Quantum effects in biology

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Abstract

Recently, there has been a growing interest and controversy about the role that quantum effects might play in some biological processes. Here, two heavily studied examples of such effects are discussed: The impact of quantum coherence in the efficiency of energy transport in photosynthesis and the radical pair mechanism in the magnetic compass of birds. In this study, a review of theoretical and experimental work that has aided understanding these effects, provides the ground for discussion regarding their biological relevance. The findings of this work suggest that quantum coherence might be crucial for the efficiency of energy transfer in photosynthetic systems, whereas more evidence are needed to support the idea of a magnetic compass based on the radical pair mechanism. In addition, gaps in the current research in these two fields are identified and recommendations for further work are made.

Introduction

The connection between quantum physics and biology and the idea that quantum effects can survive in “wet, noisy and warm” environments such as in a living organism, has fascinated the scientific community over the past few decades [1]. According to Davydov, in his book “Biology and Quantum Mechanics”, quantum mechanics is necessary to explain biological processes taking place at the extremely small atomic and molecular scales [2], while Abbott et al. in their book “Quantum Aspects of Life” claim that “quantum mechanics enabled life to emerge directly from the atomic world, without complex intermediate chemistry” [3]. It is therefore obvious why a researcher would be motivated to explore whether the role of quantum effects in biology is non-trivial or not.
While there are many examples of quantum effects in biology, such as electron tunnelling in olfaction, respiration and photosynthesis, hydrogen tunnelling in enzyme catalysis, photoisomerization in vision, quantum coherence in photosynthesis and radical pairs in bird navigation [1, 4], this work focuses on the latter two, which have been extensively studied, both theoretically and experimentally.

In photosynthesis, the solar energy captured by pigment protein complexes is transferred to the reaction center so that it can be converted to chemical energy. It has been suggested that the high efficiency of energy transfer cannot be explained solely by classical, incoherent energy transfer from molecule to molecule, but can be interpreted in terms of a wavelike energy transfer—quantum coherence. Long lived coherences have been probed in photosynthetic systems using 2D electronic spectroscopy techniques [5, 6]. It was Engel et al. in 2007 that first observed long lived coherence in the Fenna-Matthews-Olson complex at cryogenic temperatures [7].

The radical pair mechanism was first proposed in 1978 by K. Schulten [8] as the basis of magnetoreception in birds and it suggests that the magnetic compass of birds is a “chemical compass”. It is based on light initiated chemical reactions that create a pair of molecules, each having an unpaired electron spin (a radical pair), which is sensitive to external and internal magnetic fields. So far, it has been tested by exposing birds in radio-frequency oscillating fields, with the expectation that the radical pair would be sensitive to such fields and hence the magnetic compass of birds would be disrupted [9].

But why should research on the particular effects be motivated and what would their applications be in emerging technologies? Understanding of quantum coherence in photosynthesis could be used to design devices that can harness solar energy more efficiently [10, 11], whereas a better knowledge of the radical pair mechanism in avian magnetoreception would help to understand the ability of migratory birds to orientate when traversing long distances [12]. It could also be employed in the construction of an artificial compass for improved magnetic sensing [13, 11, 14].

The objective of the present study is to introduce the concept of quantum coherence and the radical pair mechanism in photosynthesis and magnetoreception in birds, respectively, and to discuss their biological relevance through an overview of recent experimental work in these fields. The first part of the paper begins with a discussion of quantum coherence in the efficiency of energy transfer in photosynthetic systems, in the frame of the Frenkel exciton model. Furthermore, it introduces the noise assisted transport model, in which the interplay of quantum coherence and decoherence
induced by the environment increases the efficiency of energy transfer [15]. It then proceeds with a review of experiments in which 2D Fourier transform electronic spectroscopy has been the tool for examination of quantum coherences. The second part of this paper moves onto a completely different topic. It explains the radical pair mechanism and its compatibility with the properties of the avian magnetic compass of birds and it continues with an outline of experimental tests for the involvement of the radical pair mechanism in magnetoreception. Moreover, this part of the paper includes a brief summary of experiments investigating the role of cryptochromes as possible magnetoreceptor molecules in the eyes of birds. Finally, the gaps resulting from research in these areas are pointed out and suggestions for further work are made.

1 Photosynthesis

1.1 Theory

Photosynthesis is the biological process in which sunlight is collected by a living organism and converted into chemical energy, which is used as a fuel for its various activities. Photosynthesis is initiated when pigment protein light harvesting complexes absorb sunlight and transfer the electronic excitation energy to the reaction center, where conversion of excited states into separated charges is driven [1, 5, 6]. The reaction centers cannot collect light as they have small absorption cross sections and they are “expensive”, while photosynthetic pigment molecules within the light harvesting complexes are “cheap” and they increase the absorption cross section of the reaction centers, allowing them to operate at very high efficiency [16, 17, 18]. The energy transfer in light harvesting systems is highly efficient, since almost all of the photons of sunlight absorbed by the pigment protein complexes reach the reaction center [5].

