Ambient nanoscale sensing with single spins using quantum decoherence

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Abstract. Magnetic resonance detection is one of the most important tools used in life-sciences today. However, as the technique detects the magnetization of large ensembles of spins it is fundamentally limited in spatial resolution to mesoscopic scales. Here we detect the natural fluctuations of nanoscale spin ensembles at ambient temperatures by measuring the decoherence rate of a single quantum spin in response to introduced extrinsic target spins. In our experiments 45 nm nanodiamonds with single nitrogen–vacancy (NV) spins were immersed in solution containing spin 5/2 Mn$^{2+}$ ions and the NV decoherence rate measured though optically detected magnetic resonance. The presence of both freely moving and accreted Mn spins in solution were detected via significant changes in measured NV decoherence rates. Analysis of the data using a quantum cluster expansion treatment of the NV-target system found the measurements to be consistent with the detection of 2500 motionally diffusing Mn spins over an effective volume of $(16 \text{ nm})^3$ in 4.2 s, representing a reduction in target ensemble size and acquisition time of several orders of magnitude over conventional, magnetic induction approaches to electron spin resonance detection. These measurements provide the basis for the detection of nanovolume spins in solution, such as in the internal compartments of living cells, and are directly applicable to scanning probe architectures.

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1. Introduction

The generation and dynamics of fluctuating nanoscale magnetic fields is central to many important processes in biology, from ion-channel function and free-radical formation in the
Figure 1. Overview of nanoscale decoherence sensing with NV spins. (a) Environmental spin baths can be detected by their effect on the NV coherence. The decoherence contribution from internal spins (green), external spins (grey) and total effect (red) on NV coherence ($T_2$) time measured with spin-echo. (b) Magnetic sources local to the NV centre include diffusing Mn$^{2+}$ spins (red), surface spins (blue) and internal nitrogen spins (green). (c) Physical and electronic energy structure of the NV centre in diamond (hyperfine structure not shown).

intra-cellular medium to neurons firing in the brain. Yet, there is a critical lack of techniques capable of detecting the small numbers of electronic or nuclear spins that are at the heart of these processes under physiological conditions. Under high vacuum and sub-kelvin operating conditions, magnetic resonance (MR) force microscopy can detect single electron [1] and as few as 100 nuclear spins in the solid-state [2] with three-dimensional imaging capability [3]. Recent work with nitrogen–vacancy (NV) centres in ultra-pure bulk diamond has also demonstrated nanovolume detection of spins at room temperature [4–7], by either matching the NV free precession to the periodic Larmor precession of external spins, or by resonantly flipping the external spins and utilizing their long coherence time. However, achieving magnetic detection of small ensembles of spins in solution using nanodiamonds as in situ sensors is a significant challenge, requiring a different approach due to the fluctuation timescales involved. This is especially relevant for the aqueous environment of living cells, where magnetic resonance imaging techniques have made tremendous progress with imaging of micron sized iron oxide particles in single cells [8], but where detection is still limited to mesoscopic scales $\sim 10 \mu m$ because of the relatively large spin ensembles of order $10^7$ required to obtain sufficient signal [9]. In addition, longitudinal spin relaxation imaging ($T_1$) using ensembles of NV centres in a bulk diamond has successfully demonstrated detection of gadolinium spins in a microfluidic device [10].

Here we report nanoscale detection of order $10^3$ electronic spins in solution by measuring the changes in decoherence rate ($T_2$) of a single spin probe in response to extrinsic target spins in its local environment. In our experiments we introduced aqueous manganese chloride around nanodiamonds containing a single-spin NV defect and detected diffusion and accretion of the target Mn$^{2+}$ spins by measuring changes in the NV decoherence time (figure 1). We use decoherence sensing [11], which exploits the sensitivity of individual quantum spin systems to minute variations in the magnetic environment, and even permits detection of fields with
zero mean, by measuring fluctuations in field amplitude [12]. In particular, the fast magnetic fluctuation rate of spins diffusing in solution is observed here, directly through the exponential nature of its effect on the NV coherence. In contrast to conventional MR imaging, where variations in spin relaxation ($T_1$) and/or dephasing ($T_2$, $T_2^*$) processes between different macroscopic regions form the basis for contrast, detection through measuring the decoherence of a single spin probe is inherently nanoscopic due to the $1/r^3$ fall-off of the dipole interaction. A useful comparison is to conventional electron spin resonance (ESR) where the local environment of ensembles of spin moieties are deduced in an average sense over the large spin ensembles, whereas our technique uses magnetic resonance on a single spin probe qubit to indirectly detect the nanoscale spin ensemble surrounding the probe.

We present the results of three experiments. First we demonstrate decoherence sensing with single spins by sequentially characterizing changes in the local NV magnetic environment for nanodiamonds in air, water (milliQ) and high-spin MnCl$_2$ using a lab-built confocal microscope with microwave control. We then confirm these results by restoring the coherence of two NV sensors by washing with spin-free acid. Finally, we use decoherence measurements to detect accretion of Mn$^{2+}$ ions onto the nanodiamond surface. A full quantum cluster expansion treatment of the NV interaction with the intrinsic and external spin baths is used to analyse the measurements. The results show that the NV-nanodiamonds used here are detecting the randomly fluctuating magnetic fields produced by nanoscale spin ensembles of order 2500 spins at ambient temperature with single-time-point detection times of a few seconds. This is an improvement of several orders of magnitude in resolution over state-of-the-art MR detection of electronic spins [9]. Just as MR detection and imaging has made critical contributions to biological imaging down to the mesoscale, the capabilities of decoherence based magnetic sensing and imaging using atomic sized NV quantum probes may offer important new opportunities for detection in nanoscale biology.

2. Decoherence sensing with NV centres in diamond

The NV centre is an atomic sized defect occurring naturally in diamond, comprised of a substitutional nitrogen atom and adjacent vacancy aligned along a ⟨111⟩ crystallographic axis (figure 1(c)). An additional captured electron gives the defect a negative charge, and a deep potential well surrounding the vacancy tightly binds the valence electrons [13] enabling production of centres in nanocrystals less than 10 nm in size [14, 15]. Far-field optical readout of the spin-1 ground state at room-temperature [16] places NV at a distinct advantage over other solid state qubits as a non-invasive sensor, since remote access and control is possible without (physical) contact. The NV system shows great promise for nanoscale magnetometry as evident from recent demonstrations for static (dc) and oscillating (ac) fields [17–21], wide-field imaging [22] and high sensitivity multi-pulse schemes [23–25]. Furthermore, the inertness of the diamond host crystal allows the NV system to be used unrestrictedly as a magnetic/fluorescent probe in biological environments [26].

