Nuclear Magnetic Resonance model of an entangled sensor under noise

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Entangled sensors have been attracting a lot of attention recently because they can achieve the sensitivity beyond that of the classical sensors. To exploit entanglement as a resource, it is important to understand the effect of noise because the entangled state is fragile against noise. Here, we provide a Nuclear Magnetic Resonance (NMR) model of an entangled sensor under engineered noise: one can implement an entangled sensor under various noisy environments. In particular, we experimentally investigate the performance of the entangled sensor under the effect of time-inhomogeneous noisy environment with which the entangled sensor holds potential to beat the classical sensors. Our “entangled sensor” consists of a multi-spin molecule solved in isotropic liquid, and we can perform the quantum sensing by using NMR techniques.

I. INTRODUCTION

Quantum sensing has been attracting a lot of attention recently as an application of quantum mechanics like quantum information technology [1] because one may achieve the sensitivity and precision beyond what is possible classically. Quantum sensing may be categorized into three according to what quantumness is employed for improving the performance of measurements: (I) quantum object such as electrons or nuclear spins, (II) quantum coherence such as superposition states or matter-wave-like nature, and (III) quantum entanglement that cannot be described classically [2]. The third may be the most quantum-like one, and various efforts have been reported along this direction. The entanglement-enhanced magnetic field sensing with atomic vapors were reported: the spin squeezing (entanglement) within the atomic internal structure [3], and the entanglement between two vapor cells [4] were employed for reducing noise. More direct approach enhancing the sensitivity of measurements with entanglement was discussed [5] and experimental efforts by using trapped ions [6–9], ultra cold atoms [10, 11], and NMR [12, 13] were reported.

A potential problem of the entangled sensor is the fragility against noise. In fact, it is theoretically pointed out that an entangled sensor in a Markovian noisy environment, where a relaxation is exponential, cannot overcome the standard quantum limit (SQL) [14]. The SQL is the consequence of the central-limit theorem [5]. On the other hand, there is a theoretical prediction that the entangled sensor can outperform the classical sensor under the effect of a time-inhomogeneous noisy environment that induces a non-exponential decay [15–18].

In this work, we investigate the behavior of the entangled sensor in engineered noisy environment with NMR. Since the performance of the entangled sensor strongly depends on the properties of the environment, systematic experimental analysis of the entangled sensor with various type of noise is essential for the realization of the quantum enhanced sensing. So our experimental investigation with NMR model would provide insight to assess the practicality of quantum sensors.

The rest of the paper is organized as follows. In Sect. 2, we closely follow Refs. [12, 13] and review how the entangled sensor is simulated with a star topology molecule. We then present the method how to prepare an engineered noisy environment following Ref. [19]. Then, these two ideas are combined: we simulate the entangled sensor under the presence of an engineered noisy environment. We show experimental results in Sect. 3, where a dynamics of the entangled sensor in a time-inhomogeneous noisy environment and a successful application of a dynamical decoupling technique [20] to the entangled sensor are shown. The last Sect. 4 is devoted to summary.

II. THEORY

In this section, we describe our strategy to combine the two ideas: (i) using a star-topology molecule as an entangled magnetic sensor, and, (ii) engineering the noisy environment that surrounds the sensor considered.

A. Molecules as a Simulator of Entangled Magnetic Sensor

Assume an isolated nuclear spin of which initial state is

\[ |\psi\rangle = \frac{|0\rangle + |1\rangle}{\sqrt{2}}, \]  

where \(|0\rangle\) and \(|1\rangle\) are two eigenstates of the standard Pauli matrix \(\sigma_x\). The system is exposed under a magnetic filed \(Bz\) where \(z\) is the unit vector along the \(z\)-axis for a period of \(\tau\), and becomes

\[ |\psi_{\tau}\rangle = \frac{|0\rangle + e^{i\gamma_{G}B\tau}|1\rangle}{\sqrt{2}}, \]  

where \(\gamma_{G}\) is the gyromagnetic ratio. Therefore, the acquired phase \(\gamma_{G}B\tau\) can be used to measure \(B\). The sensitivity of a set of \(N\) spins is proportional to \(\sqrt{N}\). It is the SQL [5, 21].

