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Phys. Rev. Lett. **109**, 220501 — Published 27 November 2012

DOI: [10.1103/PhysRevLett.109.220501](https://doi.org/10.1103/PhysRevLett.109.220501)

Entanglement and Sources of Magnetic Anisotropy in Radical Pair-Based Avian Magnetoreceptors

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One of the principal models of magnetic sensing in migratory birds rests on the quantum spin-dynamics of transient radical pairs created photochemically in ocular cryptochrome proteins. We consider here the role of electron spin entanglement and coherence in determining the sensitivity of a radical pair-based geomagnetic compass and the origins of the directional response. It emerges that the anisotropy of radical pairs formed from spin-polarized molecular triplets could form the basis of a more sensitive compass sensor than one founded on the conventional hyperfine-anisotropy model. This property offers new and more flexible opportunities for the design of biologically inspired magnetic compass sensors.

PACS numbers: 03.67.Bg, 82.30.Cf, 87.50.C-

The biophysics and biochemistry that allow birds to sense the direction of the geomagnetic field (25-65 μT) are for the most part obscure. One of the two currently popular hypotheses (the other involves biogenic iron-oxide nanostructures [1]) is founded on magnetically sensitive photochemical reactions in the retina [2]. It is thought that photo-induced radical pairs in cryptochrome, a blue-light photoreceptor protein, may constitute the primary magnetic sensor [3, 4] and a variety of supporting evidence has accumulated over the last few years (reviewed in [5–8]). If this mechanism proves to be correct, it will incontrovertibly come under the umbrella of ‘quantum biology’ [9], as an instance of Nature using fundamentally quantum behaviour – in this case the coherent spin dynamics of radical pairs – to achieve something that would be essentially impossible by means of more conventional chemistry. For this reason, the avian magnetic compass has attracted the attention of quantum information theorists and others wishing to understand the role played by spin-entanglement and to determine whether the techniques of quantum control could shed light on this intriguing sensory mechanism [10–13].

A fundamental property of radical pairs that allows sensitivity to magnetic interactions orders of magnitude smaller than $k_{\text{B}}T$ is that their chemical transformations conserve electron spin. Radical pairs are therefore created with the same spin-multiplicity (singlet or triplet) as their precursors. Owing to electron-nuclear hyperfine (HF) interactions, neither singlets nor triplets are, in general, eigenstates of the spin Hamiltonian. Consequently, the radical pair starts out in a non-stationary superposition which evolves coherently at frequencies determined by the HF interactions and also, crucially for a magnetic sensor, by the electronic Zeeman interactions with an external magnetic field [5]. Spin decoherence and spin relaxation can be slow enough to allow even an Earth-strength magnetic field to modulate the spin dynamics and hence alter the yields of the products formed by spin-selective reactions [14–16]. The anisotropy of the HF interactions leads to anisotropic reaction yields and

hence, in principle, a magnetic direction sensor [14, 17].

The singlet state – the initial state of the radical pairs formed photochemically in cryptochromes [4, 18] – is entangled:

$$|S\rangle\langle S| = \frac{1}{2}|\alpha_1\beta_2\rangle\langle\alpha_1\beta_2| + \frac{1}{2}|\beta_1\alpha_2\rangle\langle\beta_1\alpha_2| - \frac{1}{2}|\alpha_1\beta_2\rangle\langle\beta_1\alpha_2| - \frac{1}{2}|\beta_1\alpha_2\rangle\langle\alpha_1\beta_2| \quad (1)$$

(α and β are the $m_S = \pm\frac{1}{2}$ spin states of the two unpaired electrons). But other initial states are also known to result in magnetically sensitive chemistry [19]: do they too need to be entangled or is it sufficient if they are ‘merely’ coherent? Or is neither entanglement nor coherence necessary for a magnetic compass?

