Quantum Control and Entanglement in a Chemical Compass

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The radical-pair mechanism is one of the two main hypotheses to explain the navigability of animals in weak magnetic fields, enabling, e.g., birds to see Earth's magnetic field. It also plays an essential role in spin chemistry. Here, we show how quantum control can be used to either enhance or reduce the performance of such a chemical compass, providing a new route to further study the radical-pair mechanism and its applications. We study the role of radical-pair entanglement in this mechanism, and demonstrate its intriguing connections with the magnetic-field sensitivity of the compass. Beyond their immediate application to the radical-pair mechanism, these results also demonstrate how state-of-the-art quantum technologies could potentially be used to probe and control biological functions.

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Introduction.—It is known that many species, including birds, insects, and mammals, use the Earth's magnetic field for orientation and navigation [1]. To explain this remarkable ability, two main hypotheses have been proposed: a magnetite-based mechanism and a radical-pair biochemical reaction mechanism [1]. Since the radical-pair mechanism (RPM) was first proposed in pioneering work by Schulten *et al.* [2], a chemical compass model for migratory birds, based on such a mechanism [3], has been widely studied. Evidence suggests that the RPM is indeed linked to the avian magnetoreception [4]. It was recently demonstrated in spin-chemistry experiments that a photochemical reaction can act as a compass even in a magnetic field as weak as the geomagnetic field [5]. The underlying mechanism in such a chemical compass is clearly of quantum mechanical nature. However, the detailed role of quantum interactions, in giving rise to entanglement and (de)coherence, is little understood [6]. On the other hand, one can observe growing interest in the role of quantum coherence for biological processes in general [7], and specifically in photosynthesis [8]. A deeper understanding of the role of quantum mechanics in biology will eventually come along with the ability to control biological processes at the level of individual molecules. In physics, various kinds of quantum control techniques have been developed, specifically in the field of quantum information processing and quantum metrology [9,10]. The question thus naturally arises, to what extent can these or similar techniques be applied to test and refine certain biophysical hypotheses, such as the chemical compass model for animal magnetoreception? Can we use quantum technologies that have primarily been developed to control man-made microscopic systems, to study the behavior of living things—e.g., birds, fruit flies, or plants—in a detectable way?

In our work, aiming at the above questions, we will revisit the RPM and the chemical compass model using concepts and techniques from quantum information. The RPM can serve either as a magnetometer or as a compass, depending on the molecular realization. For simplicity, we will refer to both cases as "compass" in the following. First, we demonstrate how quantum control ideas can be applied to experiments in spin chemistry. We propose several protocols that can be used to either enhance or suppress the function of a chemical compass. Assuming that the RPM provides the correct explanation for magnetoreception of certain species, we predict that they would lose or regain their orientability in appropriately designed experiments using such quantum control protocols—given that such experiments could be carried out safely. Our calculations show that the RPM can not only detect weak magnetic fields, but it is also sensitive to quantum control even without the presence of a static magnetic field. These results offer a new means to study experimentally the RPM, also in comparison with other mechanisms such as those in man-made magnetometers [11,12].

Second, we investigate whether entanglement is a necessary ingredient in animal magnetoreception, which seems appealing in the light of the important role this concept has gained in fundamental discussions on quantum mechanics and its wider implications. As the sensitivity of the chemical compass depends on the initial state of the radical pair, it is natural to ask whether it needs to be quantum mechanically entangled—thereby excluding any conceivable classical mechanism—or whether classical correlations would be sufficient. We find that the answer largely depends on the radical-pair lifetime. For specific realizations of the RPM, e.g., those in recent spin-chemistry experiments [13], entanglement features prominently and can even serve as a signature of the underlying spin dynamics. However, when the radical-pair lifetime is extremely long, as is believed to be the case in the molecular candidate for magnetoreception in European robins [14], entanglement does not seem to be significant.

