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Radical-pair model of magnetoreception with spin–orbit coupling

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Abstract. The mechanism used by migratory birds to orientate themselves using the geomagnetic field is still a mystery in many species. The radical pair mechanism, in which very weak magnetic fields can influence certain types of spin-dependent chemical reactions, leading to biologically observable signals, has recently imposed itself as one of the most promising candidates for certain species. This is thanks both to its extreme sensitivity and its capacity to reproduce results from behavioral studies. Still, in order to gain a directional sensitivity, an anisotropic mechanism is needed. Recent proposals have explored the possibility that such an anisotropy is due to the electron–nucleus hyperfine interaction. In this work we explore a different possibility, in which the anisotropy is due to spin–orbit coupling between the electron spin and its angular momentum. We will show how a spin–orbit coupling-based magnetic compass can have performances comparable with the usually studied nuclear hyperfine based mechanism. Our results could thus help researchers actively

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looking for candidate biological molecules which may host magnetoreceptive functions, both to describe magnetoreception in birds as well as to develop artificial chemical compass systems.

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Growing evidence suggests quantum coherence plays an important role in hitherto unexplained biological phenomena [1]. The two most widely known examples are the recent observation of coherent energy transport in photosynthetic bacteria, that could help explain the almost unitary efficiency of energy harvesting [1, 2] and the role of coherence in the navigation ability of migrating birds [1, 3–5].

It has been proposed [4, 6, 7] that electron spin could act as a detector for the Earth's geo-magnetic field (of magnitude $0.5\,\mathrm{G} \equiv 50\,\mu\mathrm{T}$). The mechanism, called the radical pair mechanism (RPM), works as follows: upon absorption of a photon, a molecule (or part of a molecule, in cryptochrome for example) is photochemically excited, to form a radical pair with another nearby molecule (an electron is transferred to the excited acceptor from a donor molecule). This radical pair inherits its singlet or triplet nature from the molecular precursors. The Earth's magnetic field then causes oscillations of the electron spins. As radical pairs have a finite lifetime, and certain biological processes could be sensitive to the difference in metastable chemical products that result depending on the singlet or triplet nature of the radical pair at the time of decay, it has been proposed that the whole system may then be able to transduce information of the Earth's magnetic field direction into chemical signals that the bird can perceive.

The RPM model, while originally proposed as a possible explanation for magnetoreception several decades ago [4], recently gained renewed attention because it can explain some of the results of recent behavioral experiments. In these experiments the application of radio frequency fields [8, 9] or the alteration of ambient light conditions [10, 11] disrupted avian navigation. The radical pair model has also been strengthened by the discovery of a candidate radical pair system with the photo-receptor cryptochrome [12–17]. In addition, neuroanatomical evidence [18] strongly suggests that a vision-mediated pathway underlies magnetoreception in European robins, further strengthening the notion that photo-activated [10, 11] radical pairs resident in the eye could be the mechanism underlying a certain type of magnetoreception (recent evidence strongly suggests there may several different mechanisms at play [5]).

However, the radical pair model still faces some challenges. As yet, sufficient sensitivity to external fields has yet to be confirmed in *in vitro* experiments on candidate radical pairs. This is particularly demanding in terms of describing the disruption of the navigational sense of birds who are exposed to oscillating magnetic fields [8, 9, 11, 19] as weak as 15 nT. Gauger *et al* [20] showed that while the compass itself is immune to certain types of phase noise (and thus can, in some sense, operate in a classical limit), coherence must be retained for 10 s of μs, and ideally more than 100 μs, to explain this disruptive effect. A recent analysis found that the interaction of the electron spins with a spin-bath can stabilize coherence and also provide another alternative route to achieve sensitivity to the angle of the external field [21]. Finally, the RPM model demands some sort of *anisotropic* interaction to be directionally sensitive, and requires some order in the alignment of radical pairs in at least one axis [22–24], though recent work suggests, because of the selective way radical's may be photo-excited, ordering may be unnecessary [5, 25].

Most of the discussion in this topic is based on the same assumption that the anisotropy is given by the nuclear spin hyperfine interaction [4, 8]. Still, this is only one of the possible mechanisms that could lead to the needed anisotropic interaction. In this paper we investigate the role of another candidate mechanism, namely the spin–orbit coupling (SOC) in radical pair systems. Depending on the type of radical pair, SOC can either cause anisotropic g-factors (in distant radical pairs) or spin-selective transition rates (in close, or contact, radical pairs); in both cases producing a level of anisotropy suitable for a chemical compass to operate.

Anisotropic g-factors have been discussed elsewhere as a possible source of magnetic field sensitivity [20, 26–28]. In particular, Hogben *et al* [26] critically discussed SOC in cryptochromes when either dioxygen or superoxide form one half of the radical pair. The advantage of this assumption is that oxygen has little nuclear hyperfine interaction, thus enabling the combination of oxygen with the flavin adenine dinucleotide (FAD) cofactor in cryptochrome to realize the highly anisotropic nuclear spin model needed to explain the disruptive effect of external oscillating fields (the so-called Zeeman resonance). However, they argued that SOC in radical pairs involving oxygen in solution lead to rapid loss of spin-coherence due to periodic unquenching of the SOC. If the radicals are immobilized in a lattice, this effect could be suppressed. However, the strong nuclear hyperfine interaction in FAD would still dominate over anisotropy from the SOC, and hence the normal nuclear hyperfine model would probably apply. In this work we consider both the ideal situation where the SOC dominates, and in the final section when both SOC and hyperfine interactions play a role.

