Zero- and Low-field Nano-NMR with Nitrogen Vacancy Centers

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Over the years, an enormous effort has been made to establish nitrogen vacancy (NV) centers in diamond as easily accessible and precise magnetic field sensors. However, most of their sensing protocols rely on the application of bias magnetic fields, preventing their usage in zero- or low-field experiments. We overcome this limitation by exploiting the full spin $S = 1$ nature of the NV center, allowing us to detect nuclear spin signals at zero- and low-field with a linearly polarized microwave field. As conventional dynamical decoupling protocols fail in this regime, we develop new robust pulse sequences and optimized pulse pairs, which allow us to sense temperature and weak AC magnetic fields and achieve an efficient decoupling from environmental noise. The sensing scheme is applicable to common NV center based setups and opens new frontiers for the application of NV centers as magnetic field sensors in the zero- and low-field regime.

Introduction.— A bias magnetic field can lead to many undesirable effects, e.g., during the structural analysis of molecules. It induces a Zeeman interaction which then dominates over the spin-spin coupling (J-coupling), masking crucial information about the chemical bonds. Moreover, bias magnetic fields lead to perturbations in various condensed matter systems, ranging from magnetic susceptibility effects [1] to diagnosing different phases of matter [2].

Despite its success as an electric and magnetic sensor [3–7], including in the above mentioned applications [8–11], most sensing protocols developed for NV centers rely on bias magnetic fields that lift the inherent degeneracy of their ground state manifold and permit working with effective two-level systems. In recent years, scientists worked on overcoming this limitation by applying circularly polarized microwave fields, which allow to selectively address one spin state [12, 13], while working at zero- or low-field. However, this method requires special microwave structures to apply circularly polarized microwave fields, whose performance strongly depends on their phase and on the placement of the microwave structure relative to the NV center [13, 14].

We demonstrate a different approach, where we exploit the full spin $S = 1$ nature of the NV center, enabling sensing experiments at zero- and low-field. By applying linearly polarized microwave fields at a frequency equal to the NV centers zero-field splitting (ZFS), we utilize a hidden effective Raman coupling [15] to create a coherent superposition of the NV centers $|±1⟩$ spin states (we denote $|m_S = λ⟩ = |λ⟩$). Continuous application of a microwave field will thus lead to Rabi oscillations of the populations of the NV center’s ground states. We carefully analyze the observed oscillations and construct high fidelity pulse gates for sensing protocols, e.g., Ramsey, temperature and ac-sensing experiments. A similar approach has been used previously to create non-invasive bio-sensors [16] as well as for fluorescence thermometry [17, 18] and in the context of quantum information [16, 19, 20].

As linearly polarized microwave fields do not offer full phase control while working in the $|±1⟩$ subsystem of the NV center’s ground states, conventional dynamical decoupling protocols, e.g., the XY8 sequence [21, 22], are not directly applicable anymore. Furthermore, detuning from the ZFS due to e.g., hyperfine interaction and stray magnetic fields reduce the fidelity of the applied pulses, preventing the detection of weak AC magnetic fields. We overcome these problems by limiting ourselves to microwave phases of $φ = 0$ and $φ = π$, allowing us to effectively reduce the dynamics of the three-level system to an effective two-level system due to the inherent symmetry of the former. As a result, we construct robust pulse sequences to efficiently decouple the spin from environmental noise and create narrow-band filters to sense nearby AC magnetic fields. In addition, we use the GRAPE algorithm [23] to improve performance by optimizing the amplitude and phase of pairs of pulses to be used in the sequence.

Our method can be easily implemented in every common NV center based setup and is applicable at both zero- and low-field. It opens new frontiers for the investigation of condensed matter systems and the structural analysis of molecules. In combination with its bio-compatibility [24–28], small size and capability to work with nano-scale samples sizes in a broad temperature [29, 30] and pressure range [31, 32], we propose NV centers as a suitable alternative to conventional zero-field sensors [33–37].

System.— The NV center is a point defect in the diamond lattice consisting of a substitutional nitrogen atom and a vacancy on the neighboring lattice side. It’s negative charge state allows us to optically determine the electron spin state and furthermore polarize it into the
FIG. 1.  a) The NV centers ground state has a zero-field splitting of $D \approx 2.87$ GHz. A bias magnetic field lifts the degeneracy of the $m_S = \pm 1$ states by $2\gamma NB$. Hyperfine coupling to the inherent $^{14}$N nucleus leads to an additional splitting of the spin states. We combine these detuning effects to an effective detuning $\Delta$. b) Transformation into the dressed basis $(|\pm\rangle, |0\rangle)$ with $|\pm\rangle = (|+\rangle \pm |-\rangle)/\sqrt{2}$ reveals a hidden effective Raman coupling. Microwave pulses with frequency $\omega_c = D$ lead to Rabi oscillations among the three spin states with frequencies $\Omega = \sqrt{\Omega^2 + \Delta^2}$ and $2\Omega$. Depending on the ratio between detuning $\Delta$ and the applied Rabi frequency $\Omega$, the population will be trapped in $|-\rangle$. The shown example is simulated for $\Omega = 44 \text{ MHz}$ and $\Delta = 9.8 \text{ MHz}$. c) A microwave pulse with length $T$ flips the population from $|0\rangle$ to $|\phi\rangle = (1 - \exp(i\phi))/2|+\rangle - (1 + \exp(i\phi))/2|-\rangle$ [15]. To completely recover the population we have to apply a microwave pulse for the time $T'$. A pulse with length $T/2$ acts as a conventional $\pi$-pulse in the $(|\pm\rangle)$ subspace.