In recent studies, long lived quantum coherence has been suggested to be responsible for this high efficiency. But what is meant by quantum coherence in the case of light harvesting? At this point, it is useful to introduce the concept of coherence between exciton states. When a photon is captured by a light harvesting complex, an excited molecular state is created called an exciton. Excitons are linear combinations (quantum superpositions) of excited states. They extend over two or more pigment molecules and they do not have the same energies (disorder), so they tend to be localized. However, electronic coupling between pigment molecules which are not close enough for their orbitals to overlap, creates multiple delocalized ex-
cited states. In this way, coherent energy transfer occurs between excitons, despite their energy difference, in a wavelike manner. This is different from the classical Forster type energy transfer (FRTE), where excitation energy hops incoherently from molecule to molecule and the states are localized [17, 19, 20]. For the excitation to be shared coherently within the pigment groups, the coupling between them must be strong, otherwise the spread of excitation is incoherent (FRTE) [21]. The electronic interactions between pigment molecules are significant when these are closely packed [18]. A single excitation in a photosynthetic complex can be depicted by the Frenkel exciton model. The Hamiltonian in this model for an N-chromophore system can be expressed as:

\[
H_e = \sum_{m=1}^{N} E_m |m\rangle\langle m| + \sum_{n<m}^{N} V_{mn} (|m\rangle\langle n| + |n\rangle\langle m|) \tag{1}
\]

where \(E_m\) are the site energies and \(V_{mn}\) is the electronic coupling between the \(n^{th}\) and \(m^{th}\) chromophores. The state \(|m\rangle\) denotes the excited state of the chromophore \(m\) [1, 22, 23].

The electronic excitations are modulated by the protein solvating bath which surrounds excitons and induces relaxation of the excitons from high energy states to lower energy states. The system-bath Hamiltonian is given by:

\[
H_{sb} = \sum_{m} q_m |m\rangle\langle m| \tag{2}
\]

where \(q_m\) are “operators of bath coordinates”, which describe the interactions between the bath and the chromophores, including energy transfer [22, 23]. The role of the protein environment in the efficiency of energy transfer is critical. As mentioned previously, the difference in energy between sites causes them to be localized, if it is large compared to the electronic coupling between them. The system-bath interaction leads to fluctuations in site energies, which in turn gives rise to thermal dephasing (or decoherence). Due to these fluctuations, the energy levels are broadened and the gap between them is decreased, resulting in an overlap of these levels [24, 25, 26, 27]. Fluctuations in the site energies become larger as the temperature increases due to the increased vibrations in the protein bath, enhancing dephasing [28]. The interplay of dephasing and coherence is of key importance, as the combination of both coherence and decoherence results in a much more efficient energy transport compared to a perfectly coherent system, by increasing not only the rate but also the yield of excitation energy transfer. This is known as the noise-assisted transport model [24, 15].
In the case of strong coupling between chromophores, but weak system-bath coupling, the Redfield theory must be introduced, which accounts for relaxation and dephasing [29, 22]. The Redfield Master equation is given by:

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] - \hat{K} \hat{\rho}$$

where $\hat{\rho}$ is the density matrix and $\hat{H}$ represents the system Hamiltonian. The relaxation superoperator, which is denoted by $\hat{K}$, describes the relaxation dynamics. The brackets denote a commutator. The density matrix is expressed as:

$$\hat{\rho} = \sum_{ij} \langle c_i(t) c_j^*(t) | e_i \rangle \langle e_j | = \sum_{ij} \rho_{ij} | e_i \rangle \langle e_j |$$

The off-diagonal elements of this matrix, $\rho_{ij}$ stand for coherences, while the diagonal elements, $\rho_{ii} = \langle c_i c_i^* \rangle$ correspond to populations. The excitons $i$ and $j$ are represented by $| e_i \rangle$ and $| e_j \rangle$ respectively. Populations, unlike coherences, do not evolve with an oscillating phase. The rate of change of the diagonal elements is given by:

$$\frac{\partial \rho_{ii}}{\partial t} = -\sum_k (\kappa_{ii,kk} \rho_{kk} - \kappa_{kk,ii} \rho_{ii}) - \sum_{k \neq l} \kappa_{ii,kl} \rho_{kl}$$

All the $\kappa$ elements here are elements of the relaxation superoperator. The first term of this equation represents the classical, incoherent Forster resonance energy transfer between populations, whereas the second term represents coherent quantum energy transfer, which arises due to coupling between populations and coherences and indicates that populations will adopt the oscillatory behaviour of coherences. These coherences have a frequency of oscillation corresponding to the energy difference between the states [30, 31].

An advantage brought by coherence in photosynthetic systems can be described as follows: Quantum coherence allows excitations to test different pathways at the same time within the complex, thereby preventing them from being trapped in local minima in the energy landscape and improving the efficiency of energy transfer. Coherence is thought to be more important in higher plants, where the energy landscape is abnormal and it is not inclined towards the reaction center [16, 28, 32, 33].
1.2 Experiments

Two Dimensional Fourier Transform electronic spectroscopy

Apart from the theoretical work, a remarkable amount of experimental work has been carried out for the investigation of quantum coherences in photosynthetic light harvesting complexes and the interplay of these coherences with the protein environment in the energy transfer efficiency. The most common experimental tool used to probe these coherences is 2D Fourier transform electronic spectroscopy. This method makes use of three laser pulses that interact with the sample, causing it to emit a third order signal. A superposition between ground and excited states (one quantum coherence) is generated by the first laser pulse, a superposition between excited states (zero quantum coherence) is generated by the second laser pulse and a second superposition between ground and excited states (second one quantum coherence) is created by the third laser pulse. The time between the first and second laser pulses is the coherence time, $\tau$. The time between the second and third laser pulses is the waiting time, $T$, while the time between the third pulse and the signal is called the rephasing time, $t$. A 2D spectrum which associates the coherence frequency, $\omega_\tau$, and the rephasing frequency, $\omega_t$, is obtained by Fourier transformation of the signal along $\tau$ and $t$. A rephasing-photon echo (non rephasing-free induction decay) signal is detected when the coherence evolves in opposite (same) directions during the delay times, $\tau$ and $t$. The non rephasing signal can be obtained by switching the order of the first two pulses. The sum of the rephasing and non rephasing signal is equal to the overall signal. In rephasing spectra, coherences between states contribute to crosspeaks ($\omega_\tau \neq \omega_t$) and population oscillations contribute to the diagonal ($\omega_\tau = \omega_t$). The quantum beating in the diagonal contains numerous frequencies, from the zero quantum coherences of the exciton in the diagonal peak with all other excitons, while the signal in a crosspeak contains a single frequency, corresponding to the energy difference between the two excitons giving rise to this crosspeak. Thus, when the lifetime of a single coherence is to be measured accurately, the signal on the crosspeak is examined rather the signal on the diagonal [27, 28, 30, 32].

