Evolution of Quantum Discord and its Stability in Two-Qubit NMR Systems

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We investigate evolution of quantum correlations in ensembles of two-qubit nuclear spin systems via nuclear magnetic resonance techniques. We use discord as a measure of quantum correlations and the Werner state as an explicit example. We first introduce different ways of measuring discord and geometric discord in two-qubit systems and then describe the following experimental studies:

(a) We quantitatively measure discord for Werner-like states prepared using an entangling pulse sequence. An initial thermal state with zero discord is gradually and periodically transformed into a mixed state with maximum discord. The experimental and simulated behavior of rise and fall of discord agree fairly well.

(b) We examine the efficiency of dynamical decoupling sequences in preserving quantum correlations. In our experimental setup, the dynamical decoupling sequences preserved the traceless parts of the density matrices at high fidelity. But they could not maintain the purity of the quantum states and so were unable to keep the discord from decaying.

(c) We observe the evolution of discord for a singlet-triplet mixed state during a radio-frequency spin-lock. A simple relaxation model describes the evolution of discord, and the accompanying evolution of fidelity of the long-lived singlet state, reasonably well.

I. INTRODUCTION

Since its introduction by Schrödinger, entanglement has remained an extensively studied and yet a mysterious aspect of quantum theory. Entanglement appears as a by-product of the quantum formalism that assigns probability amplitudes to physical states and lets them exist in coherent superpositions. Although, it runs counter to the human intuition gained through experiences with classical systems, experimental evidence has consistently favored the existence of such superposed quantum states. Entanglement was thought to be an indispensable resource for quantum information processing, which can outperform the corresponding classical information processing. Indeed, various quantum algorithms that exploit entanglement have been proposed and successfully tested [1]. Separable (i.e. not entangled) states were considered insufficient to implement quantum information processing. That belief has changed since Ollivier and Zurek [2] as well as Henderson and Vedral [3] independently introduced a new measure of non-classical correlations named ‘discord’. Discord is based on the measure of mutual information between two parts of a system. It can be put in one-to-one correspondence with entanglement for pure states, but, unlike entanglement, it can be nonzero for separable mixed states [3].

There have been long debates on the necessity of entanglement for quantum information processing. For example, the purity of typical spin systems used in nuclear magnetic resonance (NMR) experiments is too small to exhibit entanglement; nevertheless, NMR quantum information processing is considered an efficient test bed for quantum algorithms [4-6]. Furthermore, Knill and Laflamme proposed an algorithm, called DQC1, which estimates the trace of any unitary matrix faster than any known classical algorithm [7]. Datta et al. showed that entanglement in the DQC1 algorithm is vanishingly small, and it further decays with increase in the number of qubits [8]. They also showed that the DQC1 algorithm involves nonzero discord. Thus, our present notion of quantum speed up is tied to discord rather than entanglement [9]. For a more detailed review on discord, see Ref. [10].

Discord happens to be one of the many quantities that can measure the nonclassicality of a given quantum system. Its standard definition equates discord to the difference between two classically equivalent forms of mutual information. Due to the difficulty in measuring this difference, Dakic et al. proposed an alternate quantity called ‘geometric discord’. It is the distance between the given quantum state and the closest classical state and is easier to quantify than discord [11]. We look at both of these quantities in our study.

Several experiments to demonstrate quantum correlations in liquid-state NMR systems have been performed in recent years, e.g., by measuring a suitable witness operator [12], by measuring discord [13], and by evaluating the Leggett-Garg inequality [14]. Measurements of discord in mixed states have also been performed using
optical systems \cite{13} and quadrupolar NMR systems \cite{16}. Here we report an experimental study of time evolution of discord in NMR systems. After preparing a two-qubit Werner state, we study the accumulation of discord, effects of dynamical decoupling sequences on it, and its decay due to decoherence. In Sec. II, we revisit some theoretical aspects of discord and describe different ways of measuring it for the Werner state. Then, in Sec. III, we present the experimental details and discuss the results. We conclude in Sec. IV with some inferences from our analysis.

II. THEORY

A. Discord

*Conditional Entropy:* In classical information theory the amount of information contained in a random variable $X$ is quantified as the Shannon entropy,

$$H(X) = -\sum_x p_x \log_2 p_x ,$$

(1)

where $p_x$ is the probability of occurrence of event $X$. When $H(X) = 0$, the random variable $X$ is completely determined and no new information is gained by measuring it. Hence, Shannon entropy can be interpreted as either the uncertainty before measuring a random variable or the information gained on measuring it.

Consider a bipartite system containing two subsystems (or random variables), $A$ and $B$. Conditional entropy of $B$ quantifies the uncertainty in measurement of $B$ when $A$ is known, and is represented by $H(B|A)$. Using classical probability theory, it can be expressed as

$$H(B|A) = H(A,B) - H(A) ,$$

(2)

where $H(A,B)$ is the information content of the full system and $H(A)$ is the information content of the subsystem $A$. An equivalent way of defining the conditional entropy is

$$H(B|A) = \sum_i p_i^a H(B|a = i) ,$$

(3)

where

$$H(B|a = i) = -\sum_j p(b_j|a_i) \log_2 p(b_j|a_i) ,$$

(4)

and $p(b_j|a_i)$ is the conditional probability of occurrence of event $b_j$ given that event $a_i$ has occurred. Unlike the definition in Eq. (2), the definition in Eq. (3) involves measurement of one subsystem of a bipartite system.

