An Open Quantum Systems Approach to Avian Magnetoreception

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

1. Introduction

It is generally well accepted that birds employ the earth's magnetic field in their remarkable feats of migration. The exact mechanism of this use is less well understood. Of the two main hypotheses, one suggests that ferromagnetic crystals in the birds' beaks align themselves in the earth's magnetic field and thus allow the birds to orientate themselves [1]. However, experiment demonstrates that these crystals sense magnetic intensities that are orders of magnitude bigger than the weak geomagnetic field [2]. Current consensus is that birds employ another more sensitive mechanism, a chemical compass which utilises quantum effects to 'see' the magnetic field. The detail of this compass, in the form of a radical-pair mechanism, was first proposed by Schulten *et al.* in 1978 [3]. The mechanism relies on the photo-activated creation of a radical pair in a singlet spin state, which then undergoes singlet-triplet mixing to result in different chemical signatures. This hypothesis is supported by evidence that efficient avian magnetoreception is light-dependent, requires an undamaged visual system [4] and is sensitive to weak magnetic fields [8]. One of the most convincing pieces of evidence in support of the radical pair mechanism is the experimental demonstration that oscillating radiofrequency fields cause birds to be disoriented. It was first noted in 2004 that birds are disoriented in oscillating fields of MHz range, most remarkably at a frequency of 1.315 MHz [5, 6]. This, being the Larmor frequency of a free electron in a geomagnetic field, led to speculation that one of the radicals of the pair has no hyperfine interactions. Ritz *et al.* went on to specify the other specific frequencies at which birds are disoriented, although to a much lesser degree, concluding that such disorientation would be explicable by the fact that for a radical with no hyperfine interactions the Larmor resonance would have greater effect than for a frequency corresponding to only one of the various possible energy-level splittings of the hyperfine interaction [7]. Recent experiments conducted on migratory birds over seven years at Oldenburg in Germany have also demonstrated that birds' ability to navigate effectively is compromised by anthropogenic electromagnetic radiation over a frequency range from 50 kHz to 5MHz [9].

The work documented in this paper revisits radical pair theory through an open quantum systems approach. Firstly we derive a master equation in the Born-Markov approximation which describes the dynamics of the radical pair as it dissipates in a boson bath approximating the environment. We then solve the master equation and analyse the dynamics of the radical pair. This approach is useful in its theoretical verification of experimental parameters used in other models of the avian compass, such as the lifetime of the radical pair and the rates at which singlet-triplet mixing occurs [10][11]. By varying the number of nuclear spins interacting with the radical pair we can also investigate the effects of different nuclear environments and thus conclude something about the structure of cryptochrome, the biological molecule in which it is thought that the radical pair reaction takes place [14].

2. Modelling the Radical Pair Mechanism

2.1. The System

The heart of the magnetic compass, the radical pair, results from the photo-excitation of an electron to form a spatially separated but spin-correlated electron pair. The radical pair begins in a singlet state $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$, but the hyperfine interaction of each electron with its nuclear environment, as well as with the magnetic field, induces singlet-triplet mixing. For the purposes of this research we will neglect the dipole-dipole and exchange interactions between the two electrons due to sufficient spatial separation [11][12]. We also neglect the interaction of nuclear spins as the gyromagnetic ratio is small compared to the electronic case [12].

The Hilbert space of the system is given by $\mathcal{H}_s = \mathcal{H}_e^{(1)} \otimes \mathcal{H}_e^{(2)} \otimes \mathcal{H}_n^{(1)} \otimes \mathcal{H}_n^{(2)}$ where $\mathcal{H}_e$ refers to the Hilbert space of either electron and is two dimensional while $\mathcal{H}_n$ refers to the Hilbert space of the nuclear spin environment and is of dimension $(2j+1) \times (2j+1)$. In the following we already take into account that, for example, $S_z^{(1)} = S_z^{(1)} \otimes I_e^{(2)} \otimes I_n^{(1)} \otimes I_n^{(2)}$ where I_e and I_n are the identity matrices for electron and nuclei. Thus an expression such as $S_+^{(1)} I_-^{(1)}$ uses ordinary matrix multiplication. The Hamiltonian for this system models the two electrons, labelled (1) and (2), each interacting separately, and can be written as