$|0\rangle$ ground state [38, 39] due to spin-selective intersystem crossing to a metastable singlet state between ground and excited state. It possesses an $^3A_2$ triplet ground state with a ZFS of $D \approx 2.87$ GHz as shown in Fig. 1 a). Application of a bias magnetic field along the NV centers symmetry axis lifts the degeneracy of the $|\pm 1\rangle$ states by $2\gamma NB$. Coupling to the inherent $^{14}$N nucleus and other surrounding spins causes an additional hyperfine splitting. We combine these detuning effects and approximate them with an effective detuning $\Delta$. If we apply a microwave $2\Omega \cos(\omega_c t + \varphi)S_x$ with a frequency $\omega_c = D$, the system’s rotating frame Hamiltonian becomes

$$H(D) = (\Delta|\rangle\langle -\rangle + e^{i\varphi}\Omega|0\rangle\langle 0\rangle)(|+\rangle + H.c.) \tag{1}$$

after the rotating wave approximation and reveals a hidden effective Raman coupling, through a change of basis to $(|\pm\rangle, |0\rangle)$ with $|\pm\rangle = (|+\rangle \pm |-\rangle)/\sqrt{2}$, sketched in figure 1 b). This leads to Rabi oscillations with frequencies $\Omega = \sqrt{\Omega^2 + \Delta^2}$ and $2\Omega$ between the respective dressed states. As all three states $(|\pm\rangle, |0\rangle)$ are coupled for $\Delta \neq 0$, continuous application of a microwave leads to an oscillation which is composed of both frequencies, as shown in Fig. 1 b). Due to spin flips of the nitrogen nucleus [40] the Rabi experiment will show an additional beating on the microsecond timescale since the effective detuning $\Delta$ changes.

For $\Omega > \Delta$, a microwave pulse with length $T' = \arccos(-\Delta^2/\Omega^2)/\Omega$ will, regardless of the phase $\varphi$, flip the population from $|0\rangle$ to $|\phi\rangle = (1 - \exp(i\phi))/2|+\rangle - (1 + \exp(i\phi))/2|-\rangle$ with $\phi = \arccos\left(\frac{2\Delta^2}{\Omega^2} - 1\right)$ [15], as shown in Fig. 1 c). Depending on the ratio between the effective detuning $\Delta$ and the applied Rabi frequency $\Omega$, part of the population will be trapped in the $|-\rangle$ state. To fully recover the spin state population one must apply a microwave pulse with length $T''$, shown in Fig. 1 c).

Nuclear spin detection. We use these pulse gates to construct sensing protocols for NMR experiments, e.g., a Ramsey experiment to sense the inherent $^{14}$N nucleus [16, 41], which reads as $T' - \tau - T''$, where $\tau$ is the free evolution time. All experiments are carried out in a room-temperature confocal setup with single NV centers, located several microns beneath the diamonds surface. The diamond is CVD grown (Element Six) and has a natural abundance of $^{13}$C. Linearly polarized microwave fields are applied through a simple wire spanned over the diamond’s surface. Both, zero- and low-field are achieved through a combination of permanent magnets, which in the latter case, are aligned with the NV centers symmetry axis. The zero-field is experimentally verified via a Ramsey experiment, leading to 0 G $\pm 0.12$ G, as shown in Fig. 2 a). The uncertainty of the magnetic field determination is given by the linewidth of the measured hyperfine transition, as the $|\pm 1\rangle$ states overlap. Due to the double quantum transition the observed frequencies are larger by a factor of two, which is best seen in Fig. 2 b).

The Ramsey experiment is repeated for several magnetic fields up to 5 G to demonstrate the applicability in low-field, shown in Fig. 2 c). From the measurement we can extract the hyperfine coupling $A_{ij} = $
Due to their robustness, our optimized pulse pairs are now able to cancel the erroneous signals of Fig. 3 a), and [0x0]1
[0x0]1
[0x0]4
[0x0]3
[0x0]2
[0x0]2
T
4
1
11x679]a)
[30x432]Fluorescence [a.u.]
[41x496]0
[41x593]1
[54x328]π
[54x328]a
[54x339]based on the spin echo method [49, 50], which relies on applied radio frequency fields [48]. All these protocols are e.g., from nearby nuclear spins [11, 44–47] or artificially cols are a well established method to detect AC fields, [54]. The pulses are parameterized with a time ∆ = 3 kHz Signal
XY8
0 1 2 3 4
τ [µs]
0.9
1.0
Fluorescence [a.u.]
a)
b)
c)
300 kHz Signal
Optimized
FIG. 3. a) In the presence of detuning, pulse errors of the applied π-pulses make it impossible to detect the artificially applied AC signal with a frequency of 300 kHz using classical dynamical decoupling sequences like XY8. The resulting erroneous signals completely overshadow the actual signal. Frequency detuning from D can lead to an additional envelope [19]. b) Due to their enhanced robustness against detuning, our optimized pulse pairs are able to overcome this problem leading to a clearly visible signal. c) Similar to the optimized pulse pairs, the LDD8a sequences show an exceptionally high robustness, removing all erroneous signals. The image shows an exemplary comparison between the LDD8a, optimized and XY8 sequences for a detuning of ∆ = 3.464 MHz ± 0.016 MHz.

2.166 MHz ± 0.006 MHz to the inherent 14N nucleus. In accordance to [42, 43] this leads to an estimated, shot-noise-limited sensitivity of 70 nT/√Hz ± 10 nT/√Hz for the double quantum Ramsey in low-field.

Dynamical decoupling.— Dynamical decoupling protocols are a well established method to detect AC fields, e.g., from nearby nuclear spins [11, 44–47] or artificially applied radio frequency fields [48]. All these protocols are based on the spin echo method [49, 50], which relies on a π-pulse to decouple the spin from environmental noise by population inversion. In our double-quantum system, such a π-pulse is given by a microwave pulse with length T/2 = π/Ω, as depicted in Fig. 1 c). It has been observed that this π-pulse can lead to strong erroneous signals during dynamical decoupling measurements [19]. An example is shown in Fig. 3 a), where the applied XY8 sequence [21] is not able to resolve the artificially applied 300 kHz AC signal as it is completely overshadowed by the erroneous signals. In general, conventional dynamical decoupling protocols are not able to overcome these problems as the typically used phase changes do not lead to coupling between |0⟩ and |−⟩ states because of the specific rotating frame of the double quantum system (see supplementary material [43]).