*Mutual Information:* It is the amount of information that is common to both the subsystems of a bipartite system, and is given by

$$I(A : B) = H(A) + H(B) - H(A,B) .$$

(5)

This expression can be intuitively understood with the help of Fig. 1. On the right-hand side, the first two terms quantify the information content of subsystems $A$ and $B$, respectively. So the information common to both the subsystems is counted twice. Subtracting the information content of the combined system then gives the common (or mutual) information. The result is clearly symmetric, i.e., $I(A : B) = I(B : A)$. A classically equivalent form of mutual information, also shown in Fig. 1, is

$$I(A : B) = H(B) - H(B|A)$$

$$= H(B) - \sum_i p_i^a H(B|a = i) ,$$

(6)

which removes from the information content of subsystem $B$ the conditional contribution that is not contained in subsystem $A$.

In quantum information theory, the von Neumann entropy gives the information content of a density matrix,

$$H(\rho) = -\sum_x \lambda_x \log_2 \lambda_x ,$$

(7)

where $\lambda_x$ are the eigenvalues of the density matrix $\rho$. Although the two expressions of mutual information, Eqs. (5) and (6), are equivalent in classical information theory, they are not so in quantum information theory. The reason for the difference is that the expression for mutual information given by Eq. (5) involves measurement and depends on its outcomes. Measurements in quantum theory are basis dependent and also change the state of the system. Henderson and Vedral \cite{2} have proved that the total classical correlation can be obtained as the largest value of

$$J(A : B) = H(B) - H(B|A)$$

$$= H(B) - \sum_i p_i^a H(B|a = i) ,$$

(8)

![FIG. 1: The Venn diagram representing total information $H(A,B)$, individual informations ($H(A)$, $H(B)$), conditional information ($H(A|B)$, $H(B|A)$), and mutual information $I(A : B) = J(A : B)$ in classical information theory.](image-url)
where the maximization is performed over all possible orthonormal measurement bases \( \{ \Pi_i \} \) for \( A \), satisfying \( \sum_i \Pi_i = 1 \) and \( \Pi_i \Pi_j = \delta_{ij} \Pi_i \) \cite{12}. Therefore, the nonclassical correlations can be quantified as the difference

\[
D(B|A) = I(A : B) - \max J(A : B) \ .
\]

Ollivier and Zurek named this difference ‘discord’ \cite{2}. Zero-discord states or “classical” states are the states in which the maximal information about a subsystem can be obtained without disturbing its correlations with the rest of the system.

Discord is not a symmetric function in general, i.e. \( D(B|A) \) and \( D(A|B) \) can differ. Datta \cite{18} has proved that a state \( \rho_{AB} \) satisfies \( D(B|A) = 0 \) if and only if there exists a complete set of orthonormal measurement operators on \( A \) such that

\[
\rho_{AB} = \sum_i \rho_{i}^A \Pi_i^A \otimes \rho_{B|a=i} \ .
\]

When one part of a general bipartite system is measured, the resulting density matrix is of the form given by Eq. \eqref{eq:rho_AB}. Since the state rendered on measurement is a classical state, one can extract classical correlations from it. Thus, for any quantum state and every orthonormal measurement basis, there exists a classically correlated state. Maximization of \( J(A : B) \) captures the maximum classical correlation that can be extracted from the system, and whatever extra correlation that may remain is the quantum correlation.

\section*{B. Evaluation of Discord}

Given a density matrix \( \rho_{AB} \), it is easy to construct the reduced density matrices \( \rho_A \) and \( \rho_B \) and then obtain the total correlation \( J(A : B) \) using the quantum analog of Eq. \eqref{eq:rho_AB}. Maximization of \( J(A : B) \) to evaluate discord is nontrivial, however. The brute force method is to maximize \( J(A : B) \) over as many orthonormal measurement bases as possible, taking into account all constraints and symmetries. For a general quantum state, a closed analytic formula for discord does not exist, but for certain special class of states analytical results are available \cite{19}. For example, Chen et al. have described analytical evaluation of discord for two qubit X states under specific circumstances \cite{20}. Luo has given an analytical formula for discord of the Bell-diagonal states that form a subset of the X states \cite{21}. In our work, we evaluate discord using both the brute force method and the Luo method. We use Bell-diagonal states in our experiments, but our experimental preparation of the states is not perfect. The difference between the discord values obtained by the two methods then provides an estimate of the experimental imperfections.