The rest of this paper is organized as follows: after having introduced, in section 1.1, the general features of a RPM, we will summarize, in section 1.2, the results of [20] for a RPM based on nuclear spin interaction, that has been extensively studied in the literature and which has been termed the 'reference probe model'. In sections 1.3 and 1.4 we will then investigate the efficiency of SOC-based RPM. In section 1.3 we will see in what ways a SOC-induced anisotropic g-factor can cause an efficient response to external fields. Of particular interest is the fact that very weak Δg effects (as are expected in organic radical pairs) can have a large magnetic-field sensitivity if the lifetime approaches 100 μs, giving a possible practical explanation for why the radical-pairs may need such a long lifetime [27]. We emphasize that this is not a limiting factor in the SOC model, when taken in context with the standard model of radical-pair reactions, as, when the oscillating field behavioral experiments [8, 9] are taken into account, these standard models also demand either such a long lifetime [20] or that the magneto-reception mechanism is extremely sensitive to minute changes in product yield.

The alternative is that some different models or mechanisms may arise which remove or reduce this demand [5]. In section 1.4 we discuss the effects of SOC-induced spin-dependent recombination rates that are found in contact radical pairs. We will conclude in section 2 with a comparison of the various mechanisms and suggestions for future investigations.

1. Results

1.1. General framework of the radical pair mechanism

In the RPM [4, 6] a radical pair is formed due to an optical excitation process and the associated transfer of an electron from a donor to an acceptor molecule. The excess electrons retain their initial correlation (which may be assumed to be a singlet, but can also be a triplet state without a significant change in the traditional RPM effect).

The correlated spins then evolve under the joint influence of the geomagnetic field $\boldsymbol{B}$ and of other magnetic interactions (e.g. nuclear spins, molecular fields or orbital momentum). If the evolution of the two spins is different, e.g. because one of the additional interactions is inhomogeneous (e.g. if only one of the radicals has appreciable nuclear hyperfine interactions), it will cause an oscillation between singlet and triplet states. Eventually the electrons will undergo a spin-selective recombination. The yield of the reaction is then sensitive to the dynamics of the two spins, and it can be used to measure the direction of $\boldsymbol{B}$.

The effect of the external magnetic field on the electrons is described by the Hamiltonian

$$H_B = \frac{1}{2}\mu_{\mathrm{B}}(\boldsymbol{B}\cdot\bar{g}_1\cdot\hat{\sigma}_1 + \boldsymbol{B}\cdot\bar{g}_2\cdot\hat{\sigma}_2), \tag{1}$$

where $\bar{g}_1$ and $\bar{g}_2$ are tensors describing the generally anisotropic g-factors. For clarity we have used Pauli spin matrices here, hence the factor of $1/2$. To simplify matters, an axial symmetry is usually assumed; then the magnetic field vector can be written as (including a possible external time-dependent contribution) $\boldsymbol{B} = B_0(\sin\theta, 0, \cos\theta) + B_{\mathrm{rf}}\cos\omega_{\mathrm{d}}t\,(\sin\theta', 0, \cos\theta')$, for $\theta, \theta' \in [0, \pi/2]$.

In addition, the radical pair is affected by several decoherence channels. The primary channel is spin-selective recombination into the singlet and triplet product states $|\mathbf{s}\rangle$ and $|\mathbf{t}\rangle$. This occurs when an excess electron returns from the acceptor radical to the donor radical, and can be generally described in the Lindblad form by the superoperator

$$\Sigma[\rho] = -\sum_{\alpha}\kappa_\alpha\left[\frac{1}{2}s_\alpha s_\alpha^\dagger\rho - s_\alpha^\dagger\rho s_\alpha + \frac{1}{2}\rho s_\alpha s_\alpha^\dagger\right], \tag{2}$$

where the s_α are jump operators describing the model under examination. Additional dephasing and amplitude noises can be included in the model [20], which may arise from sources like dipole interactions, magnetic fluctuators in the biological environment and so on. We will discuss this in the final section.