$$H_s = \gamma_e(\overrightarrow{B}\mathbf{S}^{(1)} + \overrightarrow{B}\mathbf{S}^{(2)}) + \lambda \sum_{k=1}^{2} \sum_{n,l=1}^{3} A_{nl}^{(k)} \mathbf{S}_n^{(k)} \mathbf{I}_l^{(k)} \tag{1}$$

where $\overrightarrow{B}$ is the magnetic field vector and

$$\mathbf{S} = (S_x, S_y, S_z) \qquad \mathbf{I} = (I_x, I_y, I_z)$$

are the vectors of spin operators for electron and nuclear spin respectively and $\gamma_e \overrightarrow{B}\mathbf{S}$ is the Zeeman interaction with electron gyromagnetic ratio $\gamma_e = -g\mu_B$, where $g = 2$ and μ_B is the Bohr magneton. The sum runs over k to include both electrons. The first electron is anisotropically coupled to its spin environment while the second is isotropically coupled, with respective hyperfine coupling tensors

$$A^{(1)} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad A^{(2)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and hyperfine coupling constant given by λ.

Following from work done in [13] we choose as a basis for the electron spin states $\{|0\rangle,|1\rangle\}$, with $|0\rangle$ the ground state and $|1\rangle$ the excited state. From this we can express the raising and lowering operators as

$$S_+ = |0\rangle\langle 1| \qquad S_- = |1\rangle\langle 0|$$

S_z in this basis is

$$S_z = \frac{1}{2}(|0\rangle\langle 0| - |1\rangle\langle 1|)$$

For the nuclear spins, j is the total angular momentum of the N spin-half nuclei, which gives $2j+1$ possible states, from $m = -j, ..., j$ where m is the magnetic quantum number. For N spins the basis can be taken as $\{|j,m\rangle, m = -j, ..., j\}$. In this basis the raising and lowering operators are

$$I_+ = \sum_{m=-j}^{j-1} A^+_{jm} |j,m+1\rangle\langle j,m| \qquad I_- = \sum_{m=-j+1}^{j} A^-_{jm} |j,m-1\rangle\langle j,m|$$

where $A^{\pm}_{jm} = \sqrt{j(j+1) - m(m \pm 1)}$. I_z in this basis is

$$I_z = \sum_{m=-j}^{j} m\,|j,m\rangle\langle j,m|$$

We now look again at the system Hamiltonian for a single electron, and, using $S_xI_x + S_yI_y = \frac{1}{2}(S_+I_- + S_-I_+)$, rewrite it as

$$H_S^{(1)} = \gamma_e B_0 S_z^{(1)} + \lambda(S_+^{(1)}I_-^{(1)} + S_-^{(1)}I_+^{(1)}) + \frac{\lambda}{2}(S_z^{(1)}I_z^{(1)})$$

where we have taken the magnetic field as pointing along the positive z axis. Using the relevant expressions above we arrive at a Hamiltonian that is not diagonal in the basis

$$\{|0,j,j\rangle, |1,j,-j\rangle, |1,j,m\rangle, |0,j,m-1\rangle\}$$

By finding eigenvalues and eigenvectors we can write the new diagonal Hamiltonian in the basis of its eigenvectors

$$\{|0,j,j\rangle, |1,j,-j\rangle, \left|\lambda^-_{jm}\right\rangle, \left|\lambda^+_{jm}\right\rangle\}$$

In this basis the system Hamiltonian looks like

$$H_S^{(1)} = \frac{1}{2}[(\gamma_e B_0 + \lambda j)\,|0,j,j\rangle\langle 0,j,j| - (\gamma_e B_0 - \lambda j)\,|1,j,-j\rangle\langle 1,j,-j|]$$
$$+ \sum_{m=-j+1}^{j} [v_1(j,m)\left|\lambda^-_{jm}\right\rangle\left\langle\lambda^-_{jm}\right| + v_2(j,m)\left|\lambda^+_{jm}\right\rangle\left\langle\lambda^+_{jm}\right|] \quad (2)$$

The diagonal system Hamiltonian for the second electron is found in the same way.

