Quantum relative entropy as a quantifier of singlet-triplet coherence in the radical-pair mechanism of biological magnetic sensing

I. K. Kominis
Department of Physics, University of Crete, 71003 Heraklion, Greece
Institute for Theoretical and Computational Physics, University of Crete, 70013 Heraklion, Greece

Radical-pair reactions pertinent to biological magnetic field sensing have been shown to be an ideal system for demonstrating the paradigm of quantum biology, the exploration of quantum coherence effects in complex biological systems. We here provide yet another fundamental connection between this biochemical spin system and quantum information science, related to the coherent spin motion driven by the magnetic interactions within these molecules. We introduce and explore a formal measure quantifying singlet-triplet coherence of radical-pairs using the concept of quantum relative entropy. The ability to quantify singlet-triplet coherence opens up a number of possibilities in the study of magnetic sensing with radical-pairs. We first use the explicit quantification of singlet-triplet coherence to affirmatively address the major premise of quantum biology, namely that quantum coherence provides an operational advantage to magnetoreception. Secondly, we use the concept of incoherent operations, which underlies the introduction of our singlet-triplet coherence measure, to show that incoherent manipulations of nuclear spins can have a dire effect on singlet-triplet coherence when the radical-pair exhibits electronic-nuclear entanglement. Finally, we study the role of magnetic interactions within the radical-pair in promoting quantum coherence, in particular unraveling a subtle effect related to exchange interactions.

I. INTRODUCTION

Radical-pair reactions \[1\], central in understanding avian magnetoreception \[2, 3\] and spin transport in photosynthetic reaction centers \[4\], have in recent years become a flourishing paradigm of quantum biology \[5, 6\], the study of quantum coherence effects in complex biological systems \[7–11\].

Indeed, it was shown that to understand the fundamental quantum dynamics of radical-pair reactions one needs to introduce quantum measurement theory, quantum coherence quantifiers and quantum trajectories elucidating the physics at the single molecule level \[12–15\]. These works also led to a new master equation describing the time evolution of the radical-pair spin dynamics \[6\], qualitatively and quantitatively departing from the theory attributed to Haberkorn \[16\], which has been traditionally used in spin chemical calculations. Moreover, quantum information concepts like violation of entropy bounds were taken advantage of to further demonstrate \[17\] the inadequacy of the long-standing theoretical foundations of spin chemistry \[18\] in a general way unaffected by the precise knowledge, or lack thereof, of molecular parameters. Most recently, quantum metrology methods were introduced to study the fundamental limits to quantum sensing of magnetic fields using radical-pair reactions and treating them as biochemical quantum magnetometers \[19\].

Following these developments, there have been several other approaches exploring radical-pair quantum dynamics \[20–22\], essentially concurring with the basic aforementioned findings, namely that a new fundamental theory based on quantum measurements is required to understand these spin-dependent biochemical reactions, that tools of modern quantum metrology are indeed useful to address their dynamics, and that in general, radical-pairs are an ideal system demonstrating the paradigm of quantum biology.

Yet apart from any quantitative or qualitative differences in accounting for radical-pair quantum dynamics in the various approaches being explored, it is broadly accepted that radical-pairs do exhibit quantum coherence, in particular singlet-triplet coherence defined by the spin space of the two electronic spins of the pair. The role of quantum coherence in magnetoreception has to some extent been addressed \[23\], but it is far from being conclusively understood. In particular, the role of singlet-triplet coherence has not been explored, since a quantitative and physically intuitive measure of singlet-triplet coherence has not been formally defined, apart from some empirical approaches \[14\]. There have also been discussions on whether a semiclassical treatment could replace coherent spin dynamics in radical-pair magnetoreception \[24\], but again, such discussions are phenomenological and of limited predictive power unless a concrete singlet-triplet coherence measure is established. This way it will be straightforward to find the classical limit of the relevant dynamics by gradually eliminating singlet-triplet coherence, while being able to exactly quantify its presence.

Interestingly, during the last few years quantum coherence measures have been formally investigated in quantum information science in the context of resource theories \[25–31\]. In this work we introduce and formally analyze quantum relative entropy as a singlet-triplet coherence measure. We rigorously prove the properties of the introduced quantifier, and offer some intuitive examples to explain its workings.

Since the theoretical formulation of the singlet-triplet coherence quantifier involves the definition of the so-called incoherent operations, we show, as a byproduct of their definition, that a class of incoherent operations originate from operating on just the nuclear spins of the
radical-pair. Having such operations out our disposal, we demonstrate that incoherently operating on just the nuclear spins can have dire consequences for the electronic singlet-triplet coherence when there is electron-nuclear entanglement. This simple and intuitively understood result opens up a number of studies on the effect of nuclear spin dynamics on the radical-pair spin dynamics.

As the main application of our singlet-triplet quantifier, we then explore the role of singlet-triplet coherence in magnetoreception. We investigate the correlation of singlet-triplet coherence with the figure of merit for the operation of radical-pair reactions as a compass. Having an explicit quantifier of singlet-triplet coherence, we can controllably suppress it while always quantifying it, and thus study the compass figure of merit as we transition from a highly coherent to highly incoherent regime.

As another application, we study the role of specific magnetic interactions in promoting such coherence, in particular the exchange interaction. We find a subtle effect alluding to optimal values of exchange couplings promoting the quantum advantage of singlet-triplet coherence.

The structure of the paper is the following. In the following subsection we motivate the need to introduce a measure of singlet-triplet coherence in simple and intuitive terms. In Sec. II we recapitulate our previous attempts at defining such a measure, which, being empirical, had several shortcomings. In Sec. III we present the definition of a singlet-triplet coherence quantifier based on relative entropy and fully analyze its properties at a formal level. In Sec. IV we study magnetoreception using the firmly established singlet-triplet coherence measure, and argue quantitatively in support of the main premise of quantum biology, namely that quantum coherence indeed provides an operational advantage to biological magnetic sensing with radical-pairs. We conclude with a summary and an outlook in Sec. V.

A. Motivation

When discussing radical-pair states, we refer to a Hilbert space comprising of two electron spins, one for each radical, and any number of nuclear spins residing in both radicals. For the simplest possible approach, one could even consider a fictitious radical-pair without nuclear spins. In such a case, the singlet-triplet (S-T) basis states of the two-electron system are denoted by $|s⟩ = (|↑⟩ - |↓⟩)/\sqrt{2}$ for the singlet, and $|t⟩$ for the triplets ($j = 0, \pm 1$), where $|t⟩ = |↑↑⟩$, $|t⟩ = (|↑⟩ + |↓⟩)/\sqrt{2}$ and $|t⟩ = (|↓⟩ + |↑⟩)/\sqrt{2}$. To motivate this work, we can ask a few questions to which are anything but obvious:

(a) Which state is "more" singlet-triplet coherent, $|ψ_s⟩ = (|s⟩ + |t⟩)/\sqrt{2}$, or $|ψ_t⟩ = (|s⟩ + |t⟩ + |t⟩ + |t⟩)/2$? Clearly, both states are pure and normalized, and both involve a superposition of the singlet and some of the triplet states, but which is "more coherent"?