The decoherence of a coherent quantum system is determined by the noise distribution in the environment and interaction strength. For NV, the Zeeman effect is larger than the Stark effect [27], so it is magnetic fields rather than electric fields which produce the greatest contribution to decoherence. Local fields arise from macroscopic sources (such as the Earth’s field), magnetic dipoles (from unpaired spins) and Biot–Savart fields (from moving charges). In ultra-pure environments, NV dephasing times exceeding a millisecond have been shown at

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Figure 2. Topology of nanodiamond sensors, inherent spin baths and cluster expansion simulations of their effect on NV coherence. (a) Atomic force microscope (AFM) profile (blue curve and inset) of an agglomeration resulting from spin-coating nanodiamond (45 nm median diameter) onto a glass substrate. Overlaid with the AFM data is a schematic depicting the intrinsic crystal spin–baths comprising strongly interacting clusters of internal nitrogen (green) and surface spins (red). (b) Cluster expansion simulation of the resulting typical magnetic fields felt by an NV centre (depth $h = 5$ nm in this case) due to the various intrinsic spin–bath sources. Surface spins are distributed with a much greater density than the internal spins, and the fluctuation frequency of the surface spins is much faster than the nitrogen spin bath. In these simulations we have assumed a mean fluctuation rate of 100 MHz and a spin density of $1 \text{nm}^{-2}$ for the surface spins. (c) NV spin-echo envelopes corresponding to the cluster state simulations in (b) as a function of depth in the nanocrystal. NV centres closer to the surface have a shorter coherence time, due to proximity to surface spin bath.

Room temperature [28], whereas for these nanodiamond studies, dipolar fields from internal nitrogen donors and spins on the diamond surface form intrinsic spin baths (see figure 2(a)) which restrict NV coherence times to below 10 $\mu$s [14]. Here we introduce spins external to the diamond lattice and surface, and detect their presence by measuring changes in the NV decoherence rate.

The effective Hamiltonian for an NV spin $\vec{S}$ in the presence of a magnetic field $\vec{B}(t)$ is
\[
H_{NV} = \hbar \vec{S} \cdot \vec{D} \cdot \vec{S} + \hbar \vec{S} \cdot \vec{A} \cdot \vec{I} + \hbar \gamma_{NV} \vec{B}(t) \cdot \vec{S},
\]
where $\gamma_{NV}$ is the NV gyromagnetic ratio and $\vec{D}$, $\vec{A}$ are the fine and hyperfine tensors which produce splitting of the order $D = 2.87$ GHz and $A \approx 2$ MHz (for $^{14}$N with nuclear spin $I = 1$) and act to partially lift the degeneracy of the NV ground state (see figure 1(e)).

We define the fluctuation regime of the magnetic environment in which the sensor is placed by the dimensionless parameter $\Theta = f_e / \gamma_{NV} B_e$, where $f_e$ is the average fluctuation rate of the field and $B_e$ its fluctuation amplitude (different environments will be denoted with a subscript) [12]. The random processes we are concerned with are characterized by zero mean fields, such that the fluctuation amplitude is described by the root–mean–square (RMS) of the field distribution, $B_e = B_{rms}$. Rapidly (slowly) fluctuating fields are characterized by the $\Theta \gg 1$ ($\Theta \ll 1$) condition. We begin by describing the effect of the intrinsic NV environment without the addition of any target spins in solution.

Internal electronic spins from nitrogen dopants in the nanocrystals provide a spin bath in the $\Theta \sim O(1)$ regime [29]. Surface spin flips occur over faster timescales providing an additional
spin bath in the $\Theta \gg 1$ regime [30]. In figure 2(b) we plot the typical magnetic fields from these distinct sources resulting from a quantum cluster expansion calculation. The relative contribution of each spin bath can be observed by applying a spin-echo pulse sequence, which refocusses slow fluctuations but retains the effect of spin baths with relatively fast dynamics. Spin-echo is a common technique in magnetic resonance spectroscopy, although here it is applied to the NV spin, rather than to the sample. To describe the effect on the NV coherence quantitatively we use an overall function for the ground state probability after spin-echo time $t$ of the form

$$P(t) = \exp \left[ -\Gamma_{\text{Ext}} t - \frac{1}{\left( \frac{\Gamma_{\text{short}}}{N} t \right)^4 + \left( \frac{\Gamma_{\text{long}}}{N} t \right)^{-1}} \right],$$

where $\Gamma_{\text{short}} = f_N / \sqrt{2} \sqrt{2} \Theta_N$ and $\Gamma_{\text{long}} = \gamma_{NV} B_N / 2 \Theta_N$ are the decoherence rates from the internal nitrogen spin bath at short and long times [12] (see appendix B) and before the addition of external target Mn$^{2+}$ spins the ‘external’ decoherence rate ($\Theta \gg 1$) is due to the surface spin bath

$$\Gamma_{\text{Ext}} \rightarrow \Gamma_{ss} = \frac{\gamma_{NV}^2 B_{ss}^2}{2 f_{ss}}.$$  

In figure 2(c) we plot the spin-echo curves corresponding to the calculations of figure 2(b) for different NV depth scenarios. When the NV is near the surface ($\sim 5$ nm) the spin-echo curve is dominated by the exponential decay of the fast fluctuating surface spins, whereas when the NV is further from the surface ($\sim 15$ nm) the spin-echo curve is also dominated at short times by the intrinsic nitrogen donor spin bath. Alternatively, the NV spin can be driven continuously with a microwave field to produce Rabi oscillations. The decay of the Rabi oscillations is also characteristic of the environmental noise spectrum [31] however, in the regime dominated by surface spins we obtain essentially the same information as from the spin-echo measurement (appendix H).

Upon introduction of MnCl$_2$ solution to the nanodiamonds, dipolar coupling to the additional magnetic sources ($S = 5/2$ Mn$^{2+}$ spins) alters the NV decoherence profile, providing new extrinsic decoherence channels (as opposed to the nitrogen and surface spin baths intrinsic to the nanodiamond) to modify equation (2) such that $\Gamma_{\text{Ext}} = (\Gamma_{ss} + \Gamma_{\text{Mn}})$. Importantly, measurement of the spin-echo profile before the addition of the spin solution allows the initial decoherence sources to be characterized. With knowledge of the initial spin environment, measurements on the same single spin probes allow us to detect changes in local magnetic fields arising from exposure to different solutions.

3. Detecting spins in solution using quantum decoherence

Figure 3 shows the spin-echo and Rabi profiles for four NV centres (referred to as NV 1–4) in air and water (green and blue traces respectively). The profiles were measured by applying 532 nm pulses with 2 $\mu$s duration and 80 $\mu$W intensity focused onto nanodiamonds through a coverslip, using a 1.4 NA oil objective. In the delay between laser pulses, microwave pulses (see figure A.1(b)) rotated the NV spin with 10–20 MHz Rabi frequencies. From the intensity of the NV fluorescence during illumination ($\sim 10,000$ counts s$^{-1}$), the spin population can be determined (see appendix A for details). As expected the Rabi profiles correlate well with the spin-echo results. The diversity in decoherence rates, with coherence times ranging from 800 ns
Figure 3. Decoherence properties of NV centres under various immersion conditions and exposure to Mn$^{2+}$ spins in solution. Top row: measured spin-echo decoherence profiles for four NV centres, performed on nanocrystals in air (green), deionized water (blue) and 1 M MnCl$_2$ (red). Fits to the data-points using equation (2) (shown as the solid lines) allow the decoherence rates under the various immersion conditions to be determined (shown in the legend with uncertainties in the last significant figure given in parentheses). Bottom row: Rabi measurements corresponding to the spin-echo data for each NV.

to 3.5 $\mu$s, indicate each NV experiences a unique nanoscale environment, due to variations in crystal size, purity and NV proximity to surface. Protons in water are paramagnetic, but with a dipole moment three orders of magnitude smaller than the electron spin, hence the addition of water has little observable effect on the magnetic environment of the nanodiamonds as measured through $T_2$. Removal or deposition of impurities at the diamond surface in water, self-diffusion of water molecules and experimental uncertainties contribute to minor differences between the measured profiles.

