

Sensitive chemical compass assisted by quantum criticality

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A radical-pair-based chemical reaction might be used by birds for navigation via the geomagnetic direction. The inherent physical mechanism is that the quantum coherent transition from a singlet state to triplet states of the radical pair could respond to a weak magnetic field and be sensitive to the direction of such a field; this then results in different photopigments to be sensed by the avian eyes. Here, we propose a quantum bionic setup, inspired by the avian compass, as an ultrasensitive probe of a weak magnetic field based on the quantum phase transition of the environments of the two electrons in the radical pair. We prove that the yield of the chemical products via recombination from the singlet state is determined by the Loschmidt echo of the environments with interacting nuclear spins. Thus quantum criticality of environments could enhance the sensitivity of detection of weak magnetic fields.

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I. INTRODUCTION

Since Schrödinger questioned “What is life?” from the general point of view of a quantum physicist [1], scientists have never stopped long-term exploration of the physical sources of living phenomena, and this even stimulated the enthusiasm for the great discovery of the DNA genetic molecule [2]. Today it seems trivial to say that life has a quantum nature, for the molecules composing living organisms obey quantum laws, but some recent discoveries are very intriguing as some optimized living processes may be based on a *nontrivial* quantum effect from quantum coherence. One example on point is the photosynthesis process. Recent experiments using two-dimensional optical spectroscopy have been able to exactly determine the time scales of various transfer processes and then show quantum coherence effects in energy transfer via collective excitations of some light-harvesting complexes [3–5].

Another prototype of the quantum coherence effect in a living process seems to appear in avian magnetoreception mechanisms [6,7], verified by some recent experiments [8–12]. Recently quantum information approaches have been used to further analyze the role of the quantum coherence phenomenon in avian magnetoreception models [13–16]. It is now believed [17,18] that magnetoreception is based on the radical-pair mechanism (RPM) [6]: a radical-pair molecule with two unpaired electrons is activated by light. When the electrons interact with their individual nuclear environments via hyperfine couplings, the spin singlet state will transit to spin triplet states even though the external field is uniform and rather weak. In response to this quantum coherent transition, the field-dependent change in the product yield of the radical-pair-based chemical reaction is enough to be sensed by the avian retina.

In spite of the rapid progress in the understanding of the RPM in the last decade, the answers to two key questions remain elusive [17]: why does the singlet-triplet interconversion respond to the extremely weak geomagnetic field ($\sim 10^{-5}$ T),

and why is it very sensitive to the field's direction? We note that the existence of nuclear environments surrounding the electron spins in the radical-pair molecule is crucial to the magnetic sensitivity of the chemical reaction. This observation motivates us to consider the role of internal quantum correlation in each environment. In this paper, following this idea, we propose a quantum-phase-transition-assisted setup as a probe of a weak magnetic field. Actually, many real-world detectors are built based on dramatic changes of systems around phase transitions, which amplify an ultraweak signal and thus enable one to probe it. Examples include bubble chamber detectors [19] and superconducting single-photon detectors [20], where the liquid-gas phase transition and superconductor-metal phase transition take place, respectively, enhancing the sensitivity of detection. We calculate the corresponding chemical product yield, which is phenomenologically described by a damping process [21]. It is discovered that the chemical product yield is determined by the time integral of the Loschmidt echo (LE). Our result shows that a chemical compass assisted by quantum criticality indeed can respond to a very weak magnetic field and be sensitive to its direction.

This paper is organized as follows: In the next section, we introduce our model describing a chemical compass assisted by a quantum phase transition (QPT) and diagonalize the total Hamiltonian by means of the Born-Oppenheimer approximation. Then we obtain the product yield of the singlet state in terms of the LE. In Sec. IV, we discuss the possibility of application in present experimental setups. Finally, we summarize the main points in the Conclusions. In addition, for the sake of self-consistency, we present the relation between the product yield and the LE and detailed calculations for the case at finite temperature and the case without interaction between nuclear spins in Appendixes A, B, and C, respectively.

II. QUANTUM-PHASE-TRANSITION-ASSISTED RADICAL-PAIR MECHANISM

Our setup is illustrated in Fig. 1. Each of the two electrons in the radical pair is uniformly coupled to its own

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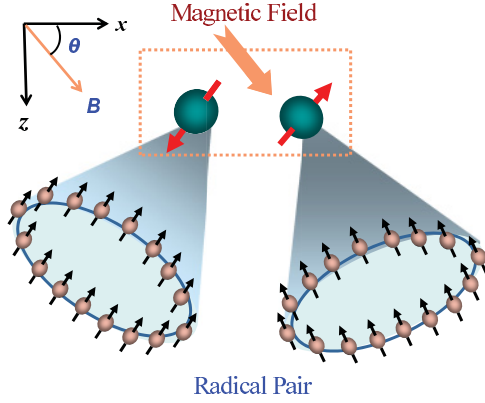


FIG. 1. (Color online) Model setup of sensitive magnetodetection based on a radical-pair chemical reaction assisted by quantum critical environments consisting of interacting spins. Two spins can be initially prepared in the singlet state and finally evolve into triplet states due to the couplings to their environments. The yield of the corresponding chemical product responds sensitively to the external magnetic field.