Expanding the spin state dimension by bringing nuclear spins into the picture, we might again ask:

(b) which state is "more" singlet-triplet coherent, $|ψ_s⟩ = (|s⟩ ⊗ |↑⟩ + |t⟩ ⊗ |↓⟩)/\sqrt{2}$ or $|ψ_t⟩ = (|s⟩ ⊗ |↑⟩ + |t⟩ ⊗ |↓⟩ + |↑⟩ + |↓⟩)/\sqrt{3}$?

Considering the fact that in states exhibiting electronic-nuclear entanglement, the nuclear spins might "spy" on the electrons, we could also ask:

(c) in which of the two states, $|ψ_s⟩$ or $|ψ_t⟩$ is singlet-triplet coherence more fragile due to physical processes involving only nuclear spins?

Finally, regarding the magnetic interactions that directly drive or indirectly affect coherent singlet-triplet oscillations in the radical-pair state, which are at the heart of spin dynamics of this system, one might also ask:

(d) which are the interactions promoting singlet-triplet coherence and why?

The lack of a straightforward and broadly understood answer to the aforementioned questions (a)-(d), and several others one could ask along these lines, demonstrates that a formal, as well as physically intuitive description of singlet-triplet coherence in radical pairs is indeed required, and this is exactly the purpose of this work.

II. DEFINITIONS AND PREVIOUS WORK

Radical-pair reaction dynamics are depicted in Fig. 1. A charge transfer following the photoexcitation of a donor-acceptor dyad DA (not shown) leads to the radical-pair (also called charge-separated state) $D^*^+^A^*^-^$, where the two dots represent the two unpaired electron spins of the two radicals. The initial state of the two unpaired electrons of the radical-pair is usually a singlet, denoted by $S^D^*^+^A^*^-^$. In theory, any other initial state is equally permissible, but in practice the precursor neutral molecule is in a singlet state, preserved by the photoexcitation process.

Both D and A contain a number of magnetic nuclei (their initial state is usually fully mixed) which hyperfine-couple to the respective unpaired electron of D and A. The resulting magnetic Hamiltonian $H$ involves all such hyperfine couplings, and extra terms accounting for the electronic Zeeman interaction with an applied magnetic field, exchange and dipolar interactions etc.

The initial electron singlet state (and for that matter the triplet-state) is not an eigenstate of $H$, hence the initial formation of $S^D^*^+^A^*^-^$ is followed by S-T mixing, a coherent oscillation of the spin state of the electrons (and concomitantly the nuclear spins), designated by $S^D^*^+^A^*^-^ \Rightarrow T^D^*^+^A^*^-^$. This coherent spin motion has a finite lifetime since charge recombination, i.e. charge transfer from A back to D, terminates the reaction and leads to the formation of the neutral reaction products. There are two kinds of neutral products, singlet and triplet. Purely singlet (triplet) radical pairs would produce singlet (triplet) neutral products at a rate $k_S$ ($k_T$). Both rates are in principle known or measurable.
parameters (in general different) of the specific molecular system under consideration.

The electronic spin basis states have been presented in Sec. I A, they are the well-known four states consisting of the singlet and triplet states \(|s⟩, |t−⟩, |t0⟩\) and \(|t1⟩\). When considering radical-pairs with nuclear spins, the tensor product structure will be explicitly given. For example, for the case of a single nuclear spin-1/2, a singlet electronic state and a spin-up nucleus will be denoted as \(|s⟩ ⊗ |↑⟩\).

### A. Singlet and triplet projectors and basis states

The singlet and triplet projection operators are

\[ Q_S = (1/4 - s1 \cdot s2) \otimes 1 \quad \text{and} \quad Q_T = (3/4 + s1 \cdot s2) \otimes 1 , \]

with 1 being the unit operator in the nuclear spin space (the dimension of the unit matrix should be evident from the context), and \(s1\) and \(s2\) the electron spins of the two radicals. The projectors \(Q_S\) and \(Q_T\) are orthogonal and complete, i.e. \(Q_S Q_T = Q_T Q_S = 0\) and \(Q_S + Q_T = 1\) (for example in the last relation \(1\) refers to the total Hilbert space electrons+nuclei).

Using the completeness property we can multiply any given radical-pair density matrix \(ρ\) from left and right with \(1 = Q_S + Q_T\) and write

\[ ρ = 1ρ1 = (Q_S + Q_T)ρ(Q_S + Q_T) = ρ_{SS} + ρ_{TT} + ρ_{ST} + ρ_{TS} \]  \hspace{1cm} (1)

where \(ρ_{SS} = Q_SρQ_S\), \(ρ_{ST} = Q_SρQ_T\), \(ρ_{TS} = Q_TρQ_S\) and \(ρ_{TT} = Q_TρQ_T\). We will make frequent use of the identity \([1]\) in the following. We can already identify \(ρ_{SS} + ρ_{TT}\) as the S-T "incoherent part" of \(ρ\), and \(ρ_{ST} + ρ_{TS}\) the S-T "coherent part" of \(ρ\), to be formally defined and quantified later.

The density matrix, the projectors and any other operator relevant to a particular radical-pair having \(M\) nuclei with nuclear spins \(I_1, I_2, ..., I_M\) have dimension \(d = 4d_{nuc}\), where 4 is the multiplicity of the two electron-spin space, and \(d_{nuc} = (2I_1 + 1)(2I_2 + 1)...(2I_M + 1)\) is the dimension of the nuclear spin space.

### B. Reaction super-operators

We first introduced the quantification of S-T coherence in radical-pairs in [13]. We will briefly reiterate the motivation for this introduction. The special property of radical-pair reaction dynamics not found in most open quantum systems usually considered in the quantum information literature is that the time evolution of their quantum state is not preserving the trace of the radical-pair density matrix \(ρ\).

At any given time interval \(dt\), the number of singlet and triplet neutral reaction products is given by

\[ dn_S = k_S dt \text{Tr}(ρQ_S) \quad \text{and} \quad dn_T = k_T dt \text{Tr}(ρQ_T) , \]

respectively. This is an incoherent and irreversible process, i.e. it is evident that any S-T coherence of the precursor radical-pairs, of number \(dn_S + dn_T\), leading to the \(dn_S\) and \(dn_T\) singlet and triplet products, is irreversibly lost. The question, however, is how to update the density matrix of the surviving radical-pairs, taking into account not only the unitary evolution driven by \(H\), but also the state-dependent recombination of radical-pairs and the reduction of their trace. In other words, if at time \(t\) the radical-pair system is described by \(ρ_t\), what is \(ρ_{t+dt}\), given that \(\text{Tr}(ρ_{t+dt}) = \text{Tr}(ρ_t) - dn_S - dn_T\)?

The answer to this question, we claim, depends on "how much" S-T coherent are the radical-pairs described by \(ρ_t\), hence the need for an S-T coherence quantifier. The reader is referred to review [9] for further details.

However, this work is decoupled from this discussion on the exact form of the reaction super-operators, because we choose \(k_S = k_T = k\), a choice that simplifies the reaction dynamics considerably.