The Fenna-Matthews-Olson complex

A paradigmatic model for the study of energy transfer in photosynthetic systems is the Fenna-Matthews-Olson (FMO) complex, from green sulfur bacteria. It consists of three monomers, with each monomer having seven
Bacteriochlorophyll (BChlα) chromophores. These are arranged in a way such that they form seven non-degenerate states. Furthermore, the FMO complex does not absorb light, but it joins the largest chlorosome to the reaction center, resulting in an efficient transfer of excitations. In addition, the protein is hydrophilic/water soluble and this aids preparation and sample handling. Finally, its structure is simple and well known and its absorption spectrum, arising from transitions in the seven chromophores, falls within the wavelength range of an ultrafast pulse generated by a Ti: Sapphire system. This makes the FMO complex compatible with ultrafast laser systems [32, 33, 34]. The structure of the FMO complex in the excitonic basis is shown in figure 1.

Figure 1: The structure of the FMO complex in the excitonic basis. The seven BChlα chromophores/sites are denoted by A-G. The black arrows indicate the zero quantum coherences between the exciton pairs 1-3 and 3-7 (modified) [34].

Investigations of coherences in light harvesting complexes

Long lived coherence in photosynthetic complexes was first observed by Engel et al. in 2007 [7]. In particular, they obtained evidence for long lived coherence in the FMO complex at 77 K, using 2D electronic spectroscopy. The 2D spectra obtained from their experimental work, taken at different waiting times, with the population time (waiting time) having a range from 0-660 fs, are shown in figure 2.

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Figure 2: Representative 2D spectra for the FMO complex shown for waiting times $T = 0, 155, 280, 600$ fs, at a temperature equal to 77 K. The black arrows indicate the exciton 1 diagonal peak, while the white arrows indicate the exciton 1-3 crosspeak [7].

The quantum beating signal in these spectra persists for 660 fs, suggesting electronic coherence between excitons. Further investigations of the exciton 1 diagonal peak and the exciton 1-3 crosspeak provide compelling evidence of quantum coherence in the FMO complex. A plot of the amplitude of the exciton 1 diagonal peak as a function of waiting time, in which the data points are connected with a Fourier interpolation, as well as the power spectrum obtained by Fourier interpolation are shown in figure 3. The power spectrum obtained experimentally is consistent with the predicted exciton spectrum, which implies that the signal from the exciton 1 diagonal peak is due to electronic coherence. The signal obtained from the exciton 1-3 crosspeak and the associated power spectrum are shown in figure 4. The fact that no beating from the exciton 1-3 crosspeak appears at early waiting times proposes that electronic coherence has been transferred from a pair of excitons to the exciton 1-3 pair at a later time and therefore that transfer of electronic coherence indeed takes place in the FMO complex. According to the theoretical work of Zhu et al. [35] and Kais et al. [36], the timescale of the quantum coherence in the FMO complex is 650 fs at 77K, which is comparable to the lifetime of the electronic coherence found in this experiment. Along with the other experimental results obtained, this shows that energy
transfer is wavelike—due to quantum coherence in the FMO complex.

Figure 3: Left: Amplitude of the exciton 1 diagonal peak as a function of waiting time, with data points connected by Fourier interpolation. Right: Power spectrum obtained by Fourier interpolation (modified) [7].

Panitchayangkoon et al. [28], have experimentally demonstrated that quantum coherence persists at a timescale of about 300 fs at 277K in the FMO complex, using 2D fourier transform electronic spectroscopy. The difference in the behavior of the rephasing and non-rephasing signals, shown in figure 5, indicates that the signal observed at 277K is due to electronic coherence. In particular, the rephasing signal on the crosspeak decays exhibiting quantum beating, while the rephasing signal on the main diagonal decays exponentially during the waiting time. Furthermore, the rephasing signal at the particular crosspeak shows quantum beating but the non-rephasing signal at the same crosspeak does not. The dephasing rate of the coherence between excitons 1 and 3 demonstrated a linear increase with temperature, which is shown in figure 6. The fact that the dephasing rate increases with temperature shows that the environment induces dephasing, because as temperature increases, the vibrations in the protein bath increase, in agreement with theory in the previous section. The lifetime of the coherence at 277K was estimated to be 300 fs, which is much shorter than the lifetime at 77 K. Apart from the long lifetime of the coherence at physiological temperature, the coherence completed almost two oscillatory cycles before being destroyed by dephasing, which satisfies the conditions for ideal transfer efficiency. The numerical calculations of Fleming et al. [37], show that quantum coherence lasts for approximately 350 fs at room temperature in the FMO complex, which agrees with the timescale of the coherence as determined by this experiment. Considering this and the fact that the beating lasts for almost two cycles, it is very likely that quantum coherence has an impact on the energy transfer in this complex.

The coherences in the light harvesting proteins phycoerythrin, PE545 and phycocyanin, PC645 from the marine cryprophytes Rhodomonas CS24 and
Figure 4: a: Signal from the exciton 1-3 crosspeak, in which the data points are connected with Fourier interpolation. b: Power spectrum for the exciton 1-3 crosspeak. The frequency corresponding to the energy difference between excitons 1 and 3 is shown with a red line [7].