\textbf{Extensive measurement method}: This method involves measurements over extensive sets of orthonormal basis vectors and maximization of \( J(A : B) \). For measurement of a single qubit in a two-qubit system, we use the orthonormal basis

\[
\{ |u \rangle = \cos \theta(0) + e^{i \phi} \sin \theta |1 \rangle \ , \ |v \rangle = \sin \theta(0) - e^{i \phi} \cos \theta |1 \rangle \},
\]

and let \( \cos \theta \in [-1, 1] \) and \( \phi \in [0, 2\pi] \) vary in small steps. For every choice of \( \theta \) and \( \phi \), we project the experimental density matrix obtained by tomography along the orthonormal basis. The postprojection density matrix is

\[
\rho' = \sum_{i=1,2} \Pi_i^A \rho_{i}^A \Pi_i^B = \sum_{i=1,2} \rho_{i}^A \Pi_i^A \otimes \rho_{B|a=i} \ ,
\]

with \( \rho_{B|a=i} = \text{Tr}[\Pi_i^A \rho] \). Discord is then obtained from the conditional density matrix \( \rho_{B|a=i} \) as per Eqs. \eqref{eq:discord} and \eqref{eq:discord_max}.

Strictly speaking, this method gives a lower bound on \( J(A : B) \), since the direction maximizing \( J(A : B) \) may not exactly match any of the points on the discrete \((\theta, \phi)\) grid. Also, when the desired state is isotropic, e.g., the Werner state, the angular variation of \( J(A : B) \) provides an estimate of the inaccuracy in the state preparation, e.g., due to inhomogeneities and pulse imperfections.

\textbf{Analytical method for the Bell-diagonal states}: As the name suggests, the Bell-diagonal states are diagonal in the Bell basis, given by

\[
|\psi^\pm \rangle = \frac{1}{\sqrt{2}}(|01 \rangle \pm |10 \rangle) \ , \ |\phi^\pm \rangle = \frac{1}{\sqrt{2}}(|00 \rangle \pm |11 \rangle) \ .
\]

The generic structure of a Bell-diagonal state is \( \rho_{BD} = \lambda_1 |\psi^- \rangle \langle \psi^- | + \lambda_2 |\phi^- \rangle \langle \phi^- | + \lambda_3 |\phi^+ \rangle \langle \phi^+ | + \lambda_4 |\psi^+ \rangle \langle \psi^+ | \). With only local unitary operations (so as not to alter the correlations), all Bell-diagonal states can be transformed to the form

\[
\rho_{BD} = \frac{1}{4} \left( 1 + \sum_{j=1}^3 r_j \sigma_j \otimes \sigma_j \right) ,
\]

where the real numbers \( r_j \) are constrained such that all eigenvalues of \( \rho_{BD} \) remain in \([0, 1]\). The symmetric form of \( \rho_{BD} \) also implies that it has symmetric discord, i.e., \( D_{BD}(A|B) = D_{BD}(A|B) \).

Luo chose the set of measurement bases as \( \{ V_{1,2} \} \), where \( V_k = |k \rangle \langle k | \) are the projection operators for the standard basis states \( |k = 0, 1 \rangle \), and \( V \) is an arbitrary \( SU(2) \) rotation matrix. A projective measurement yields the probabilities \( p_0 = p_1 = \frac{1}{2} \) and an analytical formula for the classical correlation,

\[
\max J(A : B) \left( \Pi_i^A \right) = \left( \frac{1 - r}{2} \right) \log_2(1 - r) + \left( \frac{1 + r}{2} \right) \log_2(1 + r) ,
\]

with \( r = \max\{|r_1|, |r_2|, |r_3|\} \).

For the Bell-diagonal states, the reduced density ma-
traces are $\rho_A = \rho_B = 1/2$, and the total correlation is

$$I(A : B) = 2 + \sum_{i=1}^{4} \lambda_i \log_2 \lambda_i ,$$  

(16)

where the eigenvalues $\lambda_i$ of $\rho_{BD}$ are

$$\lambda_1 = \frac{(1 - r_1 - r_2 - r_3)}{4},$$

$$\lambda_2 = \frac{(1 - r_1 + r_2 + r_3)}{4},$$

$$\lambda_3 = \frac{(1 + r_1 - r_2 + r_3)}{4},$$

$$\lambda_4 = \frac{(1 + r_1 + r_2 - r_3)}{4}.$$  

(17)

Thus the analytical formula for discord is, as per Eq. (14),

$$D_{BD}(B|A) = 2 + \sum_{i=1}^{4} \lambda_i \log_2 \lambda_i - \left(\frac{1 - r}{2}\right) \log_2 (1 - r) - \left(\frac{1 + r}{2}\right) \log_2 (1 + r).$$  

(18)

For a Werner state of the form

$$\rho_W(\epsilon) = \frac{1 - \epsilon}{4} \mathbb{1} + \epsilon |\psi^-\rangle \langle \psi^-| ,$$  

(19)

$r_j = -\epsilon$ and $r = \epsilon$. The discord is then given by

$$D_W(\epsilon) = \frac{1}{4} \log_2 \left(\frac{1 - \epsilon}{1 + \epsilon}\right) \frac{(1 + 3\epsilon)}{(1 + \epsilon)^2} + \frac{\epsilon}{4} \log_2 \left(\frac{1 + 3\epsilon}{1 - \epsilon}\right) \frac{3}{(1 + \epsilon)^2} \frac{1}{\ln 2} + O(\epsilon^3).$$  

(20)

This expression is plotted versus the purity $\epsilon$ in Fig. 2, together with the corresponding correlations $I(A : B)$ and $J(A : B)$.

