Sensitive Chemical Compass Assisted by Quantum Criticality

C. Y. Cai, 1 Qing Ai, 1 H. T. Quan, 2 and C. P. Sun 1

¹Institute of Theoretical Physics, Chinese Academy of Sciences, Beijing, 100190, China ²Department of Chemistry and Biochemistry and Institute for Physical Science and Technology, University of Maryland, College Park, MD 20742, USA

The radical-pair-based chemical reaction could be used by birds for the navigation via the geomagnetic direction. An inherent physical mechanism is that the quantum coherent transition from a singlet state to triplet states of the radical pair could response to the weak magnetic field and be sensitive to the direction of such a field and then results in different photopigments in the avian eyes to be sensed. Here, we propose a quantum bionic setup for the ultra-sensitive 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 the 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 the detection of the weak magnetic field.

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Introduction. — Since Schrödinger questioned "what is life" from the general point view of a quantum physicist [1], scientists have never stopped the long-term exploration for the physical sources of the 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 the life is of quantum for the molecules composing lives obey quantum laws, but some recent discoveries are very intriguing as some optimized living processes may be based on the nontrivial quantum effect from quantum coherence. One example in point is the photosynthesis process. Recent experiments have been able to exactly determine the time scales of various transfer processes by the 2D optical spectroscopy, and then show quantum coherence effects in energy transfer via collective excitations of some light-harvesting complexes [3-5].

Another prototype of quantum coherence effect for living process seems to appear in the avian magnetoreception mechanisms [6, 7] verified by some recent experiments [8]. Recently quantum information approaches have been used to further analyze the role of quantum coherence phenomenon in the avian magnetoreception models [9-12]. It is now believed [13, 14] that the model for magnetoreception is based on the radical-pair mechanism (RPM) [6]: the radical-pair molecule with two unpaired electrons is activated by light. When the electrons interact with their individual environments of nuclei via the hyperfine couplings, the spin singlet state will transit to the 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, a key question remains elusive [13]: why does the singlet-triplet interconver-

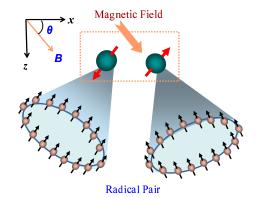


FIG. 1: (color online). Model setup of sensitive magnetodetection based on the radical pair chemical reaction assisted by the quantum critical environments consisting of interacting spins. Two spins could be initially prepared in the singlet state, and finally evolve into the triplet states due to the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

sion response to the extremely-weak geomagnetic field $(\sim 10^{-5} \mathrm{T})$, and why is it very sensitive to its direction? We notice that the existence of nuclear environments surrounding the electron spins in the radical-pair molecule is crucial to magnetic sensitivity of the chemical reaction. This observation motivates us to consider the role of internal quantum correlation in each environment. In this Letter, we propose a quantum phase transition (QPT)-assisted setup for the probe of a weak magnetic field in understanding the above conundrum. Actually a lot of real-world detectors are built based on the dramatic changes of the systems around phase transitions, which amplifies the ultra-weak signal and thus enable one to probe it. Examples include bubble chamber detectors [15] and superconducting single-photon detectors [16], where the liquid-gas phase transition and superconductor-metal phase transition take place respectively enhancing the sensitivity for detection. We calculate the corresponding chemical product yield, which is phenomenologically described by a damping process [17]. It is discovered that the chemical product yield is determined by the time integral of the Loschmidt echo (LE). Our result shows that the chemical compass assisted by quantum criticality indeed can response to a very-weak magnetic field and be sensitive to its direction.

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 quantum correlated environment, which can be described by a transverse field Ising (TFI) model [18, 19]. 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 $H'_n = H_n + g_N \mu_N B \sum_i \sin\theta I^z_{n,j}$ with

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

where $\lambda = g_N \mu_N B \cos \theta / J$ is the rescaled strength of the transverse field in unit of J being the Ising coupling constant, $q_N \mu_N$ is the nuclear magnetic moment, and n=1,2 refers to the environment of the nth electron. $I_{n,j}^x$ and $I_{n,j}^z$ are Pauli matrices of the jth nuclear spin operators. In case of 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 [20]. Here, different from all previous studies [6, 12–14, 17, 21], we explicitly consider the inter-nucleus couplings $I_{n,j}^z I_{n,j+1}^z$. This coupling competes with the Zeeman energy being 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 the dynamic sensitivity described by the sharp decay of LE near the QPT [22], which has been experimentally verified [20, 23, 24].

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

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

where σ_n^x and σ_n^z for n=1,2 are the Pauli operators for the nth electron spin, 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.