### C. First measure of S-T coherence is an \(l_2\)-norm

Our first S-T coherence quantifier [13] was introduced in analogy with the coherence for a light field pertaining to a double-slit interferometer. Specifically, we defined

\[ p_{coh} = \frac{\text{Tr}(ρ_{ST}ρ_{TS})}{\text{Tr}(ρ_{SS})\text{Tr}(ρ_{TT})} \] \hspace{1cm} (2)

The definition \([2]\) exactly aimed at quantifying the strength of the coherent part \(ρ_{ST} + ρ_{TS}\). In particular, the form of the nominator in Eq. \([2]\) was chosen because \(ρ_{ST}\) and \(ρ_{TS}\) are traceless due to the orthogonality of \(Q_S\) and \(Q_T\), but their product has a non-zero trace. For example, taking as \(ρ = |ψ⟩⟨ψ|\), with

\[ SD^+ A^- \quad TDA \]

\[ k_S \quad k_T \]

FIG. 1: Radical-pair reaction dynamics. A charge transfer following the photoexcitation (not shown here) of a donor-acceptor dyad DA produces a singlet state radical-pair \(^3D^+ \cdot A^-\), which is coherently converted to the triplet radical-pair, \(^3D^+ \cdot A^-\), due to intramolecule magnetic interactions embodied in the spin Hamiltonian \(H\). Simultaneously, spin-selective charge recombination leads to singlet and triplet neutral products with respective rates \(k_S\) and \(k_T\).
ψ = α |s⟩ + β |t₀⟩ and any coefficients α and β, it follows from (2) that $p_{coh} = 1$, i.e. any coherent superposition of |s⟩ and |t₀⟩ is maximally coherent. Considering, as a second example, a partially coherent state like

$$\rho = |\alpha|^2 |s⟩ ⟨s| + |\beta|^2 |t₀⟩ ⟨t₀| + c |s⟩ ⟨t₀| + c^* |t₀⟩ ⟨s|,$$

with $|c|^2 < |\alpha|β|^2$, it would follow that $p_{coh} = |c|^2 / |\alpha|β|^2 < 1$.

One problem of this definition is that any coherent superposition e.g. $\alpha |s⟩ + |t₀⟩$, whatever the coefficients $\alpha$ and $\beta$, is mapped into a maximum (equal to 1) coherence measure, whereas it would make intuitive sense that the more asymmetrical the superposition (e.g. the closer to one is the singlet probability) the smaller the S-T coherence should be. Yet another problem is that $p_{coh}$ measure, whereas it would make intuitive sense

$$\alpha$$

$\beta$

expression absolute value of all off-diagonal elements of $\rho$ as the $l_2$-norm, i.e. $p_{coh}$ scales with the square of the off-diagonal elements of $\rho$.

D. Second measure of S-T coherence is an $l_1$-norm

In [14] we introduced the $l_1$-norm, so-called [25] because it scales linearly with the off-diagonal elements of the density matrix.

$$C[\rho] = \frac{4}{3} \sum_{j=0,\pm} \sqrt{\text{Tr}(\rho_{ST}|T_j⟩⟨T_j|\rho_{TS})}$$

The expression in Eq. (3) was motivated by the fact that given the most general pure state of a radical-pair, $|ψ⟩ = \alpha_s|s⟩ ⊗ |\chi_s⟩ + \sum_{j=0,\pm} \beta_j|t_j⟩ |\chi_j⟩$, where $|\chi_s⟩$ and $|\chi_j⟩$ are normalized nuclear spin states, it follows that $C[|ψ⟩⟨ψ|] = \sum_{j=0,\pm} |\alpha_s\beta_j|$.

1. Shortcomings of previous definition

Our second attempt using Eq. (3) was motivated by the $l_1$-norm introduced in [25], where the authors considered a general density matrix $\rho$ and defined $\sum_{i,j,i\neq j} |\rho_{ij}|$ as the $l_1$-norm coherence measure. This is the sum of the absolute value of all off-diagonal elements of $\rho$. The expression $\sum_{j=0,\pm} |\alpha_s\beta_j|$ derived from Eq. (3) in the case of a pure radical-pair state aims at realizing exactly such a sum of ”off-diagonal” elements, now ”off-diagonal” relating to the block-diagonal decomposition of $\rho$ in the singlet and triplet subspaces (see [3] for examples).

However, this expression has two shortcomings. First, the normalizing factor of $4/3$ is incorrect, because the maximum value of the sum $\sum_{j=0,\pm} |\alpha_s\beta_j|$ is not $3/4$ but $\sqrt{3}/2$, and occurs for $|\alpha_s| = 1/\sqrt{2}$ and $|\beta_j| = 1/\sqrt{6}$. Second, the sum $\sum_{j=0,\pm} |\alpha_s\beta_j|$ is biased towards triplet states, i.e. it produces a higher coherence measure when more triplet states enter the superposition, for a given triplet character of the state. For example the superpositions $\frac{1}{\sqrt{2}}(|s⟩ + |t₀⟩)/\sqrt{2}$ and $\frac{1}{\sqrt{2}}(|s⟩ - |t₀⟩)/\sqrt{2}$ both have an excitation value of $Q_S$ equal to $1/2$, i.e. it is for both equally uncertain whether they are found in the singlet or triplet subspace upon a measurement of $Q_S$, yet the former is maximally coherent whereas the latter is not, according to Eq. (3). However, we would intuitively expect that maximum S-T coherence would be attributed to the state having maximum quantum uncertainty in a measurement of $Q_S$ or $Q_T$. Furthermore, the definition (3) is not readily amenable to a formal analysis of its properties.

All the aforementioned shortcomings of the previous definitions in Eq. (2) and Eq. (3) are alleviated by the quantifier defined in the following based on the quantum relative entropy.

III. FORMAL DEFINITION OF SINGLET-TRIPLET COHERENCE IN RADICAL-PAIRS BASED ON THE QUANTUM RELATIVE ENTROPY

We will now develop of formal theory of singlet-triplet coherence in radical-pairs using a central concept of quantum information, the quantum relative entropy, adapted to our case. The resource theory of quantum coherence is built [25] on the notion of (i) incoherent states and (ii) incoherent operations. In [25] the authors consider a $d$-dimensional Hilbert space spanned by the basis states $|i⟩$, with $i = 1, 2, ... d$, and define as incoherent states all density matrices of the form $\sum_{i=1}^{d} \delta_i |i⟩⟨i|$, where the non-negative weights $\delta_i$ sum up to unity, $\sum_{i=1}^{d} \delta_i = 1$.

In our case we consider a $d$-dimensional Hilbert space of the radical-pair under consideration, which is spanned by $d$ states, but we do not care about a ”global” coherence, but only about coherence between the singlet and triplet subspaces, hence the following definition.