Chroomonas CCMP270, respectively, have been studied by Collini et al. [38] at physiological temperature, using 2D spectroscopy. In PC645, coherences arise between the excited states $DBV_+$ and $DBV_-$ (which arise from coupling between two dihydrobiliverdin (DBV) molecules) in the centre of the protein and between the $DBV$ states and the two mesobiliverdin ($MBV$) molecules at the periphery of the protein. The quantum beating signals due to these coherences are shown in figure 7, with the plot on the left corresponding to the coherence between the $DBV$ states and the plot on the right corresponding to the coherence between the $DBV_+$ and $MBV$ states. The red lines correspond to upper crosspeaks in the rephasing spectrum and the black lines correspond to lower crosspeaks. The phase difference between the signals from the upper and lower crosspeaks is related to the sign of the energy difference between excited states (excitons) and it is a signature of
quantum coherence. In other words, coherence between excited states must carry an opposite phase if the sign of the energy difference between them is reversed, which makes this phase difference between upper and lower peaks an observation necessary in order to confirm that the signals are indeed due to electronic coherences. For example, the coherence $|DBV_+ \rangle \langle DBV_- |$, which corresponds to the upper crosspeak in the left plot, carries a phase opposite to that of the coherence $|DBV_- \rangle \langle DBV_+ |$, which corresponds to the lower crosspeak. The same applies to the coherence between the $DBV_+$ and $MBV$ states. In both plots, coherences have a lifetime longer than 400 fs, suggesting energy transfer by quantum coherence in PC645. Similar phase relationships between signals from the upper and lower crosspeaks were obtained for PE545. A slightly different method has been used by Harel, E. and Engel, G. S. [24] to examine the quantum coherence between the bands B800 and B850 from the light harvesting complex 2 (LH2) in purple bacteria, at room temperature. This method is called gradient assisted photon echo spectroscopy (GRAPES), which is a single shot version of 2D spectroscopy. The signals from a region of the upper crosspeak in the 2D spectra of LH2 were observed to have a lifetime of about 400 fs and a frequency range equal to 800-1000 cm$^{-1}$, which is much larger than the
Figure 6: The beating signals decay faster as the temperature increases and a plot of the dephasing rate against temperature shows that the dephasing rate increases linearly with temperature [28].

typical beating frequency of vibrational coherences, arising from vibrations in an individual chromophore, or vibrations in the protein bath. Moreover, the vibrational coherences would dephase very rapidly at room temperature, so they would not have such long lifetimes. Therefore, the signals are attributed to quantum coherence between the bands B800 and B850 from the LH2. Furthermore, the lifetime of this coherence is much longer than the lifetime of the coherence found by [35] to be 150 fs in the LH2, at room temperature, which demonstrates that quantum coherence can affect the energy transfer in the LH2.

Cohen et al.[39] have also used a different version of 2D spectroscopy, a coherence-specific polarization sequence, to investigate coherence dynamics in LH2. The variation in the polarization of the pulses in this method allows them to excite and detect only coherences, resulting in 2D spectra that contain only electronic coherences and not population signals. More specifically, the two excitation pulses are perpendicular to each other, which means that they can only excite coherences and not populations, while the two emission pulses are also perpendicular to each other, so they can only detect signals
Figure 7: Left: Quantum beating signals due to the coherence between $DBV$ states. The upper crosspeak, shown with a red line, represents the coherence $|DBV_+⟩⟨DBV_-|$ and the lower crosspeak, shown with a black line, represents the coherence $|DBV_-⟩⟨DBV_+|$. Right: Quantum beating signals due to the coherence between the $DBV_+$ and $MBV$ states. The phase difference between the signals from the upper and lower crosspeaks is a signature of quantum coherence (modified) [38].

corresponding to coherences. Absolute values of 2D, non-rephasing spectra at 77K, at different waiting times are shown in figure 8.

Since in rephasing spectra coherences contribute to crosspeaks, in non-rephasing spectra they contribute to the diagonal. Integration of these spectra yields the integrated intensity against waiting time, shown in figure 9. The integrated intensity depends on the short lived coherences, arising from weak coupling between chromophores, long lived coherences, arising from strong coupling between chromophores and finally on the total signal decay which is due to annihilation effects. The decay time of long lived coherences was found to be 700-900 fs, while the timescale of the short lived coherences was estimated to be about 49 fs, suggesting that the stronger the coupling between chromophores is, the longer the lifetime of the coherence. The lifetime of the long lived coherences is much longer than the lifetime of the coherence in the LH2 found by Harel, E. and Engel [24], obviously because the experiment was performed at 77K and not at room temperature, showing that the protein environment affects the lifetimes of the coherences. The experimental value for the lifetime of the long lived coherences is also larger than the theoretical value for the lifetime of the coherence in the LH2, which according to Zhu et al. [35], is 300 fs at cryogenic temperature.

The coherence dynamics between bacteriochlorophyll (denoted by B) and accessory bacteriochlorophyll (denoted by B) in the reaction center of the purple bacterium Rhodobacter sphaeroides were examined by Lee et al. [40] by the use of a two color electronic coherence photon echo experiment (2CECPE). In the 2CECPE, the first and second pulses have different ener-
Figure 8: Absolute values of 2D, non-rephasing spectra obtained using a coherence specific polarization sequence are shown at different waiting times. The spectra were obtained at 77K. In non-rephasing spectra, coherences appear on the diagonal [39].

gies (and therefore a different color) and the energies of the first and second pulses are resonant with the energies of the H and B states respectively. The lifetime of the zero quantum coherence due to superposition of the H and B states was estimated to be 440 fs at 77 K and 310 fs at 180 K. These timescales are much longer than the energy transfer timescale in the reaction center, which, as referred to the paper, is approximately 250 fs. This implies that energy transfer in the reaction center occurs in a wavelike, quantum mechanical manner. In addition, the dephasing rate of the one quantum coherence between the ground and H states was found to be much larger than the dephasing rate of the zero quantum coherence between the H and B states. This is due to the fact that the protein environment protects the zero quantum coherence by inducing fluctuations in the energies of the H and B states, keeping the energy gap between them constant. However, this is not the case for the one quantum coherence, because the fluctuations in energy induced by the environment are equal to the transition energy between the ground and the H state. This probably explains the fast dephasing of the one quantum coherence compared to the zero quantum coherence and shows that the protein environment can help to increase the lifetime of zero quantum coherences, but not the lifetime of one quantum coherences.