The form of the spin-echo decay before the addition of the Mn spins can be used to estimate the contribution of each native spin bath to the overall decoherence. For example, NV2 exhibits quartic exponential decay at short times characteristic of the internal nitrogen spin bath, whereas the exponential decay of NV4 indicates dominance of surface spins. In columns 1 and 2 of table 1 we present the decoherence rate associated with the initial surface spin bath.

3.1. Analysis of the initial surface spin bath

We first consider the control measurements in air and water. In the absence of any a priori knowledge of the initial environment, we describe the evolution of the NV and surface environment at a quantum level, using a master equation approach with a general relaxation rate $f_{ss}$ due to the surface spin dynamics. To solve the system we use a cluster expansion method [32], tracing over the bath degrees of freedom, to calculate the response of the NV
centre to the surface and internal spin baths. From the results of the cluster expansion, we determine the following dependence of the magnetic field at the NV centre:

$$B_{ss} = 277 \mu T \text{nm}^3 \times \frac{\sigma^{1/2}}{h^2},$$

(4)

where $\sigma$ is the effective surface spin density and $h$ is the depth of the NV below the diamond surface. Using equation (3), this relationship allows us to compare the relative depths of each NV ($i = 1, \ldots, 4$) below the surface, since $\Gamma^{(i)}_{ss}/\Gamma^{(j)}_{ss} = (h_j/h_i)^4$. For NV depths which are large compared to the spatial separation of surface spins, we can approximate the spin density and fluctuation rate of surface spins as being equivalent for all nanocrystals studied. Taking the depth of NV4 as a reference, we find $h_1 = (1.3 \pm 0.03) \times h_4$; $h_2 = (1.8 \pm 0.02) \times h_4$; and $h_3 = (1.4 \pm 0.02) \times h_4$.

The control measurements also provide insight into the mechanism of surface spin relaxation. Despite not knowing the precise physical origin of the surface spin relaxation, we may still rule out certain mechanisms as being responsible. Under a dipole–dipole mediated surface flip-flopping process, the cluster expansion analysis gives $f_{ss} = 5.56 \text{GHz nm}^3 \times \sigma^{3/2}$. This expression, together with equation (3), and the $\Theta \gg 1$ condition allows us to set the following upper limit for the NV depth as a function of the decoherence rate:

$$h \ll \left( \frac{2.28 \text{MHz}}{\Gamma_{ss}} \right)^{1/3} \text{nm.}$$

(5)

From equation (5), we see that even a decoherence rate as low as $\Gamma_{ss} \approx 100 \text{kHz}$ implies an NV depth much less than 2 nm below the nanocrystal surface, below the known photo-stability limit [15]. In contrast, spin–orbit coupling of sp$^2$ hybridized surface carbon to phonons results in surface spin relaxation rates of 0.1–10 GHz at 300 K [30] independent of the spin density and is therefore the more likely mechanism.

### 3.2. Detection of extrinsic manganese spins

In figure 3 (red traces) we show the effects of immersion of the nanodiamonds in 1 M MnCl$_2$ (in HCl) on the spin echo decay envelopes. Mn$^{2+}$ ions were chosen due to their high spin ground state $[\text{Ar}]3d^5$ at room temperature, characterized by an electronic spin of $S = 5/2$. A strong acid was used to prevent oxidation of Mn$^{2+}$ to a low spin state. In addition to a reduction in the coherence time, the spin-echo profiles of NVs 1, 2 and 4 become noticeably more exponential, characteristic of an additional fast magnetic noise contributing to the total profile $P(t)$. In contrast, NV3 experiences no change within the bounds of uncertainties, despite having initial decoherence comparable to the three other NV centres—implying a similar proximity to the surface. The absence of any change is attributed to close proximity to a surface not exposed to...
Figure 4. Restoration of NV quantum coherence after washing in spin-free acid. Measured spin-echo decoherence profiles for NV1 and 2, performed in air (green), 1M MnCl$_2$ (red), 1M HCl (orange). Fits to the data-points using Eq. (2) are shown as the solid lines (fit uncertainties in the last significant figure given in parentheses). The same spin-echo profiles in air and HCl confirm Mn spins are responsible for the observed changes in decoherence.

The MnCl$_2$ solution (e.g. the coverslip, or another nanodiamond). We observed that a number of other NV centres experienced minimal changes when immersed in manganese solution, which is also consistent with a greater physical separation between the NV and target manganese spins, e.g. $h > 10$ nm in the intrinsic nitrogen bath regime (figure 2(c)). AFM profilometry shows a maximal NV distance from the external Mn spins of 50 nm, further highlighting the nanoscale nature of the detection.

As a negative control, we measured the decoherence of NV1 and NV2 when immersed in a 1 M HCl solution, possessing an equivalent concentration of ions to the 1 M MnCl$_2$ solution previously detected. The restoration of quantum coherence (figure 4) confirms that the $T_2$ based decoherence detection is primarily sensitive to the presence of Mn$^{2+}$ spins rather than changes in pH, ionic diffusion, or charge transfer. The measured rates in HCl, also allow us to eliminate ambient contributions to the decoherence rate, and isolate the contribution from the Mn$^{2+}$ spins alone.

We may gain insight into the dynamics of the manganese spins using a scaling analysis to determine the dependence of the fluctuation rate on the NV depth. No depth dependence would imply an effectively frozen lattice type dipolar interaction between the Mn$^{2+}$ spins [33–35], whereas a $f_{	ext{Mn}} \propto h^{-2}$ dependence would imply a pure diffusion process with frozen magnetization. As such, we set $f_{	ext{Mn}} = \alpha h^x$ and proceed as follows to determine the scaling exponent, $x$, from the data. We first express the ratios of decoherence rates due to Mn in NV1 and NV2 as

$$
\frac{\Gamma_{\text{Mn}}^{(2)}}{\Gamma_{\text{Mn}}^{(1)}} = \left(\frac{B_{\text{Mn}}^{(2)}}{B_{\text{Mn}}^{(1)}}\right)^2 \left(\frac{f_{\text{Mn}}^{(1)}}{f_{\text{Mn}}^{(2)}}\right)^2 = \left(\frac{h_1}{h_2}\right)^{x+4}.
$$

From equation (3), we had $\frac{h_1}{h_2} = \left(\frac{\mu_{\text{Mn}}^{(2)}}{\mu_{\text{Mn}}^{(1)}}\right)^{1/4}$, and taking $\Gamma_{\text{Mn}} \sim \Gamma_{\text{Ext}}[\text{MnCl}_2] - \Gamma_{\text{Ext}}[\text{HCl}]$
Figure 5. Measurements on NV5 showing detection of Mn\(^{2+}\) spin accretion on the nanodiamond surface. Rabi and spin-echo measurements in air (green), 1 M MnCl\(_2\) solution (red), accreted MnCl\(_2\) (black) (fit uncertainties in the last significant figure given in parentheses).