Radical-pair mechanism.—We consider a photochemical reaction that starts from the light activation of a photoreceptor, followed by an electron transfer process; two unpaired electrons in a spin-correlated electronic singlet state are then carried by a radical pair. The effective environment of a radical pair mainly consists of their individual surrounding nuclei. The Hamiltonian of a radical pair is of the form [15]

$$H = \sum_{k=1,2} H_k = -\gamma_e \vec{B} \cdot \sum_k \vec{S}_k + \sum_{k,j} \vec{S}_k \cdot \hat{\lambda}_{k_j} \cdot \vec{I}_{k_j}, \qquad (1)$$

where $\gamma_e = -g_e \mu_B$ is the electron gyromagnetic ratio, $\hat{\lambda}_{k_j}$ denote the hyperfine coupling tensors, and $\vec{S}_k$, $\vec{I}_{k_j}$ are the electron and nuclear spin operators, respectively.

The initial state of a radical pair is assumed to be the singlet state $|\mathbb{S}\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$, which subsequently suffers from decoherence through the hyperfine interactions with the environmental nuclear spins. The initial state of the nuclear spins at room temperature can be approximated as $\rho_b(0) = \bigotimes_j \mathbb{I}_j / d_j$, where d_j is the dimension of the jth nuclear spin. The charge recombination of the radical pair goes through different channels, depending on the electron-spin state (singlet or triplet). In particular, the yield of products formed by the reaction of singlet radical pairs can be calculated as $\Phi_s(t) = \int_0^t r_c(t) f(t) dt$ [15], where $r_c(t)$ is the radical reencounter probability distribution, and $f(t) = \langle \mathbb{S} | \rho_s(t) | \mathbb{S} \rangle$ is the fidelity between the electron-spin state $\rho_s(t)$ and the singlet state. The ultimate activation yield $\Phi_s \equiv \Phi_s(t \to \infty)$ in cryptochrome is believed to affect the visual function of animals [3].

We have followed the established theory for the dynamics of the RPM [15,16] and computed the full quantum dynamics of the combined system of electron spins and nuclear spins. Technically, we employ the Chebyshev polynomial expansion method [17] to numerically calculate the exact evolution operator $U_k(t) = \exp(-iH_k t)$, and thereby all relevant physical quantities. We first consider the well-studied photochemical reaction of pyrene (Py-h_{10}) and N,N-dimethylaniline (DMA-h_{11}) [16], for which the hyperfine couplings are isotropic [13], and the tensor $\hat{\lambda}_{k_j}$ in (1) simplifies to a number λ_{k_j}. We study the role of entanglement in this radical-pair reaction and propose new experiments based on quantum control. We then generalize our results to the cryptochrome radical pair of FADH$^{\bullet}$-O$_2^{\bullet -}$, which is the molecular candidate believed to be involved in avian magnetoreception [14].

Magnetic-field sensitivity under quantum control.—The magnetic-field sensitivity Λ of the radical-pair reaction [Py-$h_{10}^{\cdot -}$ DMA-$h_{11}^{\cdot +}$] is quantified by $\Lambda(B) = \frac{\partial \Phi_s}{\partial B}$ [13]. We assume that the external magnetic field points in the $\hat{z}$ direction. The key ingredients in the RPM are the hyperfine interactions, which induce a singlet-triplet mixing depending on the magnetic field [15]. Using an exponential model, $r_c(t) = k e^{-kt}$, as an example for the reencounter probability distribution [15], we plot the magnetic-field sensitivity in Fig. 1(a). Our numerical simulation agrees well with experimental results in [13].

Studying the performance of the radical-pair mechanism under quantum control would allow us to test the role of entanglement and further details of the RPM in spin-chemistry experiments. As a simple example, consider a periodical pulse sequence with π pulses applied at times $t = m\tau_c$ along the $\hat{z}$ direction; the effective Hamiltonian to the first order is given by $\bar{H}_Z^{(1)} = -\gamma_e B \sum_k S_z^{(k)} + \sum_{k,j} \lambda_{k_j} S_z^{(k)} I_z^{(k_j)}$. Such kind of control can actually enhance the performance of quantum-coherence-based magnetometers; see, e.g., [11,12]. However, in case of the RPM, the magnetic-field sensitivity becomes greatly suppressed, as can be seen in Fig. 1(a). We can show that, whenever one applies more general decoupling protocols to promote quantum coherence in a radical-pair reaction, its magnetic-field sensitivity will generally be reduced [18]. This demonstrates that it is in fact the *decay* of coherence, i.e., *decoherence*, rather than coherence itself, that plays an essential role for the magnetic-field detection in RPM, different from the situation in Refs. [11,12].