Now, if we assume our sensor consists of \(N\) spins with the initial state is entangled, such as

\[ |\psi\rangle = \frac{|00\ldots0\rangle + |11\ldots1\rangle}{\sqrt{2}}, \]  

where
quantum circuit for a measurement. Because of the symmetry of the entangled sensor. We call them environment spins. (d) a basic scheme with star-topology molecules schematically shown in FIG. 1. (a, b, c) Three different interaction topologies among spins (○, ◦, and ●) discussed in this work and (d) a quantum circuit for an entangled magnetic field sensor simulation. (a) a sketch of a star-like interaction structure among spins, (b) the simplest star topology structure. The small open circles (◦’s) in (a) and (b) play the role of entangled sensors. (c) the two step star topology structure for an entangled sensor. The large open circle (○) is called the center spin, while the small open ones (◦’s) are introduced in order to generate a time inhomogeneous noisy environment acting on the entangled sensor. We call them environment spins. (d) a basic quantum circuit for a measurement. Because of the symmetry of the interaction structure, all ◦’s can be accessed globally.

then, this state will evolve into

$$|ψτ⟩ = \frac{|00...0⟩ + e^{iNγ_0 Br}|11...1⟩}{\sqrt{2}}$$

after a time τ and thus the sensitivity is proportional to the number of spins N: It is the Heisenberg Limit [5, 21].

Jones et al. demonstrated the above measurement scheme with star-topology molecules schematically shown in Fig. 1(a). They employed two molecules, trimethyl phosphite (TMP) [12] and tetramethyl silane (TMS) [13]. TMP (TMS) molecule consists of the center 31P (29Si) and three (four) methyl groups and thus the center 31P (29Si) is surrounded by 9 (12) 1H spins. The highly symmetric structure of these molecules allows to address all surrounding spins (small open circles in Fig. 1(a)) globally, and thus the operations required to measure a magnetic field can be simplified.

In this work, we employed the simplest star topology molecule that consists of the center spin (○) and the two side spins (◦’s), as shown in Fig. 1(b).

We take the initial density matrix $|0⟩⟨0| \otimes σ_0 \otimes σ_0$ [22], see also Appendix: The center spin is |0⟩⟨0|, while the two side spins are fully mixed state. When the magnetic field is applied only on the center spin (○), i.e., the star-topology structure is not effective, the density matrix becomes

$$ρ_○ = \frac{1}{8} \left( \begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{array} \right) \otimes σ_0 \otimes σ_0,$$

after the magnetic field is applied. Here, $θ = γ_0 Br$ and the subscript ○ stands for the case that the center spin is exposed to the field.

Next, let us consider the case when the magnetic field is applied on the side spins (◦’s) as shown in Fig. 1(d). Note that a co-rotating frame with the center spin is taken and accordingly it does not acquire a phase during the period τ. The initial state $\frac{1}{4} |0⟩⟨0| \otimes σ_0 \otimes σ_0$ can be decomposed to

$$\frac{1}{4} \left( |000⟩⟨000| + |011⟩⟨011| + |001⟩⟨001| + |010⟩⟨010| \right),$$

and thus, the final density matrix after the measurement operation is given as

$$ρ_σ = \frac{1}{8} \left( \begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{array} \right) \otimes |00⟩⟨00|$$

$$+ \frac{1}{8} \left( \begin{array}{cccc} 1 & e^{iθ} & 0 & 0 \\ e^{-iθ} & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{array} \right) \otimes |11⟩⟨11|$$

$$+ \frac{1}{8} \left( \begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{array} \right) \otimes |01⟩⟨01| + |10⟩⟨10|),$$

where ◦ stands for the case that the magnetic field is applied on the side spins. Note that, due to the twice large phase accumulation (2θ, instead of θ) of the initial states of |000⟩⟨000| and |011⟩⟨011|, the sensitivity with side spins interacting the magnetic fields becomes twice larger than that of the central spin.