As the evolution of the system is happening at physiological temperatures it is natural to assume the system is embedded in a dissipative bosonic environment [16]. This can be written as

$$H_I = \sum_n [g_n a_n + \bar{g}_n a_n^\dagger] \otimes [\alpha(S_x^{(1)} + S_z^{(1)}) + \alpha(S_x^{(2)} + S_z^{(2)})] \quad (3)$$

where $a_n^\dagger$ and a_n are creation and annihilation operators. The action of these operators will be described in the discussion of the derivation of the master equation below. Typically in the theory of open quantum systems one would use S_x or S_z coupling only, leading to either dissipation or decoherence. As there is currently no evidence which is the dominant interaction we include both here.

2.2. The Transition Operators

Following the approach suggested in [15] the jump operators which describe the transitions between the possible levels the system can occupy are found by taking the commutators

$$[H_S, V_k] = -\omega_k V_k \qquad [H_S, V_k^\dagger] = \omega_k V_k^\dagger$$

where $V = S_x + S_z$ follows from the interaction Hamiltonian. Transition operators V_k and $V_k^\dagger$ for the first electron take the form

$$V_1 = \left|\lambda_{j,j}^-\right\rangle \langle 0, j, j| \,, V_2 = |1, j, -j\rangle \left\langle \lambda_{j,-j+1}^+\right| ...V_k$$

where k here labels the number of transition operators and $|0, j, j\rangle$, $|1, j, -j\rangle$,$\left|\lambda_{jm}^-\right\rangle$,$\left|\lambda_{jm}^+\right\rangle$ is the diagonal basis of the system Hamiltonian for the first electron, as described above. Corresponding transition frequencies ω_1, ω_2 ... ω_k are expressed in terms of the magnetic field and the hyperfine coupling constant where negative frequencies denote energy leaving the system and vice versa. Transition operators and frequencies for the second electron are calculated in a similar manner with the isotropy of the hyperfine interaction in this case resulting in slightly different transition parameters.

The decoherence in the system is found by taking the commutator

$$[H_S, V_0] = 0$$

where the transition frequency of zero reflects the fact that there is no energy flow in or out of the system.

2.3. The Master Equation

In the interaction picture we can rewrite the interaction Hamiltonian using the transition operators as

$$\begin{aligned} H_I(t) = \sum_n [g_n a_n e^{-i\omega_n t} + \bar{g}_n a_n^\dagger e^{i\omega_n t}] \otimes [(\sum_{j=1}^{N_T} \alpha(V_j^{(1)} e^{-iw_j^T t} + V_j^{\dagger(1)} e^{iw_j^T t}) + \alpha V_0^{(1)}) \\ +(\sum_{j=1}^{N_T} \alpha(V_j^{(2)} e^{-iw_j^T t} + V_j^{\dagger(2)} e^{iw_j^T t}) + \alpha V_0^{(2)})] \end{aligned} \tag{4}$$

Here the sum runs to N_T which is the number of transition operators. As the number of nuclei increase the number of transition operators also increase, for example with only a single nucleus in the system there are only five transition operators whereas for all ten nuclei there will be fifty.