The π-pulse generates a gate which transforms the dressed states vectors as follows:

\[
|+\rangle \to -|+\rangle,
|−⟩ \to \frac{Ω^2 - Δ^2}{Ω^2 - Δ^2} |−⟩ - \frac{2ΔΩ}{Ω} e^{i\varphi}|0⟩,
|0⟩ \to \frac{Δ^2 - Ω^2}{Ω^2} |0⟩ - \frac{2ΔΩ}{Ω} e^{-i\varphi} |−⟩.
\] (2)

Much like a π-pulse in a classical dynamical decoupling sequence, our π-pulse with duration T/2 flips the state |+⟩ to |−⟩. However, part of the population in |−⟩ will be shifted to |0⟩ and vice versa unless Δ = 0. A free evolution time τ in-between two π-pulses consequently creates a superposition between all three basis vectors. After Eq. (2) the next π-pulse can then transfer even more population from the {(+), |−⟩}-plane to |0⟩, depending on the created state. When the final T′-pulse transfers the population from the {(+), |−⟩}-plane back to |0⟩, the beforehand trapped population in |0⟩ will be flipped back to the {(+), |−⟩}-plane and we observe a loss of fluorescence. Depending on the detuning Δ and the chosen free evolution time τ, this can result in a full loss of fluorescence, as shown in Fig. 3 a). Frequency detuning from the NV centers ZFS leads to an additional envelope [19]. Thus, we require new dynamical decoupling protocols or new pulses which offer a strong robustness against the detuning Δ.

Optimal control.— In order to produce high fidelity pulses which prevent the creation of such erroneous signals, we employ a version of the GRAPE algorithm [23] which makes use of automatic differentiation, similar to previous work [51]. The algorithm is implemented in the Julia programming language using the Zygote [52] and Optiijn.jl [53] packages. The optimal control pulses we introduce are robust against Rabi frequency and detuning errors by design. In addition, they also reduce the effect of errors in the zero-field splitting parameter D because they reduce the leakage from |± 1⟩ manifold to |0⟩, which causes decoherence. This is sensitive to temperature changes and a strained diamond lattice.

Decoupling sequences can be decomposed into π-pulse pairs which, when applied consecutively, produce an identity gate. We task the algorithm with finding two such optimal control pulses which both flip the spin in the |± 1⟩ manifold while not being strictly π-pulses. This extra degree of freedom allows the algorithm to generate pulses which compensate each others’ errors cooperatively [54]. The pulses are parameterized with a time dependent amplitude and phase, where the latter is restricted to ϕ = 0 or ϕ = π to mimic the control available in the experiment (see supplementary material [43]). We note that we also applied the algorithm with arbitrary ϕ but this did not lead to any significant improvement. In order to produce an experimentally viable amplitude the maximum achievable Rabi frequency is limited to Ω = 20 MHz by a sigmoid function. Each pulse has a duration of 50 ns and is discretized in 1 ns steps. Hence, each pulse has twice the time of a standard π-pulse to reach its goal. Neglecting nuclear back action the pulses are optimized to be robust to a detuning of ∆ = ±2.16 MHz caused by the 14N nucleus, a ±10 % error in the Rabi frequency and a ±100 kHz shift of D. The figure of merit is then calculated as the overlap between the final propagator and the desired identity gate. Due to their robustness, our optimized pulse pairs are now able to cancel the erroneous signals of Fig. 3 a), and
enable a precise frequency determination of the applied 300 kHz AC signal, demonstrated in Fig. 3 b).

Low-field DD sequences.— Another way to improve the robustness of the protocol is to design special zero- and low-field dynamical decoupling (LDD) sequences. They typically consist of an even number of simple \(\pi\)-pulses with duration \(\pi/2\) and we use their relative phases \(\varphi\) as a control parameter to improve performance by compensating the errors of the individual pulses cooperatively. A perfect \(\pi\)-pulse has a transition probability of 1, i.e., it inverts the population of the qubit states in the \(|\pm 1\rangle\) manifold [43]. However, due to pulse errors there can be an error in the transition probability, which we label \(\epsilon\). It proves useful to restrict the values of the phase to \(\varphi = 0\) or \(\varphi = \pi\) because we can then reduce the dynamics of the three-level system to a two-level one (see supplementary material [43]). This simplifies the derivation significantly, allowing us to obtain analytical and numerical solutions for the two-level system and apply them directly to the zero- and low-field three-level Hamiltonian (see supplementary material [43]).

We can evaluate performance by considering the fidelity of the propagator in the two-level system, which characterizes the overlap between the perfect and the actual propagators [55] \(F = \frac{1}{2} \text{Tr}[(U_0^{(n)})^\dagger U^{(n)}]\), where \(U^{(n)}\) is the actual propagator of the pulse sequence and \(U_0^{(n)}\) is its value with a perfect population inversion, i.e., when the error \(\epsilon = 0\).

In order to derive the LDD phases we perform a Taylor expansion of the error in the fidelity with respect to \(\epsilon\) around \(\epsilon = 0\) and nullify the Taylor coefficients to the highest possible order. We obtain the simplest solution for four pulses with the LDD4a (phases: \(0, 0, \pi, \pi\)) and LDD4b (phases: \(0, \pi, \pi, 0\)) sequences, which correspond to the U4a and U4b sequences from [55] (see Table I). Their fidelity error is given by \(\epsilon_{LDD4} = 2\epsilon^2\sin(2\tilde{\alpha})^2\), where \(\tilde{\alpha}\) is a phase that depends on \(\Delta, \Omega\), and the pulse separation. This is much smaller error in the fidelity in comparison to four pulses with zero phases \(\varepsilon_4 = 8\epsilon \cos(\tilde{\alpha}) + O(\epsilon^2)\), allowing for cooperative error compensation. One can derive the phases for the higher order sequences in an analogous way (see Table I for the phases and supplementary material [43] for derivation details).

