Quantum coherence and entanglement in the avian compass

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Tremendous efforts are underway to build technologies that harness the deep quantum phenomena of superposition and entanglement. These properties have proven fragile, often decaying rapidly unless cryogenic temperatures are used. Could life have evolved to exploit such phenomena [1]? Certain migratory birds have the ability to sense very subtle variations in the Earth's magnetic field [2]. Here we use recent experimental observations [3] together with the well developed 'radical pair' model of the avian compass [4], and employ a master equation with general decoherence operators in order to examine the system's vulnerability to environmental noise. Remarkably, the room temperature noise tolerance in this natural system appears greater than that of the best man-made molecular radical, N@C$_{60}$ [5]. We find that entanglement, though probably not an essential feature of this process, appears to persist to tens of microseconds, or more.

The intriguing possibility that living systems already use non-trivial quantum effects to optimise some tasks has led to a number of recent suggestions, ranging from the role of quantum physics in natural selection itself [6], through to the observation that 'warm and wet' living systems can embody entanglement given a suitable cyclic driving [7, 8]. In particular, the physics of photosynthesis has received considerable attention; a remarkable idea here is that environmental noise is not only tolerated, but even beneficial [9, 10, 11, 12]. In this letter, we examine a particularly important form of natural information processing known as magnetoreception. Unlike the other senses, the organ of magnetoreception is difficult to find, because organic tissue is mostly transparent to magnetic fields.

There are three main mechanisms explaining biological compasses: electromagnetic induction, ferromagnetism, and radical pairs (RP) [2]. Although the first two are essentially classical effects, there is growing body of evidence in certain species (including birds[4], fruit flies[13] and even plants[14]) for the RP mechanism — which relies on the quantum evolution of a spatially-separated interacting pair of electron spins. This is also supported by the growing field of spin chemistry [15, 16, 17, 18, 19] and recent experiments which were able to demonstrate a chemical compass [20].

We examine the quantum dynamics of the simplest RP model, using an open system master equation approach. Using our model together with recent experimental data, we infer a timescale for the compass mechanism and then use it to estimate a lower bound for the noise tolerance of the constituent quantum spins. Our first conclusion is that the system tolerates noise to a remarkable ex-

tent, greater than that of the best performing man-made molecular system. We speculate that this tolerance is a combination of the inherent robustness of the RP mechanism to specific noise types, together with a high level of protection from other noise sources. We then go on to examine the extent and evolution of entanglement throughout the process, and its likely significance in magnetoreception by the RP mechanism.

There have been a series of experiments in which migratory birds are captured and exposed to artificial magnetic fields[3, 21, 22, 23]. By manipulating a bird's environment and recording its response, one can make inferences about the mechanism of the magnetic sensor. For European Robins, it is found that the birds are only sensitive to the inclination and not the polarization of the magnetic field [21]. Secondly, if the ambient photons are of low energy (i.e. yellow, red), then the birds' preferred direction becomes random. If the ambient light is of higher energy (i.e. blue, green, white), then birds show a strong preference for a specific direction [22]. Finally, a very small oscillating field can disrupt the magnetic orientation behaviour [3, 23]. All these experiments can be explained with the Radical Pair Model.

The intriging idea behind the Radical Pair (RP) Model is that birds 'see' the geomagnetic field. Orientated molecules, embedded in the eye's retina, form a signal pattern dependent on the inclination of Earth's magnetic field (see Fig.1). The simplest RP model describes the spin of two electrons [4, 24] and one nucleus of the molecule. Absorption of a photon and subsequent transfer of one electron to an acceptor part of the molecule, gives rise to the radical pair. Due to the spatial seperation it now becomes meaningful to talk about electron spin entanglement. Without the hyperfine interaction both electrons would precess around the same magnetic field, leaving the singlet state invariant. With the nuclear

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interaction present, the singlet state is no longer an eigenstate of this Hamiltonian leading to an angle dependent singlet-triplet oscillation. In other words, both electrons are subject to different local operations. Recombination occurs either from the singlet or triplet state, leading to different chemical endproducts. The concentration of those products constitutes a macroscopic chemical signal, which, due to the HF interaction, is sensitive to the orientation of the molecule with the magnetic field.

