Quantum sensing and control of spin state dynamics in the radical pair mechanism

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Radical pairs and the dynamics they undergo are prevalent in many chemical and biological systems. Specifically, it has been proposed that the radical pair mechanism results from a relatively strong hyperfine interaction with its intrinsic nuclear spin environment. While the existence of this mechanism is undisputed, the nanoscale details remain to be experimentally shown. We analyze here the role of a quantum sensor in detecting the spin dynamics (non-Markovian) of individual radical pairs in the presence of a weak magnetic field. We show how quantum control methods can be used to set apart the dynamics of radical pair mechanism at various stages of the evolution. We envisage these findings having far-reaching implications to the understanding of the physical mechanism in magnetoreception and other bio-chemical processes with a microscopic detail.

I. INTRODUCTION

Spin plays a fundamental role in many chemical reactions, from photosynthesis¹ to polymerization². One of the most well-studied of those is known as the radical-pair mechanism³. There, two radicals, i.e., molecules with a free electron (S = 1/2), are brought by excitation to such a close distance between them, that their two electrons become entangled and emerge, depending on minimum energy considerations, as either in a triplet or in a singlet⁴ (in both cases, S = 1). Due to interaction with an external magnetic field and the existence of hyperfine interaction with each radical’s nuclear spins, this pair of radicals can undergo oscillations between its triplet and singlet states, with a frequency dependent mostly on the strength of this hyperfine coupling with respect to the surrounding magnetic field⁵. The radical-pair mechanism had been studied extensively using recombination fluorescence⁶, electrochemistry⁷, transient ESR⁸,⁹ and ultrafast absorption spectroscopy¹⁰–¹². All of these techniques probe samples of macroscopic scale, namely microliters or 10⁻¹³ liters or 10⁻¹⁵ sigmas. While providing a wealth of information and improving our understanding of some key processes in said mechanism, the aforementioned tools provide an ensemble average indication as to the magnetic properties one wants to explore. The radical pair mechanism is typically characterized by the spin coherence time¹³–¹⁶ and the recombination rate κ, i.e., the rate at which the pairs recombine back to their original constituents¹⁷. Our approach, using a nanoscale single-spin sensor in the form of the nitrogen vacancy center in diamond¹⁸–²⁰, shows that some of the most remarkable features of the RPM are masked by averaging, and allows us to probe this as-of-now yet un-chartered territory. Our quantum-sensing technique can assist us in determining not only the charge state of the pair²¹ but perhaps more importantly, its spin state. We introduce a detection pulse scheme for single qubit magnetometry¹⁹,²²,²³, that enables a consistent way of realizing whether the pair is in its singlet or one of its three possible triplet states. As this is a single-spin sensor operated in a detection regime where only a small amount of molecules (and hence radical pairs or spins) contributes to the signal²⁴–²⁶, we also show how quantum control schemes allow us to modify and in some instances also enhance the interaction of the radical pair with its external environment, thereby achieving a change in the ratio between the final products.

II. MODEL

We consider a prototypical model used to analyze the sensitivity of a radical pair reaction to external field (ω), wherein a radical pair (σ), composed of two electrons (spin-1/2) coupled to a nuclear spin environment (I). In addition, we also couple the radical pair spins to a sensor (spin-1), S. The Hamiltonian describing their dynamics is given by

\[ H = h_A \vec{I}_A \cdot \vec{\sigma}_A + h_B \vec{I}_B \cdot \vec{\sigma}_B + \omega (\sigma_A^z + \sigma_B^z) + g S^z (\sigma_A^+ + \sigma_B^-), \]

where \( h_{A,B} \) are the hyperfine coupling constants and \( g \) is the RP-sensor coupling strength. For simplicity we set \( h_B = 0 \), and consider a single nuclear spin as the dynamics generated by the above Hamiltonian becomes exactly solvable²⁷,²⁸. One could choose a two-level subspace spanning either by \( |−1\rangle, |0\rangle \) or \(|+1\rangle, |0\rangle \) as our computational subspace for the sensor spin. For example, in this basis of the sensor \(|±1\rangle, |0\rangle \), the above Hamiltonian can be further simplified to

\[ H = H_0 |0\rangle \langle 0| + H_± |±1\rangle \langle ±1|. \]