The performance of all LDD sequences as well as the optimized pulse pairs have been tested for detunings up to \(\Delta = 4.219\) MHz \(\pm 0.011\) MHz experimentally and numerically. All sequences achieve an exceptional high robustness against the applied detuning, removing all erroneous signals during the measurement. An exemplary measurement of the LDD8a, optimized and XY8 sequence for \(\Delta = 3.464\) MHz \(\pm 0.016\) MHz is shown in Fig. 3 c). The full numerical and experimental comparison can be found in the supplementary material [43].

As temperature measurements at zero- and low-field [17, 18] also rely on the application of a \(\pi\)-pulse, their temperature estimation might be subject to errors in the presence of detuning. These errors can be mitigated by replacing the \(\pi\)-pulse by our optimized pulses or the LDD sequences, which is exemplified by measurements in the supplementary material [43]. Finally, we note that the LDD sequences can also be combined with robust composite pulses or pulses designed by optimal control, which replace the simple rectangular pulses in the sequence. This could be especially useful in case of detuning errors in \(D\) in order to avoid leakage to \(|0\rangle\) (see supplementary material [43]).

Conclusion.— We experimentally demonstrate the application of NV centers as precise, nano-scale sensors for zero- and low-field nano-NMR experiments. We do so by applying microwave fields with a frequency equal to the NV centers ZFS, which allows us to take advantage of a hidden effective Raman coupling to construct basic pulse gates for sensing experiments. Detection of nearby nuclear spins via Ramsey measurements up to 5 G verifies the applicability of our method in both, zero- and low-field. Moreover, these measurements are able to precisely detect signals with an estimated, shot-noise-limited sensitivity of 70 nT/\(\sqrt{Hz}\) \(\pm 10\) nT/\(\sqrt{Hz}\).

Classical dynamical decoupling sequences, such as the XY8 sequence, are not directly applicable to the double quantum system and can induce strong erroneous signals. We analytically identify the responsible dynamics behind these erroneous signals. The fidelity of the applied \(\pi\)-pulses is reduced in the presence of detuning, leading to population leakage into the \(|0\rangle\) state during sensing experiments.

We use the obtained insights to construct robust dynamical decoupling protocols, which we label as LDD sequences. These sequences consist of several \(\pi\)-pulses with phases of either \(\varphi = 0\) or \(\varphi = \pi\). Moreover, we optimize the robustness of two subsequent pulses via the GRAPE algorithm, which again, leads to a robust dynamical decoupling sequence. The optimized pulse pairs and LDD sequences are experimentally and numerically analyzed for various detunings, showing an exceptionally high robustness. In addition our optimized pulse pairs and LDD sequences are able to mitigate possible errors during temperature measurements at zero- and low-field.

In summary, we present various robust sensing protocols for low-field nano-NMR (LDD) with \(n\) pulses (indicated by the number in the label of the sequence). The change of sign of all phases does not change the excitation profile. All phases are defined in radians, \(\text{mod}(2\pi)\).

| Name       | Pulses | Phases \(\varphi_k\), \(k = 1, \ldots, n\) |
|------------|--------|------------------------------------------|
| LDD4a      | 4      | \((0, 0, 1, 1)\pi\)                        |
| LDD4b      | 4      | \((0, 1, 1, 0)\pi\)                        |
| LDD8a      | 8      | \((0, 0, 1, 1, 0, 1, 1, 0)\pi\)            |
| LDD8b      | 8      | \((0, 1, 1, 0, 0, 1, 1, 0)\pi\)            |
| LDD16a     | 16     | \((0, 0, 1, 1, 0, 1, 1, 0, 1, 0, 0, 1)\pi\) |
| LDD16b     | 16     | \((0, 0, 1, 1, 0, 0, 1, 1, 0, 1, 1, 0, 0, 1)\pi\) |
center based system. Our work brings us one step closer to the ultimate goal of investigating the spin-spin coupling in molecules or various condensed matter experiments via the NV center, as it is now possible of doing so even in the absence of a bias magnetic field.

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Supplementary Information
Zero- and Low-field Nano-NMR with Nitrogen Vacancy Centers

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I. RAMSEY SENSITIVITY

After [1], the shot-noise limited sensitivity for a Ramsey measurement is given by

\[ \eta = \frac{\hbar}{\Delta m_s g_s \mu_B} \frac{1}{\sqrt{n_{avg} C e^{-\left(\tau/T_2^*\right)^p}}} \frac{\sqrt{t_I + t_r + \tau}}{\tau}. \]  

From our measurements we obtain the following parameters:

- spin quantum number difference \( \Delta m_s = 2 \),
- measurement contrast \( C = 35.5 \% \pm 0.5 \% \),
- dephasing time \( T_2^* = 2.1 \mu s \pm 0.11 \mu s \),
- decay order \( p = 2.1 \pm 0.4 \),
- initialization time \( t_I = 22.60 \) ns \( \pm 0.28 \) ns,
- readout time \( t_R = 300 \) ns \( \pm 1 \mu s \),
- average number of photons detected per measurement \( n_{avg} = 150 \frac{\text{kcounts}}{\lambda} \cdot 300 \) ns \( \pm 10 \frac{\text{kcounts}}{\lambda} \cdot 300 \) ns.

This allows us to calculate the optimal measurement time \( \tau = 1.252 \mu s \), which then leads to an estimated sensitivity of \( \eta = 70 \frac{\sqrt{\Delta f}}{\sqrt{\text{Hz}}} \pm 10 \frac{\sqrt{\Delta f}}{\sqrt{\text{Hz}}} \) for a Ramsey measurement in low-field.

We note that the measurement results are obtained with a \( \lambda = 561 \) nm laser.

II. TEMPERATURE MEASUREMENTS

In addition to magnetic field measurements the NV center in diamond can also be used for temperature measurements. To this end, the energy shift of the \( m_S = 0 \) spin state from the \( m_S = \pm 1 \) subspace is measured because the parameter \( D \) is temperature sensitive (\( \approx -74 \text{ kHz/K} \)) [2–5]. When working around zero magnetic field the sensing sequence becomes fairly simple, it consists of two \( \pi/4 \)-pulses (duration \( T/2 \)) embracing a train of \( \pi \)-pulses (duration \( T/2 \)), just like in a conventional dynamical decoupling sequence [3, 6]. In simple words, this sequence creates a superposition state of all three spin states. The train of \( \pi \)-pulses suppresses the magnetic field induced phase acquisition of states \( \{-1\} \) and \( \{+1\} \) while state \( \{0\} \) continuously acquires phase due to its energy shift \( D \). Hence, it might be called a D-Ramsey. Like the dynamical decoupling presented in the main paper also the temperature measurement sequence is affected by errors due to finite pulse lengths and detunings.