we have

\[
x = 4 \ln \left( \frac{\Gamma_{\text{Ext}}^{(2)}[\text{MnCl}_2] - \Gamma_{\text{Ext}}^{(2)}[\text{HCL}]}{\Gamma_{\text{Ext}}^{(1)}[\text{MnCl}_2] - \Gamma_{\text{Ext}}^{(1)}[\text{HCL}]} \right) \ln \left( \frac{\Gamma_{\text{as}}^{(2)}}{\Gamma_{\text{as}}^{(1)}} \right) - 4
\]

\[
x = -2.2 \pm 1.2,
\]

which suggests that the majority of the decoherence may be attributable to the self-diffusive motion of the Mn spins. The dominance of diffusion in the NV dephasing over direct Mn–Mn flip-flopping processes is perhaps not unexpected since the motion of the Mn spins reduces the mean time for dipole interaction between the Mn spins (motional narrowing). From an analysis of the magnetic field generated by motionally diffusing Mn spins in 1 M MnCl\(_2\) concentration (see appendix D) we determine an upper bound on the number of spins detected at a maximal detection standoff of 10 nm (beyond which the NV is dominated by the intrinsic spin-bath—see cluster expansion calculations in figure 2(c). Using NV4 as an example, the data corresponds to an upper bound detection of 2500 Mn spins, over an effective solution volume of \((16 \text{ nm})^3\) in a single-time-point acquisition time of 4.2 s. This is an improvement of several orders of magnitude in resolution and sensitivity over state-of-the-art ESR detection of \(2 \times 10^7\) spins over micron scales in 3600 s [9]. Due to the \(h^{-3}\) scaling of the external field variance giving rise to the decoherence change signal, reducing the size of the nanodiamond will dramatically improve the sensitivity to small spin ensembles: e.g. for NV in 7 nm nanodiamond the results indicate that less than 100 spins could be detected, with a time resolution down to 400 ms (see appendix E).

The decoherence sensing technique could equally be used to detect changes in spin density on the nanodiamond surface; for instance in monitoring chemical reactions at the surface of functionalized nanodiamonds. In a final experiment we characterized another NV centre (NV5), which was observed to have decoherence rates of \(\Gamma_{\text{Ext}}[\text{Air}]=136\ \text{kHz}\) and \(\Gamma_{\text{Ext}}[\text{MnCl}_2]=160\ \text{kHz}\). In this case the solution was left to evaporate in air resulting in precipitation from the MnCl\(_2\) solution to the nanodiamond surface. Upon re-suspension in deionized water, there...
was a significant increase in decoherence rate to 260 kHz, as can be seen in figure 5 (black trace). We attribute this to an increased surface spin density due to additional Mn$^{2+}$ spins on the nanodiamond surface.

4. Conclusion and outlook

We have demonstrated nanoscale magnetic detection of electronic spins in solution and at the surface of nanodiamonds, using the decoherence of single NV spins. Our measurements over several NV defects in separate nanodiamonds provide information on the relative location of the NV centres with respect the diamond surface and dynamic properties of the external spin environment. Our results also shed new light on the surface spin dynamics of nanodiamond. The data is supported by a detailed cluster expansion treatment and indicate the detection of order $10^3$ spins with nanoscale resolution in a single-time-point resolution of 4.2 s, which is a significant improvement over current induction-based detection of electronic spins under ambient conditions [9]. Decoherence detection using single NV spin qubit probes may be applied to arbitrary spin samples including solid-state, chemical, or biological environments where no other sensor currently exists with the desired combination of sensitivity and resolution, and is especially relevant for rapidly fluctuating environments where decoupling techniques and/or resonant driving of target spins is unfeasible. Our results correspond to $T_2$-based detection, however similar measurements using a $T_1$-based scheme [10, 11] will also open a new regime of fluctuation detection. For schemes where ultimate spatial resolution is not required, complementary techniques such as those performed recently in bulk diamond with high density NV ensembles may allow $\sqrt{N}$ improvement in sensitivity [10]. By reducing the size of the nanodiamonds to 7 nm [15], the sensitivity of the NV centre to its environment will enable single point detection times well below 1 s and detection of much smaller target ensembles, opening a new vista of novel nanomagnetic investigations of biological processes. Recent experimental demonstrations of the quantum control techniques required for decoherence detection in the complex environment of living cells [26], underpin the considerable potential of nanoscale decoherence-based biosensing [36].

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Appendix A. Methods

Type Ib nanodiamond samples (nitrogen concentration <300 ppm) were deposited onto microscope coverslips, dried in air, cleaned in oxygen plasma and mounted in a teflon fluid cell for imaging through the back of the coverslip with an oil immersion objective (figure A.1(a)). The nanodiamonds were non-detonation produced, with a size range of 40–50 nm sourced from NaBond Technologies, we observe clumping of nanodiamonds on the coverslip surface in the AFM profiles (see figure 2(a)). Microwaves were applied with an insulated wire (also immersed
Figure A.1. (a) Experimental set-up: NV nanodiamonds are introduced into a spin-rich MnCl$_2$ solution (spin target). The NV spin is controlled by an RF microwave line and read-out optically using a confocal system. (b) Quantum control protocols to measure the decoherence of the NV spin in response to the local magnetic field fluctuations.

in solution), and mounted $\sim 50 \mu$m from nanodiamonds of interest (figure A.1(a)). A magnetic field of 5 mT was applied to lift the degeneracy of the $m_s = \pm 1$ spin levels. Spin-echo profiles were normalized by fitting to the maximum population after application of a $2\pi$ microwave pulse. Pulse errors were accounted for by rejecting non-monotonically decreasing data at the start of the spin-echo before fitting (see appendix G). Changes in background fluorescence after immersion in solution, were accounted for by normalizing to the maximum and minimum fluorescence levels (proportional to spin population). Solutions were transferred by flushing the fluid cell five times before filling.

Appendix B. Theoretical description of spin-echo profile

Experimentally, different magnetic environments, can be distinguished by probing decoherence on different timescales. Of the magnetic fields local to the NV, only dipolar fields are relevant to this study [36]. The effect of rapidly fluctuating fields on the NV centre can be isolated with the application of a spin-echo ($\pi/2 - \tau/2 - \pi - \tau/2 - \pi/2$) sequence [37] (figure A.1(b)), which suppresses the effect of low frequency noise by reversing the NV evolution with the application of a $\pi$ pulse at the mid-point of the evolution. A complete decomposition of the environmental frequency spectrum can be obtained by sequentially filtering desired Fourier components [38, 39], although this provides no benefit for the fast environments investigated here and is more experimentally intensive.