Questions such as these have been addressed in two recent papers. Briegel and his group noted that randomly generated separable (i.e. not entangled) initial states could result in reaction product yields more anisotropic than those produced from an initial singlet state under the same conditions [10]. The other study, by Benjamin and colleagues, reached similar conclusions by analysing model radical pair systems, finding significant product yield anisotropies for the separable initial state [11]

$$\frac{1}{2}|S\rangle\langle S| + \frac{1}{2}|T_0\rangle\langle T_0| = \frac{1}{2}|\alpha_1\beta_2\rangle\langle\alpha_1\beta_2| + \frac{1}{2}|\beta_1\alpha_2\rangle\langle\beta_1\alpha_2| \quad (2)$$

in which T_0 is the $m_S = 0$ triplet spin state.

Here we examine the role of initial entanglement and attempt to clarify the various sources of magnetic anisotropy that might form the basis of a radical pair compass sensor in birds.

Initial radical pair states. We start by identifying chemically feasible initial electron spin states. Geminate radical pairs are normally formed by spin-conserving chemical reactions so that at the moment of their creation they are either pure singlet, described by the initial electron spin density matrix $\hat{\rho}_0 = \hat{\rho}_0(S) = |S\rangle\langle S|$, or pure triplet $\hat{\rho}_0 = \hat{\rho}_0(T) = \frac{1}{3}(\hat{1} - |S\rangle\langle S|)$. Occasionally, singlet and triplet formation channels operate in parallel [20], in

which case $\hat{\rho}_0$ is a weighted sum of $\hat{\rho}_0(\text{S})$ and $\hat{\rho}_0(\text{T})$, i.e. of $|\text{S}\rangle\langle\text{S}|$ and $\hat{1}$:

$$\begin{aligned}\hat{\rho}_0 &= \mu\hat{\rho}_0(\text{S}) + (1 - \mu)\hat{\rho}_0(\text{T}) \\ &= \frac{1}{3}(4\mu - 1)|\text{S}\rangle\langle\text{S}| + \frac{1}{3}(1 - \mu)\hat{1}\end{aligned}\quad (3)$$

Eq. (3) is also appropriate for ‘F-pairs’ [19] formed from radicals with uncorrelated spins (i.e. $\mu = \frac{1}{4}$). The operators $|\text{S}\rangle\langle\text{S}|$ and $\hat{1}$ and their linear combinations are invariant to rotations in the electron spin-space, meaning that all states that can be written in the form of Eq. (3) are isotropic. Any $\hat{\rho}_0$ that cannot be so written is necessarily anisotropic.

Significantly different initial states can occur when the radical pair comes from a molecular triplet precursor formed by intersystem crossing (ISC). This route is common in photochemical reactions of the general type:



in which the final step that creates the triplet radical pair could be homolysis (as shown) or inter- or intramolecular electron transfer, hydrogen atom transfer, etc. The formation of $\text{T}[\text{AB}]^*$ from $\text{S}[\text{AB}]^*$ requires the creation of spin angular momentum at the expense of orbital angular momentum. This process is mediated by spin-orbit coupling and is anisotropic in the molecular frame [21]. That is, the three triplet sub-levels of $\text{T}[\text{AB}]^*$ are differentially populated leading to a spin polarization in the molecular frame that is passed to the radical pair on its formation. The initial state of the radical pair may be written:

$$\hat{\rho}_0 = \sum_{q=x,y,z} p_q |\text{T}_q\rangle\langle\text{T}_q| \quad (5)$$

in which the triplet sub-state $|\text{T}_q\rangle$ ($q = x, y, z$) is spin polarized in the $q = 0$ principal plane of the triplet zero-field splitting [19, 22] (see also Supplemental Materials [23]). The initial populations of the triplet sub-states, p_q , are determined by the electronic wavefunctions of $\text{S}[\text{AB}]^*$ and $\text{T}[\text{AB}]^*$ and the spin-orbit coupling. Anisotropic ISC is known to be responsible for a variety of spin-chemical and spin-polarization phenomena [19, 22, 24, 25].

Aside from linear combinations of Eqs (3) and (5), there are no other commonly occurring initial conditions for radical pairs subject to weak magnetic fields.