In practice, the experimental density matrix obtained by tomography is not necessarily Bell diagonal. We obtain $I(A : B)$ as before, using Eq. (14). To extract the maximum value of $J(A : B)$, we drop the the off-diagonal terms, keeping only the terms in Eq. (14), and use Eq. (15). In this procedure, discord is overestimated, whenever the actual direction maximizing $J(A : B)$ is not in the Bell-diagonal state subspace.

**C. Geometric Discord**

Since the maximization of $J(A : B)$ involved in calculating discord is a hard problem, Dakic et al. introduced a more easily computable form of discord based on a geometric measure $[11]$. For every quantum state there is a set of postmeasurement classical states, and the geometric discord is defined as the distance between the quantum state and the nearest classical state,

$$DG(B|A) = \min_{\chi \in \Omega_0} \|\rho - \chi\|^2 ,$$  

(21)

where $\Omega_0$ represents the set of classical states, and $\|X - Y\|^2 = \text{Tr}(X - Y)^2$ is the Hilbert-Schmidt quadratic norm. Obviously, $DG(B|A)$ is invariant under local unitary transformations. Analytical formula for computing geometric discord for an arbitrary $A_{m \times m} \otimes B_{n \times n}$ state of a bipartite quantum system is available $[22]$. Recently discovered ways to calculate lower bounds on discord for such general states do not require tomography and, hence, are friendlier experimentally $[23, 24]$.

We follow the formalism of Dakic et al. $[11]$ to obtain geometric discord for two-qubit states. The two-qubit density matrix in the Bloch representation is

$$\rho = \frac{1}{4} \left(\mathbb{1} \otimes \mathbb{1} + \sum_{i=1}^{3} x_i \sigma_i \otimes \mathbb{1} + \sum_{i=1}^{3} y_i \mathbb{1} \otimes \sigma_i + \sum_{i,j=1}^{3} T_{ij} \sigma_i \otimes \sigma_j\right)$$  

(22)

where $x_i$ and $y_i$ represent the Bloch vectors for the two qubits, and $T_{ij} = \text{Tr}[(\rho \sigma_i \otimes \sigma_j)]$ are the components of the correlation matrix. The geometric discord for such a state is

$$DG(B|A) = \frac{1}{4} \left(\|x\|^2 + \|T\|^2 - \eta_{\text{max}}\right),$$  

(23)

where $\|T\|^2 = \text{Tr}[T^TT]$, and $\eta_{\text{max}}$ is the largest eigenvalue of $xx^T + TT^T$.

For the Werner state, as already mentioned, $x_i = 0 = y_i$ and $T$ is a diagonal matrix with $T_{ii} = -\epsilon$. Then $\|T\|^2 = 3\epsilon^2$ and all eigenvalues of $TT^T$ are $\epsilon^2$, yielding

$$DG_W(\epsilon) = \frac{1}{4} \left(3\epsilon^2 - \epsilon^2\right) = \frac{\epsilon^2}{2}.$$  

(24)

This expression is also plotted versus the purity $\epsilon$ in Fig. 2. Comparison with Eq. (23) reveals that discord and geometric discord are proportional for low-purity Werner states. Also, the numerical difference between $D_W(\epsilon)$ and $2DG_W(\epsilon)$ does not exceed 0.027 for all $\epsilon \in [0, 1]$.

The Bloch parameters $x_i, y_i$, and $T_{ij}$ provide a complete description of any two-qubit state. So tomographic measurement of these parameters determines the geometric discord exactly by Eq. (23).

**III. EXPERIMENT**

We now describe experimental evaluation of discord for two-qubit NMR systems. We measured quantum correlations for two different samples, each forming a two-qubit system, under different circumstances. Sample 1 is $^1$H and $^{13}$C spins of $^{13}$C-chloroform [see Fig. 3(b)] dissolved in deuterated chloroform (CDCl$_3$). Both $^1$H and $^{13}$C spins were on-resonant and the scalar
coupling \( (J) \) between the two spins is 219 Hz. For the proton, the \( T_1 \) and \( T_2 \) relaxation time constants are 14.5 and 5.7 s, respectively. For carbon, they are 21 and 0.25 s, respectively.

Sample 2 is \(^1\text{H} \) nuclear pairs of 5-chlorothiophene-2-carbonitrile (see Fig. 3b) dissolved in deuterated dymethylsulfoxide (DMSO-D\(_6\)). The chemical shift difference \( (\Delta\nu) \) and scalar coupling \( (J) \) between the two spins are 270 and 4.11 Hz, respectively. For each proton, the \( T_1 \) and \( T_2 \) relaxation time constants are 6.3 and 2.3 s, respectively.

All the experiments were carried out in a Bruker 500-MHz NMR spectrometer at an ambient temperature of 300 K. Precise radio-frequency (rf) gates for the experiments were synthesized by numerical optimizations as described in Refs. 22, 28. Decoherence in these systems is mainly due to the fluctuations in the local magnetic field, caused by random molecular motions in the presence of intra- and intermolecular dipolar interactions and chemical shift anisotropies. Traces of paramagnetic impurities also contribute to spin-relaxation [27].

