Optimizing a Dynamical Decoupling Protocol for Solid-State Electronic Spin Ensembles in Diamond

D. Farfurnik, A. Jarmola, L. M. Pham, Z. H. Wang, V. V. Dobrovitski, R. L. Walsworth, D. Budker, and N. Bar-Gill

1Racah Institute of Physics, Hebrew University, Jerusalem 9190401, Israel
2The Center for Nanoscience and Nanotechnology, Hebrew University, Jerusalem 9190401, Israel
3Department of Physics, University of California, Berkeley, California 94720-7300, USA
4Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, USA
5Department of Chemistry, University of Southern California, Los Angeles, California 90089, USA
6Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA
7Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA
8Helmholtz Institute, JGU, Mainz, Germany
9The Center for Nanoscience and Nanotechnology, Hebrew University of Jerusalem, Jerusalem 9190401, Israel
10Department of Applied Physics, Rachel and Selim School of Engineering, Hebrew University, Jerusalem 9190401, Israel

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We demonstrate significant improvements of the spin coherence time of a dense ensemble of nitrogen-vacancy (NV) centers in diamond through optimized dynamical decoupling (DD). Cooling the sample down to 77 K suppresses longitudinal spin relaxation $T_1$ effects and DD microwave pulses are used to increase the transverse coherence time $T_2$ from $\sim 0.7$ ms up to $\sim 30$ ms. We extend previous work of single-axis (CPMG) DD towards the preservation of arbitrary spin states. Following a theoretical and experimental characterization of pulse and detuning errors, we compare the performance of various DD protocols. We identify that the optimal control scheme for preserving an arbitrary spin state is a recursive protocol, the concatenated version of the XY8 pulse sequence. The improved spin coherence might have an immediate impact on improvements of the sensitivities of AC magnetometry. Moreover, the protocol can be used on denser diamond samples to increase coherence times up to NV-NV interaction time scales, a major step towards the creation of quantum collective NV spin states.

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In recent years, atomic defects in diamond have been the subject of a rapidly growing area of research. The most well-studied of these diamond defects is the nitrogen-vacancy (NV) color center, whose unique spin and optical properties make it a leading candidate platform for implementing quantum information processing [1–5]. However, no fundamental study yet considered the robustness of various DD protocols on NV ensembles. In this work, we perform a theoretical and experimental analysis of the performance of several DD protocols, including standard CPMG and XY-based pulse sequences as well as modifications thereon, and extract an optimized protocol for preserving a general quantum state [6–9].
3.23 3.226 3.224

a b c

Singlet States

Excited State

3.22

Fluorescence intensity of the phonon sideband [1].
pulses, and read out optically via spin-state-dependent
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pulses, and read out optically via spin-state-dependent
fluorescence intensity of the phonon sideband [1].

The NV center is composed of a substitutional nitrogen atom (N) and a vacancy (V) on adjacent lattice sites in
the diamond crystal. The electronic structure of the nega-
tively charged NV center has a spin-triplet ground state,
where the $m_s = ±1$ sublevels experience a zero-field split-
ing ($\sim 2.87$ GHz) from the $m_s = 0$ sublevel due to spin-
spin interactions [Fig. 1(a)]. Application of an external
static magnetic field along the NV symmetry axis Zeem-
man shifts the $m_s = ±1$ levels and allows one to treat the
$m_s = 0, +1$ spin manifold (for example) as an effective
two-level system. The NV spin state can be initialized
in the $m_s = 0$ state with off-resonant laser excitation,
coherently manipulated with resonant microwave (MW)
pulses, and read out optically via spin-state-dependent
fluorescence intensity of the phonon sideband [1].