The effect of the nitrogen spin bath (in the $\Theta\sim O(1)$ regime) on the spin-echo profile can be treated by addressing the two dominant timescales [12]. At short times ($t \ll 1/f_e$), magnetic field fluctuations cause a decay given by

$$D_{\text{short}}(t) \sim \exp[-(\Gamma_{N}^{\text{short}}t)^4]$$  \hspace{1cm} (B.1)
with a characteristic rate $\Gamma^\text{short}_N = f_N/\sqrt{2\gamma_\Theta N}$. At longer time-scales ($t \gg 1/f_\varepsilon$), the spin-echo decays as

$$D(t) \sim \exp[-\Gamma(t)N t]$$

with associated rate $\Gamma^\text{long}_N = \gamma N B_N/2\gamma_\Theta N$. The complete decay profile due to the internal nitrogen crystal spin bath can be approximated by asymptotically matching the short and long time scales:

$$D_N(t) = \exp\left[-\frac{1}{(\Gamma^\text{short}_N t)^{-4} + (\Gamma^\text{long}_N t)^{-1}}\right].$$

Sources of decoherence external to the crystal such as surface spin flips are relatively fast ($\Theta \gg 1$) and give rise to an overall decay of the spin-echo envelope:

$$D_{ss}(t) \sim \exp[-\Gamma_{ss} t].$$

Therefore, to describe all these effects quantitatively we use the normalized function given by equation (2) in the main text.

**Appendix C. Dynamic environmental processes**

In this section, we theoretically derive the natural timescales associated with the various physical processes taking place in this system and their effect on the dephasing rate of the NV spin.

**C.1. NV–environment interaction**

We relate the effective environmental rms magnetic field strength (in Hz, not Tesla) due to the presence of Mn spins in solution to the components of the corresponding axial magnetic field operator via

$$B \equiv \sqrt{\langle B^2 \rangle},$$

where $B_x, B_y$ and $B_z$ are defined by the total dipolar coupling of the effective environmental fields to the $x, y$ and $z$ components of the NV spin respectively. The magnetic field operators from an arbitrary Mn spin, $\vec{S}_i$, are then

$$B^i_x = \frac{\mu_0}{4\pi} \frac{\gamma_{N E} \mu_B}{R_i^3} [S_{i,x} - 3 \sin(\Theta_i) \cos(\Phi_i) (R_i \cdot \vec{S}_i)],$$

$$B^i_y = \frac{\mu_0}{4\pi} \frac{\gamma_{N E} \mu_B}{R_i^3} [S_{i,y} - 3 \sin(\Theta_i) \sin(\Phi_i) (R_i \cdot \vec{S}_i)],$$

$$B^i_z = \frac{\mu_0}{4\pi} \frac{\gamma_{N E} \mu_B}{R_i^3} [S_{i,z} - 3 \cos(\Theta_i) (R_i \cdot \vec{S}_i)],$$

where $R_i = R_i (\sin(\Theta_i) \cos(\Phi_i), \sin(\Theta_i) \sin(\Phi_i), \cos(\Theta_i))$ denotes the separation vector between the NV and a given Mn spin. Squaring these operators and taking the trace over the spin degrees of freedom, the variance of the axial field is given by

$$\langle B^2 \rangle \approx \frac{1}{3} S(S+1) A^2 \frac{1 + 3 \cos^2(\Theta_i) \gamma_\Theta N}{R_i^6},$$
where $A = \frac{\mu_0}{4\pi} \gamma_{nv} B E \mu_B = \frac{\mu_0}{4\pi} h \gamma^2$. Finally, the total variance is found by summing over all spins in the system for an NV located a distance $h$ below the diamond surface. Because of the relatively small separation of environmental spins (of order $\sim n^{-1/3}$, where $n$ is the number density of Mn spins) compared with $R$, we may treat the environmental spins as a continuum. This allows us to replace this sum with an integral over $x$ and $y$ from $-\infty$ to $\infty$, and $z$ from $h$ to $\infty$, giving

$$
\langle B_z^2 \rangle = \int n \langle B_y^2 \rangle \, d^3 \mathbf{R} = S(S + 1) A^2 \frac{n\pi}{6 h^3},
$$

which then implies an rms field strength due to all Mn spins of

$$
B_{Mn} = \frac{\mu_0}{4\pi} h \gamma^2 \sqrt{S(S + 1)} \frac{n\pi}{3 h^3} = 317 \text{ MHz nm}^3 \times \left( \frac{h}{h^3} \right)^{1/2} \sqrt{S(S + 1)} = 246 \text{ MHz nm}^{3/2} \text{ M}^{-1/2} \times \frac{c^{1/2}}{h^{3/2}} \sqrt{S(S + 1)},
$$

where $c$ is the concentration in M, or mol l$^{-1}$, of a particular chemical species in the electrolyte.

We may use this result to determine both the effective number of aqueous spins, and the effective electrolytic volume to which the NV is sensitive. If we consider a single spin placed at directly above the NV at height $h$, its variance is

$$
\langle B_{0,z}^2 \rangle = \frac{4}{3} S(S + 1) \frac{A^2}{h^6}.
$$

The effective number of such spins due to the entire environment is then

$$
N_{\text{eff}} = \langle B_z^2 \rangle / \langle B_{0,z}^2 \rangle = \frac{n\pi h^3}{8}
$$

with corresponding effective volume

$$
V_{\text{eff}} = \frac{\pi h^3}{8}.
$$

This quantity is a measure of the effective sensing volume of environmental spins to which the NV is exposed, which implies the effective spatial resolution of this sensing protocol is $\Delta L \sim \frac{3}{4} h$, which is ultimately limited by how closely an NV centre may reside to the diamond surface.

In a similar manner, the rms field due to spins on the surface of the nanocrystal may be determined by integrating expression (C.4) over the surface spin distribution. As we have restricted our interest to cases where cases the NV depth below the surface is small comprised to the nanocrystal radius, the surface distribution effectively becomes planar arrangement. Thus, fixing $z = h$, and integrating over $x$ and $y$, we obtain

$$
B_{ss} = 277 \mu T \text{ nm}^{-3} \times \frac{\sigma^{1/2}}{h^2},
$$

where $\sigma$ is the effective surface spin density and $h$ is the depth of the NV below the diamond surface.

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C.2. Environmental dipole–dipole relaxation

The coupling between a pair of environmental spins is described by the following Hamiltonian:

\[ H_{ij} = \frac{\mu_0}{4\pi \hbar} \left( \frac{\vec{S}_i \cdot \vec{S}_j - 3(\vec{r} \cdot \vec{S}_i)(\vec{r} \cdot \vec{S}_j)}{r^3} \right). \]  

(C.12)

The time evolution operator is given by

\[ U_{ij} = \exp(-iH_{ij}t). \]

Using this, we find the autocorrelation function for the axial magnetization using the corresponding Heisenberg picture operator

\[ \langle M_z(t)M_z(0) \rangle = \frac{1}{\langle \vec{S}_j^2 \rangle} \langle \vec{U}_{ij}(t)\vec{S}_j\vec{U}_{ij}\vec{S}_j \rangle = \frac{1}{2} \left( \cos(2\theta) \sin^2 \left( \frac{2(S(S+1)bt)}{r^3} \right) + \cos^2 \left( \frac{2(S(S+1)bt)}{r^3} \right) \right). \]

As the timescales associated with the dipole–dipole interaction between adjacent Mn spins is faster than their mutual self-diffusive hopping rate (see section on motional narrowing below), dipole–dipole mediated relaxation of the Mn spins will occur before the environment has undergone an appreciable geometric reconfiguration. This means that we may determine the resulting NV decoherence using a numerical disjoint-cluster expansion routine, whereby the instantaneous distribution of spins in the electrolyte is divided into small, strongly interacting clusters \[40\]. This allows the full spin-echo envelope to be factorized into contributions from each of the individual clusters. This method shows remarkable convergence for group sizes as small as three spins, meaning that the problem of determining the evolution of a bath of \( N \) spins, otherwise involving the exponentiation of a \( 15^N \times 15^N \) matrix, to \( N/3 \) calculations of each of the \( 15^3 \times 15^3 \) sized propagators for each individual cluster. These calculations may then be used to calculate the autocorrelation function of the effective magnetic field (figure C.1(a)), as described above. From this, the dependence of the associated autocorrelation time on the NV depth and Mn\(^{2+}\) concentration (figure C.1(b)), as used in the main text, may be extracted.