quantum-correlated environment, which can be described by a transverse-field Ising (TFI) model [22,23]. In an external magnetic field $B(\cos\theta\hat{x} + \sin\theta\hat{z})$, which may be the geomagnetic field, the environment is described by $H'_n = H_n + (g_N\mu_N B/2) \sum_j \sin\theta I_{n,j}^z$ with

$$H_n = J \sum_{j=1}^N (I_{n,j}^z I_{n,j+1}^z + \lambda I_{n,j}^x), \quad (1)$$

where $\lambda = g_N\mu_N B \cos\theta/(2J)$ is the rescaled strength of the transverse field in units of J , the Ising coupling constant, $g_N\mu_N$ is the nuclear magnetic moment, and $n = 1, 2$ refers to the environment of the n th electron. $I_{n,j}^x$ and $I_{n,j}^z$ are Pauli matrices of the j th nuclear spin operators. In the case of an antiferromagnetic Ising chain, i.e., $J > 0$, we can omit the longitudinal terms and $H'_n \approx H_n$ since they lead to only higher-order correction [24]. Here, in contrast to previous studies [6,16–18,21,25], we explicitly consider the internucleus coupling $I_{n,j}^z I_{n,j+1}^z$. This coupling competes with the Zeeman energy, which is proportional to the geomagnetic field, and leads to a QPT at the critical point $\lambda = 1$. A central spin uniformly coupled with each spin in this TFI system possesses dynamic sensitivity described by the sharp decay of the LE near the QPT [26], which has been experimentally verified [24,27,28].

The two unpaired electrons in the radical pair couple to the two environments E_1 and E_2 respectively with the following Hamiltonians:

$$V_n = \Omega \sin\theta \sigma_n^z + \Omega \cos\theta \sigma_n^x + Jg\sigma_n^x \sum_j I_{n,j}^x, \quad (2)$$

where σ_n^x and σ_n^z for $n = 1, 2$ are the Pauli operators for the n th electron spin, and the dimensionless coupling constant scales as $g = g_0/\sqrt{N}$ in the Van Hove limit for the interacting many-body system. All the information about the geomagnetic field is also incorporated in θ and Ω , which is the electronic Zeeman energy splitting induced by the geomagnetic field.

Due to the spin-flip terms, the time evolution governed by the total Hamiltonian $H = \sum_n (H_n + V_n)$ can be solved only with some approximation. Usually the electron spins evolve faster than the nuclear spins. Thus we can first regard nuclear spins as c numbers for formally diagonalizing the electronic Hamiltonian V_n through a generalized Born-Oppenheimer approximation [29]. The eigenstates of the electron spins are obtained as

$$|+\rangle = \cos(\alpha/2)|\uparrow\rangle + \sin(\alpha/2)|\downarrow\rangle, \quad (3)$$

$$|-\rangle = \sin(\alpha/2)|\uparrow\rangle - \cos(\alpha/2)|\downarrow\rangle, \quad (4)$$

where $|\uparrow\rangle$ ($|\downarrow\rangle$) is the spin-up (spin-down) state in the σ_x representation with corresponding eigenvalues $E_{\pm} = \pm E$ for

$$E = \sqrt{\Omega^2 \sin^2\theta + \Delta^2}, \quad (5)$$

$$\Delta = \Omega \cos\theta + Jg \sum_j I_{n,j}^x. \quad (6)$$

The mixing angle is defined as

$$\alpha = \frac{\pi}{2} - \tan^{-1} \left(\frac{\Omega \sin\theta}{\Delta} \right). \quad (7)$$

For the weak coupling ($Jg_0 \ll \Omega$) of an electron to nuclei we approximately obtain the eigenstates

$$|+\rangle \simeq \cos\theta' |\uparrow\rangle + \sin\theta' |\downarrow\rangle, \quad (8)$$

$$|-\rangle \simeq \sin\theta' |\uparrow\rangle - \cos\theta' |\downarrow\rangle \quad (9)$$

to the zeroth order of g for

$$\theta' = \frac{1}{2} \left(\frac{\pi}{2} - \theta \right) \quad (10)$$

and the eigenenergy

$$E \simeq \Omega + Jg \cos\theta \sum_j I_{n,j}^x \quad (11)$$

to the first order. The Born-Oppenheimer approximation shows that the slowly varying nuclear spins will not induce a coherent transition of the quickly varying electronic degrees, but the electronic motion provides an effective potential for the nuclear spins. In this sense, the total Hamiltonian is approximately rewritten as

$$H \simeq \sum_n (H_n^+ |+\rangle\langle +| + H_n^- |-\rangle\langle -|), \quad (12)$$

where the different effective Hamiltonians for the nuclear spins corresponding to states $|\pm\rangle$ are

$$H_n^{\pm} = J \sum_j [I_{n,j}^z I_{n,j+1}^z + (\lambda \pm g \cos\theta) I_{n,j}^x] \pm \Omega. \quad (13)$$

It can be proven that the Born-Oppenheimer approximation is generally valid even for such a large N that a QPT occurs.

III. PRODUCT YIELD AND LOSCHMIDT ECHO

The radical pair is assumed to be initially in the singlet state $|S\rangle$ which subsequently undergoes the homogeneous interaction $V = \sum_n V_n$ with the environmental nuclear spins. Then the radical pair undergoes a singlet-to-triplet transition. The charge recombination of the radical pair goes through different channels, depending on the electron-spin state (singlet

or triplet). In particular, the singlet-state product yield formed by the reaction of radical pairs can be calculated as [21]

$$\Phi_S(t) = \int_0^t r_c(t) f_S(t) dt, \quad (14)$$

where $r_c(t)$ is the radical reencounter probability distribution and $f_S(t) = \langle S | \rho_e(t) | S \rangle$ the singlet-state population at time t . Usually it is assumed [21] that

$$r_c(t) = k_S \exp(-k_S t) \quad (15)$$

with k_S the recombination rate. The ultimate product yield $\Phi_S \equiv \Phi_S(t \rightarrow \infty)$ in cryptochrome is believed to affect the visual function of animals [6]. In order to quantitatively describe the magnetic-field sensitivity of the radical-pair reaction, we shall resort to the magnetoreception sensitivity [25]

$$\Lambda(\theta) = \partial \Phi_S / \partial \theta. \quad (16)$$

In addition, we remark that the singlet-state product yield of the form given in Eq. (14) was derived from a phenomenological master equation, which might mask some underlying quantum coherence effect as pointed out in Ref. [13]. Therefore, we proposed a generalized Holstein model to describe the microscopic mechanism underlying the spin-dependent chemical reactions [30].