Here we compare the performance of temperature measurements using either eight standard \( \pi \)-pulses, four optimal control \( \pi \)-pulse pairs or two LDD4b repetitions. In all cases the microwave frequency is detuned from \( D \) by about \( 1 \) MHz. The \( \pi \)-pulse separation \( \tau \) is swept up to \( 2.6 \) \( \mu s \). Figure 1 a) shows the D-Ramsey oscillations vs. \( \tau \) with fits of exponentially decaying oscillations to the data. As there are eight \( \pi \)-pulses in each case the apparent frequency is \( 8 \) MHz instead of \( 1 \) MHz. Additionally, the residuals of data and fits are plotted. For standard \( \pi \)-pulses these residuals reach significant values compared to the D-Ramsey oscillation amplitudes. In temperature estimations this might lead to errors that can be mitigated by using either the LDD4b sequence or optimal control pulses. Figure 1 b) shows the absolute values of the fast Fourier transform of the data. All measurements reveal the main frequency peak and the standard pulses produce considerable excess noise.
FIG. 1. Temperature measurements. a) D-Ramsey oscillations with an eight \(\pi\)-pulse dynamical decoupling for 3 different cases (blue: standard pulses, orange: optimal control pulses, green: LDD4b pulses). The detuning from \(D\) is set to 1 MHz. For visibility the oscillations are stacked with an offset of 0.3 from the center of the oscillation starting with 0.3 for the standard pulses. Exponentially decaying oscillations are fit to the data. The residuals appear around 0. b) Absolute values of the fast Fourier transform of the data from panel a.

III. THE SYSTEM

We consider a three-level system (see Fig. 2a) whose dynamics in the basis \(|+\rangle, |0\rangle, |−\rangle\) is governed by the Hamiltonian

\[
H_0 = DS_z^2 + (\omega_0 + \Delta)S_z + 2\Omega \cos (\omega_c t + \phi)S_x
\]

where \(S_i, i = x, y, z\) are the spin 1 operators, \(D\) is the zero-field splitting, \(\omega_0\) is the splitting between the \(m = \pm 1\) states in the presence of a magnetic field, \(\Delta\) is a detuning, e.g., due to a hyperfine interaction, and we apply a control field with a Rabi frequency \(2\Omega\), driving frequency \(\omega_c\) and phase \(\phi\). We move to the interaction basis, defined by \(H_0^{(1)} = \omega_c S_z^2\)

\[
H_1 = U_0^{(1)}(t)\hat{H}_0 U_0^{(1)}(t) - iU_0^{(1)}(t)\hbar \frac{\partial}{\partial t} U_0^{(1)}(t)
\]

\[
= \begin{bmatrix}
(D - \omega_c) + \Delta + \omega_0 & \Omega \sqrt{2} \cos (\omega_c t + \phi) & 0 \\
\Omega \sqrt{2} \cos (\omega_c t + \phi) & 0 & \Omega \sqrt{2} \cos (\omega_c t + \phi) \\
0 & \Omega \sqrt{2} \cos (\omega_c t + \phi) & D - (\omega_c) - \Delta - \omega_0
\end{bmatrix}
\]

where \(U_0^{(1)}(t) = \exp (-i\omega_c tS_z^2)\) and we assumed that \(\omega_0 = 0\) (zero-field), resonance \(\omega_c = D\) and applied
Only for $\varphi = 0, \pi$

FIG. 2. (color online) (a) Level scheme for low-field nano-NMR sensing, which we consider in this work and the corresponding scheme in the dressed basis with $|\pm\rangle = (|+\rangle \pm |-\rangle)/\sqrt{2}$. Due to the specific rotating frame, the state $|-\rangle$ is decoupled unless $\Delta \neq 0$. (b) Three-level system with SU(2) dynamic symmetry and the level scheme in the dressed basis. Due to the different definition of the rotating frame, the phase changes in $\varphi$ can lead to a coupling on the $|0\rangle \leftrightarrow |-\rangle$ transition, thus allowing for improved quantum control. The dynamics of the three-level system with SU(2) dynamic symmetry can be obtained from the evolution of the corresponding two-level system (right). This allows for direct applications of all solutions for quantum control for the two-level system, including DD sequences, to the double quantumubit between states $|+1\rangle$ and $|-1\rangle$. Such direct application is not possible in the low-field nano-NMR level scheme unless $\varphi = 0$ or $\pi$, which we use for the derivation of the low field DD (LDD) sequences. Note that the $\Omega$ and $\Delta$ can in principle be time dependent.

the rotating-wave approximation (RWA), neglecting the terms rotating at $2\omega_c t$ in the last row.

The Hamiltonian in Eq. (3) cannot in general be presented as a combination of the operators $S_i$, $i = x, y, z$ unless the phase $\varphi = 0$ or $\pi$. In order to analyze the time evolution of the system, we compare it with a three-level system with a slightly different Hamiltonian, where such representation is possible for any $\varphi$ (see Fig. 2b). Specifically,

$$H_1 = \Delta S_z + \Omega (\cos(\varphi) S_x + \sin(\varphi) S_y)$$

where the elements in the dashed circles are the different ones from the Hamiltonian in Eq. (3), i.e., the phase of the $|-1\rangle \leftrightarrow |0\rangle$ coupling is opposite to one in the Hamiltonian in Eq. (3). This is due to the opposite direction of rotation of state $|-1\rangle$ the rotating frame of the Hamiltonian in Eq. (4), which is typically $H_0(1) = \omega_c S_z$ in comparison to $H_0(1) = \omega_c S_z^2$ for Eq. (3) (see Fig. 2). The effect of this difference is not trivial and can be understood when one analyzes the system in the respective dressed basis. Specifically, the change of the phase $\varphi$ does not allow for coupling between states $|0\rangle$ and $|-\rangle$ in the dressed basis of the Hamiltonian in Eq. (3) unlike the case for the Hamiltonian in Eq. (4), thus reducing the effect of phase changes for quantum control.