The Hamiltonian for a two-qubit NMR system, with spins \( I^A \) and \( I^B \), can be written as

\[
\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_J.
\]

Here \( \mathcal{H}_Z = -\hbar \left( \omega_A I^A_z + \omega_B I^B_z \right) \) is the Zeeman Hamiltonian, characterized by the Larmor frequencies \( \omega_A \) and \( \omega_B \), and \( \mathcal{H}_J = 2\pi J I^A \cdot I^B \) is the indirect spin-spin coupling Hamiltonian.

In thermal equilibrium at room temperature, \( kT \) is much larger than the Zeeman energy splittings. So the density matrix of a two-qubit system can be expanded as [28]

\[
\rho_{eq} = \frac{1}{4} e^{-\mathcal{H}/kT} \approx \frac{1}{4} (1 + \mathcal{P}_{eq}).
\]

**FIG. 2:** Various correlations as functions of the purity \( \epsilon \) for Werner states of the form given in Eq. (22). The inset shows the range of discord for the purity available in our NMR setup.

**FIG. 3:** (a) The molecular structure of \(^{13}\text{C} \)-chloroform, and (b) the pulse sequence for discord preparation. In (b), PFG is the pulse field gradient operation which destroys the coherences and retains the diagonal elements of the density matrix.

The identity 1 represents a background of uniformly populated levels, and the traceless part \( \mathcal{P}_{eq} = \xi (I^A_z + \frac{\omega_A}{\omega_B} I^B_z) \) is known as the deviation density matrix. Only the traceless part \( \mathcal{P} \) is manipulated by unitary transformations in all NMR experiments. For protons in a magnetic field of strength 11.7 T at room temperature, the small dimensionless number \( \xi = \hbar \omega_A/kT \approx 8 \times 10^{-5} \). The discord for this size of purity is shown in the inset of Fig. 2 by a shaded area.

### A. Preparation of non-zero discord states

We prepared the maximum discord state starting from the zero discord thermal equilibrium state \( (\rho_{eq}) \) as follows. The pulse sequence in Fig. 3 was used to prepare discord between \(^1\text{H} \) and \(^{13}\text{C} \) spins of \(^{13}\text{C} \)-chloroform. For this system, \( \omega_C/\omega_H \approx 1/4 \). An initial \( |00\rangle \) pseudopure state was prepared using the spatial averaging method [28], as shown in the first part of Fig. 3. The transformations of the traceless \( \mathcal{P}_{eq}/\xi \) under the spatial averaging pulse sequence are (as per standard notation [27])

\[
\begin{align*}
I^A_z + \frac{1}{4} I^B_z \\
\downarrow 15^\circ A \\
I^A_z \cos(15^\circ) - I^A_y \sin(15^\circ) + \frac{1}{4} I^B_z \\
\downarrow 75^\circ A_y G \xi \\
I^A_z \cos(15^\circ) + 2I^A_x I^B_z \sin(15^\circ) + \frac{1}{4} I^B_z \\
\downarrow 75^\circ A_y G \xi \\
I^A_z \cos 75^\circ \sin 75^\circ + 2I^A_x I^B_z \sin 15^\circ \sin 75^\circ + \frac{1}{4} I^B_z \\
= \frac{1}{4}(I^A_z + I^B_z + 2I^A_x I^B_z).
\end{align*}
\]

This pseudopure state was converted into a Werner state, using the second part of the pulse sequence in Fig. 3b)
with the delay $\theta/(\pi J) = 1/(2J)$:

$$\rho_{pp} = \frac{1}{4} \left[ I + \frac{\xi}{4} \left( I_x^A + I_x^B + 2 I_z^A I_z^B \right) \right]$$

$$\downarrow 90^\circ_x A, 90^\circ_x B$$

$$\frac{1}{4} \left[ I + \frac{\xi}{4} \left( -I_y^A + I_y^B - 2 I_y^A I_y^B \right) \right]$$

$$\downarrow \frac{\pi}{2}$$

$$\frac{1}{4} \left[ I + \frac{\xi}{4} \left( 2 I_x^A I_x^B - 2 I_z^A I_z^B - 2 I_y^A I_y^B \right) \right]$$

$$\downarrow 180^\circ_y A, 90^\circ_y B$$

$$\rho_W = \frac{1}{4} \left[ I + \frac{\xi}{4} \left( -2 I_x^A I_x^B - 2 I_z^A I_z^B - 2 I_y^A I_y^B \right) \right]$$

$$= \frac{1}{4} \left[ I + \frac{\xi}{4} \left( -\frac{3}{4} I + 2 |\psi^-\rangle \langle \psi^-| \right) \right]$$

$$= \frac{1 - (\xi/8)}{4} I + \frac{\xi}{8} |\psi^-\rangle \langle \psi^-|.$$ \hspace{1cm} (28)

Comparing with Eq. (19), we can see that the relevant purity parameter in this case is $\epsilon = \xi/8$.