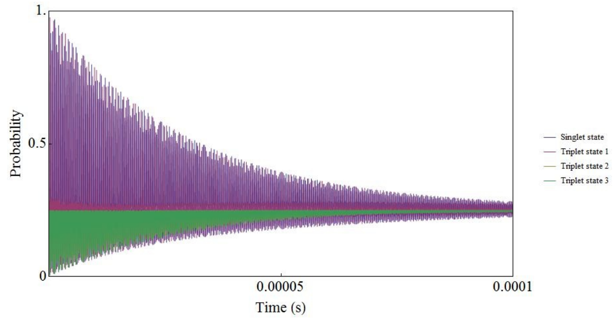

Figure 1. Radical pair dynamics for $j = \frac{1}{2}$

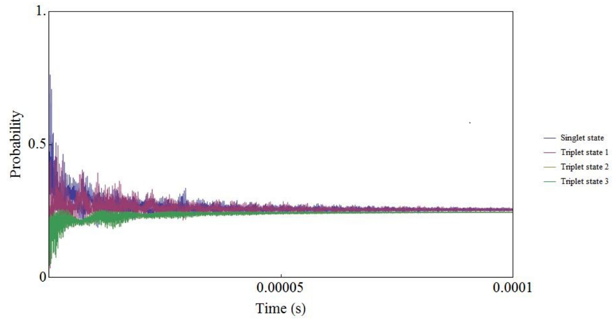

Figure 2. Radical pair dynamics for $j = 1$

In the derivation of the master equation the bath correlation functions determine the rates at which transitions happen, with the only contributions coming from

$$\left\langle a_n a_m^\dagger \right\rangle = \mathrm{Tr}_B[a_n a_m^\dagger \rho_B] = \delta_{nm}(n(\omega_n)+1) \qquad \left\langle a_n^\dagger a_m \right\rangle = \mathrm{Tr}_B[a_n^\dagger a_m \rho_B] = \delta_{nm} n(\omega_n)$$

where $n(\omega_n)$ is the Planck distibution at a specific frequency. After applying the Born-Markov approximations and completing the derivation the master equation can be expressed as

$$\frac{d}{dt}\rho_S^I = \sum_{k=1}^{2}\gamma_D[V_0^{(k)}\rho_S^I V_0^{(k)} - \frac{1}{2}\{V_0^{(k)}V_0^{(k)}, \rho_S^I\}] + \sum_{k=1}^{2}\sum_{j=1}^{N_T}\gamma_j\Big[[V_j^{(k)}\rho_S^I V_j^{\dagger(k)} - \frac{1}{2}\{V_j^{\dagger(k)}V_j^{(k)}, \rho_S^I\}]$$

$$+n(\omega_j^T)[V_j^{(k)}\rho_S^I V_j^{\dagger(k)} - \frac{1}{2}\{V_j^{\dagger(k)}V_j^{(k)}, \rho_S^I\}] + n(\omega_j^T)[V_j^{\dagger(k)}\rho_S^I V_j^{(k)} - \frac{1}{2}\{V_j^{(k)}V_j^{\dagger(k)}, \rho_S^I\}]\Big] \quad (5)$$

where γ_j is the rate of spontaneous dissipation, γ_D the rate of decoherence and

$$n(\omega_j^T) = \frac{1}{\exp\left(\frac{\hbar\omega_j^T}{k_B T}\right) - 1}$$

gives the number of thermal photons (bosons) in a mode of frequency ω_j^T at a given temperature T and k_B is the Boltzmann constant. Here the sum also runs over k in order to include both electrons. The first term describes the decoherence while the last three describe the dissipation. The first of these dissipation terms accounts for spontaneous emission and the last two terms account for stimulated emission and absorption processes respectively, these are due to thermal fluctuations at a given temperature.

3. Solving the Master Equation

3.1. Parameters

In order to investigate the dynamics of the radical pair we took the geomagnetic field to be 47μT [10]. In the relevant literature hyperfine coupling constants for organic molecules range in value. We selected $\lambda = 30$MHz [11] for the purposes of this paper. To accurately apply the model to biological systems we took the temperature to be 300K. To calculate the appropriate frequency-dependent rates of dissipation we used

$$\gamma_j = \frac{\omega_j^3}{3\epsilon_0 \pi \hbar c^3} |d|^2 \tag{6}$$

and by approximating our transitions as those of the equivalent Rydberg atom we were able to calculate the transition dipole moment to be of the order of $10^{10} e a_0$. With these parameters we were then able to simulate the evolution of the radical pair.