To demonstrate a potentially positive effect of quantum control on a chemical compass, we consider a situation where the magnetic field alternates its direction periodically at times $t = m\tau_a$, which will disturb the proper functioning of the compass. (This situation is reminiscent of an experiment with birds in an oscillating field [4], even though the cause of the compass disfunction is different here.) If we now apply π-X pulses at the same times $t = m\tau_a$, the chemical compass will recover its function, as the transitions between $|\mathbb{S}\rangle$ and $|\mathbb{T}_\pm\rangle$ induced by the residual xx hyperfine interactions are still affected by the magnetic field [see Fig. 1(a)].

Entanglement and magnetic-field sensitivity.—We have hitherto assumed, as is usually done, that the radical pair starts in a perfect singlet state, i.e., that quantum coherence is fully maintained during the pair creation. In reality, the initial state $\rho_s(0)$ of radical pairs will never be a pure singlet, but a mixed state with a certain singlet fidelity $f(0) < 1$. The value of $f(0)$ has to be sufficiently close to

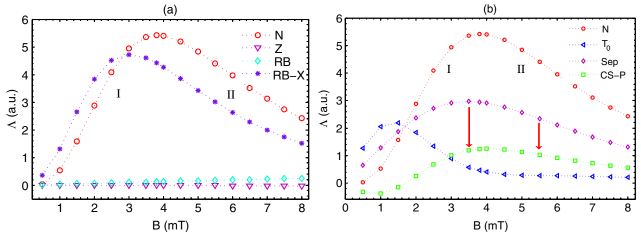

FIG. 1 (color online). Magnetic-field sensitivity Λ of the radical-pair reaction [Py-$h_{10}^{\cdot -}$ DMA-$h_{11}^{\cdot +}$] as a function of the magnetic field B. (a) N: singlet initial state; Z: under Z control; RB (RB-X): alternating magnetic field without (with) X control. (b) N: singlet initial state; T_0: triplet initial state $|\mathbb{T}_0\rangle$; Sep: optimal sensitivity for separable initial states; CS-P: applying a $\frac{\pi}{2}$-X pulse on the initial separable state $\rho_c = (|\uparrow\downarrow\rangle\langle\uparrow\downarrow| + |\downarrow\uparrow\rangle\langle\downarrow\uparrow|)/2$. The recombination rate constant is $k = 5.8 \times 10^8$ s^{-1} [13], and the control time is $\tau_c = 0.5$ ns.

unity, otherwise the state may also be described by classical correlations. We therefore ask the following question: Is entanglement, as a genuine quantum signature, needed to account for the efficiency of the magnetic compass? Or could the latter be explained by mere classical correlations? To answer this question, we have randomly chosen 5000 different initial states from the set of separable states and calculated the maximal achievable magnetic-field sensitivity for every value of B; see Fig. 1(b) ($\diamond$). We find that, in the operating region of the compass (around $B = 4$ mT), the maximal achievable sensitivity for separable states stays significantly below the sensitivity for the singlet state, and this maximum sensitivity is in fact attained by the classical mixture $\rho_c = (|\uparrow\downarrow\rangle\langle\uparrow\downarrow| + |\downarrow\uparrow\rangle\langle\downarrow\uparrow|)/2$. In turn, if nature is allowed to optimize the initial state from the full set of states, including the entangled states [e.g., $|\mathbb{S}\rangle$ and $|\mathbb{T}_0\rangle$; see Fig. 1(b)], the optimum magnetic-field sensitivity will typically be much higher than for any separable state. On these grounds one can say that entanglement is indeed helpful, and it is specifically entanglement rather than mere quantum coherence.