Minimal radical pair model. Insights into the spin dynamics of the various initial states just identified can be obtained from a minimal model [26] comprising two electron spins one of which is coupled to a spin- $\frac{1}{2}$ nucleus (e.g. ^1H). The HF interaction is axially anisotropic with an axially parameter defined in terms of the principal HF components: $\alpha = (A_\perp - A_\parallel)/(2A_\perp + A_\parallel)$ [17, 23]. Two cases are considered specifically: $\alpha = 0$ (isotropic) and $\alpha = -1$ (the anisotropic interaction that results in the largest reaction yield anisotropy for this 3-spin system

[13]). To account for the chemical reactivity of the radical pair, we adopt the ‘exponential model’ [26] in which singlet and triplet states react spin-selectively with the same first-order rate constant, k , to form distinct products. The quantum yields of these competing reactions are calculated using standard methods [17, 23, 26]. The two quantities of interest are Φ_S , the fractional yield of the product formed via the singlet pathway, referred to here as the ‘reaction yield’, and $\Delta\Phi_\text{S}$, the magnitude of its anisotropy: $\Delta\Phi_\text{S} = \max\{\Phi_\text{S}\} - \min\{\Phi_\text{S}\}$. The variation of Φ_S with the orientation of the radical pair in a 50 μT magnetic field is the basis of the compass sensor.

To begin, we choose the isotropic initial condition in Eq. (3) together with an anisotropic HF interaction ($\alpha = -1$). In the not unrealistic limit, $|a| \gg \omega \gg k$ [17, 27]:

$$\Phi_\text{S} = \frac{1}{4} + \frac{1}{12}(4\mu - 1)\cos^2\theta; \quad \Delta\Phi_\text{S} = \frac{1}{12}|4\mu - 1| \quad (6)$$

where a is the isotropic HF coupling constant, ω is the strength of the magnetic field, and θ is the angle between the symmetry axis of the HF tensor and the magnetic field vector. Φ_S is anisotropic, and therefore potentially suitable as a magnetic compass, except when the initial state is a statistical ($-\frac{1}{4} : -\frac{3}{4}$) mixture of singlet and triplet ($\mu = \frac{1}{4}$). The maximum anisotropy ($\Delta\Phi_\text{S} = \frac{1}{4}$) occurs when the initial state is pure singlet ($\mu = 1$); for a pure triplet initial state ($\mu = 0$), $\Delta\Phi_\text{S}$ is smaller by a factor of three. These results were verified by exact numerical simulations [23].

To quantify the entanglement of the various initial electron spin states considered here, we use the ‘concurrence’ $C(\hat{\rho}_0)$ proposed by Wootters [28] for a two-qubit density operator. For the initial condition in Eq. (3), $C(\hat{\rho}_0)$ is $2\mu - 1$ when $\mu > \frac{1}{2}$ and zero when $\mu \leq \frac{1}{2}$ [23]. Thus, a singlet–triplet mixture must contain more than 50% singlet for the initial state to be entangled. The pure triplet state ($\mu = 0$) is not entangled, but as we have just seen it gives rise to a significantly anisotropic reaction yield.

We now turn to a different initial condition, a linear combination of Eq. (3) (with $\mu = 0$) and Eq. (5) (with $p_x = p_y = 0$; $p_z = 1$):

$$\hat{\rho}_0 = \eta|\text{S}\rangle\langle\text{S}| + (1 - \eta)|\text{T}_z\rangle\langle\text{T}_z| \quad (7)$$

i.e. an anisotropic mixed singlet-triplet initial state in which the triplet component is 100% polarized along the molecular z -axis. In the same limit as before ($|a| \gg \omega \gg k$), but now for an *isotropic* HF interaction:

$$\Phi_\text{S} = \frac{3}{8} - \frac{1}{4}(1 - \eta)\sin^2\theta; \quad \Delta\Phi_\text{S} = \frac{1}{4}(1 - \eta) \quad (8)$$

where θ is now the angle between the triplet polarization axis (z) and the magnetic field vector. The anisotropy is maximised when $\eta = 0$ (pure $|\text{T}_z\rangle$ triplet, $\Delta\Phi_\text{S} = \frac{1}{4}$) and is at a minimum when $\eta = 1$ (pure singlet, $\Delta\Phi_\text{S} = 0$). Once again, these expressions were confirmed by numerical simulations [23]. We note that Eqs (6) and (8) predict identical maximum directional responses.