Here \( H_0 = h_A \vec{I}_A \cdot \vec{\sigma}_A + \omega (\sigma_A^z + \sigma_B^z) \), and \( H_± = h_A \vec{I}_A \cdot \vec{\sigma}_A + (\omega ± g)(\sigma_A^+ + \sigma_B^-) \). From the above equation it is clear that the coupling to the sensor leads to a modified external field for the radical pair. Due to the sensor spin-state dependent enhancement (reduction) of the effective external field seen by the radical pair, the singlet product yield \( \Phi_S \) varies with the occupation probability of the
FIG. 1. a. Schematic representation of the system, wherein the radical pair spins deposited on the surface of the diamond are sensed/controlled by a nitrogen vacancy center (NV) embedded in the diamond lattice. The inset (a1) shows the coupling of radical pair spins to their local nuclear spin environment and in (a2) the distance-dependent coupling of NV to the radical pair spins. b. The singlet-triplet oscillations and the corresponding oscillations in the contrast of the sensor (NV) are shown as a function of time. c. The asymptotic singlet state population and the sensor spin contrast (Eq. (3)) are plotted as a function of a weak external field \( \omega \). d. The average singlet production yield in the presence of the NV induced gradient field is shown for the cases of zero width (\( \eta \)) and finite width of the distribution of the coupling strengths \( g \) (see Eq. (6)). In the above simulations we have chosen all the parameters in units of the hyperfine coupling strength \( h_A \): the singlet recombination rate \( \kappa = 0.01 h_A \), and the sensor-RP coupling to be \( g = 0.1 h_A \).

sensor in either of its spin states. In turn, this leads to a visible contrast in the spin-state readout of the sensor itself. Following Ref.27 and evaluating the singlet-triplet oscillations, \( \Phi_S^0, \Phi_S^+ \) for the corresponding sensor spin-states, we find the modified singlet fraction yield, \( \Phi_S \)

\[
\Phi_S = (\Phi_S^+ + \Phi_S^0)/2, \quad C_\Phi \approx |\Phi_S^+ - \Phi_S^0|. \tag{3}
\]

Here \( \Phi_S \) is obtained by tracing out sensor degrees of freedom from exact dynamics using the above Hamiltonian. The sensor signal (contrast \( C_\Phi \)) is obtained by a Ramsey measurement, i.e., starting from the sensor state which is in a equal quantum superposition of its spin states (\( \pi/2 \)-pulse), and letting it evolve freely under the evolution generated by Eq.(2). After the free-evolution another \( \pi/2 \)-pulse is performed to map the phase accumulated during the free evolution to the population of the spin-states which is then measured to obtain \( C_\Phi \) as the population difference between the two states. After tracing out the RP degrees of freedom (see Appendix for details), the time-dependent sensor contrast is given by

\[
C_\Phi(t) = \text{Tr} \left[ \text{Re} \{ e^{iH_0 t} \rho_{RP}(0) \otimes \rho_I(0) e^{iH_1 t} \} \right] \tag{4}
\]

where \( \rho_{RP}(0) = |S \rangle \langle S | \) is the initial singlet state of the radical pair spins, and \( \rho_I(0) = 1/2I \) is the initial thermal state of the nuclear spin. One can obtain an exact expression upon simplifying the above equation, given by

\[
C_\Phi(t) = \frac{1}{\Omega_1 \Omega_2} \left[ \sin(t \Omega_1) \left( 2 \left( \Omega_1^2 + g \omega \right) \cos(gt) \sin(t \Omega_2) - 2 \omega \Omega_2 \sin(gt) \cos(t \Omega_2) \right) + \Omega_1 \cos(t \Omega_1) \left( 2 (g + \omega) \sin(gt) \sin(t \Omega_2) + 2 \Omega_2 \cos(gt) \cos(t \Omega_2) \right) \right] + 2 \Omega_1 \Omega_2 \tag{5}
\]
where \( \Omega_1 = \sqrt{a^2 + \omega^2} \) and \( \Omega_2 = \sqrt{a^2 + (w + g)^2} \). This is the central result of the paper and from this we obtain directly the dynamic behavior shown in Fig. 1(b). To obtain the asymptotic behavior of the contrast similar to the singlet fraction in the presence of the relaxation rate \( \kappa \), we integrate the contrast obtained from the singlet dynamics of the RP over all the interaction time \( t \), i.e., \( C_\Phi(\kappa) = \int_0^\infty dt C_\Phi(t)e^{-\kappa t} \). Assuming ultra-long coherence time of the sensor, the asymptotic dependence of the singlet fraction and the contrast on the external field \( \omega \) is shown in Fig. 1(c).