The impact of the protein environment on zero quantum coherences was also studied by Engel and Caram [34]. In their 2D electronic spectroscopy experiment, they determined the dephasing rates and frequencies of eight
zero quantum coherences in the FMO complex, using a linear prediction Z transform. The variations observed in the decay rates suggest that the decay rates depend on the spatial arrangement of the chromophores, which implies that the system is coupled to a phonon bath.

Three points worth to be noticed out of these experiments. First, the signals detected were distinguished from vibrational coherences or population signals and they were justifiably attributed to quantum coherences within the photosynthetic complexes. Second, these coherences were found to have a lifetime long enough to affect the energy transfer within the complexes, that is, their timescales were longer than the energy transfer timescales. Third, the fact that the dephasing rate of quantum coherences increases with temperature shows that the protein environment induces dephasing but at the same time protects quantum coherences by increasing their lifetime. Therefore, it is reasonable to conclude that the high efficiency of energy transfer in photosynthetic complexes is due to quantum coherence and its interplay with the protein environment.

Figure 9: Integrated intensity against waiting time, obtained by integration of non-rephasing spectra [39].
2 Bird Navigation

2.1 Theory

Properties of the avian magnetic compass of birds

Many species, amongst them fish, insects, amphibians, mammals, reptiles and birds are able to sense the Earth’s magnetic field, contrary to humans, in order to obtain directional and positional information [41]. In birds, the avian magnetic compass has some special properties: i) It is an inclination compass, which means that it is not based on polarity and hence cannot discriminate between magnetic South and magnetic North. It relies on the inclination of the magnetic field, that is, it points where the magnetic field lines are inclined downwards or upwards. For example, reversing the vertical or horizontal component of the magnetic field causes the birds to head in a direction opposite to their normal migratory direction. If both components are inverted, which corresponds to reversing the polarity, birds head on their normal migratory direction and their response is not affected [9, 42, 43, 44, 45]. ii) It demonstrates a functional window: If birds are exposed to intensities 30% lower or higher than the intensity of the local geomagnetic field, they become disoriented, but after some time of exposure to the new intensity they are able to orient again [9, 42, 43, 45]. iii) It is light dependent: Birds are well oriented in their normal migratory direction under monochromatic light with wavelengths from the short part of the spectrum, that is, blue and green light, or under “white” light, that is, light with wavelengths from the full spectrum. They are disoriented under light with long wavelengths (red light) [9, 42, 44].

The mechanism underlying the avian magnetic compass

Two dominant mechanisms are proposed to constitute the basis of the avian magnetic compass. The first mechanism suggests that magnetite receptors, found in the upper beak of birds, are involved in the detection of magnetic information. This magnetite-based magnetoreception is associated with forces exerted to the magnetite particles by the magnetic field, so it can be thought of as a classical mechanism [45, 46, 47, 48]. It provides information on position rather on direction, and this is achieved when the intensity of the magnetic field is recorded by the magnetite receptors [45, 47, 49]. However, it has been demonstrated that when the upper beak of birds is anaesthetized, their migratory orientation is not influenced, which means that their orientation is not affected by this mechanism [47].
The second mechanism, the radical pair mechanism, suggests a “chemical compass”, in which light initiated chemical reactions create radical pairs. The radical pair mechanism is described as follows: A donor molecule D becomes excited by light absorption and transfers an electron to an acceptor molecule A. This results to a pair of molecules, in which each molecule has an unpaired electron, and therefore an unpaired electron spin. This pair is called a radical pair. After electron transfer occurs, the radical pair is initially in a singlet excited state, in which the spins of the electrons are anti-parallel. However, transitions from the singlet state to the triplet state, in which electron spins are parallel, occurs, and vice versa. This is termed as Singlet-Triplet (S-T) interconversion [9, 44, 45, 50, 51]. The oscillation of the radical pair between the two states is a purely quantum coherent process [51, 12]. Since there is a magnetic moment associated with each of the electron spins, the S-T interconversion is affected by both internal and external fields [12]. The external field can be, for example, the geomagnetic field, which induces a splitting of energy levels, a phenomenon known as Zeeman interaction [52, 13]. Internal fields arise due to hyperfine interactions between electron spins and the magnetic nuclei of donor and acceptor molecules, and they also induce splitting of energy levels [51, 12, 52, 53]. New product states can be formed from both the singlet and triplet states, with reaction rates $k_s^f$ and $k_T$ respectively [50]. Recombination to the neutral singlet state of the two molecules, that is, before light absorption, can only occur from the singlet state, with reaction rate $k_s^r$ [50, 51]. A schematic diagram of the radical pair mechanism is shown in figure 10. If the magnetic field strength is weak compared to the strength of the hyperfine interactions, S-T interconversion is enhanced and more products are formed from both states. If the magnetic field strength is comparable to the strength of hyperfine couplings, S-T interconversion is suppressed, resulting in an increased recombination to the neutral singlet state and a decreased product formation [42, 12]. For the radical pair to be sensitive to a weak field, with a strength comparable to the Earth’s magnetic field (approximately 50 µT), the lifetime of the radical pair, which is the inverse of the reaction rate (assuming equal reaction rates) [43] must be approximately 1 µs, so that the field has enough time to affect the S-T transition and therefore the reaction yields [12, 54]. This lifetime should also be longer than the timescale of the processes that induce relaxation of the electron spins, which is equivalent to the loss of spin correlation. Such processes include the motion of the molecules [50, 12]. The combined coherent S-T interconversion and formation of products from the singlet and triplet states is represented by the
Figure 10: The radical pair mechanism. Light is absorbed by the donor molecule D, which transfers an electron to an acceptor molecule A. This creates the radical pair, initially in the singlet state. Transitions occur from the singlet to the triplet state and vice versa, which are driven by both internal and external magnetic fields [50].