The reaction yield is isotropic when $\eta = 1$ because then both the initial state $|S\rangle\langle S|$ and the spin-Hamiltonian are isotropic. The angle-dependence in Eq. (8) clearly arises because the spin dynamics depend on the direction of the magnetic field with respect to the quantization (z) axis of the initial $|T_z\rangle$ state [29]. The concurrence of the density operator in Eq. (7) is $2\eta - 1$ when $\eta \geq \frac{1}{2}$ and $1 - 2\eta$ when $\eta \leq \frac{1}{2}$. Pure singlet and pure $|T_z\rangle$ triplet thus have the same degree of entanglement but lead to very different $\Delta\Phi_S$.

Hitherto we have taken the reaction rates of the singlet and triplet states (k_S and k_T) to be identical. Once this restriction is lifted, it is even possible to have magnetic field effects when the initial state is a statistical mixture of singlet and triplet: $\hat{\rho}_0 = \frac{1}{4}\hat{\rho}_0(S) + \frac{3}{4}\hat{\rho}_0(T) = \frac{1}{4}\hat{1}$. To illustrate this point, simulations for the minimal radical pair with an anisotropic HF coupling are included in the Supplemental Materials [23]. $\Delta\Phi_S$ is non-zero except when $k_S = k_T$. That is, a radical pair can exhibit magnetic compass properties even when its initial electron spin state is neither entangled nor coherent. In this case the coherence arises during the spin evolution as a result of the differential reactivity of the singlet and triplet states.

Relation between compass properties and entanglement. A complex picture emerges from these simple considerations. Entangled initial states can give small or zero reaction yield anisotropy. Non-entangled initial states can lead to appreciable anisotropy. With two sources of anisotropic reaction yields – the initial state and the HF interactions – it is tricky to assess whether entanglement, or coherence in a given basis, is essential for magnetic compass action. For example, replacing $\hat{\rho}_0 = |S\rangle\langle S|$ (Eq. (1)) by $\hat{\rho}_0 = \frac{1}{2}|S\rangle\langle S| + \frac{1}{2}|T_0\rangle\langle T_0|$ (Eq. (2)) [11] not only removes the initial entanglement, and the coherence in the $\{|\alpha_1\beta_2\rangle, |\beta_1\alpha_2\rangle\}$ basis, it also introduces anisotropy that was not present in $|S\rangle\langle S|$. Similarly, most randomly chosen initial states [10] are anisotropic and some will give a larger $\Delta\Phi_S$ than does $|S\rangle\langle S|$ under identical conditions. In short, it appears that initial entanglement is not a particularly helpful concept when assessing the sensitivity of a radical pair compass; nor is it straightforwardly illuminating to consider the behaviour of artificial initial states.

A radical pair compass based on initial-state anisotropy. The above considerations suggest an alternative compass design in which the directionality comes from the initial condition rather than the HF interactions. In the minimal model, the initial state that gives the largest reaction yield anisotropy is $\hat{\rho}_0 = |T_q\rangle\langle T_q|$ where $q = x, y, z$ [23]. We therefore compare $|T_q\rangle\langle T_q|$ with $|S\rangle\langle S|$ using exact numerical simulations [23]. The possibility that spin-polarized triplet radical pairs might offer some advantage over singlets has been noted before but without realistic suggestions for the chemical origin of