For nuclear spins initially in the mixed state $\rho_1 \otimes \rho_2$, the initial state of the total system is $\rho(0) = |S\rangle\langle S| \otimes \rho_1 \otimes \rho_2$. Furthermore, we assume that the initial states of the environments of the two electrons are identical, i.e., $\rho_1 = \rho_2 = \rho$. Under these circumstances, one can find that the reduced density matrix for the electron spins has the simple form (as shown in Appendix A)

$$\rho_e(t) = \frac{1}{2} [|+\rangle\langle +| + |-\rangle\langle -| - L(t) |+\rangle\langle -| - L(t) |-\rangle\langle +|], \quad (17)$$

where

$$L(t) = |\text{tr}[U^+ \rho (U^-)^\dagger]|^2 \quad (18)$$

is just the *Loschmidt echo* characterizing the dynamic sensitivity of the environment in response to the perturbation [26], and $U^\pm = \exp(-iH^\pm t)$. Thus it is found that the singlet-state population $f_S(t) = \frac{1}{2}[1 + L(t)]$, which leads to the central result of our paper

$$\Phi_S = \frac{1}{2} + \frac{1}{2} k_S \int_0^\infty L(t) e^{-k_S t} dt. \quad (19)$$

Hereafter, we calculate the product yield for identical environments in an initial pure state, which corresponds to the case with absolute zero temperature. In this case, the initial state can be described by a state vector $|G\rangle$ and the LE is simplified as

$$L(t) = |\langle G | \exp(iH^- t) \exp(-iH^+ t) | G \rangle|^2, \quad (20)$$

which was explicitly given in Ref. [26]. In the following we take two specific cases into account. First, we consider the large- N case since the QPT usually occurs in this limit.

Using the analytical results for $L(t)$ obtained in Ref. [26], we approximate the product yield around the critical point as

$$\Phi_S \simeq \frac{1}{2} + \exp\left(\frac{k_S^2}{4\gamma}\right) \sqrt{\frac{\pi k_S^2}{2\gamma}} \left[1 - \text{erf}\left(\frac{k_S}{2\sqrt{\gamma}}\right)\right], \quad (21)$$

where $\text{erf}(x)$ is the error function, and

$$\gamma = \frac{8J^2 g^2 N K_c^3 \cos^2 \theta}{3\pi(1-\lambda)^2} \quad (22)$$

with K_c the cutoff momentum. For a sufficiently small k_S , i.e., $k_S \ll 2\sqrt{\gamma}$, the product yield is approximated as

$$\Phi_S \approx \frac{1}{2} + \frac{\pi k_S |1-\lambda|}{16Jg \cos \theta} \sqrt{\frac{6}{N K_c^3}}. \quad (23)$$

Since $\partial \Phi_S / \partial \lambda$ is discontinuous when $\lambda = 1$, it may serve as an indicator of the QPT.

In the opposite case, we consider a small N , where the above analysis fails. Therefore, we shall deal with it separately. For $N = 2$, we obtain explicitly

$$L(t) = 1 - \frac{16g^2 \cos^2 \theta \sin^2[\sqrt{1+4\lambda_\pm^2(\theta)t}]}{[1+4\lambda_-^2(\theta)][1+4\lambda_+^2(\theta)]}, \quad (24)$$

where

$$\lambda_\pm(\theta) = \lambda \pm g \cos \theta. \quad (25)$$

This shows that the setup for a small N cannot work as well as for a large N .

The above results are obtained for an ideal case with pure states. For practical purposes, we need to consider cases at finite temperatures. For the system considered in this paper, the LE at finite temperature can be calculated analytically as shown in Appendix B. In order to illustrate the result for a very large N , we numerically plot the product yield Φ_S vs the magnitude B and direction θ of the magnetic field at a finite temperature in Fig. 2. The product yield displays obvious dependence on both the geomagnetic field's magnitude and its direction. In addition, there is a deep valley around the top left corner. This can be seen from the fact that the LE decays in a Gaussian way around the critical point $\lambda \simeq 1$. Additionally, in

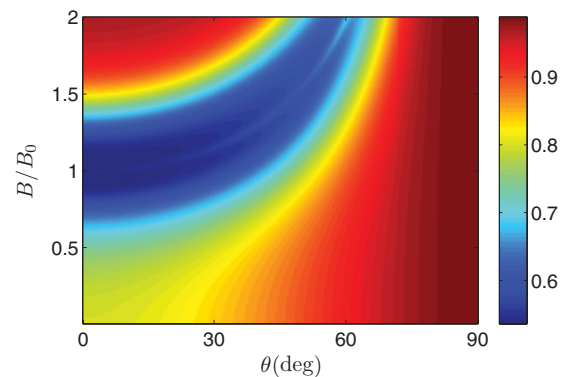


FIG. 2. (Color online) The product yield Φ_S vs the magnitude B and direction θ of the magnetic field at a finite temperature $k_B T = 0.2J$ with $N = 1000$, $g_0 = 1$, $k_S = 0.1J$, $J = 100$ Hz, $g_N = 1.905$, and $B_0 = 50 \mu\text{T}$.