We analyze the dynamics due to the Hamiltonian in Eq. (4) in order to derive robust sequences of pulses for DD in the zero-field case. As it can be presented as a combination of $S_i$, $i = x, y, z$ operators, it is said to have SU(2) dynamic symmetry (see Fig. 2b) and its dynamics can be characterized in terms of the dynamics of a corresponding two-state system [7–11]. The latter is governed by the Schrodinger Eq. $i\dot{d}(t) = \tilde{H}_{2st}(t)$, where $d(t) = [d_1(t), d_2(t)]^T$ are the probability amplitudes of the two states and

$$\tilde{H}_{2st} = \frac{\Delta}{2} \sigma_z + \frac{\Omega}{2} (\cos(\varphi) \sigma_x + \sin(\varphi) \sigma_y) = \frac{1}{2} \left[ \begin{array}{cc} \Delta & \Omega e^{-i\varphi} \\ \Omega e^{i\varphi} & -\Delta \end{array} \right],$$

where $\sigma_z, i = x, y, z$ are the respective Pauli matrices. The evolution of the two-state system is characterized by a propagator $\tilde{U}_{2st}(t)$, which connects the probability amplitudes at time $t$ with ones at the initial time $t = 0$:

$$d(t) = \tilde{U}_{2st}(t)d(0)$$

and takes the form

$$\tilde{U}_{2st} = \left[ \begin{array}{cc} a & b \\ -b^{*} & a^{*} \end{array} \right],$$

where $a$ and $b$ are the so called Cayley-Klein parameters, which can be complex with $|a|^2 + |b|^2 = 1$. We note that $\Delta$ and $\Omega$ can also be time-dependent, i.e., the Cayley-Klein parameters can characterize the evolution after a Gaussian pulse, a composite pulse, or a sequence of pulses for dynamical decoupling (DD). For example, a perfect inversion of the population of the two states, e. g., by a $\pi$ pulse, would require $a \rightarrow 0$. In addition, a perfect DD sequence, where the initial state is preserved due to refocusing of the noise, is achieved with a unity propagator, thus taking $b \rightarrow 0$. In the case of a single pulse when they $\Omega$, $\Delta$, and $\varphi$ are constant, the two parameters take the form:

$$a = \cos(\Omega t/2) - \frac{i\Delta}{\Omega} \sin(\Omega t/2),$$

$$b = \frac{i\Omega e^{-i\varphi}}{\Omega} \sin(\Omega t/2),$$

where the effective Rabi frequency $\tilde{\Omega} = \sqrt{\Omega^2 + \Delta^2}$.

Next, we demonstrate the connection between the time evolution of the three-state system in Eq. (4) and the two-state system above, following [10]. The former is governed by the Schrodinger equation $i\dot{c}(t) = \tilde{H}_1 c(t)$, where $c(t) = [c_{+1}(t), c_0(t), c_{-1}(t)]^T$ are the probability amplitudes of the system with the Hamiltonian in Eq. (4). In the case when the initial state is $c_{+1}(0) = 1$, $c_0(0) = 0$, $c_{-1}(0) = 0$, these amplitudes can be presented in terms of the corresponding ones of the two-state system by the transformation $c_{+1}(t) = d_1(t)^2$, $c_{-1}(t) = d_2(t)^2$, and $c_0(t) = 2d_1(t)d_2(t)$.
\( c_0(t) = \sqrt{2d_1(t)d_2(t)}, \quad c^{-1}(t) = d_2(t)^2 \), which leads to equation (5) [7–11]. Similarly, one can obtain the generalizations for other initial conditions and derive a propagator \( \tilde{U}_1(t) \), which connects the probability amplitudes at time \( t \) with ones at the initial time \( t = 0 \): \( c(t) = \tilde{U}_1(t)c(0) \) and characterizes the time evolution of the three-level system for any initial state. Given the propagator in Eq. (6), which describes the evolution of the corresponding two-state system, the respective propagator for the three-state system in the basis of \( \{ |+\rangle, |0\rangle, |-\rangle \} \) is \[ U_1 = \begin{bmatrix} a^2 & -\sqrt{2ab} & b^2 \\ -\sqrt{2ab} & |a|^2 - |b|^2 & \sqrt{2a^*b} \\ b^2 & \sqrt{2a^*b} & a^2 \end{bmatrix}. \] (8)

Again, we note that \( \Delta \) and \( \Omega \) can be time-dependent, i.e., they can characterize the evolution after a sequence of pulses for dynamical decoupling (DD). In addition, the requirement for a \( \pi \) pulse in the double quantum system that inverts the population of the \( \pm 1 \) states is the same as for population inversion in the corresponding two-state system, namely \( a \to 0 \). Similarly, a perfect DD sequence that refocuses dephasing of the coherence of the double quantum qubit will require a unity propagator, i.e., \( b \to 0 \). Thus, a robust pulse or a DD sequence of pulses designed for the respective two-state system would also work for the double quantum qubit. Finally, we note that the zero-field Hamiltonian in Eq. (3) can be presented as a combination of the operators \( S_i \), \( i = x, y, z \) only for the phases \( \varphi = 0 \) or \( \pi \). Thus, we restrict our set of solutions for the DD sequences to using these two phases only and derive them for the respective two-state system.