Using this approach, the relaxation rate of the axial component of the effective magnetic field belt by the NV due to the magnetic-dipole coupled Mn spins was found to be

\[ f_{\text{dip}} = 8.1 \text{ GHz nm}^3 \times n \times S(S+1) \]

\[ = 4.9 \text{ GHz M}^{-1} \times c \times S(S+1), \]  

(C.13)

which we take for the dipole–dipole contribution to \( f_e \).

C.3. Properties of effective magnetic field due to self-diffusing Mn ions

In a diffusion dominated process, the effective magnetic field dynamics are dictated by spins diffusing into and out of the region to which the NV centre is sensitive. At low spin concentrations, \( n \), the interactions between adjacent spins become less important, and fluctuation rates of the effective field as seen by the NV are instead determined by self-diffusion of aqueous spins. Consider a single spin residing at an arbitrary position \( \vec{x} = (x, y, z) \) at time \( t \),
the magnetic field operators become

$$B_i(t) = \frac{\mu_0}{4\pi} \frac{\gamma_0 g_b \mu_B}{(z^2 + x^2 + y^2)^{3/2}} \left[ S_i - 3 \frac{x^2 S_x + xy S_y + xz S_z}{z^2 + x^2 + y^2} \right]$$

During the time interval $\Delta t$, the system evolves to $(x, y, z, t) \mapsto (x + \Delta x, y + \delta y, z + \delta z, t + \delta t)$, where $\Delta x$, $\Delta y$ and $\Delta z$ are distributed according to a Brownian diffusion process. At time $t + \Delta t$ the magnetic field operators become

$$B_i(t + \Delta t) \equiv b_{xx}(t + \Delta t)S_x + b_{xy}(t + \Delta t)S_y + b_{xz}(t + \Delta t)S_z,$$

where $x, y \in (-\infty, \infty)$ and $z > h$. At some time later, $t + \Delta t$, much greater than the collision time of fluid constituents, a spin will have moved an rms distance $r = \sqrt{6D\Delta t}$ (where $D$ is the diffusion constant of the spins in solution). The magnetic field at time $t$ is given by

During the time interval $\Delta t$, the system evolves to $(x, y, z, t) \mapsto (x + \Delta x, y + \delta y, z + \delta z, t + \delta t)$, where $\Delta x$, $\Delta y$ and $\Delta z$ are distributed according to a Brownian diffusion process. At time $t + \Delta t$ the magnetic field operators become

$$B_i(t + \Delta t) \equiv b_{xx}(t + \Delta t)S_x + b_{xy}(t + \Delta t)S_y + b_{xz}(t + \Delta t)S_z,$$

where $x, y \in (-\infty, \infty)$ and $z > h$. At some time later, $t + \Delta t$, much greater than the collision time of fluid constituents, a spin will have moved an rms distance $r = \sqrt{6D\Delta t}$ (where $D$ is the diffusion constant of the spins in solution). The magnetic field at time $t$ is given by

$$B_i(t) = \frac{\mu_0}{4\pi} \frac{\gamma_0 g_b \mu_B}{(z^2 + x^2 + y^2)^{3/2}} \left[ S_i - 3 \frac{x^2 S_x + xy S_y + xz S_z}{z^2 + x^2 + y^2} \right]$$

Figure C.1. Numerical cluster expansion results for a magnetically dipole coupled aqueous solution of MnCl$_2$. (a) Autocorrelation function of the effective magnetic field experienced by the NV spin due to dipolar mediated evolution of manganese spins in solution (from 0.1 to 1 M MnCl$_2$ concentrations). (b) Extracted dipole mediated relaxation rate from the autocorrelation functions shown in (a).
And since $\text{Tr} (S_i S_j) = 0$ for $i \neq j$, we have
\[
\langle B^x_z (t) B^y_z (t + \Delta t) \rangle = b_{zz} (t) b_{zz} (t + \Delta t) \text{Tr}(S_x S_x) + b_{zy} (t) b_{zy} (t + \Delta t) \text{Tr}(S_x S_y)
\]
\[
+ b_{zz} (t) b_{zz} (t + \Delta t) \text{Tr}(S_z S_z)
\]
\[
= \frac{21}{4} \left[ b_{zz} (t) b_{zz} (t + \Delta t) + b_{zy} (t) b_{zy} (t + \Delta t) + b_{zz} (t) b_{zz} (t + \Delta t) \right].
\]
(C.16)

Expanding for $\Delta x$, $\Delta y$, $\Delta z \ll h$ (where $h$ is the NV depth), we find, to second order in $\Delta x$, $\Delta y$ and $\Delta z$
\[
\langle B(t) B(t + \Delta t) \rangle = \frac{\pi}{6} S(S + 1) \frac{n a^2}{h^3} - \frac{3\pi}{32} S(S + 1) n a^2 \frac{(\Delta x^2) + (\Delta y^2) + (\Delta z^2)}{h^5}
\]
\[
= \frac{\pi}{6} S(S + 1) \frac{n a^2}{h^3} - \frac{3\pi}{32} S(S + 1) n a^2 \frac{6D\Delta t}{h^5}
\]
\[
= \frac{\pi}{6} S(S + 1) \frac{n a^2}{h^3} \left[ 1 - \frac{9}{16} \frac{6D\Delta t}{h^2} \right].
\]
(C.17)

To obtain the autocorrelation for long times, $T = N \Delta t$, we apply this geometric scaling $N$ times
\[
B(t) B(t + N \Delta t) = B(t) B(t + T) = \frac{\pi}{6} S(S + 1) \frac{n a^2}{h^3} \left[ 1 - \frac{9}{16} \frac{6D T}{h^2} \frac{1}{N} \right]^N
\]
(C.18)

which for large $N$ becomes
\[
\langle B(t) B(t') \rangle = \frac{\pi}{6} S(S + 1) \frac{n a^2}{h^3} \exp \left[ - \frac{9}{16} \frac{6D (t - t')}{h^2} \right].
\]
(C.19)

The fluctuation rate of the effective field due to translational diffusion is then
\[
f_t = 6D \left( \frac{3}{4h} \right)^2.
\]
(C.20)

Taking the diffusion coefficient to be bounded above by that of water at 298 K, $(D = 3 \times 10^{-9} \text{m}^2 \text{s}^{-1})$ and $h \sim 5 \text{ nm}$, we find $f_t = 405 \text{ MHz}$.