To test experimentally whether the initial state of the radical pair is indeed (close to) a singlet state, one could apply a $\frac{\pi}{2}$-X pulse as the reaction starts. For an initial singlet state, the magnetic-field sensitivity will remain unchanged, whereas for an initial classical mixture it will collapse; see Fig. 1(b).

As entanglement seemingly plays a role in the RPM with Py-DMA, we have studied its dynamics and its quantitative connection to the magnetic-field sensitivity. Similar to the activation yield, we define $\Phi_E = \int_0^\infty r_c(t)E(t)dt$ to quantify the effective amount of entanglement that is present in the active radical pairs during the reaction, where $E(t)$ is chosen to be the entanglement measure of concurrence [19] at time t. The derivative $\Lambda_E = \partial\Phi_E/\partial B$ quantifies how sensitive this effective entanglement is with respect to variations of the magnetic field B.

In Fig. 2(a), we see that Λ_E and Λ are correlated in the regions I and II, displaying monotonic relations with different linear ratios. However, it can also be seen that Λ_E changes dramatically at the crossover between regions I and II. This steplike behavior relates to the discontinuity of the entanglement lifetime $T_E = \max\{t|E(t) > 0\}$ as the magnetic field increases; see Fig. 2(b). In region I, T_E is much shorter than the reaction time T_r, while it jumps to a value comparable with T_r when passing from region I to II. When we further increase the magnetic field, T_E exhibits more kinks but with smaller increments. This effect originates from the finite size of the nuclear spin bath [20] of the electron spins, and is a clear signature of the system-environment dynamics underlying the RPM [18].

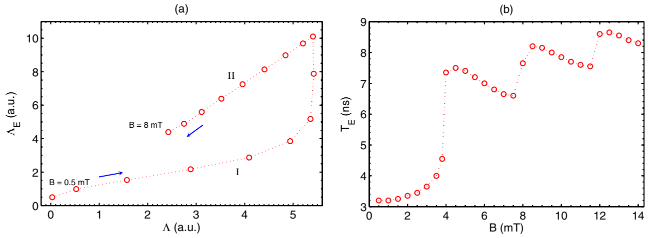

FIG. 2 (color online). Connection between entanglement and magnetic-field sensitivity [Py-$h_{10}^{\cdot -}$DMA-$h_{11}^{\cdot +}$]. (a) Sensitivity of effective entanglement Λ_E vs sensitivity of singlet yield Λ. The recombination rate is $k = 5.8 \times 10^8$ s^{-1} [13]. The blue arrows indicate variation of Λ_E and Λ when the magnetic field changes from $B = 0.5$ mT to $B = 8$ mT. (b) Discontinuity of the lifetime of entanglement T_E as a function of B.

Applications to animal magnetoreception.—In order to account for a direction sensitivity of the singlet yield, which is necessary for compass function, the hyperfine couplings must be anisotropic [3]. Here we consider an example of such a radical pair, FADH$^\bullet$-O$_2^{\bullet -}$, which was proposed as a likely molecular candidate underlying the magnetoreception of European robins [14], but it may also play this role in other species.

The direction of the magnetic field in (1) with respect to the reference frame of the immobilized radical pair is described by $\vec{B} = B(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$. Without loss of the essential physics, we assume that $\phi = 0$ and investigate the dependence of the singlet yield Φ_s on the angle θ under quantum control. First, it can be seen from Fig. 3(a) that the angular dependence of the singlet yield is much suppressed if one applies π pulses along the same direction as the magnetic field, which can distinguish the RPM from other potential mechanisms for magnetoreception [11,12]. Next, we study the scenario that the magnetic field changes its direction periodically at times $t = n\tau_a$ as in the previous section. As expected, the angular dependence is again greatly suppressed, as can be seen from the lower curve in Fig. 3(b). However, if one applies π pulses perpendicular to the direction of the magnetic field, this will reinduce an angular dependence; see Fig. 3(b). Furthermore, we find that even without a static magnetic field, quantum control can induce an angular dependence of the singlet yield as shown in Fig. 4. In other words, if one