One possible biologically detectable signal (though others have recently been proposed [27]) is the triplet or singlet yield. For example, in the normal Liouville treatment the singlet yield is

$$\Phi(\theta) = \kappa\int_0^\infty S(t)\,\mathrm{d}t, \tag{3}$$

where $S(t) = \mathrm{Tr}[Q^S \rho(t)]$, κ is the radical pair decay rate and Q^S is the projector onto the singlet states. Here, we solve the master equation, $\dot{\rho}(t) = \mathcal{L}[\rho(t)]$, where $\mathcal{L}$ is $\mathcal{L} = -\mathrm{i}[H, \cdot] + \Sigma$, and simply observe the occupation of the 'shelving' state $|\mathbf{s}\rangle$, which in the long-time limit is equivalent to the singlet yield. For a given compass model to be deemed as sufficiently sensitive one needs a large change in $\Phi(\theta)$ as a function of θ. Thus often the quantity of interest is the sensitivity

$$\Phi_\mathrm{D} = \Phi(\pi/2) - \Phi(0), \quad |\Phi_\mathrm{D}| \leqslant 1. \tag{4}$$

In the following sections we will calculate the sensitivity Φ_D both for static and oscillating magnetic fields, for three different anisotropy-inducing mechanisms (where, in absence of any anisotropy, $\Phi_\mathrm{D} = 0$).

1.2. Radical pair mechanism with nuclear hyperfine interaction

1.2.1. Hyperfine interaction. The nuclear hyperfine interaction (assuming only one of the electrons is significantly affected by the nuclear spin [7, 29]) is described by

$$H_\mathrm{Hyp} = \hat{\sigma}_1 \cdot \frac{\mathbf{A}}{2} \cdot \hat{\sigma_I}, \tag{5}$$

where $\hat{\sigma_I}$ is the nuclear spin operator, assumed for simplicity to be a single spin such that σ_I is a Pauli spin operator, and $\mathbf{A} = \mathrm{diag}(A_x, A_y, A_z)$ is the anisotropic hyperfine coupling tensor. The factor of $1/2$ allows us to directly compare the magnitude of $A/g\mu_\mathrm{B}$ to B_0 in units of μT. We also omit an additional factor of $1/2$, normally associated with the nuclear spin operator, to enable this comparison. This has been termed the reference-probe model [7], as it represents an extremely simple example with just a single nuclear spin degree of freedom, which produces a very sensitive compass against which more complex real models of radical pairs can be tested.

The spins thus evolve under the conjoint effect of the Hamiltonians in equations (5) and (1), that now takes the form (setting the g-factor as isotropic, $g = 2$)

$$H_B = \mu_\mathrm{B}\, \boldsymbol{B} \cdot (\hat{\sigma}_1 + \hat{\sigma}_2). \tag{6}$$

The Lindblad superoperator describing spin-selective recombination, and taking into account the nuclear spin states, now reads

$$\Sigma_\mathrm{Hyp}[\rho] = -\kappa \sum_{\alpha,\beta} \left[\frac{1}{2} s_{\alpha\beta} s^\dagger_{\alpha\beta} \rho - s^\dagger_{\alpha\beta} \rho s_{\alpha\beta} + \frac{1}{2} \rho s_{\alpha\beta} s^\dagger_{\alpha\beta} \right], \tag{7}$$

where $\alpha = 1, 2, 3, 4$ indexes the electronic spin states, $\beta = \uparrow, \downarrow$ the nuclear spin states and

$$s_{1\beta} = |S, \beta\rangle \langle \mathbf{s}|, \quad s_{2\beta} = |T_+, \beta\rangle \langle \mathbf{t}|, \tag{8}$$

$$s_{3\beta} = |T_0, \beta\rangle \langle \mathbf{t}|, \quad s_{4\beta} = |T_-, \beta\rangle \langle \mathbf{t}|. \tag{9}$$

We assume that the radical pairs in the singlet and triplet states have the same recombination rate, or decay rate, κ.

1.2.2. Results for static fields. The hyperfine coupling tensor was found [20] to give a large sensitivity when $A_x = A_y = A_z/2$, and $A_z/g\mu_\mathrm{B} \gg B_0$, hence the nuclear spin acts like a strong reference field. For $B_0 = 47\,\mu$T, $A_z/g\mu_\mathrm{B} = 174\,\mu$T, one obtains a sensitivity