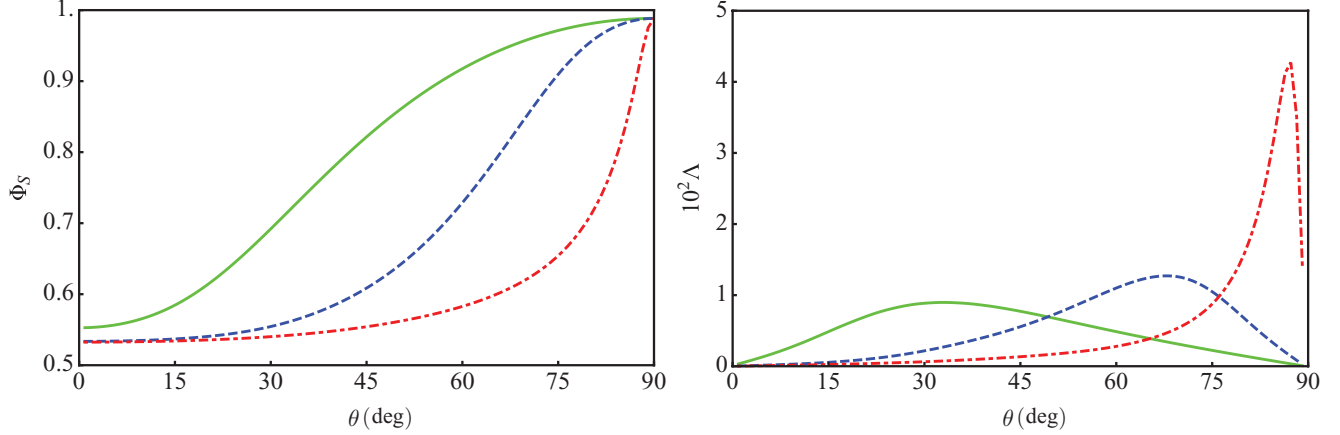


FIG. 3. (Color online) The product yield Φ_S and its derivative vs the geomagnetic field's direction θ (in degrees) for different T 's with $k_S = 0.1J$, $N = 1000$, $g_0 = 1$, $g_N \mu_N B/2 = 0.9J$, and $J = 100$ Hz: blue dashed line for $k_B T = 0.01J$, green solid line for $k_B T = 0.3J$, and red dash-dotted line for $k_B T = 0.9J$.

the regions far away from the critical point, e.g., at the top left and bottom right corners, the product yield stays nearly unity for the LE scarcely decays.

Furthermore, in order to investigate the influence of other parameters, we plot the product yield and its derivative vs direction for different temperatures in Fig. 3. The similarity among the cases at different temperatures is that there is a peak in $\Lambda(\theta)$ as it increases from zero at $\theta = 0$. It is seen that, as the temperature increases, the position of the peak moves toward $\theta = \pi/2$; meanwhile the line shape on the left-hand side becomes more and more flat. In the high-temperature limit, we would expect a sharp peak around $\theta = \pi/2$, while there is a plateau elsewhere. In this case, the device can no longer discriminate the direction. This is a reasonable result since a QPT takes place at absolute zero, and a high temperature smears the QPT. When we come to the hyperfine coupling strength g_0 in Fig. 4, we see that the situation becomes more complicated. As the coupling strength increases, the difference between the maximum and minimum of the product yield is enlarged. At the same time, the plateau in the small- θ

region becomes wider and wider. Therefore, in order to attain a considerable sensitivity for a broad region of direction, a moderate hyperfine coupling strength is required, e.g., $g_0 \sim 1$. In addition, we observe that the more slowly the singlet state reacts, the more the product yield changes along with the direction. That is because a reaction with a smaller recombination rate provides more time for the decay of the LE. This observation is consistent with the result in Ref. [17]. In addition, as the environment involves more nuclear spins, the visibility rises as the LE decays faster for a larger N .

IV. COMPARISON AND DISCUSSION

In this paper, we consider a quantum compass model with the sensitivity enhanced by quantum criticality in the nuclear environment. In order to show that this enhancement is induced by the interactions between nuclear spins, we shall make a comparison between the results with and without the interactions. Based on the calculation in Appendix C, in the