Stochastic Liouville equation:

\[
\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho] - \frac{k_s}{2} \left( P^S \rho + \rho P^S \right) - \frac{k_T}{2} \left( P^T \rho + \rho P^T \right)
\]  

(6)

The first term represents the coherent transition from the singlet to the triplet state and vice versa, the second term represents the formation of products from the singlet state and the third term denotes the formation of products from the triplet state. The symbols \( \rho \), \( P^S \) and \( P^T \) stand for the density matrix, the projection operator onto the singlet state and the projection operator onto the triplet state respectively. The square brackets denote a commutator [43, 50]. The Hamiltonian \( H \) of the radical pair is given by:

\[
H = \hat{I} \hat{A} \hat{S}_1 + \frac{1}{2} \mu_B g \vec{B} \left( \hat{S}_1 + \hat{S}_2 \right)
\]  

(7)

Where \( A \) is the hyperfine tensor, while \( \hat{I} \) and \( \hat{S}_i \) \((i = 1, 2)\) are spin operators of the nucleus and of the electrons respectively. The Bohr magneton is denoted by \( \mu_B \) and the electronic g factor is approximately equal to 2 for electrons. \( \vec{B} \) stands for the magnetic field. The Hamiltonian, as written above, models a system in which only one of the radicals has hyperfine interactions, that is, only one of the two electron spins interacts with the spin of the corresponding nucleus [43, 55]. Such a system, consisting of one nucleus and two electron spins is shown in figure 11. This implies an anisotropic hyperfine interaction, hence the term \( \hat{I} \hat{A} \hat{S}_1 \) and the hyperfine tensor \( A \) here is anisotropic. The reason for considering such a system, is because the sensitivity to an external magnetic field is increased if only one of the radicals has hyperfine interactions [44, 56]. In addition, the Hamiltonian here accounts...
only for the dominant hyperfine (first term) and Zeeman (second term) interactions and neglects dipole-dipole and exchange interactions between the electron spins of the radicals, since these interactions decrease very rapidly as the distance between the two radicals is increased [53].

Figure 11: A system consisting of one nucleus and two electron spins, in which only one of the radicals has hyperfine interactions [55].

A magnetic compass based on vision
The radical pair mechanism can explain the properties of the magnetic compass of birds: The initial step of the radical pair mechanism requires light absorption, which makes the compass light-dependent [9, 45]. Moreover, the response patterns formed across the retina of a bird due to radical pair processes are the same when the bird is looking either parallel or anti-parallel to the magnetic field lines, which implies a symmetry of these patterns around the magnetic field axis and shows that the avian compass is an inclination compass, since the patterns do not depend on the polarity of the magnetic field [42, 45]. Finally, the patterns depend on the intensity of the magnetic field, which means that when a bird is exposed to a new intensity, a new pattern is formed across its retina, but due to the symmetry of the patterns, the bird is able to understand this pattern after a certain time of exposure. This is why the bird is able to orient again in a new intensity even though it is initially disoriented [9]. The compatibility of the radical pair mechanism with the properties of the avian magnetic compass of birds makes it the most probable mechanism underlying the compass and thus gives a further motivation for testing it experimentally.
All the above show that the radical pair mechanism is related to a vision based magnetic compass. In general, the radical pairs are formed in the eyes of birds and the sensitivity of these pairs to the magnetic field can be
used to give them magnetic compass information [48, 57, 58]. The vision based magnetic compass can be realistic only if some conditions are met. First, photoreceptor molecules capable of producing radical pairs should exist in the eyes of birds. Second, the receptor cells containing these molecules should be connected to the visual transduction system. Third, the photoreceptor molecules should be aligned in the same direction within a receptor cell, and the receptor cells should in turn be arranged in a way such that all spatial directions are covered and information on magnetic direction is provided [42, 57].

2.2 Experiments

Testing the radical pair mechanism

If the radical pair mechanism is sensitive to a weak magnetic field, such as the Earth’s magnetic field, then it should also be sensitive to an oscillating radio-frequency field with a frequency corresponding to the frequency of the splitting caused by the Zeeman and hyperfine interactions. Such a field, should, in a similar way to to hyperfine and Zeeman interactions, drive S-T interconversion. Therefore, the change in the response of birds to a static geomagnetic field when an oscillating radio-frequency field is added to it, provides evidence that the radical pair mechanism is involved in magnetoreception [13, 44, 59]. Radio-frequency fields do not influence a magnetite based mechanism, so the involvement of this mechanism in the avian magnetic compass is excluded when experiments with radio-frequency fields are performed [46, 57, 49].