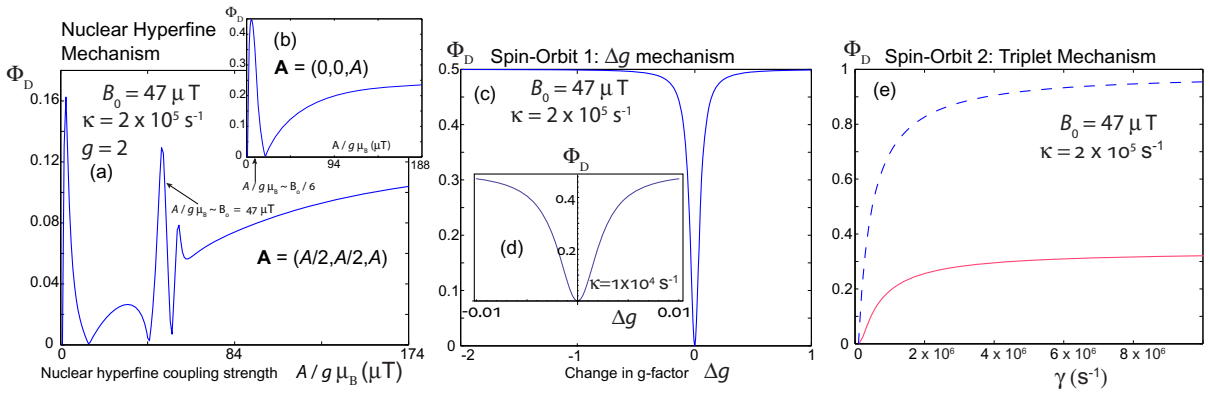

Figure 1. The sensitivity of all three RPMs, as a function of the appropriate parameter in each case. The values of the other parameters are indicated on the figures. For (a) and (b), the nuclear hyperfine mechanism, the sensitivity is shown as a function of the strength of the coupling to the nuclear spin. Panel (a) shows the just slightly anisotropic tensor, while (b) is the fully anisotropic tensor. The largest sensitivity, as discussed by Cai *et al* [30], appears for $A/g\mu_B \approx B_0/6$, but is slightly shifted due to the different value of κ employed here. Note that the resonances in (a) and (b) for small and intermediate values of A become sharper, and some are shifted, if κ is reduced. Figures (c) and (d) show the SOC Δg mechanism sensitivity as a function of Δg. Figure (c) is for the same κ as figure (a) whereas (d) is for a much longer-lived radical, and thus a much smaller κ. Such long-lived radicals are very sensitive to even small changes in g-factor. Panel (e) shows the sensitivity for the triplet mechanism, as a function of the singlet–triplet mixing rates $\gamma = \gamma_+ = \gamma_-$, for an initial pure triplet state T_0 (blue dashed curve) and a full mixture of all three triplet states (red curve).

of $\Phi_D \approx 0.1$ (see figure 1(a)). For weaker field strengths we see several sharp resonances, as the hyperfine coupling becomes comparable to the geomagnetic field. The width of these resonances are strongly dependent on the rate κ, and may not be useful for magnetoreception as they would be susceptible to small changes in the nuclear hyperfine coupling strength and κ [20]).

Recently, Cai *et al* [30] showed that an optimization of the RPM, over all parameters in the reference-probe model, gives a maximum sensitivity of $\Phi_D \approx 0.4$. This maximum occurs for a highly an-isotropic hyperfine tensor of $A_x = A_y = 0$ and $A_z/g\mu_B \approx B_0/6$ (in our definition of the nuclear hyperfine Hamiltonian, which differs from Cai *et al* by a factor of 1/2). However, as with the resonances in figure 1(a), this optimal point changes as a function of κ. A similar maximum is shown in figure 1(b), for a highly an-isotropic tensor.

1.2.3. Results for oscillating fields. The primary evidence for the RPM stems from its ability to explain behavioral experiments on certain avian species. This includes photo-sensitivity: the test subjects could not navigate when deprived of certain frequencies of light [10, 11]. It also includes disruption of the navigation sense under the influence of very weak (15–150 nT) radio-frequency oscillating magnetic fields [8, 9]. In the model we described earlier this is represented by the term B_{rf}. One can conservatively choose $B_{rf} = 150$ nT, to match the experimental