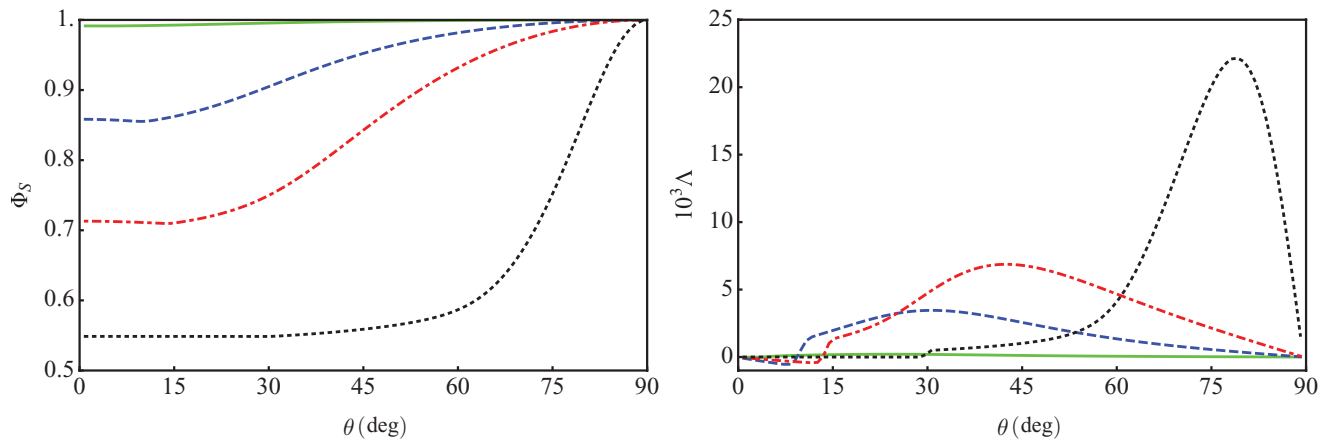


FIG. 4. (Color online) The product yield Φ_S and its derivative vs the geomagnetic-field direction θ (in degrees) for different g_0 's with $N = 1001$, $g_N \mu_N B/2 = J$, $T = 0$, and $J = 100$ Hz: green solid line for $g_0 = 0.1$, blue dashed line for $g_0 = 0.5$, red dot-dashed line for $g_0 = 1$, and black dotted line for $g_0 = 5$.

large- N and small- k_S regime, we obtain the sensitivity for the case without interactions between nuclear spins as

$$\Lambda_{\text{non}}(\theta) = \frac{-2 \sin^3 \theta}{N \cos^5 \theta}, \quad (26)$$

which diminishes as N approaches infinity. In contrast, the counterpart for the case with the interactions between nuclear spins reads

$$\Lambda(\theta) = \frac{\pi k_S |1 - \lambda| \sin \theta}{16 J g_0 \cos^2 \theta} \sqrt{\frac{6}{K_c^3}}, \quad (27)$$

which obviously remains a nonvanishing value in the infinite- N limit. Therefore, due to the presence of the interaction between nuclear spins, the sensitivity of magnetoreception is strengthened.

As far as the validity of our model is concerned, the question is whether the environments of the electrons are near the critical point. To show this, we can consider some basic organic molecules, such as diethyl-fluoromalonate in Ref. [27] or trichloroethylene in Ref. [24]. The coupling constants between nuclear spins in these molecules are about 10^2 Hz. For nuclear spins, g_N is of order 1 and μ_N is of order 10^{-27} J T $^{-1}$. Furthermore, the geomagnetic field B_0 is of order 10^{-5} T. Thus, we have the strength of the transverse field $g_N \mu_N B_0 / 2$ of order 10^2 Hz which indeed keeps the nuclear spins in these molecules in the regime near the critical point. On the other hand, the product yield may not respond to the variation of the geomagnetic-field direction as the temperature rises. In order to make our scheme work at a sufficiently high temperature, i.e., $k_B T \sim J$, we shall require a sufficiently large coupling constant between nuclear spins in the environment. Fortunately, recent progress in experiments provides us with better parameters, e.g., $J \sim$ meV in Ref. [31], which corresponds to $T \sim 80$ K.

V. CONCLUSION

We propose a RPM-based magnetodetection scheme assisted by a QPT. We have proved that the yield of the chemical product obtained via recombination from the singlet state is determined by the LE of the environment. This relation results in enhanced sensitivity of the RPM-based chemical compass. Thus, our study not only provides important insights into the mechanism of magnetoreception through a radical-pair process in a very weak field, but also sheds light on construction of a quantum bionic device for ultrasensitive magnetic-field sensing. In addition, in our bionic setup, the sensitivity is pronounced when the nuclear spin number is large and the recombination rate is small.

It may be argued that in realistic molecules, the environments of radical pairs consist of a few rather than numerous nuclei, i.e., $N \rightarrow \infty$ for a QPT. But experiments [24,27,28] have demonstrated that even for $N = 2$, there still exists dynamic sensitivity induced by quantum criticality. This result implies that dynamic sensitivity may have a close relation with a level crossing. In addition, although our scheme requires a very low temperature for the current experimental parameters, its importance also lies in the possibility of a bionic setup for sensitive magnetodetection. Last but not least, our results are

based on the TFI model, but the enhancement of LE decay due to the QPT is independent of the model [32]. Thus it is reasonable to infer that all the results obtained from the TFI model can be generalized to other models as well, such as the so-called long-range TFI model or the Lipkin-Meshkov-Glick model [23]. Detailed studies of these generalization will be given in a forthcoming presentation.

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APPENDIX A: RELATIONSHIP BETWEEN THE PRODUCT YIELD AND THE LOSCHMIDT ECHO

In this Appendix, we will present the relationship between the singlet-state product yield and the LE of the environments. In Sec. II, we found that the total Hamiltonian can be written as

$$H = \sum_{n=1,2} (H_n^+ |+\rangle_{nn} \langle +| + H_n^- |-\rangle_{nn} \langle -|), \quad (A1)$$

where H_n^\pm are the Hamiltonians of the n th electron's environment and $|\pm\rangle_n$ are the states of the n th electron's spin. By noting that the identity operator on the n th electron spin's Hilbert space can be written as $|+\rangle_{nn} \langle +| + |-\rangle_{nn} \langle -|$, we find

$$\begin{aligned} H = & |+\rangle_{11} \langle +| \otimes (|+\rangle_{22} \langle +| + |-\rangle_{22} \langle -|) \otimes H_1^+ \\ & + |-\rangle_{11} \langle -| \otimes (|+\rangle_{22} \langle +| + |-\rangle_{22} \langle -|) \otimes H_1^- \\ & + (|+\rangle_{11} \langle +| + |-\rangle_{11} \langle -|) \otimes |+\rangle_{22} \langle +| \otimes H_2^+ \\ & + (|+\rangle_{11} \langle +| + |-\rangle_{11} \langle -|) \otimes |-\rangle_{22} \langle -| \otimes H_2^-. \end{aligned} \quad (A2)$$