A. Definition of S-T incoherent states

Singlet-triplet incoherent radical-pairs are those for which the radical-pair density matrix $\rho$ has the property that $\rho = Q_S\rho Q_S + Q_T\rho Q_T \equiv \rho_{SS} + \rho_{TT}$, or equivalently, those for which the density matrix has the property that $Q_S\rho Q_T + Q_T\rho Q_S \equiv \rho_{ST} + \rho_{TS} = 0$. This definition is straightforward, since as noted in Sec. II A with regard to the identity (1), any radical-pair density matrix can be written as $\rho = \rho_{SS} + \rho_{TT} + \rho_{ST} + \rho_{TS}$ due to the completeness of the projectors $Q_S$ and $Q_T$. Let all incoherent states (for a particular radical-pair Hilbert space) define the set $\mathcal{I}$.

B. Definition of S-T incoherent operations

The authors in [25] consider a set of Kraus operators $K_n$, with $\sum_n K_n^\dagger K_n = 1$. These are called incoherent if for all $n$ it is $K_n^\dagger K_n \subset \mathcal{I}$. In our case, the two projectors
Qₗ and Qₜ qualify as a set of incoherent operations, since QₛQₗ + QₜQₗ = Qₛ + Qₜ = 1, and for any ρ ∈ I, i.e. ρ = ρₛρₛ + ρₜₜ it is QₛρₛQₗ = ρₛₛ ⊂ I and Qₜₜρₜₜ = ρₜₜₜ ⊂ I. The pair Qₛ and Qₜ are incoherent operators of central significance for discussing S-T coherence, but by no means are they the only ones.

For example, any operators acting only on the nuclear spins are S-T incoherent operators. Consider Kₙ = 1 ⊗ kₙ, where now 1 is the unit matrix in the electronic spin subspace (4-dimensional), and kₙ are trace-preserving Kraus operators acting in the nuclear spin subspace and satisfying ∑ₙ kₙ†kₙ = 1 (here 1 refers to the nuclear spin subspace). Take a density matrix ρ ∈ I. Then ρ = QₛρₛQₗ + QₜₜQₜ, so that KₙρKₙ† = KₙQₛρₛQₗKₙ† + KₙQₜₜQₜKₙ†. It can be readily seen that Qₛ and Qₜₜ commute with Kₙ, therefore KₙQₛρₛQₗKₙ† + KₙQₜₜQₜKₙ† = QₛKₙρₛQₗKₙ† + QₜₜKₙρₜₜQₜ. Since Kₙ define a trace-preserving map, KₙρKₙ† is also a physical (yet unnormalized) density matrix, call it R. Hence, finally QₛQₗρₛQₗ + QₜₜQₜQₜ = QₛQₗ = QₜₜQₜ = Qₛ + Qₜ = 1, the non-selective post-measurement state is given by QₛρₛQₗ + QₜₜQₜ. Indeed, the measurement results are qₛ = 1 or qₜ = 0. Taking place with probabilities pₛ = Tr{ρₗₗₗ} and pₜₜ = Tr{ρₜₜₜ}, with the selective post-measurement states being ρₛ = QₛρₛQₗ/pₛ and ρₜₜ = QₜₜQₜpₜₜ, respectively. The non-selective post-measurement state is pₛρₛ + pₜₜρₜₜ which indeed equals QₛQₗ + QₜₜQₜ. Since, by the theorem found in [32, 33] it is S[QₛQₗ + QₜₜQₜ] ≥ S[ρ], it follows that indeed C[ρ] ≥ 0.

3. Maximum value of C[ρ]

For any ρ it is C[ρ] ≤ 1.

Proof First, the quantum relative entropy is jointly convex in both of its arguments [34, i.e.

\[ S[λρ₁ + (1 − λ)ρ₂] ≤ λS[ρ₁] + (1 − λ)S[ρ₂] \]

for any λ ∈ [0, 1]. Applying this property for ρ₁ = ρ₂ = ρ, σ₁ = ρₛ, σ₂ = ρₜₜ, λ = pₛ, and given that pₛS[ρₛ] + pₜₜS[ρₜₜ] it follows that

\[ S[ρ] ≤ pₛS[ρₛ] + pₜₜS[ρₜₜ] \]

4. Properties of C[ρ]

We here present the basic properties of the definition [4].

1. Value of C[ρ] for incoherent states

For all ρ ∈ I it is C[ρ] = 0.

Proof This follows trivially from the definition [4], since if r ∈ I it is r = QₘᵣQₛ + QₜₜQₜ, hence C[r] = S[r] − S[r] = 0. According to [25], all incoherent states r ∈ I should have C[r] = 0, so the measure [4] satisfies this basic criterion for an acceptable coherence quantifier.

2. Minimum value of C[ρ]

Proof The proof follows from the fact that under a nonselective (or blind) measurement the entropy does not decrease. This can be found in pp. 75 of [32] and pp.92 of [33]. In our case, defining a measurement by the Kraus operators Qₛ and Qₜₜ, which satisfy QₛQₗₗₗ + QₜₜQₜₜ = QₛQₗₗₗ + QₜₜQₜₜ = Qₛ + Qₜₜ = 1, the non-selective post-measurement state is given by QₛρₛQₗₗₗ + QₜₜQₜₜ. Indeed, the measurement results are qₛ = 1 or qₜₜ = 0, taking place with probabilities pₛ = Tr{ρₗₗₗ} and pₜₜ = Tr{ρₜₜₜ}, with the selective post-measurement states being ρₛ = QₛρₛQₗₗₗ/pₛ and ρₜₜ = QₜₜQₜₜpₜₜ. Since, by the theorem found in [32, 33] it is S[QₛQₗₗₗ + QₜₜQₜₜ] ≥ S[ρ], it follows that indeed C[ρ] ≥ 0.

C. Definition of S-T coherence quantifier based on relative entropy

For any radical-pair density matrix ρ we define the singlet-triplet coherence quantifier as

\[ C[ρ] = S[QₛρₛQₗₗₗ + QₜₜQₜₜ] − S[ρ], \]

where S[r] is the von-Neumann entropy of the density matrix r. Since radical-pair reactions are non-trace preserving, the trace of the radical-pair state ρ is in general 0 ≤ Tr{ρ} ≤ 1. For the definition [4] to work, we first need to normalize the radical-pair state ρ with Tr{ρ} (see Appendix of [17] for a relevant discussion). In the following we will always imply that whenever we calculate C[ρ] we do so for radical-pair density matrices that have been appropriately normalized to have unit trace.