The effect of an oscillating field added to the local geomagnetic field, in the response of European robins during their two migration seasons, has been investigated by Thalau et al [52]. In spring, these birds migrate north-northeast and in autumn they migrate south-southwest. Their migration takes place at night. The birds where tested under green light of 565 nm wavelength, in three different conditions: In the local geomagnetic field alone, with an intensity of 46,000 nT, in the presence of a 1.315 MHz oscillating field with an intensity of 485 nT parallel to the geomagnetic field and in the presence of the oscillating field at 24° with respect to the geomagnetic field. Twelve birds were tested in spring and sixteen birds in autumn. In the local geomagnetic field alone and in the presence of the oscillating field parallel to the geomagnetic field, the birds headed in their normal migratory direction. However, when the oscillating field was superimposed to the static geomagnetic field at an angle of 24°, the response of the birds was
disrupted in both migration seasons. The headings of the birds in both seasons are shown for all three conditions in figure 12. The average heading of an individual bird at a particular condition is represented by a mean vector and the mean heading for all birds at the same condition is represented by a grand mean vector. The disruptive effect of the 1.315 MHz oscillating field when it is added at an angle to the geomagnetic field, despite its small intensity compared to that of the geomagnetic field, is attributed to the fact that its frequency is resonant with the frequency of the splitting caused by the geomagnetic field.

Ritz et al. [46] have also examined the effects of oscillating fields in the response of European robins under exposure to green light. Twelve birds were tested in five different conditions: In the local geomagnetic field alone,
with a strength of 46,000 nT as previously, in the presence of a 7 MHz oscillating field with an intensity of 470 nT at 0°, 24° and 48° with respect to the geomagnetic field and finally in the presence of a noise field with an intensity of 85 nT added to the geomagnetic field, with frequencies in the range 0.1-10 MHz. This range of frequencies corresponds to the range of frequencies of the splitting caused by hyperfine interactions. The birds headed in their proper migratory direction (north-northeast) in the presence of the geomagnetic field alone or when the 7 MHz oscillating field was parallel to the geomagnetic field, but they were disoriented when the oscillating field was at 24° or 48° to the geomagnetic field and when they were exposed to the noise field. Their responses under these conditions are shown in figure 13.

Figure 13: Headings of the twelve European robins during spring migration under five conditions: (a) in the static field alone, (b) in the presence of a noise field added to the geomagnetic field and in the presence of a 7 MHz oscillating field at (c) 0°, (d) 24° and (e) 48° relative to the static field [46].

In a similar experiment, performed by Wiltschko et al. [44], European robins were exposed to oscillating fields, with an intensity of 480 nT and at 24° relative to the local geomagnetic field lines. The birds were tested under 565 nm green light as in the previous experiments, during spring migration. The frequencies of the oscillating fields were 0.01, 0.03, 0.10, 0.50, 0.65, 1.315, 2.63 and 7 MHz. In the presence of oscillating fields with frequencies 0.01 and 0.03 MHz, the responses were identical to the responses in the geomagnetic field alone, that is, the birds were oriented northerly. The birds were slightly disoriented under exposure to the 0.10 or 0.50 MHz fields, while at the remaining higher frequencies they were completely disoriented. The authors give an approximate value of the radical pair lifetime to be 2-10 µs,
by assuming that this lifetime corresponds to the inverse of the threshold frequency at which disorientation occurs, which in this case is 0.1-0.50 MHz. The birds were also tested at the frequency corresponding to the frequency of Zeeman splitting, which, as mentioned previously is 1.315 MHz, and at 0.658 and 2.63 MHz, half and twice the resonance frequency respectively. At a field intensity of 480 nT, disorientation was observed at all three frequencies, while at lower intensities, the responses were unaffected at 0.658 and 2.63 MHz, but strongly disrupted at 1.315 MHz. Normal migratory orientation was observed at 1.315 MHz, only when the oscillating field was very weak, with a strength of 5 nT. The frequency of Zeeman splitting induced by a static geomagnetic field is proportional to the strength of the field, hence it must double when the intensity of the field is doubled. When tests were performed at an intensity twice that of the local geomagnetic field, that is, 92,000 nT, the birds were indeed disoriented at 2.63 MHz (twice the resonance frequency), even at lower intensities of the oscillating fields and oriented only at 5 nT. These observations, presented in figure 14, suggest that the disorientation at 1.315 is due to the resonance with the frequency of Zeeman splitting. The resonance at this frequency is expected for the radical pair model introduced previously, in which one of the radicals has no hyperfine interactions.

In summary, oscillating fields, at an angle with respect to the local geomagnetic field, with frequencies resonant with the frequencies of Zeeman and hyperfine interactions, cause birds to disorient. Yet, it is unclear why oscillating fields parallel to the static field produce no effect in the response of birds. Recalling that Zeeman and hyperfine interactions drive S-T interconversion, the fact that extremely sensitive responses are observed at frequencies corresponding to these interactions gives strong, but not direct evidence for the involvement of the radical pair mechanism in magnetoreception. Moreover, the possibility that these sensitive responses do not necessarily arise due to the particular resonances, but may be associated with a completely different mechanism, should be explored.

Apart from these behavioural experiments, the role of radio-frequency fields in conjunction with static fields on the recombination of photoinduced, short-lived radical pairs has been investigated. The effects of radio-frequency fields on the recombination from the singlet state of these radical pairs was found to depend on the frequency of the oscillating field and its direction with respect to the static field, as well as on the intensity of the applied static field [59, 60]. It has also been shown that a radio-frequency field alone, in the absence of an applied static field can reduce the singlet yield of a photoinduced radical pair when its frequency is resonant with the frequency of
splittings caused by hyperfine interactions [61].

Figure 14: Responses at oscillating fields of different intensities, at 0.658, 1.315 and 2.63 MHz are shown for static field strengths of 46,000 and 92,000 nT. The frequency of Zeeman splitting is 1.315 MHz at a 46,000 nT static field and 2.63 MHz at a 92,000 nT static field. Orientation at these frequencies was observed only at a 5 nT oscillating field. Tests were not performed at some frequencies and intensities which is why some diagrams are missing [44].