We show the method how to detect the acquired phases in NMR. The state $ρ_k (k = ○, ◦)$ is assumed to develop under the Hamiltonian

$$H = ω_0 σ_z 2 \otimes σ_0 \otimes σ_0 + J \left( σ_0 2 \otimes σ_0 2 \otimes σ_0 \otimes σ_0 2 \right).$$

where $ω_0$ corresponds to a Larmor frequency of the center spin and J a coupling constant between the center spin and the two side spins. The signal from the center spin is given as

$$S_c(t) = \text{Tr} \left( (σ_0 2 + iω_0 t) \otimes σ_0 \otimes σ_0 e^{-iHt} ρ_σ e^{iHt} \right).$$

Therefore, the expected normalized signals are given as

$$S_○(t) = \frac{1}{4} e^{-i/T_2} \left( e^{-iHt} + 2 + e^{iHt} \right) \cos (ω_0 t + θ),$$

$$S_◦(t) = \frac{1}{4} e^{-i/T_2} \left( e^{-iHt-iθ} + 2 + e^{iHt+iθ} \right) \cos ω_0 t,$$

where $T_2$ is a phenomenological transverse relaxation time constant that is introduced in order to express that the signal does not last forever. Equation (10) corresponds to the signal
when the field is applied on the center spin, while Eq. (11) is when on the side spins. Note the difference in the position of $\theta$ in $S_k(t)$. The three terms in the parentheses in $S_k(t)$ correspond to three peaks that are observed when $S_k(t)$’s are Fourier Transformed, see Fig. 2.

### B. Engineered Noisy Environment

Our idea to engineer the environment can be seen from Fig. 3. If System I directly interacts with Markovian Environment, it decays exponentially. If it interacts with Markovian Environment through System II, it shows various decay behaviors since System II acts as a memory of an engineered environment formed by System II and the Markovian Environment [22, 26–30].

The spins chain ($\circ - \bigcirc - \circ$ in Fig. 1(c)) is regarded as the sensor where the side spins (two $\bigcirc$’s) accumulate the phase under the external field and this phase is measured via the center spin (○), as we discussed in Sect. II A. The side spins (○’s) are surrounded by two sets of three spins (two ●’s) that we call environment spins. We regard the side spins (two ○’s) as two independent System I’s, while we do the two sets of ●’s as two System II’s. These environment spins with Markovian Environment outside them act as time-inhomogeneous noisy environments of the side spins (two ○’s) as we discussed in Refs. [22, 26, 30]. Note that we assume here that only the nearest neighbor interactions are important. After all, we can engineer the environment of the sensor ($\circ - \bigcirc - \circ$).

### III. EXPERIMENTS

In this section, we describe our approach to simulate an entangled sensor under an engineered environment with a molecule solved in an isotropic liquid. First, we show how to prepare an engineered Markovian environment and then discuss how to simulate an entangled sensor under an engineered time-inhomogeneous noisy environment.

![Fig. 2. Expected spectra calculated from $S_k(t)$ in the case of $JT_2 = 22$. (a) $\theta = 0^\circ$, (b) $\theta = 50^\circ$ for $S_C(t)$, (c) $\theta = 50^\circ$ for $S_k(t)$. The frequency differences of these peaks are $J$.](image2)

![Fig. 3. (Color online) Engineered environment. Therein, the Markovian environment indirectly interacts with System I through System II.](image3)
because $|\omega^{(j)}_0 - \omega^{(k)}_0| \gg J^{(jk)}$, or weak coupling approximation $[31]$, is satisfied here. $\omega^{(j)}_0$ is the isotropic chemically shifted Larmor frequency of the $j$'th spin, and $J^{(jk)}$ the interaction strength between the $j$'th and $k$'th spins $[27][31]$. $\omega^{(j)}_0$ and $J^{(jk)}$ were measured from the spectra of the sample without magnetic impurities and are summarized in Table I.

C. Simulation of Entangled Sensor

We implemented the quantum circuit shown in Fig. 1(d) with a standard NMR pulse sequence $[25]$. The rotation operations applied on CC are given as

$$R_C(\phi, \theta) = R(\phi, \theta) \otimes \sigma_0 \otimes \sigma_0, \quad (13)$$