The NV spin bath environment is typically dominated
by $^{13}$C nuclear and N paramagnetic spin impurities,
dependently distributed in the diamond crystal. These spin
impurities create different time-varying local magnetic fields
at each NV spin, which can be approximated as a random
local magnetic field that fluctuates on a timescale set by
the mean interaction between spins in the bath. This
random field induces dephasing of freely precessing NV
pulse sequences can suppress the effect of the spin
bath noise and thus preserve the NV spin coherence up to
a characteristic time $T_2$ [11, 21, 22]. In the ideal case of per-
fect pulses, various DD protocols (e.g., CPMG, XY, etc.)
are equally effective at preserving an arbitrary NV en-
semble spin state. Experimentally, however, off-resonant
driving due to the NV hyperfine structure [21] and other
pulse imperfections significantly affect the performance
of individual DD protocols. In order to overcome these
pulse imperfections, we optimize a DD protocol for an
ensemble of NV spins.

Figure 2(a) illustrates the general structure of the DD
protocols explored in this work. In each protocol, $(\pi)$-
pulses about a rotation axis determined by the specific
DD protocol are applied, with a free evolution interval
of time $2\tau$ between them. In the regime where the pulse
durations are short compared to the free evolution inter-
val between adjacent pulses, each pulse can be expressed
in terms of a spin rotation operator [19, 20]

$$U_k = \exp \{ -i\pi(1 + \epsilon_k)[\vec{S} \cdot \hat{n}] \}. \quad (1)$$

Equation (1) incorporates the two main types of pulse
imperfection: $\epsilon_k$ represents the deviation from an ideal
rotation angle $\pi$, and $\hat{n} = (n_x, n_y, n_z)$ is the actual
rotation axis, which can deviate from $\hat{k} = (k_x, k_y, 0)$ [Fig.
1(b)]. Generally, imperfections in the rotation angle ($\epsilon_k$
may be caused by limitations in pulse timing resolution
and amplitude stability of the MW field source, as well
as static and MW field inhomogeneity over the measure-
ment volume; and imperfections in the rotation axis may
be caused by phase instability in the MW field source.
In addition to general experimental pulse errors, the spec-
cific physical system of the NV spin ensemble introduces
additional pulse imperfections. Most notably, hyperfine
interactions between the $^{14}$N nuclear spin ($I = 1$) of
the NV center and the NV electronic spin result in three
transitions each separated by $\sim 2.2$ MHz in the, e.g., NV
$m_s = 0 ↔ +1$ resonance [21] [Fig. 1(c)].

The total evolution operator of a general DD sequence
containing $n$ $(\pi)$-pulses can then be expressed as

$$U_{DD} = U_d(\tau)U_{k_n}U_d(2\tau)U_{k_{n-1}}U_d(2\tau)\cdots U_d(2\tau)U_{k_1}U_d(\tau), \quad (2)$$

where $U_d$ is the free evolution operator. It is clear that
without compensation for pulse imperfections in the spin
rotation operators, accumulating errors will result in a se-
vere loss of coherence even in the limit of free evolution
time $\tau \to 0$. First, we study the robustness of conven-
tional CPMG and XY-based DD protocols, summarized
in Figure 2(b) (c), in order to determine which protocol
is the most robust against pulse imperfections caused by
general experimental limitations as well as those specific
to NV ensembles. Realizing that enhanced robustness
is necessary, we reduce the effects of the imperfections
by optimizing experimental parameters (see detailed ex-
perimental setup description below) and modify the ba-
sic XY sequences by introducing pulses with additional
phases [Fig. 2(d)] and concatenated cycles [Fig. 2(e)].
Similar DD protocol optimization has been performed in
the past for phosphorus donors in silicon [19] and single
NV centers [20].

In the conventional CPMG DD protocol [25], all (\(\pi\))-pulses are applied along the same axis (\(x\)) [Fig. 2(b)]; consequently, only coherence along one spin component is well-preserved. The XY family of DD protocols [20] applies pulses along two perpendicular axes (\(x, y\)) in order to better preserve spin components along both axes equally [Fig. 2(c)]. We also explored two DD protocols which introduce additional modifications on the basic XY pulse sequences in order to improve its robustness against pulse errors. The first modification, the Knill Dynamical Decoupling (KDD) pulse sequence, introduces additional phases, thereby symmetrizing the XY-plane further and reducing the effects of pulse errors due to off-resonant driving and imperfect \(\pi\)-flips. In the KDD protocol, each (\(\pi\))-pulse in a basic XY sequence is replaced by five pulses with additional phases given by \((\pi)_{60^\circ} - (\pi)_{0^\circ} - (\pi)_{90^\circ} - (\pi)_{0^\circ} - (\pi)_{60^\circ}\), where the 2\(\tau\) free evolution interval between adjacent (\(\pi\))-pulses timing is preserved [Fig. 2(d)]. The second modification employs concatenation, a recursive process in which every cycle is constructed from the previous cycles [Fig. 2(e)], and each level of concatenation corrects higher orders of pulse errors [27, 28].