Radical-Pair Evolution in Correlated Nuclear Environment.— Due to the spin-flip terms, the time evolution governed by the total Hamiltonian $H = \sum_n (H_n + V_n)$ can only be solved with some approximation. Usually the electron spins evolve faster than the

nuclear spins. Thus we can first regard nuclear spins as cnumbers for formally diagonalizing the electronic Hamiltonian V_n through a generalized Born-Oppenheimer approximation [25]. The eigen states of the electron spins are obtained as $|+\rangle = \cos(\alpha/2) |\uparrow\rangle + \sin(\alpha/2) |\downarrow\rangle$ and $|-\rangle =$ $\sin(\alpha/2) |\uparrow\rangle - \cos(\alpha/2) |\downarrow\rangle$ where $|\uparrow\rangle$ $(|\downarrow\rangle)$ is the spin-up (down) state in the representation with corresponding eigen ues $E_{\pm} = \pm E$ for $E = \sqrt{\Omega^2 \sin^2 \theta + \Delta^2}$ and $\Delta = \Omega \cos \theta + Jg \sum_{j} I_{n,j}^{x}$. And the mixing angle is defined as $\alpha = \pi/2 - \tan^{-1}(\Omega \sin \theta/\Delta)$.

For the weak coupling $(Jg_0 \ll \Omega)$ of an electron to nuclei we shall approximately obtain the eigen states $|+\rangle \simeq \cos\theta' |\uparrow\rangle + \sin\theta' |\downarrow\rangle$ and $|-\rangle \simeq \sin\theta' |\uparrow\rangle - \cos\theta' |\downarrow\rangle$ to the zeroth order of g for $\theta' = (\pi/2 - \theta)/2$ and the eigen energy $E \simeq \Omega + Jg\cos\theta \sum_j I_{n,j}^x$ to the first order. The Born-Oppenheimer approximation shows that the slowly-varying nuclear spins would not induce the coherent transition of the fast-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

$$H \simeq \sum_{n} \left(H_n^+ \left| + \right\rangle \left\langle + \right| + H_n^- \left| - \right\rangle \left\langle - \right| \right), \tag{3}$$

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

$$H_n^{\pm} = J \sum\nolimits_j \left[I_{n,j}^z I_{n,j+1}^z + (\lambda \pm g \cos \theta) I_{n,j}^x \right] \pm \Omega. \quad (4)$$

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

Product Yield and Loschmidt Echo.— The radical pair is assumed to be initially in the singlet state $|S\rangle$ which subsequently suffers from 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 electronspin state (singlet or triplet). In particular, the singlet-state product yield formed by the reaction of radical pairs can be calculated as [17]

$$\Phi_S(t) = \int_0^t r_c(t) f_S(t) dt, \tag{5}$$

where $r_c(t)$ is the radical re-encounter probability distribution, and $f_S(t) = \langle S | \rho_e(t) | S \rangle$ is the singlet-state population at time t. Usually it is assumed [17] that $r_c(t) = k_S \exp(-k_S t)$ with k_S the recombination rate. The ultimate product yield $\Phi_S \equiv \Phi_S(t \to \infty)$ 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 $\Lambda(\theta) = \partial \Phi_S/\partial \theta$, the derivative of the product yield with respect to the geomagnetic-field direction θ [21].

For nuclear spins initially in the mixed state $\rho_1 \otimes \rho_2$, the initial state of the total system is $\rho(0) = |S\rangle \langle S| \otimes \rho_1 \otimes \rho_2$. When the state of the electron is $|+\rangle$ or $|-\rangle$, the evolution of the environment is governed by H_n^+ or H_n^- respectively, and hence the initial state ρ_n will evolve into $U_n^+ \rho_n (U_n^+)^{\dagger}$ or $U_n^- \rho_n (U_n^-)^{\dagger}$ respectively. Here, the evolution operators are defined as $U_n^{\pm} = \exp(-iH_n^{\pm}t)$. This will result in the so-called adiabatic entanglement between the system and the environment [25]. For the above initial state $\rho(0)$, at time t, the reduced density matrix for the electron spins $\rho_e(t) = \operatorname{tr}_n |\psi(t)\rangle \langle \psi(t)|$ reads

$$\rho_{e}(t) = \frac{1}{2}[|+-\rangle\langle+-|+|-+\rangle\langle-+| -D(t)|+-\rangle\langle-+|-D^{*}(t)|-+\rangle\langle+-|], (6)$$

where $D(t)=\operatorname{tr}\left[U_1^+\rho_1\left(U_1^-\right)^\dagger\right]\operatorname{tr}\left[U_2^-\rho_2\left(U_2^+\right)^\dagger\right]$ is the decoherence factor. When $\rho_1=\rho_2=\rho$, D(t) is real and can be simplified to $L(t)=\left|\operatorname{tr}\left[U^+\rho\left(U^-\right)^\dagger\right]\right|^2$, which is just the *Loschmidt Echo* characterizing the dynamic sensitivity of the environment in response to the perturbation [22]. Straightforwardly, we can prove the population $f_S(t)=[1+L(t)]/2$, and obtain the product yield as

$$\Phi_S = \frac{1}{2} + \frac{1}{2} k_S \int_0^\infty L(t) e^{-k_S t} dt.$$
 (7)

This is a central result of our paper which reveals the direct relationship between the product yield and the LE.