$$Z_C(\theta) = Z(\theta) \otimes \sigma_0 \otimes \sigma_0, \quad (14)$$

where $R(\phi, \theta) = e^{-i\phi(\cos \theta \sigma_x + \sin \theta \sigma_y)/2}$ and $Z(\theta) = e^{-i\theta \sigma_z/2}$. $\theta$ in $R(\theta, \phi)$ is the rotation angle and $\phi$ defines the rotation axis in the $xy$-plane from the $x$-axis, while $\theta$ in $Z(\theta)$ is the rotation angle about the $z$-axis. The rotation operations on CSs can be implemented simultaneously thanks to the symmetry of the molecular structure and are given as

$$R_S(\phi, \theta) = \sigma_0 \otimes R(\phi, \theta) \otimes R(\phi, \theta), \quad (15)$$

$$Z_S(\theta) = \sigma_0 \otimes Z(\theta) \otimes Z(\theta). \quad (16)$$

The Hadamard gate on CC was effectively implemented with an $R_C(\pi/2, -\pi/2)$, while the pseudo CNOT gate was realized as follows

$$CNOT = e^{-i2\Delta Z_C(-\pi/2)Z_S(-\pi/2)R_C(0, \pi/2)U_E R_S(-\pi/2, \pi/2)}$$

where $U_E = e^{-i2\Delta (\sigma_x \otimes \sigma_y + \sigma_y \otimes \sigma_x)/4}$. $U_E$ was implemented by waiting for the period of $n/\Delta$, where $\Delta$ is the Larmor frequency difference between CC and CSs. $n$ is an integer and selected so that $n/\Delta \approx \pi/2 [31]$, see Table I. All $Z_S(\theta)$'s $(k = C$ or $S)$ were virtually implemented by controlling $\phi$'s in $R_S(\phi, \theta)$'s $(k = C$ or $S)$. We employed the jump-and-return pulses $[33]$ to realize $R_S(\phi, \theta)$ with concatenated composite pulses $[34]$.

Magnetic field sensing is equivalent to measuring the phase difference between the initial and final state of CC, as shown in Fig. 1. Therefore, we simulated the magnetic field by applying a $Z_S(\theta)$-rotation,

field on CC:

$$\left( R_C(-\pi/2, \pi/2) - Z_C(\theta) \right) - CNOT - \left( \frac{\tau}{2} - R_S(0, \pi) - \frac{\tau}{2} \right) - CNOT,$$

field on CSs:

$$R_C(-\pi/2, \pi/2) - (CNOT - Z_S(\theta)) - \left( \frac{\tau}{2} - R_S(0, \pi) - \frac{\tau}{2} \right) - CNOT,$$
12 mM of Fe(acac) as a magnetic impurity was used. Sensitivity [12, 35, 36] in the full-decoupling case (Fig. 5(c)). We started from the thermal state and observed fying the time development caused by the interaction between $\theta$ all H spins were about 100 ms. Figure 6 shows the spectra (the “field”) at $\tau = 3.4 \text{ ms}$. When the “field” was applied on CC, the three peaks acquired the phase $\theta = \gamma_G B t$ in real measurements. In our model, a sensor is a star-topology molecule, 2-propanol, solved in acetone-d6 with magnetic impurities on CC and CSs [19] and thus we can approximate that “magnetic field sensing” was performed under noiseless environment in the short time scale of less than 50 ms in the experiment. This approximation was confirmed with the signal did not decay almost at all in this time scale, see Fig. 7(a). In the selective decoupling case, CSs should be affected by the engineered time-inhomogeneous noisy environment formed by HSs and magnetic impurities. This noisy environment was also confirmed with the fact that the signal decay more slowly than those in (b) which indicates that dynamical decoupling was effective. When a dynamical decoupling technique is applied on a sensor, it cannot detect the DC component but can measure the AC one whose frequency is determined by the decoupling technique (XY-8). Our results in the Fig. 7(c) show the potential to realize the entanglement enhanced AC magnetic field sensor under time inhomogeneous noise, as theoretically predicted in [15-18].

**IV. SUMMARY**

We successfully modeled an entangled magnetic field sensor under various noisy environments with NMR techniques. In our model, a sensor is a star-topology molecule, 2-propanol, solved in acetone-d6 and the magnetic field is simulated by rotational pulse sequences acting on the sensor. The environment surrounding them can be engineered by adding...
Fe(III) impurity in the solvent and by selectively decoupling H spins in the 2-propanol molecule. We demonstrated the entanglement-enhanced phase sensitivity and discussed its enhancement mechanism. We also showed that the magnetic field sensing was affected by noise. Importantly, we demonstrate that, when the noise is time-inhomogeneous, the effect of the noise can be suppressed by a dynamical decoupling technique during the entanglement enhanced magnetic field sensing. Our results would provide a useful test bench to assess the practicality of quantum sensors under the effect of various types of noise.