We also varied $\theta$ from 0 to $2\pi$ in 13 steps and, for each delay, carried out tomography to measure the experimental density matrix. \[29\]. The corresponding simulated density matrices are obtained by assuming perfect pulses and carrying out a calculation similar to Eq. (28). It can be easily seen that for $\theta$ values that are odd multiples of $\pi/2$, one obtains Bell-diagonal states. The fidelity $F$ of a test density matrix $\rho_{\text{test}}$ relative to the Werner state is defined as [25]

$$F = \frac{\text{Tr}[\rho_{\text{test}} \cdot \rho_W]}{\sqrt{\text{Tr}[\rho_{\text{test}}^2] \text{Tr}[\rho_W^2]}}.$$ \hspace{1cm} (29)

Fidelities of the experimental and the simulated density matrices, as functions of $\theta$, are shown in Fig. 4(a). The discord for each value of $\theta$ is obtained using the extensive measurement method as described in Sec. II-B. Both experimental and simulated values of the discord are plotted in Fig. 4(b), in units of $\epsilon^2/\ln 2$. The state at $\theta = 0$ is related to the pseudopure $|00\rangle$ state by local unitary transformations and, therefore, has zero discord. Otherwise, for $\theta \neq 0$, nonlocal spin-spin interactions give rise to discord. For $\theta$ equal to odd multiples of $\pi/2$, one obtains Bell-diagonal states with maximum discord. For $\theta$ equal to $\pi$, the delay equals the period of the scalar coupling, implying no transformation, and the discord is periodic thereafter.

The nonzero discord in the above experiments indicate the intrinsic quantumness of nuclear spin systems even at high temperatures. Among two-qubit states of a given purity, the Werner state possesses the maximum discord. Next, we investigate the efficiency of dynamical decoupling schemes in preserving discord.

### B. Discord under Dynamical Decoupling

Dynamical decoupling (DD) is a method of preserving coherences in NMR by frequent modulation of the spin–environment interaction with the help of a series of \[\pi\] pulses \[30–33\]. The \[\pi\]-pulses effectively change the sign of the linear spin–bath interaction, and suitable time spacings between them undo the time evolution and suppress the $T_2$-type decoherence due to the bath. We applied DD sequences immediately after obtaining the Werner state as in Eq. (28) and followed that up with tomography. The CPMG DD involved a series of uniformly spaced \[\pi\] pulses separated by 4-ms delays. For comparison, we label as no-DD the evolution with the delays but without the pulses. The Uhrig DD (UDD) involved cycles of a

**FIG. 4:** (a) Fidelity relative to the Werner state of the experimental and the simulated states as a function of $\theta$, and (b) corresponding discord values in units of $\epsilon^2/\ln 2$. The maximum discord is obtained for the delay parameter $\theta = (2n + 1)\pi/2$, corresponding to preparation of Bell-diagonal states.

**FIG. 5:** (a) Fidelity of the experimental state relative to the Werner state for various DD schemes, and (b) corresponding discord values in units of $\epsilon^2/\ln 2$. 
seven pulse sequence \[32, 34]. The time-instant \( t_j \) of the \( j \)th \( \pi \) pulse in each cycle was chosen according to Uhrig’s formula \( t_j = 28 \sin^2(\pi j/16) \) ms \[53\].

Figure 5(a) shows the time dependence of fidelities relative to the Werner state for no-DD, a CPMG DD sequence, and UDD sequence. Figure 5(b) displays the corresponding discord values obtained using the extensive measurement method. We observe that the DD sequences help in protecting fidelities of two-qubit quantum states, in agreement with an earlier work \[34\]. On the other hand, there is not much difference between no-DD and DD schemes in preserving discord. We believe that the reason is the decay of purity during the DD sequences. This decay is a \( T_1 \)-type decoherence, which the DD sequences do not protect against. By definition, fidelity looks at the orientation of the quantum state relative to a target state and not its normalization. On the other hand, discord depends on the normalization of the state. Our experiments indicate that though the DD sequences help prevent the quantum state from evolving to other quantum states, they are not useful in keeping the purity from decaying.

C. Discord in Long-lived Singlet States

Here we considered a pair of nuclear spins of the same isotope, i.e. Sample 2 shown in Fig. 6(b). The closeness of their Larmor frequencies allows a spin-lock procedure \[35\], where a continuous low-amplitude resonant rf irradiation makes the spins nutate and drives the spin state toward an isotropic distribution with all \( I_z \) values equally likely. The pulse sequence for the preparation of a long-lived singlet state is shown in Fig. 6(a). The rf wave for the spin-lock had the carrier frequency \((\omega_A + \omega_B)/2\), the mean Larmor frequency of the two spins, and a nutation frequency of 2 kHz.

The average Hamiltonian in the interaction frame during the spin-lock interval is \( \mathcal{H}_{\text{int}} = 2\pi h J (I_1 \cdot I_2) \), where \( I_1 \) and \( I_2 \) are the spin operators. The singlet state, and the degenerate triplet states, form an orthonormal eigenbasis of this \( \mathcal{H}_{\text{int}} \):

\[
|S_0\rangle = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle),
\]

\[
|T_\uparrow\rangle = |00\rangle, \quad |T_0\rangle = \frac{1}{\sqrt{2}}(|01\rangle + |10\rangle), \quad |T_\downarrow\rangle = |11\rangle.
\]

As described earlier, the NMR system under ordinary conditions exists in a highly mixed state with a small purity. Leaving out the uniform distribution, the ground state is the Werner state, which is also called the long-lived singlet state (LLS) \[34, 37\]. The LLS is antisymmetric with respect to spin exchange, and is not connected to other eigenstates (i.e. symmetric triplet states) by any symmetry preserving transformations such as the nonselective rf pulses and the intrapair dipolar interaction. Therefore, the LLS can survive for durations much longer than other non-equilibrium spin states. The LLS have been used in NMR experiments for the study of slow diffusion \[38\], for ultraprecise measurement of scalar interactions \[39\], for storage and transport of parahydrogen \[40, 41\], and for preparation of high fidelity Bell states and other pseudopure states \[42\].