We performed measurements on an isotopically pure (99.99\% 13C) diamond sample with N concentration \(\sim 2 \times 10^{17}\) cm\(^{-3}\) and NV concentration \(\sim 4 \times 10^{14}\) cm\(^{-3}\) (Element Six), grown via chemical vapor deposition. The sample was placed in a continuous flow cryostat (Janis ST-500) and cooled with liquid nitrogen to 77 K, significantly reducing phonon-related decoherence to allow for NV spin coherence times \(\gg 1\) ms [17, 29]. A 532-nm laser optically excited an ensemble of \(\sim 10^4\) NV centers within a \(\sim 25 \mu m^3\) measurement volume, and the resulting fluorescence was measured with a single photon counting module. A permanent magnet produced a static magnetic field \(B_0 \sim 300\) G along the NV symmetry axis, Zeeman splitting the \(m_s = \pm 1\) spin sublevels. To coherently manipulate the NV ensemble spin state, we used a 70-\(\mu m\) diameter wire to apply a MW field resonant with the \(m_s = 0 \leftrightarrow +1\) transition. The spin rotation axes of the individual DD pulses were set through IQ modulation of the MW carrier signal from the signal generator (SRS SG384).

As discussed previously, one of the sources of pulse imperfections for NV centers is the hyperfine structure in the NV resonance spectrum; specifically, resonant driving of one of the hyperfine transitions results in detuned driving of the other two, introducing both spin rotation angle and spin rotation axis errors. We mitigate these effects by: (i) applying a strong static magnetic field \((\sim 300\) G) to polarize the 14N nuclear spins [30] into one hyperfine state which we drive [Fig. 1(c)] and (ii) applying a strong MW field to drive the NV transition with Rabi frequency \((\sim 15\) MHz) much greater than the detuning due to NV hyperfine splitting \((\sim 2.2\) MHz). Furthermore, we minimize general experimental pulse errors due to pulse timing and amplitude imperfections, MW carrier signal phase imperfections, and static and MW field inhomogeneities over the measurement volume [23]. We estimate that the pulse imperfections remaining after this optimization are characterized by \(\epsilon_k \approx 0.15\) and \(n_z \approx 0.25\).

In order to determine how well each of the four DD protocols preserves a general NV ensemble spin state, we measure the NV spin coherence of two orthogonal initial spin components \(S_x\) and \(S_y\). The \(S_x\) spin component is prepared and measured by applying the initial and final \((\pi/2)\)-pulses about the \(y\) axis; likewise, the \(S_y\) spin component is prepared and measured by applying the initial and final \((\pi/2)\)-pulses about the \(x\) axis. We first characterize the robustness of each DD protocol against pulse imperfections by measuring NV ensemble spin coherence in the short free evolution (i.e., decoherence-free) limit \(2\tau \ll T_2\) (while remaining in the regime of infinitely narrow MW pulses) and normalizing against the NS ensemble spin coherence of a 1-pulse Hahn-Echo measurement in the same limit. We plot the experimental results in Figure 3(b) for each of the DD protocols as a
Figure 3: Relative contrast in the decoherence-free limit ($\tau \ll \frac{\Delta}{2\pi}$) of DD protocols as a function of number of pulses. For clarity purposes, the simulation is separated from the experimental results. (a) Simulation of the effect of non-ideal ($\pi$)-pulses according to Equation (2). All XY8-based sequences performed similarly for initialization at $S_x$ and $S_y$. (b) Experimental results. The relative contrast is determined via normalizing with a Hahn-Echo measurement in the decoherence-free limit. At the perpendicular axis, the contrast of XY-based sequences is similar, but the CPMG contrast vanishes completely, as demonstrated in the supplemental material [23].