At first sight, the quantum relative entropy is not present in the definition [4]. However, equation [4] readily follows by first defining, along the lines of [25],

\[ C[ρ] = \min_{δ ∈ I} S[ρ|δ|], \]

where now S[ρ|δ|] = Tr{ρ log ρ} − Tr{ρ log δ} is the quantum relative entropy of the radical-pair density matrices ρ and δ. Indeed, by denoting

\[ \hat{ρ} = QₛρₛQₗₗₗ + QₜₜQₜₜ, \]

and for δ ∈ I it is [25] S[ρ|δ|] = S[ρ|δ|] + S[ρ] − S[ρ]. However, since the quantum relative entropy is always positive or zero, S[ρ|δ|] ≥ 0, it is seen that minδ∈I S[ρ|δ|] = 0, the minimum obviously taking place for δ = ρ, since it is known that for any density matrix r it is S[r|r] = 0. Hence C[ρ] = S[ρ|ρ] = S[ρ] − S[ρ].
Now, the interpretation of the quantum relative entropy $S[\rho||\sigma]$ is the extent to which one can distinguish two different states $\rho$ and $\sigma$, in particular by a series of quantum measurements and their resulting statistics. Let us first consider $S[\rho||\rho_S]$. This reflects the extent to which by doing some measurement on $\rho$ we can use the measurement statistics to distinguish $\rho$ from $\rho_S$. We can choose as measurement the measurement of $Q_S$, the result of which can be either 0 or 1. Clearly if the state we were measuring was $\rho_S = Q_S \rho Q_S / \text{Tr} \{Q_S\}$, we would only obtain 1 for every measurement performed in $N$ identically prepared systems. But if the state of each of those identical copies is $\rho$, measuring $Q$ we will obtain 1 only some of the times. The probability to obtain 1 in all $N$ such measurements will clearly be $p_S^N$. This is the probability that $\rho_S$ would “pass” our test and we would confuse the actual state $\rho$ with $\rho_S$. But it is known that for an optimal measurement using $N$ identical copies of our system, the probability that we will mistakenly confuse $\rho$ for $\rho_S$ is $2^{-NS[\rho||\rho_S]}$. Our choice of measurement is not necessarily optimal, hence $2^{-NS[\rho||\rho_S]} \leq p_S^N$, or $S[\rho||\rho_S] \leq -\log[p_S]$. We can similarly show that $S[\rho||\rho_T] \leq -\log[p_T] = -\log[1-p_S]$. Finally, using the inequality we get

$$C[\rho] \leq \mathbb{H}[p_S, p_T],$$

where $\mathbb{H}[p_S, p_T] = -p_S \log p_S - p_T \log p_T = -p_S \log p_S - (1-p_S) \log(1-p_S)$ is the Shannon entropy of the pair of probabilities $\{p_S, p_T\}$. Since this Shannon entropy has maximum 1 (when the logarithms are calculated with base 2), the maximum occurring for $p_S = p_T = 1/2$, we finally show that the maximum of $C[\rho]$ is 1.

4. Singlet-triplet coherence of pure states

Pure radical-pair states $|\psi\rangle$ saturate the bound $[9]$, i.e. it is $C[|\psi\rangle\langle\psi|] = \mathbb{H}[p_S, p_T]$, where $p_S = \text{Tr}\{|\psi\rangle\langle\psi| Q_S\}$.

Proof: The most general pure state of a radical-pair can be written as

$$|\psi\rangle = \alpha_s |s\rangle \otimes |x_s\rangle + \sum_{j=-1}^{1} \beta_j |t_j\rangle \otimes |x_j\rangle,$$

where $|x_s\rangle$ and $|x_j\rangle$ are nuclear spin states “living” in a nuclear spin space of dimension $d_{nuc}$ (defined in Sec. II A), dependent on the number and spin of nuclear spins of the particular radical-pair. Setting $\rho = |\psi\rangle\langle\psi|$, in order to calculate $C[\rho]$, we need to calculate the entropies $S[\rho]$ and $S[\rho]$ of the former is zero since $\rho$ is a pure state. To calculate the latter, we write

$$\hat{\rho} = Q_S \rho Q_S + Q_T \rho Q_T$$

$$= |\alpha_s|^2 |s\rangle \langle s| \otimes |x_s\rangle \langle x_s| + |\phi_T\rangle \langle \phi_T|,$$

where for brevity we denoted by $|\phi_T\rangle = \sum_{j=-1}^{1} \beta_j |t_j\rangle \otimes |x_j\rangle$ the triplet-subspace component of the most general pure state $|\psi\rangle$. The matrix $\hat{\rho}$ clearly has a block-diagonal form, one block being the singlet and the other the triplet subspace. To calculate $S[\hat{\rho}]$ we need to find the eigenvalues of $\hat{\rho}$. They are easily obtained by finding the eigenvectors and corresponding eigenvalues of $\hat{\rho}$ by construction.

For example, the state $|s\rangle \otimes |x_s\rangle$ is an eigenvector of the singlet block diagonal of $\hat{\rho}$ with eigenvalue $|\alpha_s|^2 = \text{Tr}\{Q_S \rho Q_S\} = p_S$. Remaining in this singlet subspace block-diagonal, we can span the nuclear spin space with $d_{nuc}$ orthogonal basis states, one being $|x_s\rangle$ itself. Hence the other $d_{nuc} - 1$ eigenvalues of the singlet block-diagonal of $\hat{\rho}$ are zero. Similarly, the unnormalized state $|\phi_T\rangle$ is an eigenstate of $|\phi_T\rangle \langle \phi_T|$ with eigenvalue $|\phi_T\rangle \langle \phi_T| = |\beta_+|^2 + |\beta_0|^2 + |\beta_-|^2 = \text{Tr}\{Q_T \rho Q_T\} = p_T$. We can clearly span this triplet subspace with $3d_{nuc}$ orthogonal basis states, one of which is $|\phi_T\rangle$ itself. Hence the other eigenvalues of $|\phi_T\rangle \langle \phi_T|$ are zero. Thus, the state $\hat{\rho}$ has two nonzero eigenvalues, $p_S = \text{Tr}\{Q_S \rho Q_S\}$ and $p_T = \text{Tr}\{Q_T \rho Q_T\} = 1 - p_S$, hence the coherence measure of the most general pure radical-pair state is exactly equal to $\mathbb{H}[p_S, p_T]$.

5. States with maximum singlet-triplet coherence

It readily follows that the states having maximum $S\text{-}T$ coherence, equal to 1, are all pure states of the form $|\psi\rangle_{\text{maxC}} = 1/\sqrt{2} |s\rangle \otimes |x_s\rangle + \sum_{j=-1}^{1} c_j |t_j\rangle \otimes |x_j\rangle$, where $\sum_{j=-1}^{1} |c_j|^2 = 1/2$, while $|x_s\rangle$ and $|x_j\rangle$ are arbitrary normalized nuclear spin states.

6. Connection with quantum uncertainty

For the general pure state $|\psi\rangle$ of Equation (10) it can be easily seen that the quantum uncertainty of $Q_S$, given by $\Delta q_S \equiv \sqrt{\langle Q_S | \psi \rangle^2 - \langle Q_S | \psi \rangle^2}$, is $\Delta q_S = \sqrt{|\alpha_s|^2 (1 - |\alpha_s|^2)}$. Evidently, $\Delta q_S$ is maximized for $|\alpha_s| = 1/\sqrt{2}$, i.e. the maximally coherent pure states $|\psi\rangle_{\text{maxC}}$ also have maximum uncertainty in their singlet (or equivalently triplet) character. This is intuitively satisfactory, since thinking at the level of a simple qubit, we intuitively relate the maximum coherence state $\{|0\rangle + |1\rangle\}/\sqrt{2}$ with the fact that this state is maximally uncertain regarding a measurement in the computational basis $\{|0\rangle, |1\rangle\}$.