**IV. DERIVATION OF THE LDD SEQUENCES**

We derive the low-field DD (LDD) sequences by considering their effect in the absence of a sensed field. Then, unwanted errors, e.g., detuning \( \Delta \) or variation in the Rabi frequency \( \Omega \) cause errors in the DD sequence propagator, which leads to loss of contrast. In order to derive the LDD sequences we reparameterize the two-state system propagator in Eq. (6) by

\[ \hat{U}_{2st} = \begin{bmatrix} \sqrt{\epsilon e^{i\alpha}} & \sqrt{1-\epsilon}e^{-i\beta} \\ -\sqrt{1-\epsilon}e^{i\beta} & \sqrt{\epsilon}e^{-i\alpha} \end{bmatrix}, \] (9)

where \( p = 1-\epsilon \) is the transition probability, i.e., the probability that the qubit states in the two-level system will be inverted after the interaction, \( \epsilon \in [0,1] \) is the unknown error in the transition probability, \( \alpha \) and \( \beta \) are unknown phases. In case of a perfect pulse, the transition probability becomes \( p = 1 \) and \( \epsilon = 0 \). However, this is often not the case, e.g., due to frequency or amplitude drifts or field inhomogeneity, which make \( \epsilon \neq 0 \). Such errors can be compensated by applying phased sequences of pulses, where the phases of the subsequent pulses are chosen to cancel the errors of the individual pulses cooperatively up to a certain order [12–14].

If the pulses are time separated, the propagator of the whole cycle [free evolution for time \( \tau/2 \)-pulse–free evolution for time \( \tau/2 \)] changes by taking \( \alpha \to \alpha + \Delta \).

Additionally, a shift with the phase \( \varphi_k \) at the beginning of the \( k \)-th pulse in a DD sequence leads to \( \beta \to \beta + \varphi_k \) [12, 13]. We note that we make no assumptions about the the pulses, except for the RWA, coherent evolution, and the assumption that effect of the pulse and free evolution before and after the pulse on the qubit is the same during each pulse (except for the effect of the phase \( \varphi_k \)).

Thus, the propagator of the \( k \)-th pulse takes the form

\[ U(\varphi_k) = \begin{bmatrix} \sqrt{\epsilon e^{i\alpha}} & \sqrt{1-\epsilon}e^{-i\beta+\varphi_k} \\ -\sqrt{1-\epsilon}e^{i\beta+\varphi_k} & \sqrt{\epsilon}e^{-i\alpha} \end{bmatrix}. \] (10)

Assuming coherent evolution during a sequence of \( n \) pulses with different initial phases \( \varphi_k \), the propagator of the composite sequence then becomes

\[ U^{(n)} = U(\varphi_n) \ldots U(\varphi_1), \] (11)

and the phases \( \varphi_k \) of the individual pulses can be used as control parameters to achieve a robust performance and can take the values 0 or \( \pi \) to correspond to the low-field system. We can evaluate the latter by considering the fidelity [13]

\[ F = \frac{1}{2} \text{Tr} \left( U^{(n)}_0 U^{(n)} \right)^\dagger \equiv 1 - \varepsilon_n, \] (12)

where \( U^{(n)}_0 \) is the propagator of the respective pulse sequence when \( \epsilon = 0 \), i.e., when the pulse performs a perfect population inversion and \( \varepsilon_n \) is the error in the fidelity, where the label \( n \) shows the number of pulses in the DD sequence. For example, the fidelity of a single pulse is given by \( F = \sqrt{1-\epsilon} \). We note that this measure of fidelity does not take into account variation in the phase \( \beta \), which is important when we apply an odd number of pulses. However, the latter is fully compensated when we apply an even number of pulses with perfect transition probability. Thus, we use the fidelity measure in Eq. (12) as it usually provides a simple and sufficient measure of performance when we apply an even number of pulses. All phase shifts are assumed to be either \( \phi_k = 0 \) or \( \pi \), so that they could be used for the propagator in the zero-field case.

First, we consider the case with two pulses in a sequence, i.e., \( n = 2 \). The fidelity error is given by

\[ \varepsilon_2 = 2\epsilon \cos \left( \alpha + \frac{\varphi}{2} \right)^2, \] (13)

where we assumed without loss of generality that \( \varphi_1 = 0 \). As we can see, we cannot in general reduce the error in the fidelity by choosing a particular phase \( \varphi_2 \) as it will work only for particular values of \( \alpha \) and thus only for particular detunings \( \Delta \).

Second, we consider the case with four pulses in a sequence, i.e., \( n = 4 \). In order to derive the phases we
perform a Taylor expansion of the error in the fidelity with respect to $\epsilon$ around $\epsilon = 0$ and nullify the first order Taylor coefficient for any $\alpha$. The solution is given by the LDD4a (phases: 0, $\pi$, $\pi$, $\pi$) and LDD4b (phases: 0, $\pi$, $\pi$, 0) sequences, which correspond to the U4a and U4b sequences from [13] (see Table I in the main text). Their fidelity error is given by

$$\varepsilon_{\text{LDD4}} = 2\epsilon^2 \sin (2\alpha)^2,$$

which is much smaller error in the fidelity in comparison to the error in the fidelity for two pulses $\varepsilon_2 \sim \epsilon$ as $\epsilon < 1$. It is also much smaller than the error for four pulses with zero phases $\varepsilon_4 = x - x^2/8$, where $x = 8\epsilon \cos (\alpha)$. We note that these solutions are not unique as the phases of these and the following LDD solutions can be shifted by an arbitrary phase and are defined mod($2\pi$). Again, we restrict ourselves only to $\varphi = 0$ or $\pi$ in order for these solutions to be directly applicable for the three-level system of the zero-field Hamiltonian.

Next, we derive sequences for second order error compensation. Again, we derive the phases by performing a Taylor expansion of the error in the fidelity with respect to $\epsilon$ around $\epsilon = 0$ and nullify or minimize the Taylor expansion coefficients up to the highest possible order for any $\alpha$. We require $n = 8$ pulses to nullify both the first and second order coefficients. There are multiple solutions and the simplest ones LDD8a and LDD8b are given in Table I in the main text. Their phases are obtained by combining LDD4a and LDD4b one after the other and the error in the fidelity becomes

$$\varepsilon_{\text{LDD8}} = 8\epsilon^3 \sin (2\alpha)^2 (1 - \epsilon \sin (2\alpha)^2),$$

which is usually much smaller than the error of the fidelity of a single LDD4 sequence or an LDD4 sequence, repeated twice, with the latter being $\varepsilon_{\text{LDD4+LDD4}} = 8\epsilon^3 \sin (2\alpha)^2 (1 - \epsilon^2 \sin (2\alpha)^2)$.