C.4. Motional narrowing of the dipole–dipole fluctuation rate

Because of the diffusive motion of spins in the electrolyte, the effective fluctuation rate due to dipolar flip-flops may, in some cases, be reduced significantly. This is because any two spins may not interact long enough for a magnetization exchange to occur with an appreciable probability. We may use a semi-classical argument to estimate this revised relaxation timescale.

Whilst two spins are in contact (i.e. they exist temporarily as a nearest-neighbour pair before the diffusion process redistributes them), we assume they are sufficiently close that no terms from the full dipolar interaction may be ignored. If the spins are in contact for a time $\delta t$, the rate of rotation rate of one of the spin vectors may be taken straight from equation (C.13), and the total polar angle rotation during this time will be
\[
\delta \theta = 4S(S + 1) \frac{b}{\langle r \rangle^3} \delta t,
\]
(C.21)
where $\langle r \rangle \approx \frac{1}{2}n^{-1/3}$ is the average separation of spins in the electrolyte. Over a long period of time, $t \gg \delta t$, these angular shifts will accumulate in a fashion reminiscent of a random walk. Hence, by the central limit theorem, the total accumulated angular shift will be normally distributed with variance of $N = t/\delta t$ times the variance of a single shift, that is

$$\Delta \theta^2 = \frac{t}{\delta t} (\delta \theta)^2 = t \delta t \left[ 4S(S+1) \frac{b}{\langle r \rangle^3} \right]^2.$$  \hfill (C.22)

Using the above analysis of diffusive motion, the effective dwell time over which the interaction takes place is

$$\delta t = \frac{1}{D_{\text{Mn}}} \left( \frac{4 \langle r \rangle}{3} \right)^2.$$ \hfill (C.23)

Hence, the motionally narrowed relaxation rate is then

$$f_{\text{narr}} = \frac{1}{2} \frac{\delta \theta^2}{\delta t} = \frac{1}{5} \frac{f_{\text{dip}}^2}{n^{2/3} D}.$$ \hfill (C.24)

This analysis, of course, hinges on the assumption that the ‘hopping rate’, $R_{\text{hop}} = 1/\delta t$, is much faster than the dipolar flipping rate, $f_{\text{dip}}$, otherwise the fluctuation can be attributed to dipolar flip-flops alone. The crossover point at which motional narrowing becomes important occurs when $1/\delta t \sim f_{\text{dip}}$, or when

$$D \left( \frac{3 \langle r \rangle}{4} \right)^2 = 2S(S+1) \frac{\mu_0}{4\pi} \hbar \gamma^2 \frac{4\pi^2 n}{3}$$

$$\Rightarrow n = \left[ \frac{D}{S(S+1)} \frac{3}{32} \left( \frac{\mu_0}{4\pi} \hbar \gamma^2 \right)^{-1} \right]^3.$$ \hfill (C.25)

For the specific case of MnCl$_2$, we have $S = 5/2$. To estimate the diffusion coefficient of manganese, we note that atomic manganese has a mass 55/18 times that of water. Given that the number density of water molecules is roughly three orders of magnitude greater than that of Mn, most collisions involving an Mn atom will be with a water molecule, thus each molecular collision will result in a Mn atom changing its velocity by a factor 18/55 less than that of the corresponding water molecule. Thus if the expected translational variance of a water molecule during time interval $t$ is $\langle r_{\text{H}_2\text{O}}^2 \rangle = D_{\text{H}_2\text{O}} t$, that of the Mn atom will be $\langle r_{\text{Mn}}^2 \rangle = (18/55)^2 \langle r_{\text{H}_2\text{O}}^2 \rangle = (18/55)^2 D_{\text{H}_2\text{O}} t$. Thus the effective diffusion constant for Mn is $D_{\text{Mn}} = (18/55)^2 D_{\text{H}_2\text{O}} \approx 0.3 \text{ nm}^2 \text{ ns}^{-1}$ at 300 K. Thus, the concentration below which motional narrowing becomes important is

$$c \approx 1 \mu\text{M}$$ \hfill (C.26)

which is well below the regimes considered in this work. This result is essentially due to the fact that both dipolar relaxation and effective hopping rate increase with the aqueous spin concentration, albeit with a differing power-law dependence.
Appendix D. Additional spin-echo profiles

We observed no changes in the spin-echo profile for several NV centres when immersed in 1 M MnCl₂. We attribute these null results to the strong spatial dependence of the dipolar coupling between the NV centre and external spins. The random position of each NV centre in its respective nanodiamond means that each NV is at a different distance from the manganese solution. AFM profilometry of nanodiamonds on coverslips give an average nanoparticle height of \( \approx 50 \text{ nm} \). However, to observe dipolar coupling between single spins over this distance requires an NV coherence time \( > 1 \text{ ms} \). The large size of the nanodiamonds with respect to the sensing volume of each NV centre means that we observe a range of sensitivities for NV centres in different nanodiamonds. The spin-echo profiles of two NV centres, NV6 and NV7 showing no significant change in \( T_2 \) time under immersion in MnCl₂ is shown in figure D.1.

Appendix E. Time resolution

We analyse the acquisition time required to detect manganese spins, using NV4 as an example. We consider monitoring the fluorescence intensity at the \( T_2 \) time-point of the spin-echo curve, and setting a fluorescence threshold to indicate a positive result. At the \( t = 0.696 \mu s \) free evolution time-point, the difference in fluorescence intensity between the air and the MnCl₂ measurements is 2.63\%. By setting a fluorescence reduction of 1.32\% as the threshold, we can determine the minimum number of photons required to correctly identify the presence of Mn spins with a 95\% confidence level. Noise in the experiment is dominated by photon shot-noise, meaning we can use the Poisson distribution to calculate

\[
P[(x = X) > \text{Threshold}, \lambda = \text{Threshold} \times 0.9868] < 0.05, \quad (E.1)
\]

where \( \lambda \) is the count rate in the presence of Mn (at a level 1.32\% below the threshold), and \( x \) is the detected number of photons. Evaluating equation (E.1) with the Poisson cumulative distribution function, yields 15 270 photons required to obtain a 95\% certainty. The experiment

Figure D.1. Additional spin-echo profiles. The spin-echo decoherence profiles for two NV centres (NV6 and NV7), performed in air (green), deionized water (blue) and 1 M MnCl₂ (red) showing no significant change in coherence time in each solution. Fits to the data-points according to equation (2) (main text) are shown as the solid lines.
consists of performing a spin-echo sequence on the NV spin, followed by an excitation pulse lasting 2\(\mu\)s, and a waiting period of 2.2\(\mu\)s, before repeating multiple times to collect enough photons. Signal collection only occurs in the first 600 ns of the excitation pulse, with an average 0.061 photons collected during this time period. As a result 2.5 \times 10^5 averages, taking a total time of 1 s, are required before enough signal is obtained. In figure E.1 we plot the spin-echo profile for NV4 after two different acquisition times, showing the scaling of the noise as a function of acquisition time. In the legend we show the single-point detection time when monitored at the \(T_2\) time for each data set.