Chryptoochrome: A possible magnetoreceptor molecule

The only photoreceptor molecules which are known to produce radical pairs upon light excitation in birds are cryptochromes. Cryptochromes are flavoproteins which are located in the retina of birds and are excited upon absorption of blue-green light, which is the colour of light under which birds are well oriented [44, 45, 57, 58, 62, 63]. Cryptochromes have also been found in plants and animals [64]. However, if cryptochromes are to function as the sensory molecules mediating magnetic information in birds, they should satisfy the criteria discussed in the previous section, that is, they should form radical pairs with long lifetimes in the eyes of birds and they should be aligned in receptor cells connected to the visual transduction system. In the retina of European robins, three types of cryptochromes, eCRY1a,
eCRY1b and eCRY2 have been identified [63]. In addition, it has been shown that cryptochrome 1 (CRY1) is present in the retina of garden warblers and that it is located in ganglion cells which demonstrate high activity (convey information from the eyes to the brain) during night, when these birds migrate [65]. An experimental study has revealed that the ganglion cells in the retina of garden warblers are linked through a specific visual pathway to the Cluster N, a forebrain area which is a component of the visual system in birds and it is active during night [66]. Cluster N is vital for magnetoreception, since European robins which had their Cluster N destroyed, could no longer orient using their magnetic compass [48]. The connection between the Cluster N and the ganglion cells proves that the ganglion receptor cells, containing the cryptochromes, are connected to the visual system. In addition, transient absorption measurements have shown that cryptochrome 1a forms radical pairs in the retina of a migratory garden warbler, with millisecond lifetimes, when illuminated with 355 nm blue light. These lifetimes are fairly longer than the typical radical pair lifetime of 1 µs, at which a weak magnetic field can have a significant effect on the S-T interconversion [67]. Nonetheless, this result has limitations, as birds orient well not only under blue light, but under green light, too. Finally, Cry1a proteins were found to be orderly aligned in the outer parts of ultraviolet/violet (UV/V) cones in the retina of European robins. The receptor cells-UV/V cones were observed to be distributed in a uniform way throughout the retina, that is, in a way that all spatial directions are covered [68].

Although these experiments provide direct evidence that cryptochrome satisfies the criteria that a candidate photoreceptor molecule mediating magnetic information should meet, there is a lack of conclusive experimental evidence that cryptochromes are the molecules constructing the basis of a vision based, light dependent magnetoreception. Since there are no other known photoreceptor molecules in birds capable of producing radical pairs, the radical pair mechanism cannot be of biological relevance and thus cannot be the mechanism affecting magnetic compass orientation, if cryptochromes are not the molecules intervening magnetic field information. Considering also that the experiments discussed previously do not provide direct evidence that the radical pair mechanism is associated with magnetoreception, the statement that this mechanism is necessary for birds to perform magnetic compass orientation is questionable.
Conclusions

The main goal of this study was to investigate the effect of quantum coherence in the efficiency of energy transfer in photosynthesis and the role of the radical pair mechanism in the avian magnetoreception in birds. It was found that quantum coherence and its interplay with the environment might play a significant role in the efficiency of energy transfer. This conclusion is based on several experimental evidence. The signals detected in the experiments described in section 1.2 were indeed due to quantum coherences and not due to population oscillations or vibrational coherences. Furthermore, these coherences survived long enough to have an impact on the energy transfer in photosynthetic systems, since their lifetimes were comparable to the timescales of the energy transfer. Moreover, the protein environment was found to induce dephasing, destroying coherences, but at the same time, increasing their lifetime. However, it should be noticed that in these experiments, the excitations within the light harvesting antenna complexes were generated using laser pulses, that is, coherent light. Observations of quantum coherence in experiments in which excitations are created by incoherent light, such as sunlight, have not been reported so far. It is therefore unknown whether quantum coherence in this case would still have an impact in the efficiency of energy transfer or not [4]. Future experiments utilizing incoherent light for the excitations within the complexes could shine light regarding what would happen in this situation.

As for the radical pair mechanism in bird navigation, it has been shown that oscillating fields at an angle with respect to the geomagnetic field, with frequencies resonant with the frequencies of the energy level splittings due to hyperfine and Zeeman interactions, can disrupt the magnetic compass orientation of birds. Although the sensitive responses at these frequencies give strong evidence that the radical pair mechanism operates in the magnetic compass of birds, they might be related to a completely different mechanism or they might be just a simple coincidence. Future work should investigate this possibility. Even if the responses at the particular frequencies are indeed associated with the radical pair mechanism, this mechanism can be important for magnetic compass orientation only if there is a receptor molecule in the eyes of birds, satisfying the criteria discussed in section 2.1. Hitherto, only cryptochromes are known to produce radical pairs in birds. Even though it has been shown that they satisfy the required criteria, there is a lack of sufficient, conclusive experimental evidence that cryptochromes are the molecules mediating magnetic information in birds. This leaves open questions concerning the existence and identity of a magnetorecep-
tor molecule and consequently the necessity of the radical pair mechanism for birds to perform magnetic compass orientation. In the coming years, researchers should investigate the essentiality of the radical pair mechanism in avian magnetoreception by further study of the properties of cryptochromes. In the case that the cryptochrome is not the primary sensory molecule in birds, future research could result in identification and characterization of the photoreceptor molecule underlying the light dependent compass.

Acknowledgements

This work was supervised by [supervisor name] with additional support from [PhD student name] PhD student, in the Quantum Information group at the University of Leeds.

References


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