The CPMG protocol maintains the highest relative contrast for the spin component along the spin rotation axis of the DD pulses ($S_z$) but the lowest relative contrast for the spin component along the perpendicular axis ($S_y$) [23], as expected. The relative contrast of XY-based sequences is comparable for both spin components [23] but drops as the number of pulses increases, indicating that while the XY-based protocol is able to symmetrically compensate for pulse errors and thus preserve an arbitrary NV ensemble spin state, accumulating pulse errors due to imperfect compensation eventually limit the sequence to $\sim 500$ pulses. Within the XY family, we compared XY4, XY8, and XY16 pulse sequences [24] and found XY8 to show the best performance [24].

The KDD protocol, which introduces more spin rotation axes to further symmetrize pulse error compensation, and the concatenated protocol, which constructs the pulse sequences recursively in order to correct for higher orders of pulse errors both improve upon the conventional XY8 sequence, maintaining higher relative contrast for both spin components to $> 500$ pulses. Note that the measurements are in qualitative agreement with the simulations. Quantitatively, however, there is a disagreement, and the experimental results for the relative contrast are slightly lower than the simulation suggests. In particular, the contrast of the concatenated XY8 protocol does not change with the number of pulses according to the simulation, which disagrees with the experimental data. This disagreement is likely caused by the interplay between pulse errors and decoherence effects, which was not taken into account in the simulation and will be the subject of a future research.

Figure 4: Experimental results of the coherence time of DD sequences as a function of the number of pulses, after initialization at $S_x$. The results after initialization at $S_y$ are shown in the supplemental material [23].

The measured NV ensemble spin coherence time is plotted as a function the number of pulses for each DD protocol in Figure 4. The CPMG, XY8, and concatenated XY8 protocols all extend the NV spin coherence time as expected, given the nitrogen-impurity-dominated spin bath environment [22]. However, the KDD protocol is less effective at extending the NV spin coherence time; this underperformance is probably due to the fact that the phase difference between adjacent pulses in KDD (sometimes 60°) is smaller than in other sequences (90°), making phase errors more significant [23].

In conclusion, after optimizing experimental parameters to minimize pulse imperfections, we found the most robust DD protocol for preserving an arbitrary spin state in an NV ensemble system to be the concatenated XY8 pulse sequence. By compensating for higher order pulse errors, the concatenated XY8 sequence maintains higher
relative contrast than the conventional XY8 sequence and is expected to ultimately outperform the KDD sequence for larger numbers of pulses. Furthermore, the concatenated XY8 sequence achieves longer NV ensemble spin coherence times than the KDD sequence. At 77 K, we measured an extension of the arbitrary spin state of an ensemble of $\sim 10^4$ NV centers by a factor of $\sim 40$ and up to $\sim 30$ ms.

The optimized DD protocol determined in this work may already have an immediate impact in improving the sensitivity of NV magnetometry [3] and, moreover, may be useful for quantum information applications. The sample in this work has nitrogen density $\sim 2 \times 10^{17}$ cm$^{-3}$ and NV density $\sim 4 \times 10^{14}$ cm$^{-3}$, corresponding to N-to-NV conversion efficiency $\sim 0.2\%$ and typical NV-NV interaction time $\sim 150$ ms. Using standard sample processing techniques, such as electron irradiation [4], to modestly improve the N-to-NV conversion efficiency to $\sim 1\%$, the concatenated XY8 pulse sequence can increase the NV ensemble spin coherence time to the NV-NV interaction time. In such a case, MREV-based techniques [31] can be applied to average out the NV-NV interactions and introduce effective Hamiltonians [10], thereby creating self engineered quantum states (e.g. squeezed states) in NV ensemble systems.

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[23] See supplemental material.