3.2. Preliminary Results and Conclusions

The results for two possible variations of the radical pair mechanism can be seen above. Figure 1 demonstrates singlet-triplet mixing where each electron in the pair interacts with a single nuclear spin only, while Figure 2 shows singlet-triplet mixing for the electrons each interacting with two nuclear spins, taking into account the different possible alignments of these spins. In both instances the lifetime of the radical pair is of the order of microseconds, a surprisingly long-lived coherence which nonetheless verifies values arrived at through various methods elsewhere in the literature where coherence times have even been suggested to be of the order of milliseconds [17]. The difference in our approach as compared, for example, to Gauger *et al.*, [10] being that instead of estimating rates from experiment we have derived our model from first principles. The agreement of our derived lifetime with those estimated in the literature suggests the feasibility of our open quantum approach.

Being as there are only two of the ten proposed cases reported here it is too early for any absolute conclusions. One of the intentions of the research is to compare, for example, the effects of half integer as opposed to integer spin for the nuclear environment. As it stands it would appear that dissipation happens slower in the case of half integer spin, even though the lifetimes are comparable. This would have to be verified for all ten cases. The dissipation in the $j = \frac{1}{2}$ case also appears smoother whereas in the $j = 1$ case there is an initial more rapid decline in the singlet state. These results might suggest that the presence of additional nuclear spins or their configuration in relation to the radical pair either enhance or destroy the coherence.

As mentioned already in the introduction to this paper Mouritsen *et al.* have recently published a report gleaned from seven years of double-blind experiments that demonstrated the disorientation of migratory birds under the influence of anthropogenic electromagnetic radiation over a frequency range from 50 kHz to 5MHz [9]. This is important new evidence that radiation at frequencies deemed safe can functionally disrupt complex biological organisms. The use of quantum theory as applied to avian magnetoreception in the radical pair mechanism offers a possible model to explain this effect and, as such, has a valuable contribution to make.

References

[1] Kirschvink J and Gould J 2000 *BioSystems*, **13** 181–201.
[2] Mouritsen H and Ritz T 2005 *Current Opinion in Neurobiology*, **15** 406–414.
[3] Schulten K, Swenberg CE, and Weller A 1978 *Z. Phys. Chem.*, **NF111** 1–5.
[4] Wiltschko W *et al.* 2002 *Nature*, **419** 467–470.
[5] Thalau P, Ritz T, Stapput K, Wiltschko R, Wiltschko W, 2004, *Naturwissenschaften* **92**, 86–90

[6] Ritz T, Thalau P, Phillips JB, Wiltschko R and Wiltschko W, 2004, *Nature* **429**, 177–179
[7] Ritz T, Wiltschko R, Hore PJ, Rodgers CT, Stapput K, Thalau P, Timmel CR and Wiltschko W 2009, *Biophysical Journal Volume* textbf96 3451–3457
[8] Ritz T, Adem S and Schulten K 2000 *Biophys. J.*, **78** 2 707–718.
[9] Mouritsen H *et al* 2014 *Nature*, **509** 353–356.
[10] Gauger EM *et al* 2011 *Physical Review Letters*, **106** 040503.
[11] Rodgers CT and Hore PJ 2009 *PNAS*, **106** 2 353–360.
[12] Tiersch M and Briegel HJ 2012 *arXiv preprint:1204.4179v2 [physics.bio-ph].*
[13] Tarrant J 2011 NITheP Internship Project supervised by Goldstein K, Petruccione F and Sinayskiy I.
[14] Solov'yov IA, Domratcheva T, Shahi ARM and Schulten K 2012 *J. Am. Chem. Soc.*, **134** 18046.
[15] Sergi A, Sinayskiy I and Petruccione F 2009 *Physical Review A*, **80** 1 012108.
[16] Breuer HP and Petruccione F 2002 *The Theory of Open Quantum Systems* Oxford University Press, Oxford.
[17] Walters ZB 2013 *arXiv preprint:1208.2558v3 [physics.bio-ph].*