We employ the Hamiltonian corresponding to the system once the two electrons have become separated. The anisotropic hyperfine tensor, coupling the nucleus and electron 1, is conveniently written in its diagonal basis

$$\mathbf{A} = \begin{pmatrix} A_x & 0 & 0 \\ 0 & A_y & 0 \\ 0 & 0 & A_z \end{pmatrix}$$

and we assume an axially symmetric (or cigar-shaped) molecule with $A_z = 10^{-5}$ meV and $A_x = A_y = A_z/2$. This is the simplest assumption that can provide us with directionality. It is also possible to choose a more general tensor with lower symmetry, though such a choice complicates the analysis (necessitating the use of two angles to describe the orientation). Nevertheless, we have compared the two and found that the results are qualitatively similar. The Hamiltonian is

$$H = \hat{I}\mathbf{A}\hat{S}_1 + \gamma\mathbf{B}\cdot(\hat{S}_1 + \hat{S}_2),$$

where $\hat{I}$ is the nuclear spin operator, $\hat{S}_i = (\sigma_x, \sigma_y, \sigma_z)_i$ are the electron spin operators ($i = 1, 2$), $\mathbf{B}$ is the magnetic field vector and $\gamma = \frac{1}{2}\mu_0 g$ = the gyromagnetic ratio with μ_0 being Bohr's magneton and $g = 2$ the g-factor. The factor $1/2$ in the gyromagnetic ratio accounts for the fact that we have a spin one-half system, but we will use Pauli matrices such as $\sigma_z = \text{diag}\{1, -1\}$ etc. Generally
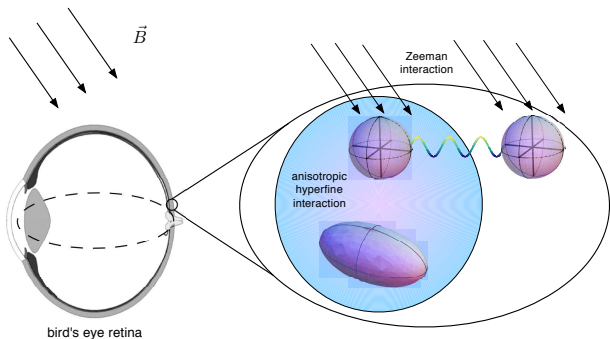

FIG. 1: Schematic of the bird's eye. The back of the eye contains numerous molecules, fixed with specific orientations. In the simplest RP model, each such molecule involves three crucial components (see inset): there are two electrons, initially photo-excited to a singlet state, and a nuclear spin that couples to *one* of the electrons. This coupling is anisotropic, so that the molecule has a directionality to it.

the magnetic field which we employ is

$$\begin{aligned} \mathbf{B} =\ & B_0(\cos\varphi\sin\vartheta, \sin\varphi\sin\vartheta, \cos\vartheta) \\ & + B_{\text{rf}}\cos\omega t(\cos\phi\sin\theta, \sin\phi\sin\theta, \cos\theta), \quad (1) \end{aligned}$$

where $B_0 = 47\ \mu$T is the Earth's magnetic field in Frankfurt [3], and the angles describe the orientation of magnetic field to the basis of the HF tensor. $B_{\text{rf}} = 150$ nT is an additional oscillatory field only applied in our simulations where explicitly mentioned. For resonant excitation with the uncoupled electron spin, $\hbar\omega = 2\gamma B_0$, so that $\nu = \omega/(2\pi) = 1.316$MHz.

Because of the axial symmetry of the HF tensor we can set $\varphi = 0$ and focus on the ϑ in the range $[0, \pi/2]$ without loss of generality. Furthermore, for the oscillatory field, we set $\phi = 0$ and introduce $\kappa = \theta - \vartheta$ as the angle enclosed by oscillatory and static field.

We model the dynamics of the system with a quantum master equation (ME) approach. We employ operators representing the relaxation processes; specifically, we include two 'shelving states' which represent the system having decayed either from an electron singlet state, or from one of the triplet states. Ultimately one of these two forms of relaxation will occur. The three spins span an 8 dimensional Hilbert space to which we therefore add two further levels $|S\rangle$ and $|T\rangle$ for the singlet and triplet decay outcomes, respectively. The populations of these levels will then correspond the singlet and triplet yield.