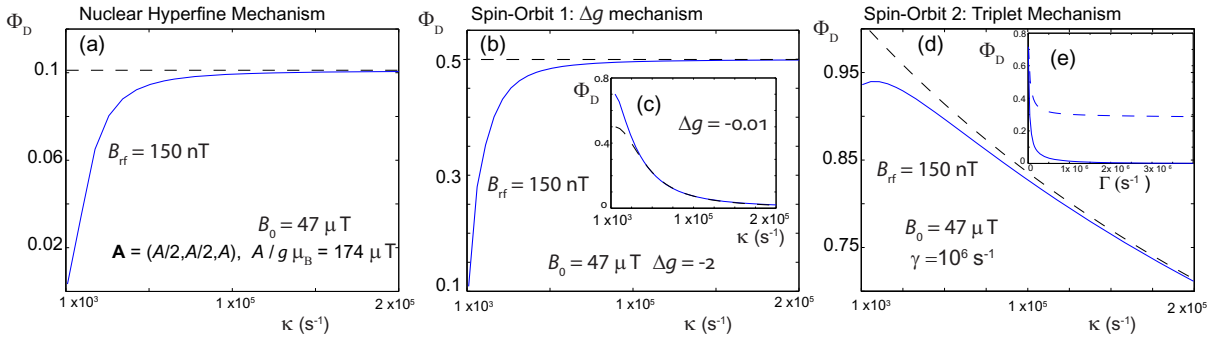

Figure 2. The sensitivity Φ_D as a function of recombination rate κ, with an external field strength $B_0 = 47\,\mu$T and both $B_{rf} = 0$ (black dashed lines) and $B_{rf} = 150$ nT (blue curves). In all cases κ was cut off at a lower value of $1 \times 10^3\,s^{-1}$. Panel (a) is for a strong nuclear hyperfine coupling $A_z/g\mu_B = 174\,\mu$T, with a semi-anisotropic tensor, which exhibits an almost complete loss as $\kappa \to 10^3\,s^{-1}$ (these results are identical to those in [20]). Panel (b) shows the sensitivity for the SOC Δg mechanism with $\Delta g = -2$. The disruption due to the oscillating field is similar to the hyperfine one, with significant changes in the sensitivity only appearing for remarkably small κ. Panel (c) shows the effect of the oscillating field for $\Delta g = -0.01$. In contrast to the previous examples, the sensitivity is increased when the oscillating field is switched on. More precisely, and not shown in the figures, for small κ switching on the oscillating field reduces the yield of $\Phi(0)$ while that of $\Phi(\pi/2)$ is generally unaffected. Arguably this could also lead to a disruption of the magnetic sense, though in a different way than the 'normal' flattening of the $\Phi(\theta)$ profile [20]. (d) The sensitivity for the triplet mechanism, for a pure initial triplet state. In this case the overall behavior is slightly different from the hyperfine and Δg mechanisms, with the overall sensitivity increasing as κ is decreased, and the rf-field having less of a profound effect on the magnitude. The inset (e) shows the effect of an additional dephasing and decoherence on the triplet mechanism. The solid line is for six equal additional decoherence operators (see main text), while the dashed line is just dephasing in the σ_z basis, and in both cases $\kappa = 2 \times 10^5\,s^{-1}$.

conditions (though disruption was seen also for much smaller field magnitudes), $\omega_d = \mu_B g B_0/\hbar$, which for $B_0 = 47\,\mu$T gives $\omega_d/2\pi = 1.32$ MHz, and in all of the following results we set $\theta' = \theta + \pi/2$, as this maximizes the effect of the time-dependent contribution. This induces Rabi-oscillations in the 'free' electron state at a frequency proportional to the field strength B_{rf}. This is an extremely slow frequency compared to the other system parameters, and for it to have any effect on the singlet yield it is immediately clear that κ must be exceptionally slow. For any non-negligible effect on the singlet yield [20] one needs a rate $\kappa < 10^4\,s^{-1}$, which corresponds to a lifetime exceeding $100\,\mu$s. This is shown in figure 2(a), where the yield is unaffected by the oscillating field unless κ is exceptionally small. Now that we have set the stage with the traditional nuclear hyperfine model of the radical-pair compass, we will next outline how SOC can fulfill a similar role.

1.3. Radical pair mechanism with spin–orbit coupling (SOC) in distantly bound radical pairs

1.3.1. SOC and anisotropic g-factor. The Hamiltonian responsible for SOC is of the form [31]

$$H_{\mathrm{SOC}} = \sum_j \zeta_j \mathbf{L}_j \mathbf{S}_j, \tag{10}$$

where $\mathbf{L}_j$ and $\mathbf{S}_j$ are, respectively, the orbital momentum and the spin operator of electron j and the sum is over the valence electrons. The value ζ_j is termed the SOC constant and it includes the screening effect due to the presence of inner electrons. The effect of the Hamiltonian in equation (10) depends upon the symmetry of the system. In atoms the valence orbitals along different axes (e.g. P_x, P_y and P_z) are degenerate and transitions between them thus couple with the spin degree of freedom. In molecules, this degeneracy is usually lifted, and the SOC effect can thus be quenched (its strength depends in this case on the ratio between the SOC constant and the splitting between the orbitals). Of particular interest for us is the case in which the degeneracy is only partially lifted, as in axial molecules, in which the two orbitals orthogonal to the molecular axis (that we will assume to be z) are still degenerate. In these molecules the SOC effect will thus be quenched in the x–y plane but present along the z direction, leading to an anisotropic g-factor. Physically we can visualize this phenomenon as a current that flows around the z-axis, due to the fact that the unpaired electron can freely jump between the degenerate x and y orbitals. This current will then create a magnetic field along the z-axis, that will couple with the z component of the electron spin.

The interaction of the radical pair with an external magnetic field will thus be described by the Hamiltonian with an anisotropic g-factor. According to the reference-probe model logic, we will study the sensitivity of the system using, in equation (1), a g-factor of the form

$$\begin{aligned} \bar{g}_1 &= 2, \\ \bar{g}_2 &= (2, 2, 2 + \Delta g), \end{aligned} \tag{11}$$

that is, only the second radical has a significant g-factor anisotropy.

In most organic molecules such effects are quenched ($\Delta g \approx 10^{-2}$–10^{-3}), but in simpler radical pairs [26], or radicals containing heavy atoms, they can be extremely large ($\Delta g \approx 2$). The two spins will thus evolve under the effect of equation (1) with the anisotropic g-factor defined in equation (11) and they will be subject to a spin-selective recombination, analogous to the case of the hyperfine interaction, described in the Lindblad form as

$$\Sigma_{\mathrm{SOC}}[\rho] = -\kappa \sum_\alpha \left[\frac{1}{2} s_\alpha s_\alpha^\dagger \rho - s_\alpha^\dagger \rho s_\alpha + \frac{1}{2} \rho s_\alpha s_\alpha^\dagger \right], \tag{12}$$

where $\alpha = 1, 2, 3, 4$, $s_1 = |S\rangle\langle \mathbf{s}|$, $s_2 = |T_+\rangle\langle \mathbf{t}|$, $s_3 = |T_0\rangle\langle \mathbf{t}|$ and $s_4 = |T_-\rangle\langle \mathbf{t}|$.