In Fig. 1(c) we show the effect of magnetic field \( (\omega) \) on the singlet yield of a one-proton radical pair (see Eq. (1)). It has been shown previously that the singlet product yield shows an abrupt change even by a tiny magnetic field in the low-field limit and for a slow recombination rate \( \kappa \). We observe a similar behavior in the sensor contrast, \( C_\Phi \), with \( \omega \). The singlet fraction shown here is the steady state population obtained in the long-time limit where the coherent singlet-triplet mixing and the incoherent mixing caused by the relaxation are in equilibrium. One could also analyze the dynamics for times shorter than the relaxation time as shown in Fig. 1(c). The singlet-triplet oscillations are also seen on the sensor contrast. As opposed to the fast oscillations in the singlet fraction caused by the hyperfine interaction \( h_A \), the oscillation frequency of the sensor contrast is due to the small coupling strength \( g \ll h_A \).

### III. ENSEMBLE SENSING

While the above analysis holds for a single RP with a given interaction strength \( g \) to the sensor holds in general, in a practical setting, an ensemble of RPs is drop-casted on top of the diamond surface or on the apex of an AFM tip and then scanned with respect to the NV. Due to this the sensor interacts with a large number of RPs within a sensing volume that is determined by the distance between the surface and the sensor. Owing to interaction with a large number of RPs both the singlet production rate and the sensor contrast get affected due to the averaging over the effective field generated by the sensor on the different RPs and vice-versa. In order to accommodate this we now integrate the functions given in Eq. (3) over some distribution for \( g \), i.e.,

\[
\Phi_S(\eta) = \int dg e^{-\eta(g-g_0)^2} \Phi_S(g),
\]

\[
C_\Phi(\eta) = \int dg e^{-\eta(g-g_0)^2} C_\Phi(g).
\] (6)

For increasing width of this distribution the oscillations seen in the single RP limit eventually vanishes in the large \( N \)-limit. A similar behavior can also be seen for finite time in Fig. 1(c), where we directly plot the time-dependent behavior of the triplet-pair production \( \Phi(t) \) from the unitary evolution generated by Hamiltonian given in Eq. (1). The characteristic oscillations of the triplet fraction shown in the Fig. 1(d) indicate the singlet-triplet oscillations. In the presence of interaction with the sensor, the dampening of the oscillations can be understood as an additional random phase \( \phi \) (see Appendix) introduced by the sensor coupling, leading to a gradual loss of coherent behavior of the triplet-pair production in time. Both the asymptotic and finite time analysis clearly display the role of an additional sensor interaction both for sensing the RP dynamics, and in turn influencing its production rate. This influence can be further induced in a controlled manner if one employs coherent control of the sensor spin (see Appendix).

### IV. EXPERIMENTAL IMPLEMENTATION

Apart from the theoretical model shown here, we also propose an apparatus for sensing and controlling the RP spin state as described above. This consists of a scanning confocal microscope for the initialization and read-out of the NV state, as is schematically shown in Fig. 2(a). Green laser (520 nm) is used for excitation, and the NV fluorescence in the range of 650 nm to 800 nm is collected and focused onto an avalanche photodiode. The microscope is integrated with a variable magnetic field implemented by either a permanent magnet (Nd-FeB or SmCo) on an XYZ stage for a room temperature setup or a set of three pairs of split Helmholtz coils for a low temperature measurement. In addition, a microwave antenna is positioned near the NV center for spin state manipulation of both the NV spin and the RP state. Finally, for RPs based on the Flavin-Tryptophan pair, a pulsed blue diode (460 nm) is to be positioned such that the RPs can be created. A schematic of such an apparatus is shown in Fig. 2(a).

Using a single NV center in diamond, our approach to detect the spin state of the radical pair relies on a triple-electron resonance (TEER) sequence introduced by us in Ref. 26. This entails a preliminary frequency scan of each radical’s Larmor precession frequency, taking into account a small shift between the two radicals in the pair due to dipole-dipole interaction, as written in the second term of Eq. (1). Combining this with the proposed protocol for the pair’s charge state determination, our spin state scheme can allow us to distinguish between the different triplet spin states, as well as giving a threshold below which we can safely establish that the RP is in the singlet state. In Fig. 2(b) we show the original and modified TEER pulse sequence for detecting the exact spin state of the RP. In Fig. 2(b) the NV’s normalized contrast when employing this pulse sequence while varying the time between microwave pulses, \( \tau \), is shown and the four spin states of the two-electron system (RP) become clearly distinguishable.
FIG. 2. a. A schematic representation of the experimental setup displaying a diamond substrate with RP spins on its surface. We also show the initialization and readout mechanism of the sensor spin state through the green laser (520 nm) and detection through its red side-band emission (650 – 800 nm). A blue LED (460 nm) is used to initialize the RP mechanism that will be sensed through the NV center in the diamond lattice. b. We show the modified DEER pulse sequence (b1) in b2 wherein a π-pulse is replaced by a π/2-pulse to differentiate the singlet and triplet states as shown in the plot on the right, where we vary the free evolution time τ, and initialize the RP in various spin states.