With the usual definiton of singlet $|s\rangle$ and triplet states $|t_i\rangle$ in the electronic subspace, while $|\uparrow\rangle$ and $|\downarrow\rangle$ describing the states of the nuclear spin, we define the following decay operators:

$$\begin{aligned} P_{S,\uparrow} &= |S\rangle\langle s, \uparrow| \\ P_{T_0,\uparrow} &= |T\rangle\langle t_0, \uparrow| \\ P_{T_+,\uparrow} &= |T\rangle\langle t_+, \uparrow| \\ P_{T_-,\uparrow} &= |T\rangle\langle t_-, \uparrow| \end{aligned}$$

and similarly for the 'down' nuclear states. This gives us a total of two singlet projectors and six triplet projectors. For simplicity and because this choice corresponds exactly to the expression for singlet yield used in previous literature, all eight projectors have the same decay rate $\Gamma_P = k$.

For our model we start from a initial density matrix $\rho(0)$ corresponding to the electrons in a pure singlet state, and a completely mixed nuclear state, i.e.,

$$\rho(0) = id_n \otimes |s\rangle\langle s| = |s, \downarrow\rangle\langle s, \downarrow| + |s, \uparrow\rangle\langle s, \uparrow|.$$

The decay to the two shelving levels is then described using a standard quantum optical ME with above decay operators which effectively discrimate singlet and triplet decay events

$$\dot{\rho} = -\frac{i}{\hbar}[H, \rho]_- + k\left(\sum_{i=1}^{8} P_i\rho P_i^\dagger - \frac{1}{2}\left(P_i^\dagger P_i\rho + \rho P_i^\dagger P\right)\right)(2)$$
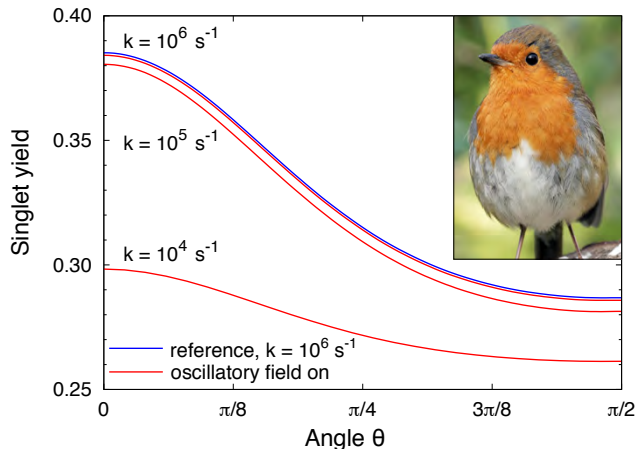
FIG. 2: **Angular dependence of the singlet yield in the presence of an oscillatory field.** The blue reference curve shows the singlet yield obtained in the Earth's magnetic field with $B_0 = 47\mu$T), which is independent of the decay rate k for $k \leq 10^7$ s^{-1}. For better visibility, the blue curve has been shifted upwards by 0.001. The red curves show the singlet field when a 150 nT magnetic field oscillating with a frequency resonant with the Zeeman splitting of the uncoupled electron (1.316 MHz) magnetic field is superimposed perpendicular to the direction of the static field. We see that this only has an appreciable effect on the singlet yield once k is of order 10^4 s^{-1}. Inset: a European Robin (© David Jordan)
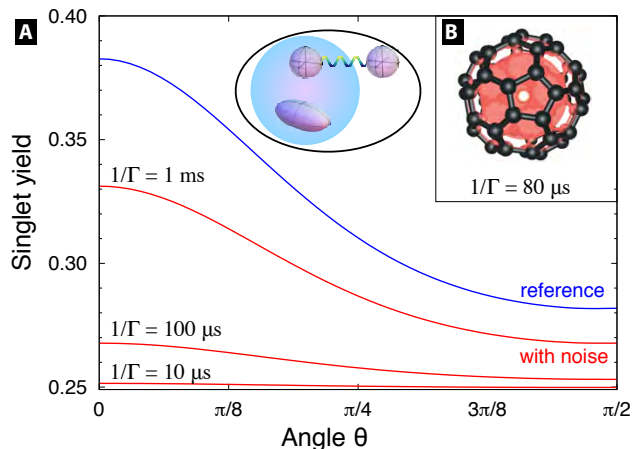

FIG. 3: **Angular dependence of the singlet yield in the presence of noise**. A) All curves were obtained using $k = 10^4$. The blue curve provides a reference in the absence of noise and the red curves show the singlet yield for different noise rates given. It is apparent from the plot that a noise rate $\Gamma > 0.1k$ has a dramatic effect on the magnitude and contrast of the singlet yield. B) The N@C$_{60}$ molecule, which has a measured decoherence time of 80 μs at room temperature.

