Reported-spin-assisted $T_1$ relaxometry

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A single spin quantum sensor can quantitatively detect and image fluctuating electromagnetic fields via their effect on the sensor spin’s relaxation time, thus revealing important information about the target solid-state or molecular structures. However, the sensitivity and spatial resolution of spin relaxometry are often limited by the distance between the sensor and target. Here, we propose an alternative approach that leverages an auxiliary reporter spin in conjunction with a single spin sensor, a diamond nitrogen vacancy (NV) center. We show that this approach can realize a $10^4$ measurement speed improvement for realistic working conditions and we experimentally verify the proposed method using a single shallow NV center. Our work opens up a broad path of inquiry into a range of possible spin systems that can serve as relaxation sensors without the need for optical initialization and readout capabilities.

The detection of fluctuating electromagnetic fields lends important insight into the dynamics of solid-state systems, for example, the local current and spin fluctuations in magnetic and correlated electron systems [1–6], decoherence processes in quantum systems [7–11], and chemical and biological processes [12–15]. Single-spin quantum sensors constitute a powerful tool for detecting fluctuating fields; in a technique called relaxometry, fluctuating fields with a spectral component matched to the energy splitting of the sensor spin reduce the spin’s relaxation time $\tau_1$ [16]. Single-spin relaxometry features noninvasive and quantitative measurement of the fluctuating fields as well as high spatial resolution down to the nanometer scale.

Nitrogen vacancy (NV) centers in diamond are a prominent example of a solid-state spin qubit sensor, exhibiting a wide temperature operating range, compatibility with other systems, high sensitivity, and high spatial resolution. Relaxometry with NV centers has been used to probe magnetic fluctuations near the diamond surface to better understand surface-induced decoherence [8–11], detect spin waves in magnetic systems [17, 18], image local conductivity and current flow of condensed matter systems [19–21], perform spectroscopy of electronic spins [22], and detect magnetic nanoparticles [23] and magnetic ions [24–26]. The proximity of the sensor to its target is critical to achieving high spatial resolution and high sensitivity, and becomes particularly important for relaxometry when targeting the detection of single spins (nuclear or electronic), as the dipolar magnetic fluctuating field signal from a single spin die off as $1/r^6$, with $r$ being the sensor-target separation [24, 27]. Further, the need for proximity is made more acute in imaging experiments when long measurement times can lead to significant drifts in the sensor-target distance that may render the images unrecognizable.

Bringing NV centers close to the diamond surface is one natural approach to reduce sensor-target separation for improved relaxometry. However, NV centers with high-grade properties cannot be made arbitrarily shallow for many reasons: firstly, the yield rate of an implanted nitrogen atom forming an NV center declines dramatically near the surface [28], and secondly, near-surface NVs tend to exhibit increased charge instabilities [29–31] and shorter coherence times [10, 32]. Overcoming these challenges is an active area of study.