For simplicity, $|\pm\rangle_1 \otimes |\pm\rangle_2$ is denoted by $|\pm\pm\rangle$ and the above formula can be rewritten as

$$\begin{aligned} H = & |++\rangle \langle ++| \otimes (H_1^+ + H_2^+) \\ & + |--\rangle \langle --| \otimes (H_1^- + H_2^-) \\ & + |+-\rangle \langle +-| \otimes (H_1^+ + H_2^-) \\ & + |-+\rangle \langle -+| \otimes (H_1^- + H_2^+). \end{aligned} \quad (A3)$$

Thus one finds that this Hamiltonian does not lead to a transition between two different electron spin states, e.g., the transition between $|--\rangle$ and $|+-\rangle$ is forbidden. For the system we considered, the initial state of the electron spins is a singlet state, i.e., $|S\rangle = (|+-\rangle - |-+\rangle) / \sqrt{2}$. Therefore the electron spin system will evolve in the subspace $V = \text{span}\{|+-\rangle, |-+\rangle\}$. Confined in this subspace, the Hamiltonian of the total system can be written in the following matrix form (in the basis $\{|+-\rangle, |-+\rangle\}$):

$$\begin{aligned} H|_V = & \begin{bmatrix} H_1^+ + H_2^- & 0 \\ 0 & H_1^- + H_2^+ \end{bmatrix} \\ = & \begin{bmatrix} H_1^+ & 0 \\ 0 & H_1^- \end{bmatrix} \otimes \begin{bmatrix} H_2^- & 0 \\ 0 & H_2^+ \end{bmatrix}, \end{aligned} \quad (A4)$$

and the corresponding evolution operator is

$$U(t) = \exp(-iH|_V t) \\ = \begin{bmatrix} U_1^+(t) & 0 \\ 0 & U_1^-(t) \end{bmatrix} \otimes \begin{bmatrix} U_2^-(t) & 0 \\ 0 & U_2^+(t) \end{bmatrix}, \quad (\text{A5})$$

where $U_n^\pm(t) = \exp(-iH_n^\pm t)$ for $n = 1, 2$. Thus the state of the total system at time t is $\rho(t) = U(t)\rho(0)U^\dagger(t)$, and since $\rho(0) = |S\rangle\langle S| \otimes \rho_1 \otimes \rho_2$ its explicit expression is

$$\rho(t) = \frac{1}{2} [|+-\rangle\langle +-| \otimes U_1^+ \rho_1 (U_1^+)^\dagger \otimes U_2^- \rho_2 (U_2^-)^\dagger \\ + |+-\rangle\langle -+| \otimes U_1^- \rho_1 (U_1^-)^\dagger \otimes U_2^+ \rho_2 (U_2^+)^\dagger \\ - |+-\rangle\langle -+| \otimes U_1^+ \rho_1 (U_1^+)^\dagger \otimes U_2^- \rho_2 (U_2^-)^\dagger \\ - |+-\rangle\langle +-| \otimes U_1^- \rho_1 (U_1^-)^\dagger \otimes U_2^+ \rho_2 (U_2^+)^\dagger]. \quad (\text{A6})$$

For the above state of the total system at time t , the reduced density matrix for the electron spins $\rho_e(t) = \text{tr}_N[\rho(t)]$ reads

$$\rho_e(t) = \frac{1}{2} [|+-\rangle\langle +-| + |+-\rangle\langle -+| \\ - D(t)|+-\rangle\langle -+| - D^*(t)|-+\rangle\langle +-|], \quad (\text{A7})$$

where we have used $\text{tr}\rho_n = 1$ for $n = 1, 2$, and

$$D(t) = \text{tr}[U_1^+ \rho_1 (U_1^-)^\dagger] \text{tr}[U_2^- \rho_2 (U_2^+)^\dagger] \quad (\text{A8})$$

is the decoherence factor. When the initial states of the environments of the two electrons are identical, i.e., $\rho_1 = \rho_2 = \rho$, $D(t)$ is real and can be simplified to

$$L(t) = |\text{tr}[U^+ \rho (U^-)^\dagger]|^2, \quad (\text{A9})$$

which is the LE of the environment. Then the singlet-state population is

$$f_S(t) \equiv \langle S | \rho_e(t) | S \rangle \\ = \frac{1}{2} [1 + L(t)], \quad (\text{A10})$$

which leads to the product yield as

$$\Phi_S = \frac{1}{2} + \frac{1}{2} k_S \int_0^\infty L(t) e^{-k_S t} dt. \quad (\text{A11})$$

Thus we have established the central result of our paper, which reveals the direct relationship between the product yield and the LE.

APPENDIX B: LOSCHMIDT ECHO AT FINITE TEMPERATURE

In this Appendix, we will give the explicit expression for the LE at finite temperature via the method in current paper. In this paper, we are mainly concerned with the TFI model described by the Hamiltonian

$$H(\lambda) = J \sum_j (I_j^z I_{j+1}^z + \lambda I_j^x). \quad (\text{B1})$$

After a combination of Jordan-Wigner and Fourier transformations, for a sufficiently large N ,

$$H = \sum_{k>0} H_k, \quad (\text{B2})$$

where

$$H_k = \eta_k (c_k^\dagger c_k + c_{-k}^\dagger c_{-k}) - i \Delta_k c_k^\dagger c_{-k}^\dagger + \text{H.c.}, \quad (\text{B3})$$

$$\eta_k(\lambda) = -2J(\lambda - \cos k), \quad (\text{B4})$$

$$\Delta_k = -2J \sin k, \quad (\text{B5})$$

and c_k^\dagger (c_k) are the creation (annihilation) operations after the transformations. Here we have discarded the constant terms because they do not contribute to the LE.