For comparison, we performed a more general approach with coherent decay from each basis state into its own corresponding bin level, with subsequent projection onto singlet and triplet components. That approach gives rise to identical system dynamics and singlet yield and so is unnecessarily complicated for the problem at hand.

In the absence of noise operators (discussed below) it is possible to compare the predictions of our full ME approach with the singlet yield integral that is commonly used in the prior literature. Specifically, we compare the ultimate population of our singlet 'shelf' $|S\rangle$ with the quantity $\Phi = \int_0^\infty \langle\psi^-|Tr_n(\rho(t))|\psi^-\rangle ke^{-kt}dt$. As expected, we find that in the limit where k is small, i.e. the process takes a long time compared to the rate at which the coherent dynamics take place, the two quantities agree.

We now wish to determine an appropriate choice for our parameter k in Eqn. 2. In Ref. 3, the authors report that a perturbing magnetic field of frequency of 1.316 MHz (i.e. the resonance frequency of the 'remote' electron) can disrupt the avian compass. They note that this immediately implies a bound on the decay rate (since the field would appear static for sufficiently rapid decay). Here we aim to refine this bound on k by considering the oscillating magnetic field *strength* which suffices to completely disorient the bird's compass, i.e. 150 nT. (Indeed,

even a 15 nT field was reported as being disruptive, but to be conservative in our conclusions we take the larger value here.) To model this effect, we activate the oscillatory field component defined in Eqn. 1 and examine the singlet yield (i.e. the eventual population of shelving state $|S\rangle$) as a function of the angle between the Earth's field and the molecular axis. Consistent with the experimental work, we find that there is no effect at such weak fields when the oscillatory field is parallel to the Earth's field. Therefore for our analysis we set the oscillatory field to be perpendicular. The results are shown in Figure 2. We conclude that if the oscillating field is to disorient the bird, as experiments showed, then the decay rate k should be approximately 10^4 s^{-1} or less. For higher values of k (shorter timescales for the overall process) there is no time for the weak oscillatory field to significantly perturb the system; it relaxes before it has suffered any effect. Such a value for the decay rate is consistent with the long RP lifetimes in certain candidate cryptochrome molecules found in migratory birds[25].

Taking the value $k = 10^4$ s^{-1}, we are able to move to the primary question of interest: how robust this mechanism is against environmental noise. There are several reasons for dehorence. For example dipole interaction, electron-electron distance fluctuations and other particles' spin interaction with the electrons will cause decoherence. We describe generic environmental noise with a standard Lindblad ME technique [26], where the following dissipator is additional to the terms in Eqn. 2 above:
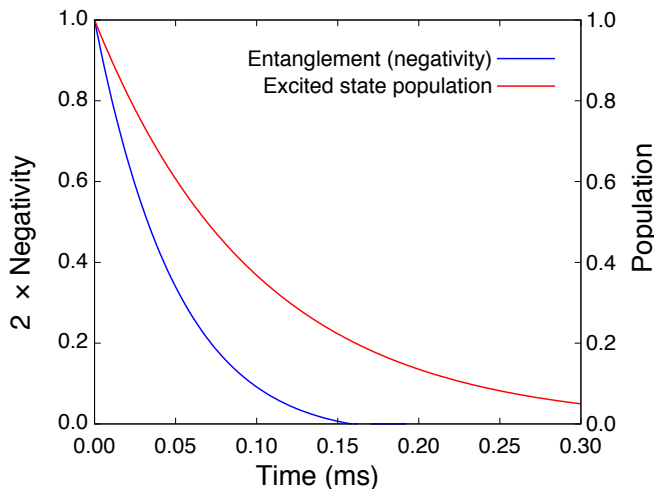
FIG. 4: A plot indicating the decline and disappearance of entanglement in the compass system, given the parameter k and the noise severity Γ defined above. Here the angle between the Earth's field and the molecular axis in $\pi/4$, although the behavior at other angles is similar. The entanglement metric is negativity as defined in the text.