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Appendix A

In the preceding work [19], we systematically studied the three cases when the environments consisted of 1, 3, and 12 spins + Markovian environment generated by magnetic impurities. We add another case study here, 6 spins + Markovian environment by using 2-propanol solved in acetone d6.

The longitudinal relaxation times, $T_1$'s, of the $^{13}$C spins of the 0.41 M 2-propanol sample solved in acetone d-6 without magnetic impurities were measured to be 20 s (CC) and 8 s (CSs). Therefore, within the time scale much shorter than these $T_1$'s, the $^{13}$C chains in the 2-propanol molecules can be approximated as an isolated system. We added magnetic impurities (Fe(III)acac) and prepared 4 samples, as shown in Table II.

TABLE II. Measured $T_1$'s, $T_2$'s of CC and $T_1$ of HSs are summarized. $C_m$: the concentration of the magnetic impurity (Fe(III)acac), $T_1$: the longitudinal relaxation time constant of CC, $T_2^0$: the relaxation time constant of the signal in the full-decoupling case, $T_2^0$': the relaxation time constant of the signal in the selective-decoupling case, and $T_1$(HSs): the longitudinal relaxation time constant of HSs' spins.

| Sample | $C_m$ (mM) | $T_1$ (s) | $T_1$ · $C_m$ (mM·s) | $T_2^0$ (ms) | $T_2^0$ · $C_m$ (M·s) | $T_2^0$' (ms) | $T_1$(HSs) (ms) |
|--------|------------|----------|----------------------|--------------|----------------------|--------------|----------------|
| 1      | 12         | 1.3      | 3.0 × 10$^2$         | 3.5 × 10$^{-2}$ | 3.0 × 10            | 93           |
| 2      | 26         | 0.64     | 1.0 × 10$^2$         | 2.6 × 10$^{-2}$ | 3.9 × 10            | 43           |
| 3      | 47         | 0.36     | 9.9 × 10$^2$         | 4.7 × 10$^{-2}$ | 3.8 × 10            | 24           |
| 4      | 94         | 0.17     | 6.4 × 10$^2$         | 6.0 × 10$^{-2}$ | 3.9 × 10            | 17           |

In the full-decoupling case, small but not negligible direct influence of the Markovian environment on CC should be observed. $T_1$'s of CC in Table II are inversely proportional to the magnetic impurity concentration $C_m$ which implies that this $T_1$ is determined by the impurity [26]. On the other hand, in the selective-decoupling case, the interaction between CC and the Markovian environment through HSs (system II) should be added although it is expected to be small. Therefore, we obtain the engineered environment which consists of 6 spins + Markovian Environment and that it causes a non-exponential decay of CC [19]. We note, however, that the large interactions between CC and CSs ($J^{CC,CSs} = 2\pi \cdot 34$ rad/s) compared with those between CC and HSs ($J^{CC,HSs} = 2\pi \cdot 4.4$ rad/s) prevent from observing the above subtle non-exponential dynamics.

In order to observe the above subtle non-exponential dynamics, let us re-examine the thermal state $\rho_{th}$ of the three

FIG. 8. (Color online) FID signals of Sample 1, 2, 3, and 4 in Table II. The initial states were $|+\rangle|+\rangle \otimes (|01\rangle|01\rangle + |10\rangle|10\rangle)$. The real parts of the FID signals are shown in red, while the imaginary in black. The full-decoupling (left panels) and selective decoupling case (right panels). The black dashed curves in the left panels are exponential fittings to the real parts of the FID signals. The green (blue) curves in the right panels are calculated real (imaginary) part of the FID signals [19]. The blue curves overlap the experimental data and thus hardly visible.
\[ \rho_{\text{th}} \approx \frac{\sigma_0 + \epsilon|0\rangle\langle0|}{2} \otimes \frac{\sigma_0}{2} \otimes \frac{\sigma_0}{2} \] 

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