**Appendix F. Effective number of spins detected with a single NV centre and associated temporal resolution**

The magnetic field variance from a single target spin external to the diamond (distance \(r\) to the NV) is

\[
\langle B_i^2 \rangle \sim S(S + 1) \left( \frac{\mu_0 gM_B \mu_B}{4\pi r^3} \right)^2.
\]

So the total variance is

\[
\langle B^2 \rangle = 4\pi n \int_h^\infty \langle B_i^2 \rangle r^2 dr \sim S(S + 1) \frac{4\pi n}{3} \left( \frac{\mu_0 gM_B \mu_B}{4\pi} \right)^2 \frac{1}{h^3}.
\]

Hence the effective number of particles detected at a NV depth of \(h\) is

\[
N_p = \frac{\langle B^2 \rangle}{\langle B_i^2 \rangle} = \frac{4\pi n h^3}{3}.
\]
In terms of the concentration [Mn], we obtain (\(N_A\) is Avogadro’s constant)

\[
N_p = 10^3 \times \frac{4\pi N_A h^3}{3} \times [\text{Mn}] \approx 2500 \ \text{Mn spins}
\]

for the 1 M solution and a maximal detection depth of \(\sim 10\) nm.

We obtain a scaling relation for the total measurement time in terms of the intrinsic \(T_2\) and decoherence rate as follows. The magnetic field sensitivity of an NV magnetometer with a 1 \(\mu s\) decoherence time is \(\eta_B = B_{\text{min}} \sqrt{T} = 1 \mu \text{T Hz}^{-1/2}\), where \(T\) is the total measurement time. So for an arbitrary intrinsic \(T_2\), the sensitivity is

\[
\eta = \eta_B \sqrt{\frac{T_2}{1 \mu \text{s}}}.
\]

This type of magnetometer measures the field by detecting a phase shift, \(\phi = \gamma B t\). If the free precession time is \(t = T_2\), then we multiply both sides of the above equation by \(\gamma T_2\) to give

\[
\phi \sqrt{T} = \eta_B \gamma T_2 \sqrt{\frac{T_2}{1 \mu \text{s}}}.
\]

If instead of a phase shift due to a magnetic field, we measure a phase decay due to a decoherence source of \(\phi = \Gamma T_2\), where \(\Gamma\) is due to extrinsic sources, and \(T_2\) is due to intrinsic sources, then

\[
\Gamma \sqrt{T} = \gamma \eta_B \sqrt{\frac{T_2}{1 \mu \text{s}}}.
\]

So the total measurement time is

\[
T = \left(\frac{\gamma \eta_B}{\Gamma}\right)^2 \frac{T_2}{1 \mu \text{s}}
\approx 400\ \text{ms}.
\]

Appendix G. Normalization of spin-echo curves

Extraction of accurate decay rates from the spin-echo measurements requires correct normalization and analysis of the data. Here we discuss the data analysis of the spin-echo profiles. The fluorescence intensity before application of coherent microwave pulses provides the initial population in the \(m_s = 0\) state. For an infinitesimally short 2\(\pi\) pulse with no pulse errors, the spin population and therefore fluorescence intensity is the same directly after application of a 2\(\pi\) pulse. The population decay, in the absence of coherent coupling to single/few spins, is then monotonically decreasing. Pulse errors however, lead to a reduced initial population and incomplete refocusing in the spin-echo sequence (see figures G.1(a) and (b)). As a result the evolution becomes akin to a Ramsey sequence at short times, with beating occurring and non-monotonically decreasing evolution. To reduce the effect of pulse errors, initial data points were neglected until the spin-echo followed a monotonically decreasing decay and then renormalized. Analysis of control experiments with deliberate pulse errors yielded the same fitting parameters as experiments without pulse errors (see figure G.1(c)). Therefore, by taking into account experimental imperfections, we can robustly measure the component decoherence rates even in the presence of large pulse errors.
errors. One consequence is that timescales before the first data point cannot be addressed, and neglecting short time data points produces a greater uncertainty in the extracted rates. In experiments on NVs 1–7, pulse errors were below the 20% level.

For spin-echo profiles where the driving Rabi frequency was close to the same order as the hyperfine splitting, an additional source of modulation occurs in the spin-echo profiles. This modulation arises from incomplete driving of all three hyperfine transitions, and with slightly different Rabi frequencies. These additional hyperfine modulations were also removed from the fitted data.

Appendix H. Decay of Rabi envelopes

The NV spin can be driven continuously with a microwave field to produce Rabi oscillations, with the decay of the Rabi oscillations also characteristic of the environmental noise spectrum [31]. In the regime dominated by surface spins we obtain essentially the same information as from the spin-echo measurement. To see this we first note that because the coupling to adjacent surface spins is much stronger than the coupling between surface spins and the NV centre, the influence of the surface spins may be regarded as a semiclassical field. Hence, the dephasing in a Rabi experiment due to the surface will be purely exponential and may be treated using a master equation approach for the reduced density matrix for the ensemble averaged dynamics of the NV. Once obtaining the solution for the probability of the system being in the initial spin state at later times, we integrate over a spectral density of width $f_{ss}$ to obtain an overall Rabi profile decay rate of $\Gamma_{\text{Rabi}} \approx B^2/f_{ss}$. The envelope is assumed to have an exponential shape due to the faster surface spin dynamics in agreement with the spin-echo case.

The Rabi data is less conclusive than the spin-echo data, due to several confounding factors. Firstly, the decay of the Rabi envelope depends on the strength of the driving field. To circumvent this, efforts were made to ensure the Rabi frequency was kept constant across experiments, but the addition of different chemical solutions affected power coupling to the

*Figure G.1*. The effect of pulse errors on the spin-echo profile. (a) Experimental spin-echo profiles of a single NV spin in type Ib diamond with: a correct $2\pi$ pulse length of 80 ns (green), an applied pulse length of 72 ns (blue, 10% error), 64 ns (red, 20% error) and 56 ns (orange 30% error). (b) Short time effect of pulse errors on the spin-echo profile. For increased pulse errors, the population after application of a $2\pi$ pulse is reduced and beating occurs. (c) Spin-echo profiles after removal of short time data points and renormalization.
Table H.1. NV Rabi frequency (MHz) across experiments, uncertainties are negligible.

|       | Air   | Water | MnCl₂ |
|-------|-------|-------|-------|
| NV1   | 12.00 | 17.99 | 11.19 |
| NV2   | 21.66 | 21.91 | 21.63 |
| NV3   | 16.43 | 16.40 | 13.55 |
| NV4   | 17.41 | 17.99 | 18.05 |

microwave wire and limitations in the microwave amplifier meant that different Rabi frequencies were unavoidable. Table H.1 lists the Rabi frequency obtained in each experiment. However, in the case where the environmental fluctuation rate is very broad compared to the Rabi frequencies (as we have here), then increasing or decreasing the Rabi frequency has little effect on the decay rate. Instabilities in the applied microwave power can also contribute to decay of the Rabi envelope, and in contrast to the decoupling effect of the Rabi oscillation, are exacerbated as the driving field is increased [41]. As a result we have not explicitly analysed the Rabi experiments.

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