Here we propose an alternative approach that leverages

![FIG. 1. (a) Schematic of the proposed experiment. To detect the magnetic fluctuations (red contours) from a target spin (yellow), an optically addressable NV center in diamond senses a change in the relaxation time $T_{1,R}$ of a reporter spin at the diamond surface. The close proximity of the reporter spin to the target spin amplifies the signal. (b) Pulse sequence and corresponding quantum circuit diagram (bottom) [33] used for measuring $T_{1,R}$. After optical initialization of the NV center (dark green), microwave pulses control the spin states of NV center (light green) and reporter spin (blue), followed by optical readout of the NV (dark green). (c) Simulated NV coherence as a function of $\tau_r$ as measured by the pulse sequence shown in (b), for an NV 4.5 nm deep. In the absence of a target spin, the black curve shows the signal corresponding to the reporter spin’s intrinsic $T_1$, 30 $\mu$s in this case. The red curve shows a faster decay when a nearby Gd$^{3+}$ spin, 3 nm from the reporter spin in this case, reduces $T_{1,R}$ to 11.6 $\mu$s.](image-url)
an auxiliary spin that resides closer to, or even at, the diamond surface (Fig. 1(a)) to sense fluctuating fields. This reporter spin acts as the relaxation sensor, whereas a nearby NV center, comfortably deeper in the diamond, serves as a local optical readout of the reporter spin state [34, 35]. Compared to direct NV relaxometry, this method features improved sensitivity and spatial resolution while circumventing the reduced NV coherence and charge stability associated with the diamond surface. In essence, the main advantage of the reporter relaxometry method stems from the fact that the reporter translates an incoherent magnetic field signal, which decays as $1/r^6$, into a coherent magnetic signal emanating from the reporter spin with a $1/r^3$ dependence. Furthermore, the proposed approach offers access to an additional range of detection frequencies determined by the reporter spin’s energy splitting, which is distinct from the NV sensor’s splitting. In this paper, we analytically examine the dependence of the relaxation signal on NV and reporter spin properties, finding a measurement speed increase up to $10^4$-fold compared to conventional NV relaxometry as relevant parameters are varied in real working conditions. For concreteness, we benchmark performance using a specific example of detecting and imaging a single Gadolinium ($\text{Gd}^{3+}$) ion, a commonly used spin label for bio-structural imaging, but we remark that the results are broadly applicable to other target systems. We then experimentally verify the proposed pulse sequence with a single NV center strongly coupled to a nearby reporter spin, whose relaxation time is tuned via a stochastic driving technique [36]. Finally, the challenges and future outlook of this novel approach are discussed.

We consider a single reporter spin located at the diamond surface near a single NV center, as shown in Fig. 1(a). Although the reporter spin can come in any form, its primary requirement is a long intrinsic $T_1$. We note that single spins at the diamond surface have been detected with $100$-$\mu$s-scale relaxation times [26, 37], which are sufficiently long for the protocols proposed here. For simplicity, we discuss the case of spin-1/2 reporter spins, but the analysis can be extended to systems with larger spins.

The proposed reporter-spin relaxometry protocol is shown in Fig. 1(b). This protocol probes the correlation time of the magnetic field signal produced by the reporter spin, which is equal to its relaxation time $T_{1,R}$, via its dipolar coupling to the NV using double electron electron resonance (DEER) techniques. The sequence constitutes a correlation measurement of the NV center’s environment seen through the filter function set by the NV pulse sequence, an “xyy” Hahn echo like sequence in this case. Importantly, by matching $\tau_{NV}$, to the inverse of the NV-reporter dipolar spin coupling rate $k_s$, the sequence selectively probes the coupling between the reporter spin and NV. Therefore, the two separate “xyy” DEER sequences are equivalent to two CNOT gates in quantum circuit representation [33]. The correlation time of such coupling is then imprinted onto the NV coherence, which can be measured via differential photoluminescence read-out of the NV center’s spin state [11]. In effect, the NV center acts as a “flag” qubit whose state changes if the reporter spin flips during the correlation sequence [38]. We note that to probe more weakly coupled reporter spins, one has to extend $\tau_{NV}$, and the Hahn echo may need to be replaced by dynamical decoupling sequences such as XY8 with corresponding microwave pulses on the reporter spin.