1.3.2. Results for static fields. In order to measure the efficiency of the anisotropic g-factor as compass we solve the full numerical model described above. We have also compared our numerical results to the analytical results from the Liouville equation approach in [30] (which is easily adapted to include the anisotropy in the g-factor). In figure 1(c) we show the sensitivity Φ_{D}, as a function of Δg for $\kappa = 2 \times 10^5\,\mathrm{s}^{-1}$, and in (d) $\kappa = 1 \times 10^4\,\mathrm{s}^{-1}$. We find that in figure 1(c) a large sensitivity $\Phi_{\mathrm{D}} = 0.5$ arises for $|\Delta g| > 0.5$.

Interestingly, if $|\Delta g|$ is small, one needs a smaller κ to saturate the sensitivity. For $\kappa = 1 \times 10^4\ \mathrm{s}^{-1}$, as shown in figure 1(d), the magnetic sensitivity is saturated for values as

small as $|\Delta g| \approx 0.01$. One could argue that this could explain the need for the exceptionally long lifetime of radical pairs. In the nuclear hyperfine case, a long lifetime is arguably unnecessary to saturate the compass sensitivity, but is needed to explain the disruption effects of weak oscillating fields. Of course, this disruptive effect is not a functional necessity of the compass, so the difficulty is in explaining why the radical pairs would have a long lifetime which is functionally not useful. An alternative scheme was recently proposed [27] to give this long lifetime (and, incidentally, coherence time) a functional role. The dependence we show here, of the sensitivity of a SOC mechanism with a small Δg on the long lifetime of the radical pair, could, in principle, also explain this phenomenon.

1.3.3. Results for oscillating fields. As with the nuclear hyperfine mechanism, the SOC must also be able to explain the rather demanding results of the behavioral experiments. The behavior of a general Δg mechanism under oscillating fields was presented in the supplementary information of [20], albeit without reference to the source of the anisotropy. Here we make a similar examination and find that for large Δg, as with the nuclear hyperfine field, that the SOC-compass is only sensitive to the external field for very small κ (see figure 2(b)). For the interesting case of a small shift $\Delta g = -0.01$, we show in figure 2(c) that the effect of the oscillating field is different from the large Δg and nuclear hyperfine case. As κ becomes small the sensitivity is increased in the presence of the oscillating field. Arguably this could still cause a disruptive behavioral effect, depending in exactly what way the singlet yield is transduced into a directional signal by the avian host.

A similar argument was recently made in [32], where they noted that the application of additional weak static fields, causing disruption of the magnetic sense, does not reduce the sensitivity of the normal reference-probe model, but shifts the overall 'curve', implying there is a 'window' of operation. With static fields, it was observed that the disruptive effect was temporary, and eventually the birds adjusted and were once more able to navigate [33, 34]. If very weak anisotropic g-factors, mediated by SOC, is the cause of magnetic sensitivity in these species, then a similar argument may be applicable. The effect of oscillating fields would not suppress the sensitivity, as in the nuclear hyperfine or strong Δg mechanisms, but would shift the sensitivity curve out of an operational window. Of course, if such an effect is directly analogous to that of static fields, then also the disruptive effect should be temporary.

1.4. Radical pair mechanism with SOC in contact radical-pairs

1.4.1. Triplet mechanism. The second possible SOC effect is the so-called triplet mechanism [35] that can occur in closely bound, or contact, radical pairs. As in this case the pair can be considered as a single system, the SOC Hamiltonian in equation (10) can give rise to transitions involving at the same time a variation of the orbital and spin degrees of freedom. This results in an anisotropic, incoherent transition from the triplet states to the singlet ground state. For our purposes we model this as follows: unlike in the previous cases, we assume the radical pair is created either in one of the triplet states or an equal mixture of all the triplet states. The triplet states are then coupled to each other because of the external magnetic field and in turn undergo their normal recombination into the triplet product state at a rate κ, as before. The effect of the spin–orbit interaction then in this case is to induce an incoherent inter-system crossing transition from the triplet states to the singlet recombination product or ground state, the rate or frequency of which is dependent on the original triplet state. Since the relative triplet state

occupations depend on the orientation of the external field, this creates, as with the previous mechanisms, a singlet state product which is sensitive to the angle of the external field.

We include this in the standard radical pair model, akin to the approach taken in [35], by allowing for spin-selective transitions from the triplet states to the singlet product. The Lindblad superoperator thus reads

$$\Sigma_{\mathrm{Tot}} = \Sigma_{\mathrm{SOC}} + \Sigma_{\mathrm{TM}}, \tag{13}$$

where Σ_{SOC} is defined in equation (12) and describes the usual channels and Σ_{TM} is given by

$$\Sigma_{\mathrm{TM}}[\rho] = -\sum_{\alpha} \gamma_{\alpha} \left[\frac{1}{2} s_{\alpha} s_{\alpha}^{\dagger} \rho - s_{\alpha}^{\dagger} \rho s_{\alpha} + \frac{1}{2} \rho s_{\alpha} s_{\alpha}^{\dagger} \right], \tag{14}$$

with $\alpha = -, 0, +$, $\mathrm{s}_{+} = |T_{+}\rangle\langle \mathbf{s}|$, $\mathrm{s}_{-} = |T_{-}\rangle\langle \mathbf{s}|$ and $\mathrm{s}_0 = |T_0\rangle\langle \mathbf{s}|$. Note in this case the g-factors are now isotropic.