$$\dot{\rho} = \begin{matrix} \text{above} \\ \text{terms} \end{matrix} + \sum_i \Gamma_i \left(L_i \rho L_i^\dagger - \frac{1}{2} \left(L_i^\dagger L_i \rho + \rho L_i^\dagger L_i \right) \right) \ (3)$$

Noise operators L_i are σ_x, σ_y, σ_z for each electron spin individually (i.e. tensored with identity matrices for the nuclear spin and the other electron spin). This gives a total of six different noise operators L_i and we use the same decoherence rate Γ for all of them. We are now in a position to determine the approximate level of noise which the compass suffers, by finding the magnitude of Γ for which the angular sensitivity fails. This is shown in Fig. 3. Conservatively, we can say that when $\Gamma \geq k$, the angular sensitivity is highly degraded. This is remarkable, since it implies the decoherence time of the two-electron compass system is of order $100 \ \mu s$ or more! For comparison, the best laboratory experiment involving preservation of a molecular quantum state has accomplished a decoherence time of $80 \mu s$[5].

It is interesting to ask, what is the significance of entanglement between the spins in the avian compass? Having inferred approximate values for the key parameters, we can plot an appropriate entanglement measure over the course of the process, from the initial singlet generation to the eventual decay. The metric we use is negativity:

$$N(\rho) = \frac{||\rho^{T_A}||}{2}$$

where $||\rho^{T_A}||$ is the trace norm of the partial transpose of the system's density matrix. The transpose is applied to the uncoupled electron, thus performing the natural partitioning between the electron, on one side, and the coupled electron plus its nucleus, on the other. Fig. 4 shows how this negativity evolves under our noise model. Clearly, the initial singlet state is maximally entangled. Under noise, entanglement falls off at a faster rate than the decay of population from the excited state.

Although a physical mechanism for pure dephasing is somewhat questionable, we can apply such noise in our model to investigate the role of entanglement in this process. We have studied the effect of pure dephasing noise on the system and observed far less degradation on angular visibility for a given strength Γ, than the generic x, y, z noise model described above. Interestingly, if we begin the simulation with a completely dephased state: $(|s\rangle\langle s| + |t_0\rangle\langle t_0|)/2$, then the classical correlations are still sufficient for achieving adequate angular visibility. Thus, entanglement does not appear to play an essential role in the efficiency of the avian compass.

In summary, we used an open system master equation approach to examine the implications of recent experimental data on European Robins upon spin coherence in biological magnetoreception. We have been conservative in our line of inference (indeed, we could reasonably have started with an oscillatory field of 15 nT rather than 150 nT) and yet found remarkably long spin coherence times under a general noise model. We further conclude that while entanglement does not appear necessary to the process of avian magnetoreception under the RP mechanism, it is most likely not only present, but persists out to long times.

We note that in the final stages of preparation of this manuscript, a related work has appeared which considers a chemical magnetometer in the context of quantum control [27].

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[1] P. C. W. Davies: *Does quantum mechanics play a nontrivial role if life*, BioSystems **78** , 69-79 (2004).

[2] Sonke Johnsen, Kenneth J. Lohmann: *Magnetoreception in animals*,Physics Today, (2008).

[3] T. Ritz, R. Wiltschko, P. J. Hore, C. T. Rodgers, K. Stapput, P. Thalau, C. R. Timmel, and W.Wiltschko:

Magnetic Compass of Birds Is Based on a Molecule with Optimal Directional Sensitivity, Biophysical Journal, **96** 34513457, (2009).

[4] T. Ritz, S. Adem, K Schulten:*A Model for Photoreceptor-Based Magnetoreception in Birds*, Biophysical Journal Volume **78** , 707-718, (2000).