Since there are two invariant subspaces spanned by $|00\rangle_{k,-k}$ and $|11\rangle_{k,-k}$, $|01\rangle_{k,-k}$ and $|10\rangle_{k,-k}$, respectively, the above Hamiltonian reads $H_k = H_k^{\text{odd}} \oplus H_k^{\text{even}}$. Here, for the subspace with an odd number of total excitations,

$$H_k^{\text{odd}} = \eta_k 1_{k,-k}, \quad (\text{B6})$$

where $1_{k,-k} \equiv |01\rangle_{k,-k} \langle 01|_{k,-k} + |10\rangle_{k,-k} \langle 10|_{k,-k}$. By subtracting the constant η_k , we have

$$H_k^{\text{odd}} = 0_2. \quad (\text{B7})$$

For the subspace with an even number of total excitations, on subtracting the same constant η_k , we have

$$H_k^{\text{even}} = \eta_k \sigma_k^z + \Delta_k \sigma_k^y. \quad (\text{B8})$$

By rotating around the x axis with the angle θ_k , we diagonalize the Hamiltonian as

$$H_k^{\text{even}} = \varepsilon_k S_k^z, \quad (\text{B9})$$

where the eigenenergy is

$$\varepsilon_k = \sqrt{\eta_k^2 + \Delta_k^2}, \quad (\text{B10})$$

and the mixing angle θ_k is determined by

$$\sin \theta_k = \frac{\Delta_k}{\varepsilon_k}, \quad (\text{B11})$$

$$\cos \theta_k = \frac{\eta_k}{\varepsilon_k}. \quad (\text{B12})$$

In total,

$$H_k = \varepsilon_k S_k^z \oplus 0_2. \quad (\text{B13})$$

Hereafter, we shall calculate the thermal state of the environment as

$$\exp(-\beta H) = \prod_{k>0} [\exp(-\beta \varepsilon_k^- S_k^z) \oplus 1_{k,-k}] \quad (\text{B14})$$

and

$$\text{tr} \exp(-\beta H) = \prod_{k>0} Z_k, \quad (\text{B15})$$

where

$$Z_k = 2 + 2 \cosh(\beta \varepsilon_k^-). \quad (\text{B16})$$

As a result, the normalized density matrix for a thermal state reads

$$\rho = \prod_{k>0} \frac{1}{Z_k} [\exp(-\beta \varepsilon_k^- S_k^z) \oplus 1_{k,-k}]. \quad (\text{B17})$$

For the two relevant Hamiltonians

$$H^\pm = H(\lambda_\pm(\theta)), \quad (\text{B18})$$

the corresponding evolution operators are

$$U_{\pm} = \prod_{k>0} [\exp(-i\varepsilon_k^{\pm} S_k^z) \oplus 1_{k,-k}], \quad (\text{B19})$$

where

$$\varepsilon_k^{\pm} = \sqrt{(\eta_k^{\pm})^2 + \Delta_k^2}, \quad (\text{B20})$$

$$\eta_k^{\pm} = \eta_k(\lambda_{\pm}(\theta)). \quad (\text{B21})$$

Therefore, for two environments in the same initial state, the LE $L(t) \equiv |\text{tr}(U_+ \rho U_-^\dagger)|^2$ reads

$$L(t) = \prod_{k>0} \frac{A_k^2 + B_k^2}{[1 + \cosh(\beta\varepsilon_k^-)]^2}, \quad (\text{B22})$$

where

$$A_k = [\cos^2 \alpha_k \cos(\varepsilon_k^+ - \varepsilon_k^-)t + \sin^2 \alpha_k \cos(\varepsilon_k^+ + \varepsilon_k^-)t] \times \cosh(\beta\varepsilon_k^-) + 1, \quad (\text{B23})$$

$$B_k = [\cos^2 \alpha_k \sin(\varepsilon_k^+ - \varepsilon_k^-)t - \sin^2 \alpha_k \sin(\varepsilon_k^+ + \varepsilon_k^-)t] \times \sinh(\beta\varepsilon_k^-), \quad (\text{B24})$$

$$\alpha_k = \frac{1}{2}(\theta_k^- - \theta_k^+), \quad (\text{B25})$$

$$\theta_k^{\pm} = \tan^{-1}(\Delta_k/\eta_k^{\pm}). \quad (\text{B26})$$

Having obtained the above result independently, we found that it had already been given in Ref. [33]. We remark that the LE here is defined differently from in Ref. [34].

APPENDIX C: PRODUCT YIELD WITHOUT INTER-NUCLEAR-SPIN COUPLINGS

In order to investigate the effect of the inter-nuclear-spin couplings, we calculate the product yield without them. The relevant Hamiltonian is

$$H = h^{(1)} + h^{(2)} \quad (\text{C1})$$

with

$$h^{(k)} = \frac{1}{2}g_e\mu_B\vec{B} \cdot \vec{\sigma}_k + \frac{1}{2}g_N\mu_N\vec{B} \cdot \vec{I}_k + g\sigma_k^x I_k^x, \quad (\text{C2})$$

where we have defined the collective operators

$$I_k^\alpha = \sum_{j=1}^N I_{kj}^\alpha \quad (\alpha = x, y, z), \quad (\text{C3})$$

$$I_k^{\pm} = \frac{1}{2}(I_k^x \pm iI_k^y), \quad (\text{C4})$$

which in combination with the basis $\{|j, m\rangle\}$ satisfy

$$\frac{1}{2}I_k^z|j, m\rangle = m|j, m\rangle, \quad (\text{C5})$$

$$I_k^{\pm}|j, m\rangle = \sqrt{(j \mp m)(j \pm m + 1)}|j, m \pm 1\rangle. \quad (\text{C6})$$