Figure 1(c) shows the expected signal for the example case of detecting a single, proximal fluctuating $\text{Gd}^{3+}$ spin, a spin label with a large electronic spin of $\mathcal{S} = 7/2$ and fast GHz-scale spin dynamics [12, 39]; ensembles of $\text{Gd}^{3+}$ spins have been interfaced with and detected by NV centers [24, 26, 27, 40]. The $\text{Gd}^{3+}$ produces a rapidly fluctuating magnetic field, which reduces the correlation time of the reporter spin and manifests clearly as a faster NV population decay. (See SI for details.) The small reduction in NV coherence as can be seen from short $\tau_c$ is caused by the relaxation of reporter spin during the “xyy” DEER. The NV parameters used in the simulations are experimentally measured on an implanted shallow NV (NV1) in a chemical vapor deposition-grown diamond sample. The parameters are $T_2 = 8.4$ $\mu$s, and $T_{1,NV} = 3.5$ ms, and the NV depth is measured via proton NMR [41, 42] to be 4.5 nm. The reporter spin is assumed to be located on the diamond surface at a position where the dipolar coupling to the NV is maximized, $T_{1,R}$ is assumed to be 30 $\mu$s, and $\tau_{NV}$ is set to 912 ns to match the inverse of the dipolar coupling strength $k_s$ [35].

To quantitatively compare the performance of the proposed reporter-spin-assisted relaxometry protocol with direct NV relaxometry, we first discuss how a target fluctuating magnetic field external to the diamond imprints itself on the relaxation time of a single spin (either the NV center or the reporter spin):

$$\frac{1}{T_1'} = \frac{1}{T_1} + N_S \frac{\gamma_{NV} \gamma_R}{2} [S_B(\omega) + S_{B_s}(\omega)],$$

(1)

where $T_1'$ is the spin’s intrinsic relaxation time without the external fluctuating fields, $\gamma_{NV}$ and $\gamma_R$ are the gyromagnetic ratios of NV and reporter spin, $S_B$ is the noise spectral density of the magnetic field experienced by the spin, $N_S = 3$ for the NV spin (or $N_S = 2$ for spin-1/2 reporter), and $\omega$ is the transition frequency of the spin. Assuming a Lorentzian spectrum of the fluctuating field, Eq. (1) can be written as

$$\frac{1}{T_1'} = \frac{1}{T_1} + N_S \gamma_{NV} \gamma_R \langle B^2 \rangle \frac{\tau_c}{1 + \omega^2 \tau_c^2},$$

(2)

where $\langle B^2 \rangle = \langle B_x^2 \rangle + \langle B_y^2 \rangle$ is the variance of the magnetic field transverse to the quantization axis of the spin and is proportional to $1/r^6$ (see Supplementary Material for details of derivation), and $\tau_c$ is the correlation time of magnetic field from a fluctuating $\text{Gd}^{3+}$, which we take to be 0.35 ns, as reported in the literature [43].
Figure 2 plots the speed enhancement of the reporter spin relaxometry protocol over the direct NV relaxometry protocol, varying several parameters to highlight in which situations reporter spins are an advantageous choice. The qualitative picture that emerges from the four plots is that longer intrinsic reporter $T_{1,R}^\prime$, longer NV $T_2$, smaller reporter-NV-$Gd^{3+}$ separations, and deeper NV centers enhance the benefits of reporter relaxometry, culminating in a 10$^4$-fold speed enhancement for a 10-15 nm deep NV with $T_2 = 100 \mu$s and a $Gd^{3+}$ spin located ~3 nm above a reporter spin with $T_{1,R}^\prime = 30 \mu$s (Fig. 2c-d). We note that these are all experimentally confirmed values [11, 26, 30, 42]. A lower (higher) NV $T_2$ would shift the location of maximal speed enhancement in Fig. 2c to smaller (larger) reporter-NV separations ($r_{\text{reporter-NV}}$), and reduce (enhance) the speed enhancement value ($t_{\text{NV}}/t_R$) (plots are shown in the SI). We assume the use of the spin-to-charge conversion (SCC) readout technique for all cases here, where the readout noise level is experimentally verified on NV1 [44]. The speed enhancement is obtained by computing the ratio $t_{\text{NV}}/t_R$; $t_R$ is the averaged minimal time required to detect a reduction in reporter $T_{1,R}$ if using reporter relaxometry,