7. Additional comments

Finally, all other conditions of an acceptable measure of coherence defined in [29], like (i) monotonicity under incoherent completely positive and trace preserving maps, (ii) monotonicity under selective measurements on average and (iii) convexity, are automatically satisfied as
has been shown in for the relative entropy measure defined therein.

E. Examples

1. Fictitious radical-pair with no nuclear spins

We will first consider the simplest system, a fictitious radical-pair with no nuclear spins, hence a four-dimensional Hilbert space spanned by $|s\rangle$ and $|t_j\rangle$, with $j = 0, \pm 1$. This example can be treated analytically and illustrate the properties of singlet-triplet coherence in a transparent way. In fact, high magnetic fields, at which the magnetic Hamiltonian is dominated by the electronic Zeeman terms, readily lead to this approximation and in such cases singlet-triplet mixing is driven by a difference in the $g$-factor for the electronic spins in the two radicals $[36]$. Explicitly, consider a Hamiltonian $H = \omega_1 s_{1z} + \omega_2 s_{2z}$, where $\omega_1$ and $\omega_2$ are the Larmor frequencies of the electrons in the two radicals, taken to be different. If the initial state is $|\psi_0\rangle = |s\rangle$ it is easily shown that $|\psi_t\rangle = \cos \frac{\Omega t}{2} |s\rangle - \sin \frac{\Omega t}{2} |t_0\rangle$, where $\Omega = \omega_1 - \omega_2$. Thus the singlet and triplet probabilities are $p_S = \cos^2 \frac{\Omega t}{2}$ and $p_T = \sin^2 \frac{\Omega t}{2}$, respectively.

The state $|\psi_t\rangle$ is pure, hence it has zero entropy, $S(\rho_t) = 0$, where we set $\rho_t = |\psi_t\rangle \langle \psi_t|$. The incoherent state $\tilde{\rho}_t = Q_S \rho Q_S + Q_T \rho Q_T$ is $\tilde{\rho}_t = p_S |s\rangle \langle s| + p_T |t_0\rangle \langle t_0|$. It readily follows that the eigenvalues of $\tilde{\rho}_t$ are $p_S$ and $p_T$, hence $S[\tilde{\rho}_t] = -p_S \log p_S - p_T \log p_T$. Thus the coherence measure for $|\psi_t\rangle$ is $C[|\psi_t\rangle \langle \psi_t|] = S[\tilde{\rho}_t] - S[\rho_t] = -p_S \log p_S - p_T \log p_T$. In Fig. 2a we plot the time evolution of the singlet probability $p_S = \text{Tr}(\rho_t Q_S)$ and the S-T coherence measure $C[\rho_t]$. Evidently, $C[|\psi_t\rangle \langle \psi_t|]$ is zero when $|\psi_t\rangle$ is a pure singlet or a pure triplet, and reaches its maximum value of 1 in between the maxima of $p_S$, i.e. at those times where we have the most uncertain coherent superposition of $|s\rangle$ and $|t_0\rangle$, of the form $\frac{1}{\sqrt{2}} (|s\rangle \pm |t_0\rangle)$.

We can now introduce a singlet-triplet dephasing through the operation $\rho \rightarrow \rho - K_\rho dt (Q_S \rho Q_T + Q_T \rho Q_S)$, i.e. by removing from $\rho$ its coherent part $\rho_{ST} + \rho_{TS}$ at a rate $K_\rho$ (we will elaborate more about this in the following section). In the presence of such an S-T dephasing mechanism, a pure initial state necessarily evolves into a mixed state, which in general satisfies the master equation $d\rho/dt = -i[H, \rho] - K_\rho dt (Q_S \rho Q_T + Q_T \rho Q_S)$. This is easy to solve analytically in the considered example, since the problem is essentially reduced to a two dimensional system spanned by $|s\rangle$ and $|t_0\rangle$. For $K_\rho < 2|\Omega|$ the off-diagonal density matrix elements are oscillatory and decay exponentially at a rate $K_\rho/2$. An analytic expression can be obtained for the time-evolved density matrix $\rho_t$, but it is a bit cumbersome. For $K_\rho < 2|\Omega|$ an excellent approximation is $\rho_t = \frac{1}{2} (1 + e^{-K_\rho t/2 \cos \Omega t}) |s\rangle \langle s| + \frac{1}{2} (1 - e^{-K_\rho t/2 \cos \Omega t}) |t_0\rangle \langle t_0| + \frac{1}{2} e^{-K_\rho t/2 \sin \Omega t} |s\rangle \langle t_0| - \frac{1}{2} e^{-K_\rho t/2 \sin \Omega t} |t_0\rangle \langle s|.

The singlet probability is now $\text{Tr}(\rho_t Q_S) = \frac{1}{2} (1 + e^{-K_\rho t/2 \cos \Omega t})$. The eigenvalues of $\rho_t$ and $\tilde{\rho}_t$ are $e_1 = \frac{1}{2} (1 - e^{-K_\rho t/2 \cos \Omega t})$, $e_2 = \frac{1}{2} (1 + e^{-K_\rho t/2 \cos \Omega t})$, and $\tilde{e}_1 = \frac{1}{2} (1 - e^{-K_\rho t/2 \cos \Omega t})$, $\tilde{e}_2 = \frac{1}{2} (1 + e^{-K_\rho t/2 \cos \Omega t})$, respectively. Thus we can readily calculate the entropies $S[\rho_t]$ and $S[\tilde{\rho}_t]$, and from them $C[\rho_t] = S[\tilde{\rho}_t] - S[\rho_t] = -e_1 \log e_1 - e_2 \log e_2 + e_1 \log e_1 + e_2 \log e_2$. These analytic results for $\text{Tr}(\rho_t Q_S)$ and $C[\rho_t]$ are now shown in Fig. 2b.

2. Incoherent operations on nuclear spins

The phenomenological wealth of coherence phenomena increases dramatically by considering realistic radical-pairs involving one ore more nuclear spins. In particular, plots similar to Fig. 2 can also be produced by introducing just one nuclear spin and calculating the evolution of S-T coherence in various scenarios. However, here we will explicitly mention as a second example a more subtle effect having to do with the fact that the pair $\{Q_S, Q_T\}$ are not the only incoherent operations, as mentioned in Sec. III B. As shown in the previous example, singlet-triplet dephasing and concomitant decrease in the S-T measure

![Figure 2](image-url)
C can be readily induced by performing a measurement of the "singlet character" of the radical-pair density matrix. This measurement is described by the Kraus operators $K_1 = Q_S$ and $K_2 = Q_T$ and leads to the previously mentioned master equation including the S-T dephasing term proportional to $K_d$. But with the presence of nuclear spins, there is yet another mechanism, irrelevant to the electronic spins, by which S-T dephasing can be produced. This can happen when there is electronic-nuclear entanglement.