1.4.2. Results for static fields. Generally, any anisotropic choice of γ_{α} rates will introduce an angular dependence. We follow the example of [35] and choose $\gamma_0 = 0$, $\gamma_{+} = \gamma_{-} = \gamma$. The exact dependence or form of these parameters will depend on the microscopic features of the given radical, thus this choice is again in the spirit of an ideal 'reference-probe' model. In figure 1(e) we plot the sensitivity as a function of γ. The red lower curve shows the sensitivity for an initial complete mixture of the three triplet states, while the blue curve shows the sensitivity for an initial pure triplet state T_0, which produces an overall much larger variation in magnitude.

1.4.3. Results for oscillating fields. Again, this mechanism, if one were to use it as an explanation of the magnetoreception phenomena, must be able to explain the disruptive-field effect. Figure 2(d) shows the singlet products for an initial pure triplet state, both with and without the time-dependent external field switched on $B_{\mathrm{rf}} = 150\,\mathrm{nT}$. In this mechanism the sensitivity itself is still a function of decreasing κ, as with a zero κ the one-way triplet to singlet transition will completely dominate the long-time occupations, ultimately giving unit occupation of the singlet yield. The effect of the oscillating field is weaker than that seen for the nuclear hyperfine and Δg mechanisms, but in commonality with those other mechanisms it occurs for $\kappa < 1 \times 10^4\,\mathrm{s}^{-1}$.

We also point out that the 'zero-field effect' may play a role in this triplet mechanism. This is a spin–spin interaction effect, in the presence of SOC, which splits the triplet states even under zero-external magnetic field. For a radical-pair of dioxygen and the FAD cofactor in cryptochrome, Hogben *et al* [26] found that the zero-field effect prevented the normal nuclear hyperfine interaction from being able to explain the presence of external oscillating fields. Depending on the particular radical-pair one is studying this may also apply to our discussion here, and negatively affect the efficacy of the triplet mechanism.

1.4.4. Role of coherence and noise. The role of quantum coherence in the RPM is quite subtle. As discussed in the introduction [20], one can introduce strong pure dephasing which does not affect the efficacy of the magnetic compass (though other choices of decoherence do reduce the sensitivity drastically). However, even pure dephasing alone does effect the ability of the external oscillating field to disrupt the compass. Some studies [30] have shown that the environment can improve the sensitivity of the compass response, with a maximum for an intermediate level of arbitrary decoherence (both dephasing and dissipation). For the

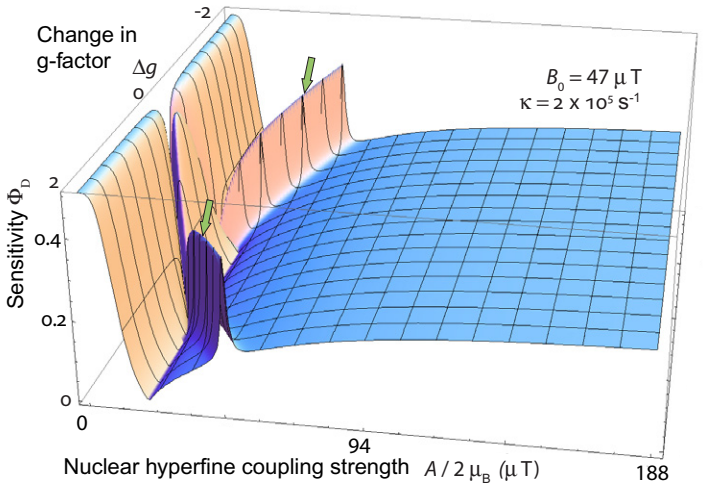

Figure 3. Sensitivity Φ_D as a function of Δg and nuclear field strength $A/g\mu_B$, $B_0 = 47\,\mu$T and $\kappa = 2 \times 10^5\,s^{-1}$. Generally speaking, the combined effect of SOC and nuclear hyperfine interaction only reduces the sensitivity, but for small hyperfine coupling there are two peaks, indicated by the green arrows, where the combination of both effects can increase the sensitivity.

normal hyperfine mechanism this has been discussed in great detail in other works [20, 30, 36]. For the Δg mechanism one expects similar results, and some examples were discussed in the supplementary information of [20].

For the triplet mechanism we make a similar analysis, and introduce a set of six Lindblad operators

$$L_i[\rho] = \Gamma_i \left[\sigma_i^\alpha \rho \sigma_i^\alpha - \rho\right], \tag{15}$$

where $i = 1, 2$; α indicates spin 1 or 2 and $\alpha = x, y, z$. We find, as shown in figure 2(e), that large 'general' decoherence (i.e. equal rates on all six Lindblad terms), has a detrimental effect on the sensitivity of the compass. Dephasing in the σ_z basis alone reduces but does not completely eliminate the sensitivity even for relatively large rates (though this is different from the dephasing in the eigenbasis which was shown to have no effect on the compass [20]). The 'increase' in sensitivity with environmental noise discussed in other works typically arises for for arbitrary, possibly non-orthogonal, angles in equation (4), and we do not discuss that case here.