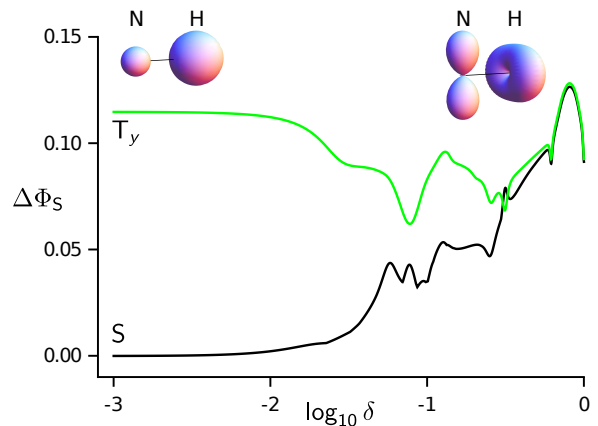


FIG. 1. (color online). Reaction yield anisotropy, $\Delta\Phi_S$, calculated [23] for a radical pair in which one radical contains a ^1H nucleus (spin- $\frac{1}{2}$) and a ^{14}N nucleus (spin-1). $k = 10^6 \text{ s}^{-1}$ and $\omega = 50 \text{ } \mu\text{T}$. The HF coupling parameters (in mT) are: $a_H = -0.8$; $T_{H,xx} = 0.8 \delta$; $T_{H,yy} = -0.6 \delta$; $T_{H,zz} = -0.2 \delta$; $a_N = 0.4$; $T_{N,xx} = -0.5 \delta$; $T_{N,yy} = -0.5 \delta$; $T_{N,zz} = 1.0 \delta$. $\hat{\rho}_0 = |S\rangle\langle S|$ (black) and $\hat{\rho}_0 = |T_y\rangle\langle T_y|$ (green). Also shown are representations of the hyperfine tensors for $\delta = 0$ (left) and $\delta = 1$ (right).

such initial states [29].

Figure 1 shows the reaction yield anisotropy of a radical pair inspired by the flavin adenine dinucleotide radical, FADH^\bullet , formed photochemically in cryptochromes [30]. One radical contains ^1H and ^{14}N nuclei with isotropic HF couplings approximately equal to those of the proton and nitrogen (H5 and N5 [23]) in the central ring of the tricyclic isoalloxazine ring system of FADH^\bullet (these being the two largest HF interactions in FADH^\bullet [31]). The anisotropic components of the two interactions were also modelled on FADH^\bullet , but with a uniform scaling by a factor of δ (defined in the figure caption), in the range 0.001 – 1.0. For the smaller values of δ , the spin-Hamiltonian is essentially isotropic. When the initial state $\hat{\rho}_0$ is a 100% spin-polarized triplet, $\Delta\Phi_S$ has significant magnitude for all values of δ . In contrast, when $\hat{\rho}_0 = |S\rangle\langle S|$, $\Delta\Phi_S$ is essentially zero until the HF tensors become significantly anisotropic ($\delta \approx 0.1$). By the time the HF anisotropy is comparable to that in FADH^\bullet (i.e. $\delta \approx 1.0$), both initial states give very similar directional responses to the 50 μT applied magnetic field. This suggests that a spin-polarized triplet geminate radical pair with isotropic HF interactions could operate as a compass sensor just as well as an initial singlet state with anisotropic HF interactions.

Indeed, there are circumstances in which, other things being equal, the anisotropy of the initial state might offer a more sensitive compass than one based on HF anisotropy. Biologically plausible radical pairs are likely to have many magnetic nuclei (mostly ^1H and ^{14}N) with differently aligned HF tensors. Simulations suggest that the directional information potentially available from in-