Consider in particular a pure radical-pair state of the form $|\psi\rangle = (|s\rangle \otimes |\uparrow\rangle + |t_0\rangle \otimes |\downarrow\rangle)/\sqrt{2}$. Ignoring for the moment the electronic states $|t_1\rangle$ and $|t_{-1}\rangle$, so that the electron spin subspace "looks" two-dimensional, the state $|\psi\rangle$ is clearly a maximally entangled state of two qubits, one spanned by the states $|s\rangle$ and $|t_0\rangle$ and the other by $|\uparrow\rangle$ and $|\downarrow\rangle$. Now, suppose we perform a measurement on the nuclear spin only, e.g., in the $z$-basis, using the Kraus operators $K_1 = \mathbb{1} \otimes |\uparrow\rangle \langle \uparrow|$ and $K_2 = \mathbb{1} \otimes |\downarrow\rangle \langle \downarrow|$, which evidently leave the electrons untouched. Yet, because of the electron-nucleus entanglement, these incoherent operators will also damp S-T coherence, as easily seen by setting $\rho = |\psi\rangle \langle \psi|$ and considering $K_1 \rho K_1 + K_2 \rho K_2 = 1/2 (|s\rangle \langle s| \otimes \mathbb{1}) + 1/2 (|t_0\rangle \langle t_0| \otimes \mathbb{1}) + 1/2 (|\uparrow\rangle \langle \uparrow| \otimes \mathbb{1}) + 1/2 (|\downarrow\rangle \langle \downarrow| \otimes \mathbb{1})$. The state $\rho$ is maximally S-T coherent, while the state $K_1 \rho K_1 + K_2 \rho K_2$ has zero S-T coherence.

IV. SINGLET-TRIPLET COHERENCE AS A RESOURCE FOR MAGNETORECEPTION

Having defined a measure for S-T coherence, we will now explore whether S-T coherence is a resource for biological magnetic sensing, in particular for radical-pair magnetoreception. That is, we will focus on the compass aspect of the radical-pair mechanism, and attempt to figure out the role S-T coherence plays in the workings of precise heading estimation. As we will show, this is not an innocuous question, and care should be exercised in claiming whether or not S-T coherence provides an operational advantage to the compass.

A. Some introductory comments

To be explicit, it is known that an anisotropic hyperfine coupling can render the radical-pair reaction yields dependent on the angle $\phi$ of the external magnetic field with respect to a molecule-fixed coordinate frame. As is usually the case, let us consider a single-nuclear-spin radical pair, with Hamiltonian

$$H = \mathbf{s}_1 \cdot \mathbf{A} + \omega \cos \phi (s_{1x} + s_{2x}) + \omega \sin \phi (s_{1y} + s_{2y}), \quad (12)$$

where $\mathbf{A}$ is the hyperfine tensor coupling the electron spin $s_1$ of one radical with the single nuclear spin $I$ of that radical, and $\omega$ the external magnetic field lying on the $x-y$ plane and producing the Zeeman terms of the two electronics spins. Both $\mathbf{A}$ and $\omega$ are in units of frequency, and as usual we omit the nuclear Zeeman term. We will now calculate the singlet reaction yield as a function of the angle $\phi$, always starting at $t = 0$ with a singlet state for the electrons and a fully mixed nuclear spin state, $\rho_0 = Q_S/\text{Tr}(Q_S)$. As mentioned in Sec. II B, we assume that $k_S = k_T = k$, in which case the quantum dynamics of the radical-pair reaction are simplified, and the differences between our master equation and Haberkorn’s are less exacerbated. In particular, when $k_S = k_T = k$ it is $d\rho/dt = e^{-kt}R$, with $dR/dt = -i[H, R] - k(Q_S R Q_T + Q_T R Q_S)$ according to our theory, whereas $dR/dt = -i[H, R]$ according to Haberkorn’s, i.e. we have an additional dephasing term $-k(Q_S R Q_T + Q_T R Q_S)$ inherent in our description of the dynamics. In the following we will anyhow use a significantly stronger dephasing term of the form $-K_d(Q_S R Q_T + Q_T R Q_S)$, with $K_d \gg k$, hence it really does not matter for this discussion which of the two master equations we use.

In any case, we will now calculate the singlet reaction yield, $Y_S(\phi) = \int_0^\infty dt k \text{Tr} \{\rho(t) Q_S\}$, and plot it is a function of $\phi$ in order to define the figure of merit for the compass function of the reaction. We explicitly include the time dependence of the density matrix to remind the reader that $\rho_t$ is the density matrix at time $t$, evolved by the master equation starting from $\rho_0$, and the yield $Y_S$ depends on $\phi$ since the Hamiltonian $H$, affecting the evolution of $\rho_t$, depends on $\phi$.

An example of such a $\phi$-dependence of $Y_S$ is shown in Fig. 3. What we define as figure of merit is the maximum slope of the function $Y_S(\phi)$, because it is this slope that determines the useful compass "signal", i.e. the change of the reaction yield resulting from a change of heading $\phi$ around $\phi_0$. In the following we will quantify this figure of merit with the quantity $\delta Y_S = \max_{\phi_0} |Y_S(\phi_0 + \epsilon) - Y_S(\phi_0 - \epsilon)|$.

B. Correlation of $\delta Y_S$ and $\mathcal{C}$

We will now explore the connection between singlet-triplet coherence as quantified by $\mathcal{C}$ and the figure of merit of the compass, $\delta Y_S$, as defined before. In particular, since $\mathcal{C}$ depends on the time-dependent density matrix $\rho_t$, we define a mean value of $\mathcal{C}[\rho_t]$ along the whole reaction as $\overline{\mathcal{C}} = \int_0^\infty dt k e^{-kt} \mathcal{C}[\rho_t]$. We remind the reader that in order to calculate $\mathcal{C}[\rho_t]$ using the definition (11), we always have to first normalize $\rho_t$ by $\text{Tr} \{\rho_t\}$ (since this trace changes with time due to the reaction), and then calculate the entropies in (11).

We use the Hamiltonian of Eq. (12), and for completeness we add an exchange term of the form $-J S_1 S_2$. We use a diagonal hyperfine tensor, randomizing all three diagonal elements $A_{jj}$, with $j = x, y, z$. We also randomize the exchange coupling $J$. For each set of parameters $A_{xx}$, $A_{yy}$, $A_{zz}$ and $J$ we calculate $\delta Y_S$ and $\mathcal{C}$. Additionally, we calculate the mean values along the reaction of the singlet and triplet expectation values, $\langle Q_S \rangle_t = \int_0^\infty \langle Q_S(t) \rangle dt$. We also calculate the slope of $\delta Y_S$ as a function of $\omega$. The results are shown in Fig. 4. We can see the presence of a regime in which $\delta Y_S$ is strong and $\mathcal{C}$ is small, which we shall call a "hidden regime", and we conjecture that the hidden regime is the regime in which $\mathcal{C}$ concealed under the noise.
over the sample of 5000 points of these distributions. The triple character of the radical-pair state, quantified by the average values along the reaction of the singlet and triplet populations, as seen in Figs. 4(d1)-4(d4), are not affected by the increasing $K_d$. In other words, we have a process by which an initially singlet radical-pair state is coherently transformed into a triplet, and back and forth, but it is the underlying coherence and not the population exchange that seems to be directly connected with the figure of merit $\Delta Y_S$. It should be clear that we were able to arrive at these conclusions because we have an explicit quantifier of S-T coherence.