The rf pulses prior to the spin-lock prepare a state which is a mixture of the \(|S_0\rangle \) and \(|T_0\rangle \) states,

\[
\rho(0) = \frac{1}{4} + \frac{\xi}{4} \left(|S_0\rangle\langle S_0| - |T_0\rangle\langle T_0|\right).
\]

During the spin-lock, rf irradiation mixes various components of states with the same spin, and the \(|T_0\rangle \) state rapidly equilibrates with the other triplet states. Furthermore, all other coherences created due to pulse imperfections also decay towards the background \[43\]. On this equilibration, which takes a few seconds, the system reaches the Werner state,

\[
\rho_{\text{LLS}} = \frac{1 - (\xi/3)}{4} \mathbb{1} + \frac{\xi}{3} |S_0\rangle\langle S_0| = \rho_W (\epsilon = \xi/3).
\]

This Werner state has a purity that differs from the one prepared from Sample 1, i.e., Eq. (28).

To study the evolution of the density matrix state during spin-lock, we applied the spin-lock for a variable duration \( \tau \) and then carried out tomography to measure the traceless part of the density matrix \( \rho(\tau) \). We find that \( \rho(\tau) \) gradually evolves towards the Werner state \( \rho_W \), remains in that state for several tens of seconds, and ultimately decays towards the uniform state \( \mathbb{1}/4 \) that is the asymptotic eigenstate of the spin-lock evolution after the decay of all spin correlations.

We monitored fidelity of the experimental state relative to the Werner state at 17 spin-lock durations, \( \tau = 2^n \) ms with \( n = \{0, 1, \ldots, 16\} \). As shown in Fig. 7(a), it starts with a value of 0.85, reaches a maximum of 0.99 after a few seconds, and then decreases. The real parts of the deviation density matrices \( \tilde{\rho}_W \) and \( \tilde{\rho}(\tau) \), with \( \tau =...
16.4 s corresponding to the maximum fidelity 0.99, are compared in Figs. 6(c) and 6(d).

Although fidelity is a good measure of how close a test density matrix is to the target density matrix, it does not capture the global decay of the purity of the density matrix. To monitor the decay of the purity as well as the closeness of the traceless parts of the density matrices, we use attenuated fidelity, as shown in Fig. 7(a), we determined $\lambda_2^{-1} = 0.75$ ms and $\lambda_2^{-1} = 26$ s. These values indicate the rapid equilibration of the triplet states and the long-lived nature of the singlet state. It can be noticed that $\lambda_2^{-1}$ is comparable to the rf period during the spin-lock, and $\lambda_2^{-1}$ is significantly longer than spin-lattice relaxation time constants ($T_1$ values).

We also measured discord during the spin-lock evolution using the methods described in Sec. II, and the results are plotted versus the spin-lock duration in Fig. 7(b). The results for the extensive measurement method $D(B|A)$ and geometric discord $DG(B|A)$ essentially agree (when scaled by appropriate factors), as expected for accurate methods, and indicate that measurement errors in our experiments are rather small. By looking at angular variation of $J(A : B)$ in the extensive measurement method, at $\tau = 16.4$ s when the state is closest to the isotropic Werner state, we estimate that the imperfections in our prepared LLS state give around 3% error to discord values.

The discord $D_{BD}(B|A)$ obtained by assuming that the state is of Bell-diagonal form is an overestimate initially but becomes almost the same as the other two determinations beyond $\tau = 1 ms$. That means that artifact off-diagonal coherences are present in our prepared state, but they decay rapidly on a time scale comparable to $\lambda_2^{-1}$. The discord value for the two-parameter model of Eq. (35) is also shown in Fig. 7(b). It is accurate once the state becomes Bell-diagonal, but is unable to model the initial behavior. The reason for the initial discrepancy is that the off-diagonal components missing from Eq. (35) alter both $I(A : B)$ and $J(A : B)$. Later evolution and the asymptotic vanishing of discord after long durations of spin-lock is governed by the time scale $\lambda_2^{-1}$.

IV. CONCLUSIONS

Over the years, several hypotheses have been proposed to characterize the nonclassical part of quantum correlations, e.g., entanglement, violation of Bell-type inequalities, uncertainty relations, quantum discord, and so on. They are not all equivalent, especially for mixed states. Quantum discord aims to be the most inclusive of all of these, and we have focused our attention to the study of its dynamics in this work.