FIG. 3. Spin-state dependent singlet yield is shown for single RP-sensor coupling. For the simulations we set the recombination rate $\kappa = 0.01 h_A$, which also sets the resolution for the sensor and $g = 0.5 h_A$.

V. QUANTUM CONTROL

The experimental difficulty in clearly resolving the singlet triplet oscillations stems from the ensemble dynamics of the RP spins in the presence of external field, as shown in Fig. 1(d). One can use the sensor coupling instead to resolve individual RP’s as shown in Fig. 3. For this we choose the computational basis for the sensor spin as $| -1 \rangle$, $| 0 \rangle$. Due to this the effective field seen by a given RP is $\omega - g$. By scanning the external field $\omega$, one finds an enhanced singlet fraction when the total effective field becomes zero. As shown in Fig. 3, the peak is centered around the value of the external field, and the width is determined by the recombination rate $\kappa$. The aspect of quantum control arises when one changes the spin state of the sensor from $m_s = +1$ to $m_s = -1$ in a controllable way.

VI. CONCLUSION AND OUTLOOK

The use of a quantum sensor, i.e., a true two-level system as the detection tool opens a wide range of possibilities for optimization and control which are not accessible to macroscopic or classic objects. Namely, it allows us to decouple the target spin from its surrounding spin bath and even make use of potentially helpful nuclear spins in the immediate vicinity of the radicals, such as those which are hyperfine coupled to them. We find that even such a basic protocol (before optimization) can lead to a visible enhancement of the triplet/singlet ratio, and hence in effect we show control over at least one stage of the radical pair mechanism. As mentioned above, this can be further improved by polarizing the radicals’ neighboring nuclear spins. A fully polarized nuclear spin species, for example could result in nearly a two-fold increase in the sensor contrast when compared to its thermal polarization. Moreover, due to the quantum nature of both the NV and the RP, it is possible to devise a model which takes such a single spin sensor and an $N$-sized collection of radicals pairs, and show that as one reduces the number of pairs in the sensor’s vicinity, one can obtain a significantly improved visibility contrast for reading out the state of the pairs.

To conclude, we have shown here the role of a quantum sensor in sensing and controlling the RP mechanism to weak external fields, both for the case of single
and ensemble RPs. We have also given modified multi-electron electron resonance spectroscopy pulse sequences to clearly distinguish the four different singlet/triplet configurations, and find the conditions for the optimal sensitivity in terms of magnetic field strength, hyperfine interaction and recombination rate. We have also shown a preliminary quantum control aspect wherein modulation of sensor spin state can have dramatic effect on the RP dynamics and we envisage that additional tailor-made protocols can improve this even further. Our results continue a line of theoretical proposals for detecting various aspects of the phenomenon known as the radical pair mechanism, which can now be considered for experimental realization as the technical aspects of assembling the appropriate setups are being constantly tackled and resolved.

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APPENDICES

Appendix A: Dynamics

The time-evolution operator corresponding to the Hamiltonian (Eq. (2)) is given by

\[ U = U_0 \langle 0 | \langle 0 | + U_{\pm 1} \langle \pm 1 | \langle \pm 1 | \right] \tag{A1} \]

where \( U_0 = e^{iH_0t} \) and \( U_{\pm 1} = e^{iH_{\pm 1}t} \). Starting from an initial state of the sensor in \( |\psi_S\rangle = \frac{1}{\sqrt{2}} (|0\rangle + |1\rangle) \), and the RP in a singlet state \( |\psi_\sigma\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \), the time-evolved state for the total system can be found using

\[ \rho(t) = U \rho(0) U^\dagger \tag{A2} \]

where \( \rho(0) = |\psi_S\rangle \langle \psi_S| \otimes |\psi_\sigma\rangle \langle \psi_\sigma| \otimes \frac{1}{2} \hat{I}_A \), where the nuclear spin state is taken to be a thermal state, i.e., a fully mixed state \( \frac{1}{2} \hat{I}_A \). The reduced state of RP spins and their coupled nuclear spins can be obtained by tracing out the sensor degrees of freedom, and vice-versa respectively as

\[ \rho_{\sigma,ts}(t) = Tr_S \rho(t), \quad \rho_S(t) = Tr_{\sigma,ts} \rho(t). \tag{A3} \]