To be precise, however, we should limit the affirmative answer to this statement: what the previous findings demonstrate is that singlet-triplet coherence allows for a quantum advantage not present in conditions of singlet-triplet incoherence. Whether such advantage is actually realized in nature, or in other words, whether the actual molecular parameters of the naturally occurring compass are such that the compass operating point is among those exhibiting large S-T coherence is a different question. However, this is not of fundamental interest for quantum biology. In contrast, what is of interest is what is in principle possible with such biochemical spin-dependent reactions. If it is found that they naturally work in a regime of large S-T coherence it would be quite an exciting finding, but even if this is not the case, knowing what is in principle possible would allow for the design of an artificial compass (or magnetometer in general) taking advantage of quantum coherence effects.

Put differently, since the correlation coefficient of $\Delta Y_S$ with $\bar{C}$ is at the level of 0.3 (see Fig. 4b), the mean of $\Delta Y_S$ over the 5000 points is seen to drop with the decreasing mean of $\bar{C}$ (see Fig. 4b), but not excessively, i.e., $\Delta Y_S$ is much more significant in order the explore the effect of suppressing S-T coherence.

The main results of this simulation, making a clear case that S-T coherence is indeed a resource for magnetoreception, are shown in Fig. 4c. Moreover, the correlation between the correlation coefficient (around 0.3) between $\Delta Y_S$ and $\bar{C}$, respectively.

We will now interpret the aforementioned observations. The first question to ask is, does singlet-triplet coherence provide a quantum advantage to the operation of the compass? The answer should clearly be affirmative, because of three facts: (a) Due to the correlation between $\Delta Y_S$ and $\bar{C}$ at a specific value of $K_d$, large values of S-T coherence $\bar{C}$ are on average connected with large figures of merit $\Delta Y_S$ for the compass. (b) Strong S-T dephasing produced by increasing $K_d$ leads to small values of $\bar{C}$ and small values of $\Delta Y_S$. (c) At the same time the average singlet and triplet populations, as seen in Figs. 4(d1)-4(d4), are not affected by the increasing $K_d$. In other words, we have a process by which an initially singlet radical-pair state is coherently transformed into a triplet, and back and forth, but it is the underlying coherence and not the population exchange that seems to be directly connected with the figure of merit $\Delta Y_S$.

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D. The role of the exchange interaction

The exchange interaction is known to play a subtle role in magnetoreception [38][39]. To explore the role of exchange interactions, we included them in the Hamiltonian, with an exchange coupling in the interval \(-10k \leq J \leq 10k\). Now we split this interval into 5 subintervals of width \(\Delta J = 4k\), and study the correlation of the figure of merit \(\delta Y_S\) with the S-T coherence \(\overline{C}\). The result is plotted in Fig. 5a for the case \(K_d = k\), i.e the case where the dynamics are described by our master equation. In the same figure (right y-axis) we also plot the mean value, \(\langle \langle \delta Y_S \rangle \rangle\), of \(\delta Y_S\) for those same subintervals of \(J\).

The behavior of \(\langle \langle \delta Y_S \rangle \rangle\) with \(J\) is known since the work of [38], i.e. it is already known that large values of \(J\) suppress the figure of merit \(\Delta Y_S\).\) of the compass, as is evident in Fig. 5b. We here observe two additional, counterintuitive effects. Namely, (i) for small values of \(J\) the correlation between singlet-triplet coherence \(\overline{C}\) and the figure of merit \(\delta Y_S\) is significantly suppressed, to recover for large values of \(|J|\). (ii) Moreover, there is also an asymmetry in \(\text{Corr}\{\delta Y_S, \overline{C}\}\) between \(J > 0\) and \(J < 0\).

The interpretation of both of these observations is rather challenging, and we will at the moment only offer an educated guess. It is conceivable that they originate from the positions of level crossings in the eigenvalues of the magnetic Hamiltonian, in particular from the complex interplay of energy shifts between the singlet and triplet states produced by the exchange interaction on the one hand, and on the other hand Zeeman shifts of the triplet states.

However, there is a subtle conjecture to be made, resting on two points. Firstly, it is again noted that the absolute value of the figure of merit \(\delta Y_S\) is small for large values of \(J\).
and $\bar{C}$ for the interval $|J|/k < 2$, and for all four values of $K_d$. As mentioned before, this correlation is small for $K_d = 1$, and also for $K_d = 0$. But the correlation recovers for larger values of $K_d$. Based on this, we anticipate that there is another regime of the reaction dynamics, which we have not addressed in this work, and where the correlation could be significant even for small $|J|$. Namely, we here considered equal recombination rates $k_S = k_T = k$, in order to simplify reaction dynamics and decouple from the ongoing discussion on the form of the reaction super-operators. However, the regime $k_T \gg k_S$ is also interesting, and based on Fig. 4, it is conceivable that in this regime there is a large correlation between figure of merit and S-T coherence for all values of the exchange coupling $J$. The study of this possibility will be undertaken elsewhere.

V. CONCLUSIONS

Quantum coherence is a fundamental resource for modern quantum technology. Its formal quantification has been established in recent years, in fact along the lines used to quantify entanglement, which came before. One quantifier of quantum coherence is the quantum relative entropy between the density matrix describing the quantum state of the system under consideration and its diagonal version.

We have here adapted this quantifier to radical-pairs, defining singlet-triplet coherence as the relative entropy between the radical-pair density matrix and its block-diagonal version in the singlet-triplet subspaces. We have then established the properties of this singlet-triplet coherence quantifier at a formal level. Having an explicit quantifier of singlet-triplet coherence, one can study the fundamental properties of biological magnetic sensing in various regimes, for example in regimes where the relevant spin states are highly coherent or highly incoherent.

By doing so, we have shown that singlet-triplet coherence is indeed a quantum resource for magnetoreception, since (i) it is highly correlated with the figure of merit of the radical-pair compass, (ii) both singlet-triplet coherence and the figure of merit decrease significantly in the presence of singlet-triplet dephasing, and (iii) the singlet/triplet populations remain on average unaffected by such dephasing. Thus, due to the observations (i)-(iii) we conclude that it is not the singlet-triplet population exchange but the underlying singlet-triplet coherence that promotes precise heading of the radical-pair compass. Finally we explored the subtle role played by exchange interactions in promoting the correlation between singlet-triplet coherence and the figure of merit of the chemical compass. Along the same lines one could explore the role of other interactions entering the Hamiltonian, in particular when more nuclear spins are included.

Last but not least, while defining the incoherent operations needed in the formulation of singlet-triplet coherence quantification, we gave an example where incoherent
operations on nuclear spins only can have a significant effect on the singlet-triplet coherence, which is of electronic nature. This can happen when nuclear spins and electrons in the radical-pair are entangled, which is in general the case. This observation opens up a promising direction of studying the effects of nuclear spin dynamics, e.g. the interaction with the environment of the radical-pair’s nuclear spins, and their consequences on radical-pair spin dynamics.

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