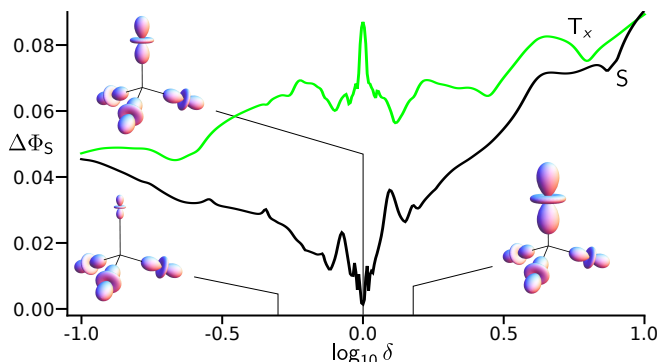


FIG. 2. (color online). Reaction yield anisotropy, $\Delta\Phi_S$, calculated [23] for a radical pair in which one radical contains four ^1H nuclei, all of which have axially anisotropic HF interactions with $a = 0$. The symmetry axes of the four HF tensors are directed towards the vertices of a tetrahedron. Three of the tensors have principal values: $T_{11} = T_{22} = -1.0$, $T_{33} = 2.0$ mT. The fourth is identical apart from a uniform scaling of the principal values by a factor δ . $k = 10^6 \text{ s}^{-1}$ and $\omega = 50 \text{ } \mu\text{T}$. $\hat{\rho}_0 = |\text{S}\rangle\langle\text{S}|$ (black) and $\hat{\rho}_0 = |\text{T}_x\rangle\langle\text{T}_x|$ (green). Also shown are representations of the hyperfine tensors for $\delta = 0.5$, $\delta = 1.0$, and $\delta = 1.5$.

dividual HF tensors tends to be scrambled in a multi-nuclear radical pair, resulting in a greatly reduced $\Delta\Phi_S$ [23]. A simple illustration of this effect is given in Fig. 2 which shows simulations of the reaction yield anisotropy for a spin system in which one of the radicals contains four spin- $1/2$ nuclei with tetrahedrally disposed axial HF tensors. When all four tensors are identical, the reaction yield anisotropy for $\hat{\rho}_0 = |\text{S}\rangle\langle\text{S}|$ vanishes, by symmetry. However, when the symmetry is reduced to C_{3v} , by scaling the principal components of one of the HF tensors by a factor δ (defined in the figure caption), the value of $\Delta\Phi_S$ increases but does not approach that afforded by $\hat{\rho}_0 = |\text{T}_x\rangle\langle\text{T}_x|$ until $|\log_{10} \delta|$ reaches ca. 1.0. Thus it appears that the compass properties of a radical pair with many mutually cancelling HF interactions could be ‘rescued’ by having a triplet, rather than a singlet, initial condition, provided the triplet is spin-polarized by anisotropic intersystem crossing.

Discussion. Having identified the initial spin-states in which radical pairs may be formed by chemical reaction, we revisited earlier attempts to determine the importance of entanglement and coherence as determinants of the anisotropic responses of radical pair magnetoreceptors. It appears that the use of artificial initial spin-states for this purpose [10, 11] is somewhat confounded by their intrinsic anisotropy, the effects of which may dominate the anisotropy conferred by the HF interactions. From these considerations it emerges that the anisotropy of radical pairs formed from spin-polarized molecular triplets could form the basis for a magnetic compass that is more sensitive than one based on the conventional HF-anisotropy model [2] in particular when the HF couplings are not

strongly anisotropic or when the individual effects of multiple HF anisotropies tend to counteract one another.

Would a triplet radical pair compass be compatible with cryptochrome as the primary magnetoreceptor? In the cryptochromes investigated hitherto (bacterial [16], plant [4] and frog [18]), flavin-tryptophan radical pairs are formed as *singlets*. However, avian cryptochromes may behave differently, and there are precedents for triplet radical pairs in other flavoproteins [32, 33]. Superficially, it appears that flavins may be suitable for an initial triplet-state compass: intersystem crossing in both flavin mononucleotide and riboflavin at near-neutral pH results in fractional populations of the zero-field triplet sub-levels of $p_x = \frac{1}{3}$, $p_y = \frac{2}{3}$, $p_z = 0$ [34]. Within the minimal model discussed above, this would lead to a high reaction yield anisotropy, two-thirds that of the maximum possible [23].

The use of spin-polarized triplets should open new channels for the design of bio-inspired molecular devices for sensing the direction of weak magnetic fields.

We thank DARPA (QuBE: N66001-10-1-4061) and the EPSRC for financial support.

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