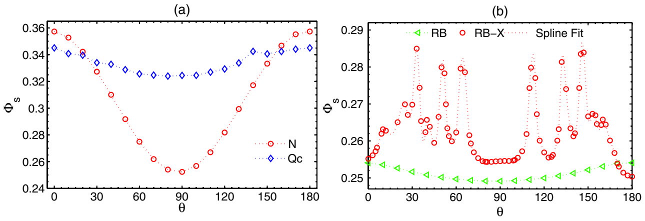

FIG. 3 (color online). Singlet yield Φ_s of the radical-pair reaction [FADH$^\bullet$-O$_2^{\bullet -}$] as a function of θ, at $B = 46$ μT. (a) N: without quantum control; Q_c: applying π pulses along the direction of the magnetic field. (b) RB (RB-X): effect of an alternating magnetic field, without (with) additional quantum control pulses perpendicular to the direction of the magnetic field. For comparison, the RB curve has been shifted downwards by 0.1. The recombination rate is $k = 5 \times 10^5$ s^{-1} and the control times are $\tau_c = \tau_a = 10$ ns.

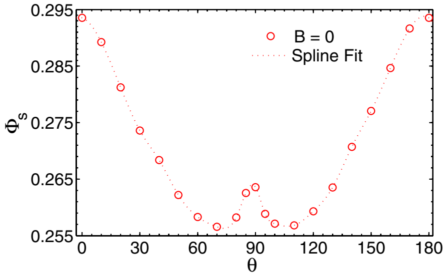

FIG. 4 (color online). Singlet yield Φ_s of the radical-pair reaction [FADH$^\bullet$-O$_2^{\bullet -}$] as a function of the angle θ, relative to the direction in which the π pulses are applied. There is no external static magnetic field, i.e., $B = 0$. The recombination rate is $k = 5 \times 10^5$ s^{-1}, and the control time $\tau_c = 100$ ns.

were able to design a behavior experiment with animals that use a chemical compass to sense the magnetic field, in such an environment they would lose or regain their orientability, depending on the applied control fields. This would provide further evidence for the RPM as the underlying mechanism, and it could help to narrow down the possible candidates of radical pairs in animal magnetoreception. It is, however, not clear how such experiments could be carried out safely.

Different from Py-DMA, we find that here the entanglement only exists in a time range (~10 ns) that is much shorter than the expected radical-pair lifetime (~2–10 μs). We have also computed the achievable sensitivity of the compass for different initial states and found that a substantial part of all separable states can account for an angular dependence that is even higher than for the singlet state [18]. This means that—in contrast to Py-DMA—the radical-pair entanglement does not seem to be a necessary ingredient for a chemical compass based on FADH$^\bullet$-O$_2^{\bullet -}$.

Summary and outlook.—We have demonstrated how quantum control can influence radical-pair reactions and the function of a chemical compass. The presented protocols can, in principle, be applied to existing spin-chemistry experiments, even though the implementation of coherent spin control [21,22] in this context needs to be further developed. They might also provide a route for future experiments with biological systems (including animals or plants) that are expected to exploit the RPM; in this case a much more careful study would be required.

We found interesting connections between entanglement and the magnetic-field sensitivity when the radical-pair lifetime is not too long compared to the coherence time. Otherwise, the roles of coherence and entanglement seem to be insignificant. Whether or not birds or other animals use entanglement for their ability to orient themselves in the Earth's magnetic field remains an open question, whose answer will depend on the specific molecular realization of their chemical compass.

As a biomimetic application of practical relevance, it would be interesting to explore the possibility of simulating a radical-pair mechanism in more controllable quantum systems, such as nitrogen-vacancy centers in diamond [11,12,23], to design an ultrahigh fidelity sensor for the detection of weak fields or forces.

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