1.5. Combined SOC and nuclear hyperfine

One may imagine that in many realistic situations nuclear hyperfine and SOC co-exist [26, 31]. In earlier radical-pair experiments it was generally noted that the combination of both effects tends to reduce the magnetic sensitivity of the reactions. Using the analytical results of Cai *et al* [30] we can plot the sensitivity as a function of both Δg and nuclear hyperfine coupling strengths (however only for the hyperfine tensor $(0, 0, A_z)$). We show the resultant singlet yield sensitivities in figure 3. In the parameter regimes where the sensitivity is highest for each individual mechanism alone we find that the introduction of the other mechanism

generally reduces the sensitivity. While there is a large maximum for intermediate levels of nuclear hyperfine coupling where non-zero SOC increases the sensitivity (as marked by the green arrows on the figure) if κ is decreased these maxima become increasingly 'narrow', and may not represent a robust parameter regime. These maxima are broadened somewhat if one performs a maximization of the sensitivity over all angles in $\Phi(\theta)$, but the behavior remains qualitatively the same.

1.6. Distinguishing SOC and nuclear hyperfine mechanisms

One may be able to distinguish a mechanism based on strong SOC Δg effects from the others (nuclear hyperfine, triplet mechanism, weak SOC Δg) by further behavioral experiments with oscillating fields. Till now a disruptive effect was found [8, 9] when the oscillating field frequency matched the Zeeman splitting of a radical with $g \approx 2$. Further experiments may find a disruptive effect when the frequency matches the energy splitting of the other radical with strong Δg. Such disruptive effects are expected to be difficult to observe in radicals with nuclear hyperfine interactions due to the large spread of very weak resonances one expects in that case, when the true nuclear hyperfine interaction is with many nuclear spins (see the supplementary information of [9] for a detailed discussion). Similarly, we expect the weak Δg mechanism should not exhibit any additional resonances, and thus disruption should only occur for the approximately free Zeeman splitting frequency in that case. A full investigation of the effect of a disruptive oscillating fields as a function of frequency, for a range of strong anisotropic Δg tensors, and an analysis of the strength of these effects is a possible interesting avenue of future work.

Secondly, the weak Δg and triplet mechanisms may be distinguishable from the strong Δg and nuclear hyperfine mechanisms because of the way the disruptive effect of the oscillating field affects the singlet yield in those cases. We have shown in this work, for the weak Δg and triplet mechanisms, that the yield is altered under applied oscillating fields, but not entirely suppressed. As pointed out earlier, it has been found that the application of static fields caused a temporary disruption of the magnetic sense [33, 34]. In the standard radical-pair model static fields were seen to cause a shift of the singlet yield [32], not a suppression. Logic dictates that if birds were able to adapt to the disruptive effect of oscillating fields, this would be an argument in favor of a shift, not a suppression, of the yield, as seen with static fields, and thus may indicate in favor of the weak Δg or triplet mechanisms. Whether such adaptation was looked for in experiments so far [8, 9] is not clear.

2. Discussion

We have shown that spin–orbit effects can, in principle, induce strong magnetic field sensitivity and satisfy the experimental criteria needed as a candidate for magnetoreception. Our main result is that the Δg mechanism becomes more prominent as the radical recombination rate κ is reduced, providing an explanation for why such a small κ might be needed by the RPM.

If the lifetime of the spin-coherence of the radicals is truly 100 μs then it seems possible that the Δg mechanism could arise and play a role even in organic molecules. As discussed in the introduction, the prime candidate so far is the FAD radical in cryptochrome. However, such a radical is not a good host of a SOC mediated mechanism as FAD has substantial nuclear hyperfine interactions [25], which will inevitably dominate over any weak SOC effects

[37, 38], even if additional inorganic radicals are involved [26]. This does not mean that SOC in an alternative radical is not a feasible mechanism for hosting the magnetic sense of birds, as it is also difficult to explain the frequency-selective disruptive effect of oscillating fields [8, 9] if both radicals contain strong nuclear hyperfine interactions, and additional difficulties arise even if FAD forms a radical pair with dioxygen or superoxide (which have no nuclear hyperfine interactions) [26].

This ultimately leaves open the question of the precise host radical for the magnetoreception mechanism. Our results would primarily be relevant for a radical-pair with no, or minimal, nuclear hyperfine interaction, particularly inorganic radicals where SOC effects are large, though our results suggest even a very weak Δg anisotropy can induce a magnetic field sensitivity on the lifetimes apparently demanded by some behavioral experiments [8, 9]. In addition, apart from providing an alternative route to a magnetically-sensitive radical pair reaction to describe avian magneto-reception, our results may help in identifying a broader range of radical pairs which can be used in artificial weak-magnetic-field sensors [39, 40].

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