Having rotated the system around the y axis with angle $\pi/2 - \theta$, we obtain

$$h_{\text{rot}}^{(k)} = \frac{1}{2}g_e\mu_B B\sigma_k^z + \frac{1}{2}g_N\mu_N B I_k^z + g(\sin\theta\sigma_k^x + \cos\theta\sigma_k^z)(\sin\theta I_k^x + \cos\theta I_k^z). \quad (\text{C7})$$

Furthermore, under the rotating-wave approximation, the Hamiltonian is approximated as

$$h_{\text{eff}}^{(k)} \simeq \frac{1}{2}g_e\mu_B\sigma_k^z + \frac{1}{2}g_N\mu_N I_k^z + g\cos^2\theta\sigma_k^z I_k^z + g\sin^2\theta(\sigma_k^+ I_k^- + \sigma_k^- I_k^+). \quad (\text{C8})$$

Hereafter, we will omit the subscript ‘‘eff’’ for simplicity.

Obviously, there are invariant subspaces of $h^{(k)}$ as follows:

$$F_0 = \text{span}\{|\downarrow 0\rangle\},$$

$$F_i = \text{span}\{|\downarrow i\rangle, |\uparrow i-1\rangle\}, \quad 1 \leq i \leq N,$$

$$F_{N+1} = \text{span}\{|\uparrow N\rangle\},$$

where $|\downarrow i\rangle$ is short for $|\downarrow\rangle \otimes |j = N/2, m = -N/2 + i\rangle$, and $|\uparrow i\rangle$ for $|\uparrow\rangle \otimes |j = N/2, m = -N/2 + i - 1\rangle$. In the invariant subspace F_i , the eigenstates of

$$H|_{F_i} = \begin{pmatrix} H_{i1} & H_{i2} \\ H_{i2} & H_{i3} \end{pmatrix} \quad (\text{C9})$$

with matrix elements

$$H_{i1} = \frac{g_e\mu_B}{2}B - \left(\frac{N}{2} - i + 1\right)(g_N\mu_N B + 2g\cos^2\theta), \quad (\text{C10})$$

$$H_{i2} = g\sin^2\theta\sqrt{i(N-i+1)}, \quad (\text{C11})$$

$$H_{i3} = -\frac{g_e\mu_B}{2}B - \left(\frac{N}{2} - i\right)(g_N\mu_N B - 2g\cos^2\theta) \quad (\text{C12})$$

are straightforwardly obtained as

$$|E_i^+\rangle = \cos\alpha_i|\uparrow i-1\rangle + \sin\alpha_i|\downarrow i\rangle, \quad (\text{C13})$$

$$|E_i^-\rangle = -\sin\alpha_i|\uparrow i-1\rangle + \cos\alpha_i|\downarrow i\rangle \quad (\text{C14})$$

with eigenenergies

$$E_i^{\pm} = \frac{1}{2}[(H_{i1} + H_{i3}) \pm \sqrt{(H_{i1} - H_{i3})^2 + 4H_{i2}^2}]. \quad (\text{C15})$$

Here, the mixing angle α_i satisfies

$$(H_{i1} - E_i^+) \cos\alpha_i + H_{i2} \sin\alpha_i = 0. \quad (\text{C16})$$

Suppose the initial state of the electron pair is a singlet state, and the two nuclear ensembles are in their ground states. The initial state $|\psi(0)\rangle = |S\rangle \otimes |0\rangle \otimes |0\rangle$ can be rewritten in the above eigenbasis as

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}[\cos\alpha_1(|E_1^+ E_0\rangle - |E_0 E_1^+\rangle) - \sin\alpha_1(|E_1^- E_0\rangle - |E_0 E_1^-\rangle)]. \quad (\text{C17})$$

At time t , the total system evolves into

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}[\cos\alpha_1 e^{-i(E_1^+ + E_0)t}(|E_1^+ E_0\rangle - |E_0 E_1^+\rangle) - \sin\alpha_1 e^{-i(E_1^- + E_0)t}(|E_1^- E_0\rangle - |E_0 E_1^-\rangle)] = [e^{-i(E_1^+ + E_0)t} \cos^2\alpha_1 + e^{-i(E_1^- + E_0)t} \sin^2\alpha_1]|S00\rangle + [e^{-i(E_1^+ + E_0)t} - e^{-i(E_1^- + E_0)t}] \frac{\sin(2\alpha_1)}{2\sqrt{2}}|T_-\rangle \otimes (|10\rangle - |01\rangle), \quad (\text{C18})$$

where $|T_-\rangle = |\downarrow\downarrow\rangle$ and

$$E_0 = \frac{1}{2}(g_e\mu_B + Ng_N\mu_N)B + \frac{N}{2}g \cos^2\theta. \quad (\text{C19})$$

Therefore, the probability of the electron spins being in the singlet state is

$$f_S(t) = 1 - \sin^2(2\alpha_1) \sin^2(E_1^+ - E_1^-)t. \quad (\text{C20})$$

The corresponding product yield is

$$\Phi_S = 1 - \frac{2}{\zeta}Ng^2 \sin^4\theta, \quad (\text{C21})$$

where

$$\zeta = \left[\left(\frac{g_e\mu_B}{2} - g_N\mu_N \right) B + 2(N-1)g \cos^2\theta \right]^2 + k_\zeta^2 + 4Ng^2 \sin^4\theta. \quad (\text{C22})$$

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