It is well known that under ordinary NMR conditions, the purity of an ensemble of nuclear spin systems is below the threshold to exhibit entanglement. However, successful demonstrations of NMR quantum information processing indicate that quantum correlations do exist in such ensembles. In our work, we have, first, revisited the theoretical basis of discord as well as geometric discord and then have described how they can be produced, manipulated, and monitored for an experimental density matrix, using the Werner state as a specific example. We have also implemented several checks in our investigations to keep track of experimental imperfections.
The experimental study of discord was carried out in two different systems. In one system, we studied preparation of discord using an entangling pulse sequence, and evolution of discord under dynamical decoupling sequences. Under DD, discord did not show much improvement, but there was clear improvement in fidelity, which implies that DD protects against $T_2$-type decoherences but not against $T_1$-type decoherences. In the second system, we used the construction of the long-lived singlet state to prepare the Werner state and examined its evolution under rf spin-lock. We can describe the accompanying evolution of fidelity and discord reasonably well using a simple relaxation model. In both systems, the experimentally observed behavior and the fit parameters are in good agreement with expectations from theory and simulations.

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[1] R. Horodecki et al., Rev. Mod. Phys. 81, 865 (2009).
[2] H. Ollivier and W.H. Zurek, Phys. Rev. Lett. 88, 017901 (2002).
[3] L. Henderson and V. Vedral, J. Phys. A 34, 6899 (2001).
[4] V. Athalye, S.S. Roy and T.S. Mahesh, Phys. Rev. Lett. 107, 070501 (2011).
[5] E. Knill and R. Laflamme, Phys. Rev. Lett. 81, 5672 (1998).
[6] M. Carravetta et al., Phys. Rev. Lett. 107, 070501 (2011).
[7] G. Passante et al., Phys. Rev. A 84, 044302 (2011).
[8] A. Datta, A. Shaji and C.M. Caves, Phys. Rev. Lett. 100, 050502 (2008).
[9] K. Modi et al., Phys. Rev. X 1, 021022 (2011).
[10] B. Dakic, V. Vedral and C. Brukner, Phys. Rev. Lett. 105, 190502 (2010).
[11] R. Auccaise et al., Phys. Rev. Lett. 107, 070501 (2011).
[12] D. Leung, A. Shaji and C.M. Caves, Phys. Rev. A 85, 024302 (2012).
[13] A.S.M. Hassan, B. Lari and P.S. Joag, Phys. Rev. A 85, 024302 (2012).
[14] S. Luo and S Fu, Phys. Rev. A 82, 034302 (2010).
[15] S. Luo and S Fu, Phys. Rev. A 82, 044302 (2011).
[16] A. Datta, PhD thesis, The University of New Mexico, arXiv:0807.4490 (2008); arXiv:1003.5256 (2010).
[17] D. Girolami and G. Adesso, Phys. Rev. A 83, 052108 (2011).
[18] Q. Chen et al., Phys. Rev. A 84, 042313 (2011).
[19] S. Luo, Phys. Rev. A 77, 042303 (2008).
[20] S Luo and S Fu, Phys. Rev. A 82, 034302 (2010).
[21] S. Rana and P. Parashar, Phys. Rev. A 85, 024102 (2012).
[22] D. Girolami and G. Adesso, Phys. Rev. A 83, 017901 (2012).
[23] E.M. Fortunato et al., J. Chem. Phys. 126, 214501 (2007).
[24] K. Modi et al., Phys. Rev. Lett. 101, 200501 (2008).
[25] T.S. Mahesh and D. Suter, Phys. Rev. A 74, 062312 (2006).
[26] S. Meiboom and D. Gill, Rev. Sci. Instr. 29, 688 (1958).
[27] G. Palao and M.H. Levitt, J. Magn. Reson. 177 (2008).
[28] A. Datta, PhD thesis, The University of New Mexico, arXiv:0807.4490 (2008); arXiv:1003.5256 (2010).
[29] A.K. Grant and E. Vinogradov, J. Magn. Reson. 193, 177 (2008).
[30] W.S. Warren et al., Science 323, 1711 (2009).
[31] S. Meiboom and D. Gill, Rev. Sci. Instr. 29, 688 (1958).
[32] A.K. Grant and E. Vinogradov, J. Magn. Reson. 193, 177 (2008).
[33] W.S. Warren et al., Science 323, 1711 (2009).
[34] S.S. Roy, T.S. Mahesh and G.S. Agarwal, Phys. Rev. B 83, 062326 (2011).
[35] G. Pileio and M.H. Levitt, J. Magn. Reson. 130, 214501 (2004).
[36] M. Caravettta, O.G. Johannessen and M.H. Levitt, Phys. Rev. Lett. 92, 153003 (2004).
[37] M. Caravettta and M.H. Levitt, J. Am. Chem. Soc. 126, 6228 (2004).
[38] S. Cavadini et al. J. Am. Chem. Soc. 127, 15744 (2005).
[39] G. Pileio, M. Caravettta and M.H. Levitt, Phys. Rev. Lett. 103, 083002 (2009).
[40] A.K. Grant and E. Vinogradov, J. Magn. Reson. 193, 177 (2008).
[41] W.S. Warren et al., Science 323, 1711 (2009).
[42] S.S. Roy and T.S. Mahesh, Phys. Rev. B 82, 052302 (2010).