	Theory of Exciton-Charge Transfer State Coupled Systems
Journal citation:	Chem. Phys. Lett. 432 (2006) 301
DOI:	10.1016/j.cplett.2006.10.055

5.3 Paper III

	G. S. Engel, T. R. Calhoun, E. L. Read, T. K. Ahn,
Authors:	T. Mančal, Y.-C. Cheng, R. E. Blankenship
	and G. R. Fleming
Title:	Evidence for wavelike energy transfer through Quantum
	coherence in photosynthetic complexes
Journal citation:	Nature 446 (2007) 782
DOI:	10.1038/nature05678

5.4 Paper IV

Authors:	A. Nemeth, F. Milota, T. Mancal, V. Lukeš,
	H. Kauffmann and J. Sperling
Title:	Vibronic modulation of lineshapes in two-dimensional
	electronic spectra
Journal citation:	Chem. Phys. Lett. 459 (2008) 94
DOI:	10.1016/j.cplett.2008.05.057

5.5 Paper V

Authors:	T. Mancal and L. Valkunas
Title:	Exciton Dynamics in Photosynthetic Complexes:
	Excitation by Coherent and Incoherent Light
Journal citation:	New J. Phys. 12 (2010) 065044
DOI:	10.1088/1367-2630/12/6/065044

5.6 Paper VI

Authors :	N. Christensson, H. F. Kauffmann, Tonu Pullerits and T. Mančal
Title:	Origin of Long Lived Coherences in Light-Harvesting Complexes
Journal citation:	J. Phys. Chem. B 116 (2012) 7449
DOI:	10.1021/jp304649c

5.7 Paper VII

Authors:	A. Chenu, N. Christensson, H. K. Kauffmann and T. Mančal
Title:	Enhancement of Vibronic and Ground-State Vibrational Coherences in 2D Spectra of Photosynthetic Complexes
Journal citation:	Sci. Rep. 3 (2013) 2029
DOI:	10.1038/srep02029

5.8 Paper VIII

Authors:	T. Mančal
Title:	Excitation Energy Transfer in a Classical Analogue of Photosynthetic Antennae
Journal citation:	J. Phys. Chem. B 117 (2013) 11282
DOI:	10.1021/jp402101z

5.9 Paper IX

Authors:	A. Chenu, P. Malý and T. Mančal
Title:	Dynamic Coherence in Excitonic Molecular Complexes under Various Excitation Conditions
Journal citation:	Chem. Phys. 439 (2014) 100
DOI:	10.1016/j.chemphys.2014.05.008

5.10 Paper X

Authors:	V. Perlik, J. Seibt, L. J. Cranston, R. J. Cogdell, C. N. Lincoln, J. Savolainen, F. Sanda, T. Mančal, and J. Hauer
Title:	Vibronic coupling explains the ultrafast carotenoid-to-bacteriochlorophyll energy transfer in natural and artificial light harvesters
Journal citation:	J. Chem. Phys. 142 (2015) 2012434
DOI:	10.1063/1.4919548

5.11   Paper XI

5.12   Paper XII