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 LE is simplified as $L(t) = |\langle G| \exp(iH^-t) \exp(-iH^+t) |G\rangle|^2$, which was explicitly given in Ref. [22]. 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 analytic results about L(t) obtained in Ref. [22], we approximate the product yield around the critical point as

$$\Phi_S \simeq \frac{1}{2} + \exp\left(\frac{k_S^2}{4\gamma}\right) \sqrt{\frac{\pi k_S^2}{2\gamma}} \left[1 - \operatorname{erf}\left(\frac{k_S}{2\sqrt{\gamma}}\right)\right], \quad (8)$$

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

$$\gamma = \frac{8J^2g^2NK_c^3\cos^2\theta}{3\pi(1-\lambda)^2} \tag{9}$$

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

$$\Phi_S \approx \frac{1}{2} + \frac{\pi k_S |1 - \lambda|}{16Jg \cos \theta} \sqrt{\frac{6}{NK_c^3}}.$$
 (10)

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

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

$$L(t) = 1 - \frac{16g^2 \cos^2 \theta \sin^2(\xi t)}{[1 + 4(\lambda - g \cos \theta)^2] \xi^2},$$
 (11)

where $\xi = \sqrt{1 + 4(\lambda + g\cos\theta)^2}$. It shows that the setup for a small N can not work as well as it for a large N. The detailed discussions about dependence of Φ_S on N are visually given in the supplementary material.

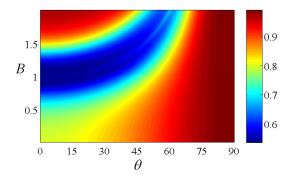


FIG. 2: (color online). The product yield Φ_S vs the magnitude B and direction θ of the magnetic field at a finite temperature T=0.2 with $N=1000,\ g_0=1,\ k_S=0.1,$ and J=1.

Sensitive Magnetodetection at Finite Temperatures.— The above results are obtained for an ideal case with pure states. For the practical purpose, we need to consider the cases at finite temperatures. 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 magnetic field at a finite temperature in Fig. 2. Obviously, the product yield displays its dependence on both the geomagnetic field's magnitude and direction. Besides, 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 the regions far away from the critical point, e.g., at the top-left and bottom-right corners, the product yield nearly stays unity for the LE almost does not decay.

Furthermore, in order to investigate the influence of other parameters, we plot the product yield vs direction for different temperatures and recombination rates in Fig. 3. The similarity among the cases with different temperatures is that there is a peak for $\Lambda(\theta)$ as it increases from zero at $\theta=0$. It is seen that as the temperature increases, the position of the peak moves towards $\theta=\pi/2$, 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 platform elsewhere. In this case, the bird can no longer discriminate the direction. This is a reasonable result since a QPT takes place at the absolute

zero, and a high temperature smears the QPT. When we come to the recombination rate k_S in Fig. 3(c), we see that the slower 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 LE. The magnetic-field sensitivity in Fig. 3(d) clearly confirms our analysis. In addition, as the environment involves more nuclear spins, the visibility rises as the LE decays faster for a larger N.

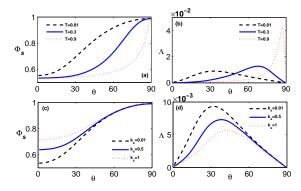


FIG. 3: (color online). The product yield Φ_S and its derivative Λ vs the geomagnetic field's direction θ for different T in (a) and (b) with $k_S=0.1$, and for different k_S in (c) and (d) with T=0.01. In all figures, we set $N=1000,\ g_0=1,\ B=0.9$ and J=1.

Conclusion.— We proposed a RPM-based magnetodetection scheme assisted by the QPT. We have proved that the yield of the chemical product via the recombination from the singlet state is determined by the LE of the environments. This relation results in the enhanced sensitivity of the RPM-based avian compass. Thus, our study does not only provide important insights to the mechanism of magnetoreceptor through a radical-pair process in a very-weak field, but it also shields new light on building a quantum bionic device for ultra-sensitive magneticfield 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 the avian retina, the environments of radical pairs consist of a few nucleus rather than numerous nucleus, i.e., $N \to \infty$ for a QPT. But the experiments [20, 23, 24] however demonstrated that even for N=2, there still exists the dynamic sensitivity induced by quantum criticality. This result implies that dynamic sensitivity may have a close relation with the level crossing. Besides, although our scheme requires a very-low temperature for the current experimental parameters, its importance also lies in the possible 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 QPT is independent of the model [26]. Thus it is reasonable to infer that all the results obtained from TFI model can be generalized

to other models as well, such as the so-called long-range TFI model, or Lipkin-Meshkov-Glick model [19]. Detailed studies of these generalization will be given in a forthcoming paper.

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