[5] J. J. L. Morton, A. M. Tyryshkin, A. Ardavan, K. Porfyrakis, S. A. Lyon and G. A. D. Briggs: *Electron spin relaxation of $N@C_{60}$ in CS_2,*, J Chem Phys **124** 014508, (2006)

[6] S. Lloyd: *A quantum of natural selection*, Nature Physics **5**, 164 (2009).

[7] H. J. Briegel, S. Popescu: *Entanglement and intramolecular cooling in biological systems? A quantum thermodynamic perspective*, arxiv: 0806.4552

[8] J.-M. Cai, S. Popescu, H. J. Briegel:*Dynamical entanglement in oscillating molecules*, arXiv:0809.4906

[9] G. S. Engel, T. R. Calhoun, E. L. Read, T.-K. Ahn, T. Mančal, Y.-C. Cheng, R. E. Blankenship, G. R. Fleming: *Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems*, Nature, **446**, 782-786 (2007).

[10] M. Mohseni, P. Rebentrost, S. Lloyd, A. Aspuru-Guzik: *Environment-assisted quantum walks in photosynthetic energy transfer*, J. Chem. Phys. **129**, 174106 (2008).

[11] M.B. Plenio, S.F. Huelga: *Dephasing assisted transport: Quantum networks and biomolecules*, New. J. Phys. **10**, 113019 (2008).

[12] M. Sarovar, A. Ishizaki, G. R. Fleming, K. Birgitta Whaley, *Quantum entanglement in photosynthetic light harvesting complexes*, arXiv: 0905.3787.

[13] R. J. Gegear, A. Casselman, S. Waddell, and S. M. Reppert: *Cryptochrome mediates light-dependent magnetosensitivity in Drosophila*, Nature **454**, 1014 (2008).

[14] M. P. Galland, T. Ritz, R. Wilschko, and W. Wilschko:*Magnetic intensity affects cryptochrome-dependent response in Arabidopsis thaliana*, Planta. **225**, 615 (2006).

[15] C. R. Timmel, K. B. Henbest: *A study of spin chemistry in weak magnetic fields*, Phil Trans Roy Soc London A **362**, 2573-2589, (2004).

[16] Y. Liu, R. Edge, K. Henbest, C. R. Timmel, P. J. Hore, P. Gasta :*Magnetic field effect on singlet oxygen production in a biochemical system*,Chem.Commun., 174176 (2005).

[17] T. Miura, K. Maeda, T. Arai: *The Spin Mixing Process of a Radical Pair in Low Magnetic Field Observed by Transient Absorption Detected Nanosecond Pulsed Magnetic Field Effect*, J. Phys. Chem. A **110**, 4151-4156, (2006).

[18] C T. Rodgers: *Magnetic Field Effects in Chemical Systems*, Pure Appl. Chem., **81**, No.1, 87-111, (2009).

[19] C. T. Rodgers, P.J, Hore: *Chemical magnetoreception in birds: The radical pair mechanism*, PNAS, **106** 2, 353-360, (2009)

[20] K. Maeda et al.:*Chemical compass model of avian magnetoreception*, Nature, **453**, 387 (2008).

[21] W. Wiltschko, R. Wiltschko: *Magnetic compass of European robins* Science, **176** 6264, (1972).

[22] W. Wiltschko, R. Wiltschko: *Magnetic compass orientation in birds and its physiological basis* Naturwissenschaften, 89:445452, (2002).

[23] T. Ritz, P. Thalau, J.B. Philips, R. Wiltschko, W. Wiltschko:*Resonance effects indicate a radical-pair mechanism for avian magnetic compass*, Nature, **429**, 177 (2004).

[24] K. Schulten, C. E. Swenberg, and A. Weller, *A biomagnetic sensory mechanism based on magnetic field modulated coherent electron spin motion*, Z. Phys. Chem. **NF111**, 1 (1978).

[25] Liedvogel et al.:*Chemical Magnetoreception: Bird Cryptochrome 1a Is Excited by Blue Light and Forms Long-Lived Radical-Pairs*, PLoS ONE, **10** e1106, (2007).

[26] M. A. Nielsen and I. C. Chuang *Quantum Computation and Quantum Information, Cambridge* Cambridge University Press 2000.

[27] J.-M. Cai, G. G. Guerreschi, H. J. Briegel: *Quantum control and entanglement in a chemical compass* , arXiv:0906.2383