Finally, derive LDD sequences that compensate errors to the third order. We require $n = 16$ pulses to nullify the first, the second and the third order coefficients of the Taylor expansion of the fidelity error. Again, there are multiple solutions and the simplest ones LDD16a and LDD16b are given in Table I in the main text. Their phases are obtained by nesting the LDD8a and LDD8b sequences in the (0, $\pi$) sequence and the error in the fidelity becomes

$$\varepsilon_{\text{LDD16}} = 8\epsilon^4 \sin (4\alpha)^2 + O(\epsilon^5),$$

which is usually much smaller than the error of the fidelity of a single LDD8 sequence or an LDD8 sequence, repeated twice. It is also possible to derive higher order error compensating sequences in a similar way.

We note that the restriction of $\varphi = 0$ or $\pi$ leads to a higher number of pulses, needed to achieve a certain order of error compensation in the two-level system in comparison to the use of arbitrary $\varphi$. For example, the UR sequences [12] use arbitrary phases and can achieve the second and third order of error compensation with $n = 6$ and $n = 8$ pulses, respectively. However, these are not directly applicable for the zero-field Hamiltonian.

The LDD sequences can directly be used for error compensation in the zero field three level system, defined by the Hamiltonian in Eq. (3) and they perform error compensation for any initial state. A numerical simulation of the fidelity for different sequences is shown in Fig. 3, demonstrating the remarkable robustness of the sequences. We note that for the initial state $|+\rangle$ after the effective $\pi/2$ pulse in our experiment, a simple DD sequence of two pulses with $\varphi_1 = 0$ and $\varphi_2 = \pi$ is also very efficient. However, it does not compensate errors for an arbitrary initial state.

Finally, we note that the LDD sequences can also be combined with robust composite pulses, which can replace the simple rectangular pulses in the sequence. This could be especially useful in case of detuning errors in $D$ in order to avoid leakage to state $|0\rangle$. We have found in our simulations that it is particularly useful to replace the simple rectangular pulses with a composite pulse that consists of two adjacent pulses, where the first pulse has a pulse area of $3\pi/4$ with phase 0, immediately followed by a $\pi/4$ pulse with phase $\pi$. This composite pulse acts as a robust $\pi$ pulse, uses only $\varphi = 0$ or $\pi$ and has a very modest total pulse area of $2\pi$. Other longer composite pulses with alternating phases have been proposed in [15]. Another alternative is to design pulses by optimal control and nest them in the LDD sequences. We note that even more efficient sequences might be possible to design by numerical optimization but these were not necessary in our experiment.

V. EXPERIMENTAL COMPARISON OF DD SEQUENCES

An experimental comparison between the different LDD sequences, the optimized pulses and a standard XY8 sequence for detunings up to $\Delta = 4.219$ MHz $\pm$ 0.011 MHz is shown in Fig. 4. The integrated fluorescence over a fixed period of time (from $\tau = 0.125$ $\mu$s to $\tau = 2.105$ $\mu$s) is used as a measure to determine the robustness of the applied sequences. As pulse errors result in a drop of fluorescence, the measure will decline as well, which is best seen for the XY8 sequence. Both, the optimized pulse pairs and the different LDD sequences show a strong robustness against the applied detunings, enabling dynamical decoupling experiments at zero- and low-field. We furthermore investigate the performance of the different sequences numerically. Fig. 3 shows a full numerical comparison between the different LDD sequences and the optimized pulse pair for a pulse spacing of $\tau = 1/(2 \cdot 300$ kHz), equal to the presented AC field sensing in the main part. Each top figure shows the evolution of the pulse target Rabi frequency and phase, while the bottom part shows the corresponding fidelity of state $|+\rangle$ for $\alpha \in [-0.2, 0.2]$ and $\Delta \in 2\pi[-4.32, 4.32]$ MHz. The parameter $\alpha$ is the deviation of the Rabi frequency $\Omega = \Omega_0(1 + \alpha)$, where the target magnitude of
FIG. 3. Simulations for a Rabi frequency $\Omega = \Omega_0(1 + \alpha)$, where the target magnitude of the Rabi frequency is $\Omega_0 = 2\pi \cdot 20$ MHz. All sequences use rectangular pulses with a duration of 25 ns each, except for the Optimal control case, where each of the two optimized pulses is 50 ns long. The time separation between the centers of each pulse is $\tau = 1/(2 \times 300$ kHz) $\approx 1.67$ µs.

The top figure shows the evolution of the pulse target Rabi frequency and phase (note that the pulse durations are longer than the actual ones for better visibility). The bottom figures show the corresponding fidelity of state $|+\rangle$ after the DD pulses for $\alpha \in [-0.2, 0.2]$ and $\Delta \in 2\pi [-4.32, 4.32]$ MHz for (a) Standard rectangular pulses with a zero phase, (b) the XY8 sequence, (c) DD with pulses, designed by optimal control (see text), (d) LDD4a, (e) LDD4b, and (f) LDD8a, (g) LDD8b, (h) LDD16a, (i) LDD16b. Note that the optimal control pulses were designed to achieve a high fidelity in the range of $\pm 2.16$ MHz and $\pm 0.1$ for detuning and Rabi error respectively.

The Rabi frequency is set to $\Omega_0 = 2\pi \cdot 20$ MHz. While a standard pulse with zero phase (3 a)) the widely used XY8 sequence (3 b)) clearly show the lack of robustness against detuning, which will then lead to the observed pulse errors, the optimized pulse pair and the different LDD sequences clearly show a significant improvement.
FIG. 4. The optimized pulse pairs, as well as the LDD sequences show an exceptional robustness against the detuning $\Delta$. We use the integrated fluorescence over a fixed period of time as a measure of the robustness. Pulse errors will lead to a loss of fluorescence as shown by the XY8 sequence. The difference between the different LDD sequences and the optimized pulses are within the error for the given detuning.

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