For the above initial state of the sensor, the RP state

\[ \rho_{\sigma,ts}(t) = \frac{1}{2} [U_0 \rho_{\sigma,ts}(t) U_0^\dagger + U_1 \rho_{\sigma,ts}(t) U_1^\dagger] \tag{A4} \]

Due to the above symmetry, the total singlet fraction will also be \( \Phi_S = \langle \Phi_S^1 + \Phi_S^0 \rangle / 2 \).

Appendix B: Triplet fraction

Based on the one-proton radical pair model presented in Ref. 27, we calculate \( \Phi_T(t) = 1 - \Phi_S(t) \), where

\[ \Phi_S(t) = \frac{3}{8} + \frac{1}{8} \frac{\omega^2}{\Omega^2} + \frac{1}{8} \frac{h^2}{\Omega^2} f(\Omega) + \frac{1}{8} \left( 1 - \frac{\omega}{\Omega} \right) \left( \frac{1}{2} h + \frac{1}{2} \omega + \frac{1}{2} \Omega \right) + \frac{1}{8} \left( 1 - \frac{\omega}{\Omega} \right) \left( \frac{1}{2} h - \frac{1}{2} \omega - \frac{1}{2} \Omega \right) + \frac{1}{8} \left( 1 + \frac{\omega}{\Omega} \right) \left( \frac{1}{2} h - \frac{1}{2} \omega + \frac{1}{2} \Omega \right) + \frac{1}{8} \left( 1 + \frac{\omega}{\Omega} \right) \left( \frac{1}{2} h + \frac{1}{2} \omega - \frac{1}{2} \Omega \right). \]

Here \( h \) is the hyperfine coupling strength in rad/sec, \( \omega \) is the Zeeman interaction term or magnetic field in rad/sec, \( \Omega = \sqrt{h^2 + \omega^2} \) and \( f(x) = \cos(xt + \varphi) \). Note that \( \varphi \) was not included in the original derivation and accounts for a random phase for each radical pair. We take a magnetic field of 50 µT and a hyperfine interaction strength of 14 MHz.

We consider a radical pair initially formed in a singlet configuration, and evolves under both the hyperfine interaction with its neighboring nuclear spins and with the external (Zeeman) field. For the current discussion we neglect their intra-spin interaction and consider their interaction with a nearby probe spin, the NV center. From the coherent evolution of the pair \( \rho(t) \) the singlet state dynamics can be evaluated as

\[ P_S(t) = |S_0\rangle \langle \rho(t)|. \tag{B1} \]

where \( \rho(t) \) is obtained by tracing out the degrees of freedom of the nuclear and probe spins. Further, upon considering the radical-pair recombination mechanisms, the decay of singlet products, or the singlet yield in RP mechanism is simply captured through

\[ P_S(k, t) = \int_0^t dt P_S(t)e^{-kt}. \tag{B2} \]
Appendix C: Quantum Control

The ability to control the singlet product yield through the quantum sensor becomes possible due to the sensor spin-state dependent evolution of the radical pair. Upon coherently flipping of the sensor spin, the singlet yield could be manipulated and hence to its sensitivity to low fields and low recombination rates. To see this, we write down the evolution operator corresponding to the above Hamiltonian, given by

\[ U = U_0 |0\rangle \langle 0| + U_1 |1\rangle \langle 1|. \] (C1)

Let us consider a \( \pi \)-flip operation on the sensor spin, followed by the time evolution. This leads to a modified time-evolution operator, given by

\[ V_1 = U e^{i \pi S_x} U = U_1 U_0 |1\rangle \langle 0| + U_0 U_1 |0\rangle \langle 1|. \] (C2)

Upon the application of \( M \) (even) \( \pi \)-pulses, the final evolution operator takes the simple form

\[ V_M = U \cdots e^{i \pi S_x} U e^{i \pi S_x} U \\
= (U_1 U_0)^{M/2} |1\rangle \langle 0| + (U_0 U_1)^{M/2} |0\rangle \langle 1|. \] (C3)

From the above evolution the singlet yield is additionally dependent on the stroboscopic interruptions of evolution for every time \( \tau \).