$$t_R = \frac{(\text{SNR})^2 C_{\text{SPN}}^2}{2(\Delta S)^2} t_{\text{seq}},$$

where $\Delta S$ is the change of the signal due to the reduced $T_{1,R}$; SNR is the desired signal-to-noise ratio, $C_{\text{SPN}}$ is the ratio between experimental measurement uncertainty and the spin projection noise limit, and $t_{\text{seq}}$ is the total duration of the pulse sequence including the initialization and readout time. $t_{\text{NV}}$ is computed analogously using Eq. 3 with the corresponding $\Delta S$ and $t_{\text{seq}}$ for direct NV relaxometry. For each point in the simulations shown in Fig. 2, the readout and measurement times are optimized to minimize $t_R$ and $t_{\text{NV}}$ separately, and the details are discussed in SI. We note that the speed enhancements shown in Fig. 2 will be even more significant if a standard 532 nm NV photoluminescence readout is used instead of SCC readout techniques, because SCC readout techniques are more effective for the longer pulse sequences associated with direct NV relaxometry compared to reporter relaxometry [20].

Reportor relaxometry can also be combined with scanning probe microscopy (SPM) [20, 23, 25, 45] to achieve better spatial resolution than conventional NV relaxometry imaging in a given measurement time as well as providing faster imaging for a given sensitivity. In reporter-spin-assisted scanning relaxometry, a reporter spin is in-
The measurement is performed with a single NV center that is strongly coupled to a nearby g=2 spin-1/2. (a) Pulse sequence of reporter relaxometry with additional stochastic driving of the reporter spin during τr. Incoherent spin dynamics caused by stochastic driving with Rabi frequency |Ωs| and linewidth Δν reduces T1,R of the reporter spin. (b) NV coherence for various stochastic driving powers, indicating reduced reporter spin auto-correlation with increased Ωs. Solid lines are mono-exponential decay fits. (c) Extracted reporter spin relaxation rate as a function of 2|Ωs|^2/Δν. Black solid line is the theoretical behavior expected from Eq. (4).

Another benefit of reporter spin relaxometry is that it can probe fluctuating fields in a different frequency range than direct NV relaxometry, in particular giving access to a lower frequency range in moderate static magnetic fields (the NV probes higher frequencies because of its large zero-field splitting). Probing a lower frequency range provides a stronger fluctuating signal for many types of noise baths, such as a Lorentzian noise spectrum. We note that the speed and spatial resolution comparisons in Fig. 2 and 3 conservatively assume identical NV and reporter spin transition frequencies, but a smaller reporter spin transition frequency could yield a larger reduction in the relaxation time. Further, reporter spin relaxometry can be used in conjunction with NV relaxometry to gain more spectral information about the sensing target.

Our work opens up a broad path of inquiry into a range of possible reporter spin systems that can serve as relaxation sensors without the need for optical initialization and readout capabilities. While engineering single reporter spins at the diamond surface is challenging, there are several promising candidates. Naturally occurring surface spins located on the diamond surface have been detected and measured to have remarkably long T1 = 100 µs [32, 35, 42, 47–50], though further work is necessary to confirm their microscopic origin and engineer their properties. Reporter spins can also be engineered...
via ion implantation or chemical synthesis and pattern-
ing of molecules [51, 52], ions encapsulated in fullerene
[53], rare-earth ions, and radical spin labels [54, 55].

In conclusion, we propose a novel method that utilizes
reporter spins in conjunction with optically addressable
NV centers in diamond to improve the measurement sen-
sitivity and spatial resolution of conventional NV $T_1$ relax-
ometry sensing and imaging. We quantitatively com-
pare the speed and spatial resolution of this method to
conventional NV $T_1$ relaxometry, and find a wide range of
parameter space in which reporter spin relaxometry pro-
vides substantial gains. Proof-of-principle experiments
confirm the ability of the proposed sequence to quan-
titatively probe the relaxation of a single, dark reporter
spin. This work motivates the development of engineered
reporter spins and some candidates are proposed.

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